1961

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Recommended Citation

Moye, Anthony Joseph, "The autoxidation of resonance stabilized carbanions " (1961). *Retrospective Theses and Dissertations*. 1978.
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MOYE, Anthony Joseph, 1933–
THE AUTOXIDATION OF RESONANCE STABILIZED CARBANIONS.

Iowa State University of Science and Technology
Ph.D., 1961
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

THE AUTOXIDATION OF
RESONANCE STABILIZED CARBANIONS

by

Anthony Joseph Moye

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical-Organic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1961

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ACKNOWLEDGEMENT

I would like to express my sincere thanks and appreciation to Professor Glen A. Russell for his ready advice and encouragement during the course of the research described herein. Particularly I want to express my gratitude to Professor Russell for his patience during the extended period of thesis preparation.

I also want to thank my wife, Betty, for her steadfastness and encouragement, and her aid in preparing and typing early drafts of the thesis.

Thanks are due also to the members of the Russell Research Group for their friendship, encouragement, and experimental assistance. Particularly, I want to make known my indebtedness to the Messers. Williamson, Ito, and Hendry for their invaluable aid in bringing this dissertation preparation to a satisfying conclusion.

Finally, I would like to express my gratitude to the Proctor and Gamble Co., the Eastman Kodak Co., and the Iowa State Research Institute for financial aid during my graduate career.

INTRODUCTION

The increasing practical and theoretical significance of the phenomenon of *autoxidation* of organic substances has been well documented by the appearance of several excellent reviews[1-4]. The varied nature of the products produced by the action of oxygen on organic substrates in neutral media has been satisfactorily accounted for through the agency of peroxy radicals as reactive chain propagating intermediates.[5]

In spite of this plethora of autoxidation data, the reaction of molecular oxygen with organic substrates in alkaline media has received very little serious attention. However, such a reaction is of potential value for several reasons. Firstly, a study of the reaction of a carbanion with oxygen ought to yield valuable information as to the nature of the initiation process, i.e., either a one or a two electron transfer could conceivably occur.

$$(1)\quad R:^{-} + \cdot\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{O}}\cdot \longrightarrow R\cdot + {}^{-}:\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{O}}:$$

---

[1] R. Criegee, *Fortschr. chem. Forsch.*, *1*, 508 (1950).

[2] L. Bateman, *Quart. Revs.*, *8*, 147 (1954).

[3] C. Walling, "Free Radicals in Solution", John Wiley and Sons, Inc., New York, 1957, Chapter 9.

[4] G. A. Russell, *J. Chem. Educ.*, *36*, 111 (1959).

[5] A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides", Interscience Publishers, New York, 1954.

(2) $R:^{-} + \cdot\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{O}}\cdot \longrightarrow R-\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{O}}:^{-}$

Secondly, since the expected hydroperoxides are often unstable[6] under such conditions the nature of the oxidation products is important. Finally, in many cases, organic compounds, inert toward molecular oxygen in neutral media, are rapidly autoxidized in basic solution. An understanding of the factors affecting such reactivity is of obvious interest.

The present work is a result of the recent publication by Tsuruta, Fueno, and Furukawa[7] wherein a free radical pathway was proposed for the oxidative dimerization of *p*-nitrotoluene in alkaline media through the agency of air or oxygen. In view of the extreme reactivity of oxygen toward radical species[8,9], such a reaction mechanism would appear to be unlikely.

My initial efforts, therefore, were spent in examining alternate mechanistic possibilities. I ultimately found that the original suggestion made by the Japanese workers was not

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[6] H. Hock and W. Susemihl, *Ber.*, *66*, 61 (1933); N. Kornblum and H. E. DeLaMare, *J. Am. Chem. Soc.*, *73*, 880 (1951).

[7] T. Tsuruta, T. Fueno, and J. Furukawa, *J. Am. Chem. Soc.*, *77*, 3265 (1955).

[8] The rate constant for the reaction $R\cdot + O_2 \longrightarrow R-O-O\cdot$ where R = 1-tetralyl has been determined as 6.8×10^7 liters/mole-sec., by C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc. London*, *A198*, 252 (1949).

[9] A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.*, *78*, 1017 (1956). These workers report that toward a polystryrenyl radical oxygen is about 10^6 times as reactive as styrene.

without merit. As a result of this initial investigation I have become further concerned with the intriguing problem of the reaction of carbanions with molecular oxygen. Further, I have approached the problem of oxidative dehydrogenations, in particular those of alcohols, and report herein on this subject also.

In connection with the experimental study of the reactivity of oxygen toward carbanions I have attempted to present a representative review of published literature on this subject. It should be appreciated that, with certain exceptions, most of the pertinent references are not concerned with the elucidation of mechanistic features. I have endeavored to be reasonably selective in this review and submit it in the hope that future investigators in this area may find such a study useful.

REVIEW OF LITERATURE

Oxidation of p-Nitrotoluene and Its Derivatives

The enhancement of the reactivity of the methyl group of ortho or para-nitrotoluene by the action of alkali is well known. In the presence of base p-nitrotoluene will even undergo condensation reactions with aromatic aldehydes, a reaction characteristic of reactive nucleophilic species. The oft cited example of the formation of anthranilic acid in low yield by the action of alkali on o-nitrotoluene[10,11] in the absence of air offers additional testimony as to this enhanced reactivity.

No less dramatic is the reactivity exhibited by p-nitrotoluene under similar conditions. The initial report in this area is that of Perkin[12] who noted the formation of "p-azotoluene" and a considerable amount of red-brown amorphous material in the treatment of p-nitrotoluene with sodium amalgum.

The complexity of the highly colored condensation products in this reaction was confirmed by Klinger[13] and by

---

[10] H. Klinger and R. Pitschke, Ber., 18, 2551 (1885).

[11] R. Scholl, Monats., 34, 1011 (1913).

[12] W. H. Perkin, J. Chem. Soc., 37, 546 (1880).

[13] H. Klinger, Ber., 15, 866 (1882); ibid., 16, 941 (1883).

Bender and Schultz[14]. These latter workers were able to isolate, in good yield, p,p'-diaminostilbenedisulfonic acid from the Zn dust reduction of the highly colored amorphous product resulting from the extended treatment of p-nitrotoluene-2-sulfonic acid with alcoholic potassium hydroxide. It is interesting to note that the presence of an acidic fraction in the product distribution resulting from basic treatment of p-nitrotoluene[13] has been largely overlooked.

In a careful re-investigation of this remarkable reaction, Fischer and Hepp[15] reported the isolation of significant quantities of the dimeric products, p,p'-dinitrobibenzyl and p,p'-dinitrostilbene. The major reaction product was an orange-yellow crystalline compound of molecular formula $C_{28}H_{20}N_4O_4$. A probable structure for this product has been suggested by Green[16] on the basis of extensive experimentation into the practical application of this reaction to the synthesis of dye intermediates. His structure, the dinitroazodistilbene (I), is reasonable in the light of existing data.

$$O_2N\text{-}C_6H_4\text{-}CH{=}CH\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_4\text{-}CH{=}CH\text{-}C_6H_4\text{-}NO_2$$

I

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[14] F. Bender and G. Schultz, ibid., 19, 3234 (1866).

[15] O. Fischer and E. Hepp, ibid., 26, 2231 (1893).

[16] A. G. Green, J. Chem. Soc., 85, 1424 (1904).

The formation of nearly quantitative yields of p,p'-dinitrobibenzyl and/or p,p'-dinitrostilbene derivatives (depending on reaction conditions) in the presence of an oxidizing agent (sodium hypochlorite) seemed to provide the first clue as to a possible pathway of the reaction[17,18]. In his review of stilbene based dye materials, Green[16] had suggested that the first stage in the oxidative dimerization of p-nitrotoluene derivatives in alkaline solution was the oxidation of the methyl group to an unstable intermediate. This was followed by rapid condensation of this intermediate to the observed products of the reaction.

In order to provide a more secure experimental basis for these suppositions the oxidation of various 2-substituted p-nitrotoluenes was studied[19,20]. The variation of the substituent group from sulfonic acid to phenylsulfone to sulfonamide led to the interesting result that while a temperature of 60° was necessary to effect reaction of the first named compound the latter two substituted p-nitrotoluenes reacted rapidly in the cold in the reaction in alkaline solution with sodium hypochlorite as oxidizing agent. The

---

[17] C. Ris and C. Simon, Ber., 30, 2618 (1897).

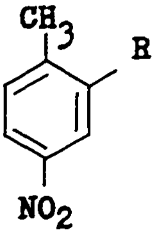
[18] A. G. Green and A. R. Wahl, ibid., 30, 3097 (1897); ibid., 31, 1078 (1898).

[19] A. G. Green, F. Marsden, and F. Scholefield, J. Chem. Soc., 85, 1432 (1904).

[20] A. G. Green, A. H. Davies, and R. S. Horsfall, ibid., 91, 2076 (1907).

products were a mixture of *cis* and *trans* *p*-nitrostilbene derivatives, in yields of 50 to 70%, *trans* predominating. The use of air as oxidizing agent led to the same products albeit in lower yield. In order to account for a seemingly inordinate amount of saponification of the phenylsulfone when air was used as the oxidizing agent, the formation of hydrogen peroxide was postulated. This thesis was confirmed by the addition of lead acetate to the reacting mixture, filtering off the lead peroxide formed and evolution of chlorine gas on the addition of hydrochloric acid[19].

The fact that the same deeply colored unstable intermediate products seemed to be formed either by treatment of the stilbenes with reducing agents in alkaline solution or on initial addition of potassium hydroxide solution to the *p*-nitrotoluene derivatives led to the assignment of a nitrosostilbene structure to this stage of reaction. The deep color was accounted for on the basis of a quinoid form of this nitroso compound. In order to further explain the qualitative difference in reactivity of a series of compounds of the type



R = SO_3H, SO_2Ph, Cl, CN, NO_2

Rate of reaction more rapid than p-nitrotoluene (R=H). Only stilbenes formed on oxidation. (Intermediates, blue color).

R = H, CH_3, OCH_3, CO_2H	Rate same or slower than *p*-nitrotoluene, products mainly bibenzyl. (Intermediates, red color).

a second reaction stage was postulated. In other words, the proposed reaction path was

$$(1)\quad 2\ O_2N\text{-}C_6H_4\text{-}CH_3 \longrightarrow O_2N\text{-}C_6H_4\text{-}CH_2\text{-}CH_2\text{-}C_6H_4\text{-}NO$$

$$(2)\quad O_2N\text{-}C_6H_4\text{-}CH_2CH_2\text{-}C_6H_4\text{-}NO \longrightarrow ON\text{-}C_6H_4\text{-}CH = CH\text{-}C_6H_4\text{-}NO$$

$$(3)\quad O_2N\text{-}C_6H_4\text{-}CH_2\text{-}CH_2\text{-}C_6H_4\text{-}NO \xrightarrow{OX.} O_2N\text{-}C_6H_4\text{-}CH_2CH_2\text{-}C_6H_4NO_2$$

$$(4)\quad ON\text{-}C_6H_4CH = CHC_6H_4\text{-}NO \xrightarrow{OX} O_2N\text{-}C_6H_4\text{-}CH = CH\text{-}C_6H_4\text{-}NO_2$$

The two states of reaction (1) and (3) were presumed to be more or less concurrent with (2) and (4) according to the reactivity of the particular *p*-nitrotoluene derivative chosen. Since the ultimate reaction product (bibenzyl or stilbene) depends on the reactivity of the derivative chosen it is supposed that only the most reactive of these will proceed via a second condensation stage, i.e., step (2). In general, air or oxygen served adequately as oxidizing agent, although in the case of 2,4-dinitrotoluene ($R = NO_2$), only violet-brown amorphous products could be isolated[21]. In this instance iodine seemed to be the oxidizing reagent of choice, leading to the tetranitro-stilbene in good yield.

Several other mechanisms have also been proposed for this

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[21] A. H. Green and J. Baddiley, *ibid.*, **93**, 1721 (1908).

reaction. Plisov[22] assumed an initial tautomerization to an *ortho* quinoid structure, by the action of alkali, followed by condensation to a nitroso bibenzyl derivative. The stilbenes were formed from the bibenzyl by a sequence of steps, involving tautomerization, followed by addition of hydroxyl, elimination of water, etc. No allowance is made in this mechanism for the apparent lack dimerization in the *o*-nitrotoluene series. Porai-Koshitz[23] proposed a mechanistic pathway for the *ortho* reaction involving a series of intermediates leading in turn to the nitroso alcohol or aldehyde, these in turn finally ending up as anthranilic acid by a series of additions of water, isomerizations, and removals of water. The dimeric *para* products presumably arise through condensation of the initial oxidation intermediates.

The variety of products obtained by the action of hot 70% potassium hydroxide in air or nitrogen atmosphere on *o*-nitrotoluene were rationalized by Lock and Stitz[24] who assumed that the formation of anthranilic acid involved *tris*-hydroxylation of the methyl group with evolution of hydrogen and the formation of *o*-nitrobenzoic acid as a primary step.

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[22] A. J. Plisov, *Ukrainskii Khem. Zhur.*, *4*, Sci. Pt., 241 (1929); [Original not available for examination, abstracted in *C. A.*, *24*, 1108 (1930).]

[23] A. E. Porai-Koshitz, *Anilinokrasochnava Prom.*, *4*, 261 (1934); [Original not available for examination, abstracted in *C. A.*, *29*, 139 (1935).]

[24] G. Lock and F. Stitz, *Ber.*, *73*, 1377 (1940).

The hydrogen evolved then serves as reducing agent to form anthranilic acid. In support of this theory a 15.7% yield of o-nitrobenzoic acid was isolated in a reaction of o-nitrotoluene in 70% potassium hydroxide carried out at 200° in a stream of air.

Although, as has been previously indicated, o-nitrotoluene normally reacts in the presence of base to form anthranilic acid, dimeric products have been isolated from reactions taking place under especially mild conditions. For example, Lapworth[25] isolated o,o'-dinitrobibenzyl upon treatment of o-nitrotoluene with ethoxide ion in a reducing solvent. In liquid ammonia (-33°C) the action of sodium diphenylamide on o-nitrotoluene yielded 36% of the ortho bibenzyl dimer[26].

This peculiar oxidative dimerization has attracted the attention of organic theorists in the early 1930's who were able to accomodate the results only by novel theories concerning the reactivity of organic molecules[27,28]. The reaction has found practical application as the basis for synthetic attempts to find new chemotherapeutic amidines[29]

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[25] A. Lapworth, J. Chem. Soc., 79, 1275 (1902).

[26] F. W. Bergstrom, I. M. Granara, and V. Erickson, J. Org. Chem., 7, 98 (1942).

[27] W. Bradley and R. Robinson, J. Chem. Soc., 1932, 1254.

[28] E. C. S. Jones and J. Kenner, ibid., 1931, 1846.

[29] J. N. Ashley and J. O. Harris, ibid., 1946, 567.

as a route to synthetic estrogens[30], and as the method of choice for synthesis of p,p'-dinitrobibenzyl[31,32].

Efforts to unravel the intricate mechanism of this reaction have continued. Treves[33] has demonstrated the efficacy of the use of catalysts to increase yields, p-benzoquinone yielding the best results. The conversion of p,p'-dinitrobibenzyl to p,p'-dinitrostilbene through the agency of alkali in the presence of oxygen was also noted[34]. In addition, other nitro compounds, e.g., p-nitroethylbenzene[34,35], p,p'-dinitrodiphenylmethane[34], mono-p-nitrodiphenylmethane[36], p-nitropropylbenzene[30], and 2,4,6-trinitrotoluene[37], have been reported to undergo similar oxidative condensation.

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[30] Huang-Minlon, J. Am. Chem. Soc., 70, 2802 (1948).

[31] R. C. Fuson and H. O. House, ibid., 75, 1325, 5744 (1953).

[32] H. O. House, Org. Syntheses, 34, 35 (1954).

[33] G. R. Treves, J. Am. Chem. Soc., 70, 875 (1948).

[34] R. Oda and T. Tsuruta, Repts. Chem. Research Inst. Kyoto Univ., 16, 6 (1947).

[35] K. A. Krupennikova, Uchenye Zapiski Kazakh. Univ., 16, 94 (1954); [Original not available for examination, abstracted in C. A., 51, 1910 (1957).]

[36] P. J. Beger, Z. Krist., 57, 303 (1922).

[37] W. Will, Ber., 47, 712 (1914). The work of this last investigator on the alkaline condensation of TNT has not been reproduced by other workers, e.g., W. H. Rinkenbach and H. A. Aaronson, J. Am. Chem. Soc., 52, 5040 (1930); A. H. Blatt and A. W. Rytina, ibid., 72, 403 (1950).

This vast accumulation of data coupled with experiments of their own design led Tsuruta, Fueno, and Furukawa[7] to propose a different reaction mechanism. On the basis of some rather tenuous kinetic results on the oxygen absorption of p-nitrotoluene and p-nitrophenylacetic acid in alkaline medium they derived the rate expression

$$(5)\quad v = (k_1 + k_2\,[O_2])\,na^m$$

where n is the concentration of p-nitro compound, a is the mean ionic activity, m is 1 with water as solvent and 2 with methanol as solvent, and k_1 and k_2 are specific rate constants. The postulated reaction mechanism is presented below.

$$(6)\quad O_2N\text{-}C_6H_4\text{-}CH_2X + KOR \xrightleftharpoons{K} O_2N\text{-}\overset{\ominus}{C}_6H_4\text{-}CHX,\ \overset{\oplus}{K} + HOR$$

$$(7)\quad O_2N\text{-}C_6H_4\text{-}\overset{\ominus}{C}HX,\ \overset{\oplus}{K} \xrightarrow{k'1} ON\text{-}C_6H_4\text{-}\dot{C}HX + \cdot OK$$

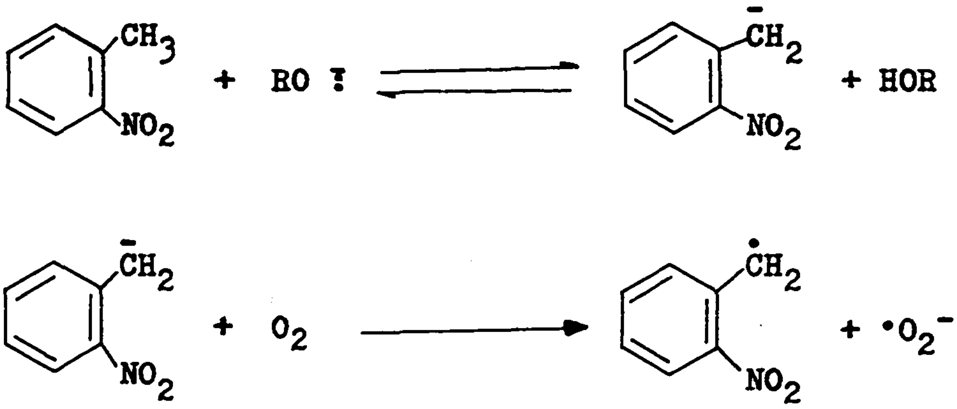
$$(8)\quad O_2N\text{-}C_6H_4\text{-}\overset{\ominus}{C}HX,\ \overset{\oplus}{K} + O_2 \xrightarrow{k'2} O_2N\text{-}C_6H_4\text{-}\dot{C}HX + \cdot O_2K$$

$$(9)\quad ON\text{-}C_6H_4\text{-}\dot{C}HX + O_2 \longrightarrow O_2N\text{-}C_6H_4\text{-}\dot{C}HX + O$$

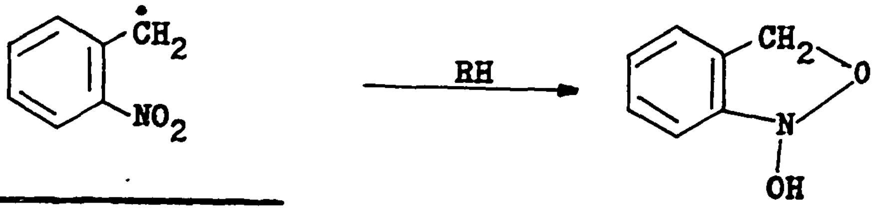
$$(10)\quad 2\ O_2N\text{-}C_6H_4\text{-}\dot{C}HX \longrightarrow \text{dimeric products}$$

The mechanism involves the initial formation of a carbanion that "readily loses oxygen" to form a nitroso radical; also involved is the transfer of an electron to an oxygen molecule to form the p-nitrobenzyl radical. Since the "nitroso group rapidly absorbs oxygen", the products of the reaction result from dimerization of these radicals. In spite of the well-documented reactivity of free radicals toward oxygen[3,4,8,9] no mention was made of any other reaction products or additional reaction stages.

Utilizing some of the same type of radical intermediates a reasonable rationalization of the formation of anthranilic acid from *o*-nitrotoluene would appear to entail the processes



The known affinity of carbon radicals for attack of nitro groups[38,39] coupled with the unfavorable steric interactions in any resonance hybrids involving the nitro group lead to the formation of a cyclic structure, a precursor of anthranil (II). Subsequent reaction of the anthranil in



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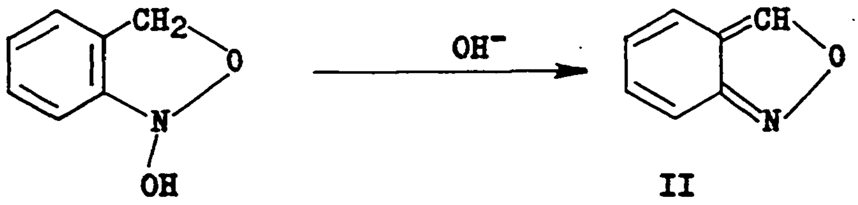
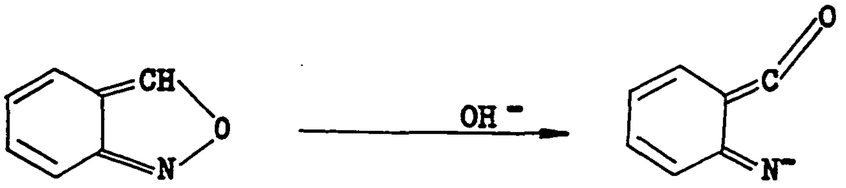
[38] P. D. Bartlett, G. S. Hammond, and H. Kwart, *Disc. Faraday Soc.*, **2**, 342 (1947).

[39] N. Inamoto and O. Simamura, *J. Org. Chem.*, **23**, 408 (1958).



II

basic media, perhaps through the intermediacy of ketene type structures resembling III[40] followed by hydration, would lead



III

to anthranilic acid.

Nitro compounds other than the nitrotoluenes react with oxygen or air in the presence of base in various ways. For example, nitrobenzene in the presence of potassium hydroxide and a stream of air or oxygen yields *o*-nitrophenol to the extent of 50%[41].

Hawthorne and Hammond[42] have reinvestigated a novel oxidation reaction of *tris*-(*p*-nitrophenyl)-methane in the presence of base and oxygen. Although the parent compound is totally inert to oxygen at 140° even in the presence of

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[40] G. Del Re, *Tetrahedron*, *10*, 81 (1960).

[41] A. Wohl, *Ber.*, *32*, 3486; *ibid.*, *34*, 2444 (1901).

[42] M. F. Hawthorne and G. S. Hammond, *J. Am. Chem. Soc.*, *77*, 2549 (1955).

initiator the anion autoxidizes rapidly at room temperature[43]. The products are hydroperoxide, carbinol and traces of *p*-nitrophenol.

An appealing initiation step for this process, as well as other carbanion oxidation, would appear to be the one electron transfer

$$R = \underline{p}\text{-}NO_2 \text{ phenyl}$$

$$(11)\quad R_3C:^- + O_2 \longrightarrow R_3C\cdot + \cdot O_2^-$$

This reaction followed by the sequence

$$(12)\quad R_3C\cdot + O_2 \longrightarrow R_3COO\cdot$$

$$(13)\quad R_3COO\cdot + R_3C:^- \longrightarrow R_3COO:^- + R_3C\cdot$$

provides a satisfactory explanation of the hydroperoxide formation. Since the hydroperoxide is stable to alkali an alternative rationalization was necessary to account for the presence of large amounts of carbinol in the product. Hawthorne and Hammond therefore proposed the novel one electron transfer oxidation-reduction reaction

$$(14)\quad R_3C:^- + R_3COOH \longrightarrow R_3C\cdot + R_3CO\cdot + {}^-:OH$$

This suggestion has been received with somewhat less than widespread approval[44]. Among other alternatives for the

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[43] O. Fischer and G. Schmidt, *Z. Farben u. Textilchemie*, *3*, 1 (1904); [Original not available for examination, abstracted in *Chem. Zentr.*, *75 I*, 460 (1904).]

[44] Walling, *op. cit.*, p. 465.

formation of carbinol is the interesting possibility of a nucleophilic displacement on oxygen[45]. A number of such reactions have recently been discussed by Edwards[46].

$$(15)\quad R_3C{:}^- + R_3COOH \longrightarrow R_3CO{:}^- + R_3COH$$

The mode of formation of *p*-nitrophenol is not completely clear although a free radical process involving the Wieland rearrangement may be postulated[47].

$$2\ R_3COO\cdot \longrightarrow 2\ R_3CO\cdot + O_2$$

$$R_3CO\cdot \longrightarrow R_2\dot{C}OR$$

$$R_2\dot{C}OR + O_2 \xrightarrow{RH} R_2COR(OOH)$$

$$R_2COR(OOH) + R_3C{:}^- \longrightarrow R_3COH + R_2CO + RO^-$$

R = *p*-nitrophenyl

Oxidation of Aliphatic Nitro Compounds

The air oxidation of aliphatic nitro compounds (nitrocyclohexane, 2-nitropropane) in the presence of a

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[45] G. A. Russell, *J. Am. Chem. Soc.*, *76*, 1595 (1954).

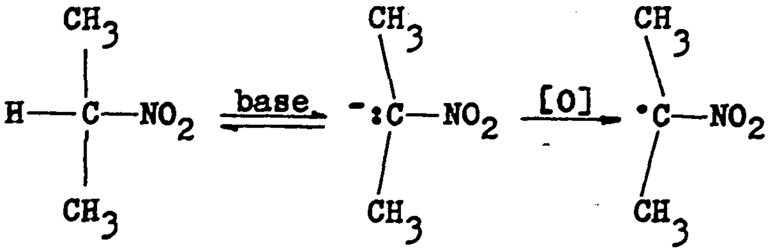
[46] J. O. Edwards, "Nucleophilic Displacement on Oxygen in Peroxides", in J. O. Edwards, ed., "Peroxide Mechanism Symposium, Brown University, 1960", Interscience Pub. Corp., New York, N. Y., in press.

[47] P. D. Bartlett and J. D. Cotman, Jr., *J. Am. Chem. Soc.*, *72*, 3095 (1950).

deficiency of aqueous bases has been suggested as a method of preparing the corresponding dinitro dimers[48]. The formation of *vic*-*t*-dinitro -alkanes in the oxidation of *sec*-alkane nitronates by such one electron oxidizing agents as sodium persulfate and potassium ferricyanide has been attributed to the intermediacy of 2-nitro-2-propyl radicals[49].

The autoxidation of 2-nitropropane in basic solution has been investigated by Russell[45]. The overall reaction leads to the formation of acetone and nitrite ion. The reaction rate is a function of pH and is autocatalytic. Evidence for a free radical chain process has been accumulated; the rate of oxygen absorption is accelerated by catalytic amounts of ferric and other metal ions and completely inhibited by the addition of arsenic trioxide. Russell suggests the ion-radical chain

Initiation



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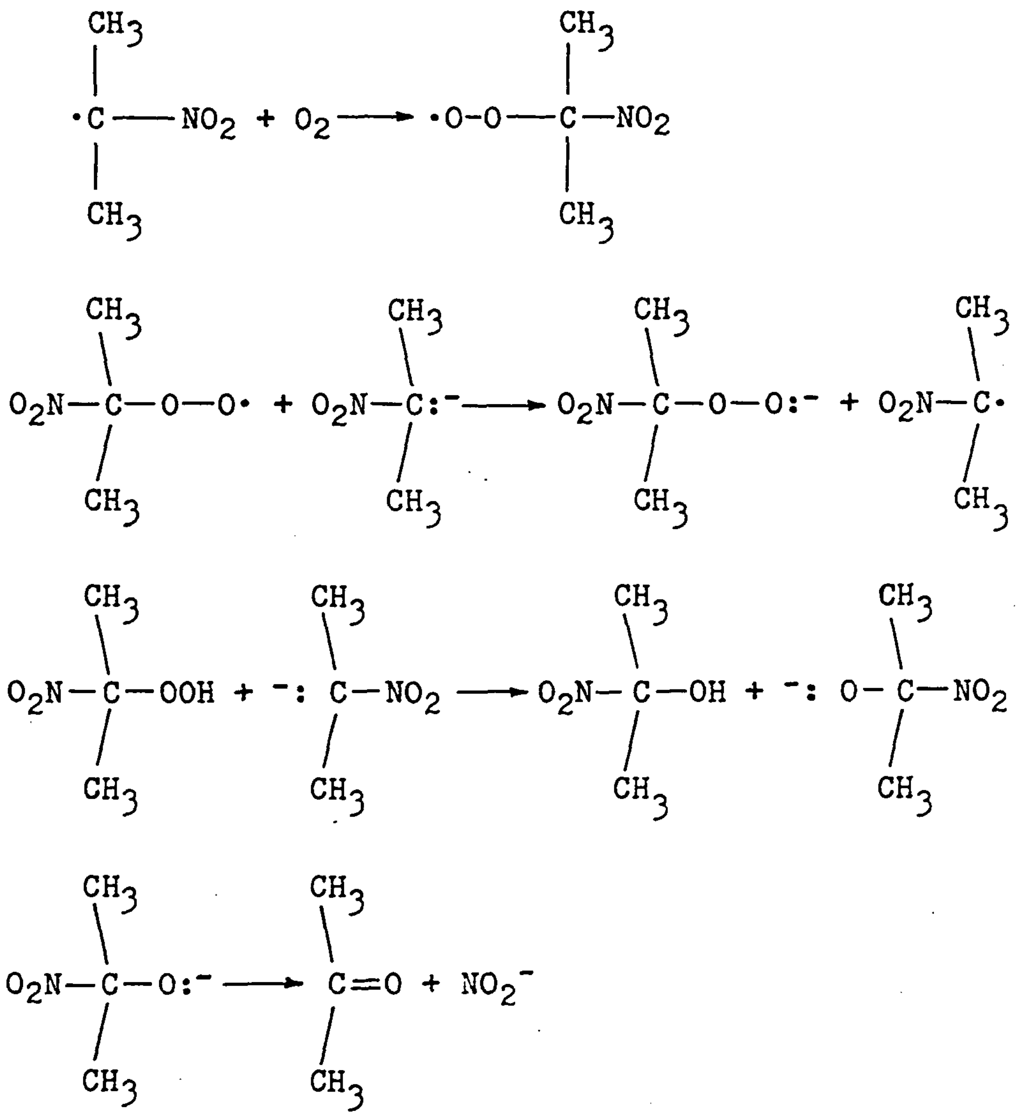
[48] C. S. Coe, E. C. Attuné, and T. F. Doumani, U. S. Patent, 2,465,974 (March 29, 1949); [Original not available for examination; abstracted in *C. A.*, *43*, 4683d (1949).]

[49] H. Schechter and R. B. Kaplan, *J. Am. Chem. Soc.*, *75*, 3980 (1953).

Propagation



The formation of nitrite ion in the reaction of potassio-9,10-dihydro-9,10-(11-methyl-12-nitroethano)-anthracene has been attributed to the intervention of a similar autoxidative process[50].

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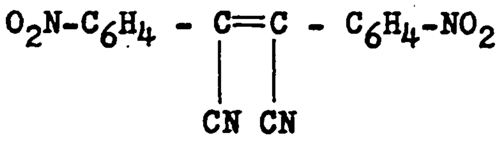
[50] W. E. Noland and R. Libers, Abstracts of Papers, Symposium on Nitro Aliphatic Chemistry at Purdue University, Lafayette, Indiana, May 25-26, 1961, Department of Chemistry, Purdue University, Lafayette, Indiana, p. 3.

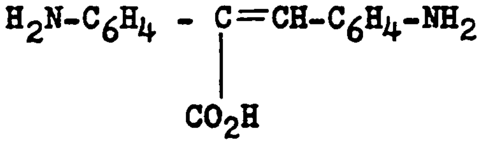
Oxidation of Acetonitrile Derivatives

Although the extreme sensitivity toward oxygen of alkaline solutions of p-nitrophenylacetonitrile has been appreciated for some time[51] no definitive investigations have been forthcoming[52]. Nerdel, Klamann, and Ebing[53] have accounted for the "chromoisomerism" of the sodium salt of p-nitrophenylacetonitrile in polar solvents on the basis of inter-intra-molecular oxidation-reduction reactions that produce a variety of dyestuffs. An extremely careful and efficient product study yielded, among others, the compounds



$$O_2N\text{-}C_6H_4 - \underset{CN}{C} = \underset{CN}{C} - C_6H_4\text{-}NO_2$$

IV



$$H_2N\text{-}C_6H_4 - \underset{CO_2H}{C} = CH\text{-}C_6H_4\text{-}NH_2$$

(after catalytic hydrogenation)

V

The 4,4'-dinitro-α, α'-dicyanostilbene (V) had been previously prepared by oxidation of the sodium salt of

---

[51] R. S. Stearns and G. W. Wheland, J. Am. Chem. Soc., 69, 2025 (1947).

[52] C. H. Langford and R. L. Burwell, Jr., ibid., 82, 1503 (1960) have commented on the difficulty in obtaining reliable pK_a values for this compound because of the "rapid" oxidation of the anion.

[53] F. Nerdel, D. Klamann, and W. Ebing, Ann., 632, 55 (1960).

p-nitrophenylacetonitrile with iodine[54]. Undoubtedly, the reaction pathway is very much like that previously discussed in the nitrotoluene series.

In the absence of any base, solutions of substituted acetonitriles do not absorb any oxygen[55]. However, in the presence of a strong base, oxygen is slowly absorbed, and ketones or acids are formed in good yield, depending upon the nitrile used. In the presence of a trace (1 mole per cent) of copper salts the reaction takes a different course, predominant dimerization occurs. Representative results obtained with diphenylacetonitrile are portrayed in Table 1. Quantitative yields of the dimeric product are also obtained on oxidation with alkaline permanganate (acetone solvent) and ferricyanide. Strangely enough when 10% of water is added to the alkaline acetone solution of permanganate the product is exclusively benzophenone (85%).

The autoxidation of methylphenylacetonitrile in the presence of base (piperidine) and catalytic amounts of copper salts yielded dimethyldiphenylacetonitrile (17%) and acetophenone (56%). Under similar conditions cyclohexylphenylacetonitrile gave only cyclohexylphenylketone (25 to 32%); phenylacetonitrile gave benzoic acid (75%); and dimethylacetonitrile gave only traces of acetone along with

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[54] G. Heller, ibid., 332, 279 (1904).

[55] M. S. Kharasch and G. Sosnovsky, Tetrahedron, 3, 97 (1958).

Table 1. Oxidation of diphenylacetonitrile at room temperature

Nitrile conc. (mole/liter)	Solvent	Base (m/l)	Catalyst	Products	
				TPSN[a]	Ph_2CO
0.02	CH_3OH	0.025 NaOMe	——	0	90-100
0.02	Pip[b]	0.0002 NaOMe or Triton B	——	20	50
0.01	Pip[b]	——	CuBr	80	0
0.01	Pip[b]	——	$CuBr_2$	95	0
0.01	Et_2NH	——	CuBr	10	70
0.005	En[c]	——	CuBr	88	0
0.005	CH_3OH	0.0045 KOH	$CuBr_2$	10	(?)
0.005	CH_3OH	0.027 NaOMe	$CuBr_2$	95	0

[a] Tetraphenylsuccinonitrile

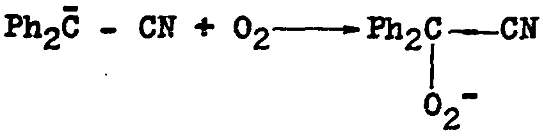
[b] Piperidine

[c] Ethylenediamine

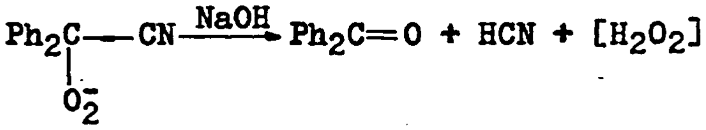
unchanged starting material[55].

On the basis of these results, Kharasch and Sosnovsky propose the mechanism

(16) $Ph_2CHCN \xrightarrow{B^-} Ph_2\bar{C}—CN + HB$

(17) 

$$Ph_2\bar{C} - CN + O_2 \longrightarrow Ph_2\underset{\displaystyle O_2^-}{\underset{|}{C}}—CN$$

(18) 

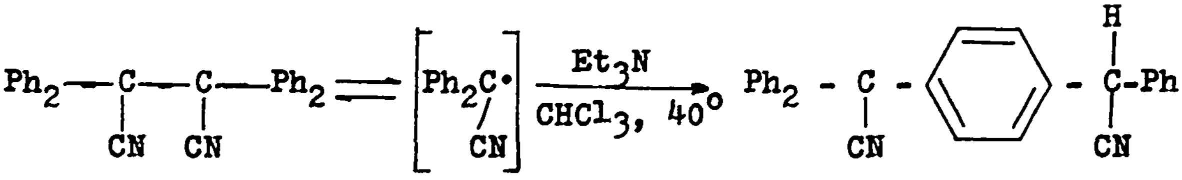
$$Ph_2\underset{O_2^-}{C}-CN \xrightarrow{NaOH} Ph_2C{=}O + HCN + [H_2O_2]$$

(19) $Ph_2\overset{-}{C}-CN + Cu(II) \longrightarrow Ph_2\underset{\bullet}{C}CN + Cu(I)$

(20) $2\ Ph_2\underset{\bullet}{C}CN \longrightarrow$ dimer.

The product distribution in the presence of copper salts was assumed to be dependent on competition between steps (17) and (19).

The reported high yields of tetraphenylsuccinonitrile seem anomalous when considered in light of the reported experiments of Wittig and coworkers[56,57,58]. Basic solvents, according to these workers, catalyze the dissociation of the dimer to form an "isodinitrile"[56,57].



VI

VII

At 40°C in chloroform the dimer has a half-life of 270 min[58]. The observation that the diphenylcyanomethyl radical (VI) is unaffected by oxygen even at 100°C may prove pertinent in any

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[56] G. Wittig and W. Hopf, Ber., 65, 760 (1932).

[57] G. Wittig and H. Petri, Ann., 513, 26 (1934).

[58] G. Wittig and O. Pockels, Ber., 69, 790 (1936).

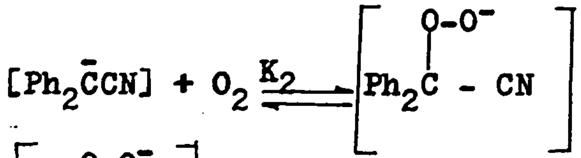
mechanistic arguments concerning this reaction. The intervention of the same radical in the formation of TPSN by reaction of diphenylacetonitrile with nitrate esters has been proposed by Emmons and Freeman[59]. These workers also note that air has no effect on the yield of TPSN.

A kinetic study of the autoxidation of diphenylacetonitrile has been reported by Garrett[60]. From the examination of the reaction products and the oxygen absorption data the reaction is pictured as

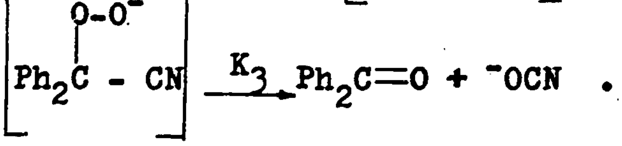
$$Ph_2CHCN + O_2 + NaOH \longrightarrow Ph_2C{=}O + NaOCN + H_2O\ .$$

No catalysis or inhibition could be demonstrated implying that the reaction is not of a free radical nature. The reaction mechanism postulated is

$$(21)\quad Ph_2CHCN + OH^- \xrightleftharpoons{K_1} [Ph_2\bar{C}CN] + H_2O$$

(22) 

$$(22)\quad [Ph_2\bar{C}CN] + O_2 \xrightleftharpoons{K_2} \left[Ph_2\overset{O-O^-}{\overset{|}{C}} - CN \right]$$

(23) 

$$(23)\quad \left[Ph_2\overset{O-O^-}{\overset{|}{C}} - CN \right] \xrightarrow{K_3} Ph_2C{=}O + {}^-OCN\ .$$

The reaction mechanism suffers the defect of the uniqueness

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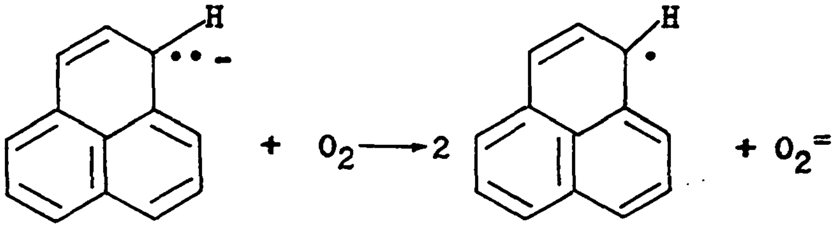
[59] W. D. Emmons and J. P. Freeman, J. Am. Chem. Soc., 77, 4416 (1955).

[60] B. R. Garrett, "The Autoxidation of Diphenylacetonitrile," unpublished Ph. D. thesis, Library, University of Delaware, Newark, Delaware, 1959.

of reaction (22). Although the combination of an anion with oxygen is not impossible, it is certain to be a complex and energetically unfavorable process since it implies the pairing the odd electrons of oxygen[61].

Oxidation of Aralkyl Hydrocarbons

The red perinaphthyl anion (VIII) reacts with oxygen rapidly and quantitatively to yield the blue perinaphthyl radical (IX)[62,63]. The reaction apparently proceeds via the electron transfer



VIII
red

IX
blue

The radical undergoes a slow further reaction with oxygen,

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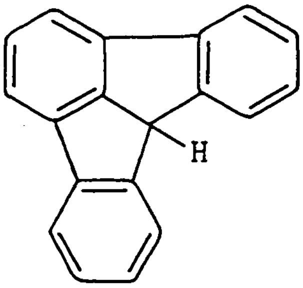
[61] L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, New York, 1960, p. 353, places the energy difference between the ${}^3\Sigma$ and ${}^1\Sigma$ states of oxygen at 37.8 k-cal/mole. (In this connection, see also G. Herzberg, "Spectra of Diatomic Molecules", 2nd ed., D. Van Nostrand Co., Inc., New York, 1950, p. 346.)

[62] D. H. Reid, Chem. Ind., 1956, 1504.

[63] V. Boekelheide and C. F. Larrabee, J. Am. Chem. Soc., 72, 1245 (1950).

yielding peropyrene and perinaphthenone[62]. The acidic hydrocarbon fluoradene (X)[64] apparently undergoes a similar electron transfer process in alkaline solution. However, in this case the radical instantaneously dimerizes, even in the presence of significant quantities of oxygen, forming a 12,12'-bifluoradenyl.



X

The recent report[65] of a hydrocarbon even more acidic than fluoradene, i.e., 1,5-bis-diphenylenepentadiene-(1,4) (XI) includes the observation that the anion is unstable to oxygen. Thus, the occurence of a one-electron transfer step from an anion to molecular oxygen would appear to be adequately demonstrated.

Other hydrocarbons, somewhat less acidic than those mentioned above, also undergo autoxidation in alkaline media. For example, di-__-naphthylfluorene, in acetone solution,

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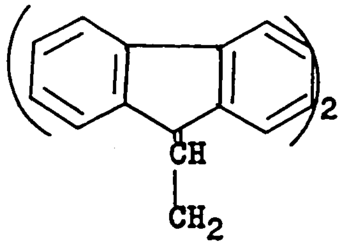
[64] H. Rapoport and G. Smolinsky, *ibid*., *82*, 934 (1960), report a pK_a' value of 11 ± 0.5 in water.

[65] R. Kuhn and H. Fischer, *Angew. Chem*., *73*, 435 (1961).



XI

when treated with methanolic potassium hydroxide, absorbs oxygen readily and yields 85-90% of di-α-naphthofluorenone[66]. The reaction is apparently of sufficient generality to serve as the basis of a color test for the fluorene type structure[67].

Sprinzak[68] has reported on the "ionic autoxidation" of fluorene and several of its derivatives. He demonstrated that solutions of fluorenes in pyridine in the presence of a small amount of Triton B absorb oxygen rapidly to form fluorenones in excellent yield. The insensitivity of the reaction to various additives (catalysts and inhibitors) and the lack of any induction period, even in the dark, led Sprinzak to propose an ionic mechanism. In the case of 9-alkyl substituted fluorenes the products of oxidation

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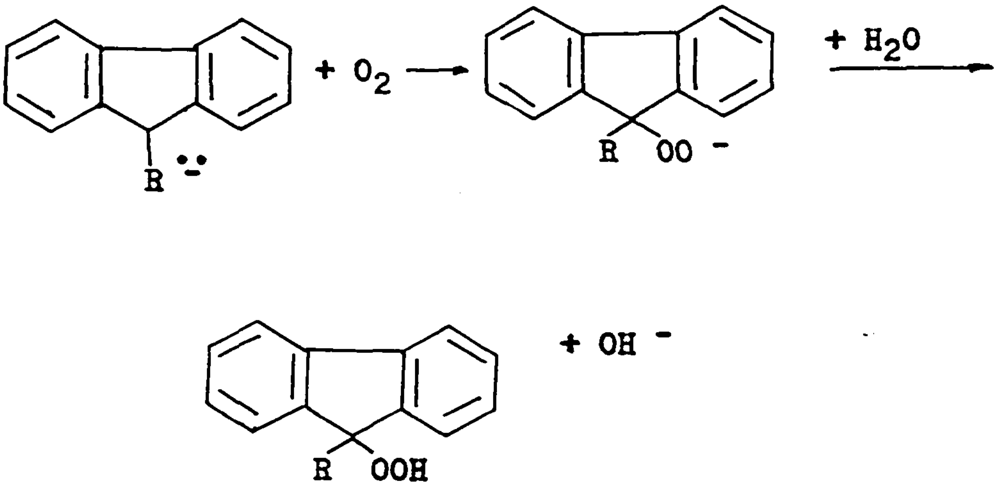
[66] A. Wanscheidt, Ber., 59, 2092 (1926).

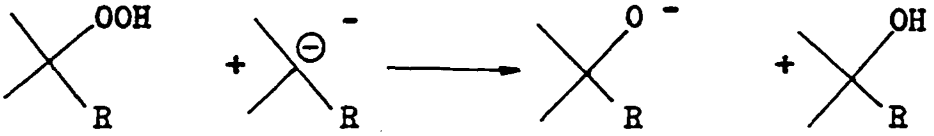
[67] A. A. Vansheidt, J. Gen. Chem. (U. S. S. R.), 4, 875 (1934); [Original not available for examination, abstracted in C. A., 29, 2160 (1935).]

[68] Y. Sprinzak, J. Am. Chem. Soc., 80, 5449 (1958).

(24)



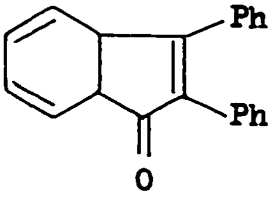
(25)



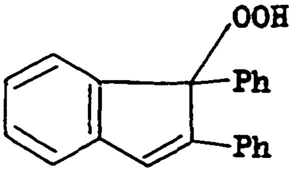
consist of a mixture of the corresponding fluorenol and the hydroperoxide. Quantitative conversion to hydroperoxide occurred at low reaction temperatures (-15°) or by gradual addition of the hydrocarbon to the pyridine Triton B mixture. In the case of fluorene, no hydroperoxide could be detected even at -40°. Presumably, decomposition to fluorenone is rapid even at low temperatures.

Although indene undergoes destructive oxidation under these conditions, the substituted 2,3-diphenylindene yields a 50:50 mixture of 2,3-diphenylindone (XII) and 1-hydroperoxy-1,2-diphenylindene (XIII) upon oxidation at -40°. At room temperature, XII was again formed along with 1-hydroxy-1,2-diphenylindene and the epoxide of 2,3-diphenylindone (XIV).

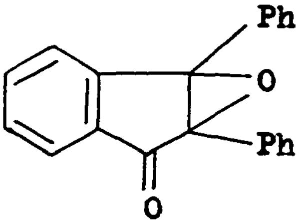
Methylene and hydroxymethylene groups adjacent to



XII



XIII



XIV

aromatic rings have been converted to carbonyl groups by passing air through a mixture of the powdered compound and ordinary or sodium methoxide treated alumina[69]. The fact that these reactions appear to take place on the solid phase may be of special importance.

In addition to these autoxidative processes, the phenomena of oxidative dehydrogenation occurs readily in alkaline media with specifically constructed molecules. We have previously noted the formation of stilbene derivatives from bibenzyls (vide supra). Vansheidt[70] has observed the

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[69] E. F. Pratt and L. E. Trapasso, ibid., 82, 6405 (1960).

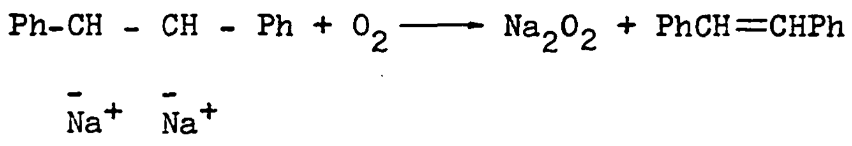
[70] A. A. Vansheidt, J. Russ. Phys. Chem. Soc., 58, 39, 249 (1926); [Original not available for examination, abstracted in C. A., 21, 581, 3616 (1927).]

facile dehydrogenation of bifluorenyls in alkaline solutions to form di-biphenylene-ethene derivatives and has suggested the scheme

(26) $Ar_2CH\text{-}CHAr_2 + 2\ KOH \rightleftharpoons Ar_2CK - CKAr_2 + 2\ H_2O$

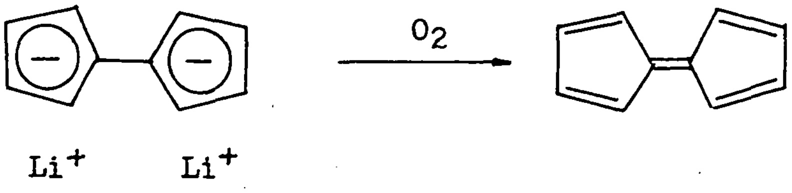
(27) $Ar_2CK\text{-}CKAr_2 + O_2 \longrightarrow Ar_2C{=}CAr_2 + K_2O_2$

This scheme finds ready analogy in the oxidation of the di-sodium adduct of stilbene as reported by Schlenk, et al.[71],

(28) 

$$\underset{\bar{}\ Na^+}{Ph\text{-}CH} - \underset{\bar{}\ Na^+}{CH} - Ph + O_2 \longrightarrow Na_2O_2 + PhCH{=}CHPh$$

Recently, Doering[72] has utilized the oxidation of the di-lithium salt of dicyclopentyl (XV) to prepare the interesting hydrocarbon fulvalene (XVI).



XV XVI

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[71] W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, Ber., 47, 473 (1914).

[72] W. von E. Doering, "Tropylium and Related Molecules", in International Union of Pure and Applied Chemistry, "Theoretical Organic Chemistry", pp. 35-48, Butterworth's Scientific Publications, London, 1959, p. 46.

Oxidation of Phenols

The oxidation of phenols or phenolate anions by one electron transfer oxidizing agents affords phenoxy ("aroxyl") radicals[73]. The existence of these free radicals was apparently first suggested by Pummerer and Frankfurter[74]. The recent isolation of a stable phenoxy radical (2,4,6-tri-t-butylphenoxy) in the solid state has served as a resounding confirmation of this early suggestion[75,76].

In general, simple phenols are relatively stable toward oxygen and are only slowly converted to colored products in alkali[77]. A study of the oxidation products shows that oxidative condensations as well as degradations occur. For example, the oxidation of 2,6-di-t-butyl-4-methylphenol (DTBC) yields 3,5,3',5'-tetra-t-butyl-4,4'-dihydroxy-1,2-diphenylethane and 3,5,3',5'-tetra-t-butylstilbene-4,4'-quinone as alkali insoluble products. Campbell and

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[73] H. Erdtmann and C. A. Wachmeister, "Phenoldehydrogenation as a Biosynthetic Reaction", in "Festschrift Arthur Stoll", pp. 144-165, Birkhauser, Basel (Switzerland), 1957.

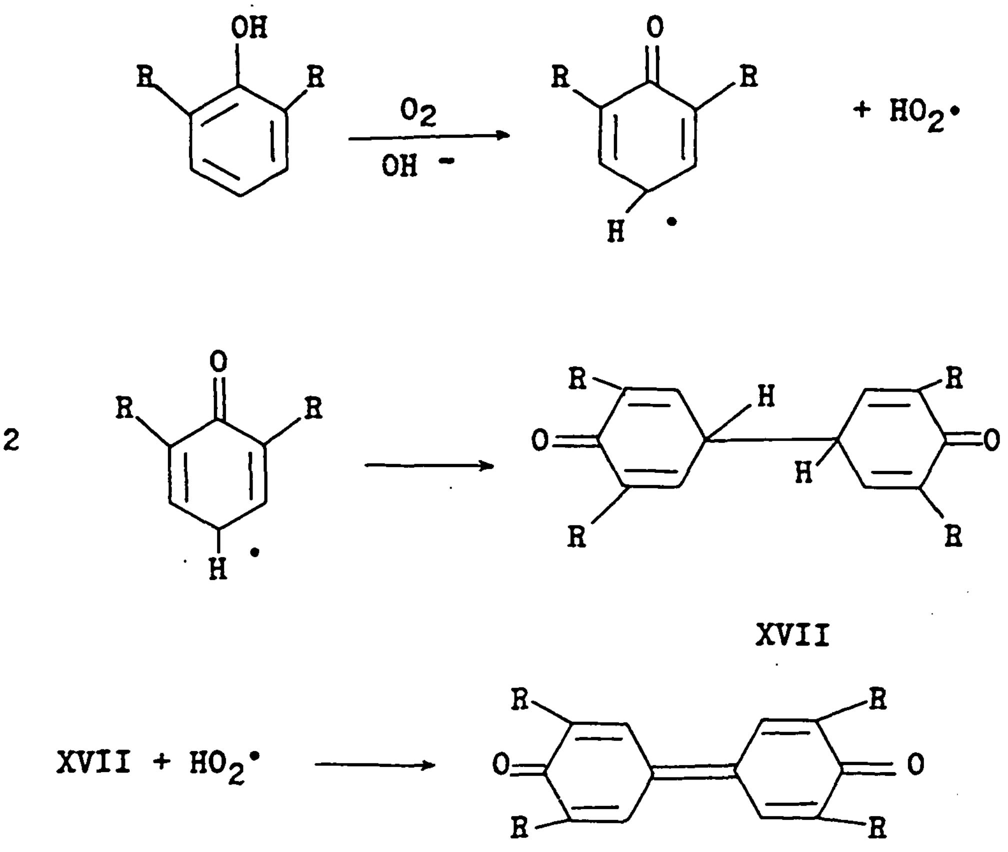
[74] R. Pummerer and E. Frankfurter, Ber., 47, 1472 (1914); ibid., 52, 1416 (1919).

[75] C. D. Cook, J. Org. Chem., 18, 261 (1953); C. D. Cook and R. C. Woodworth, J. Am. Chem. Soc., 75, 6242 (1953).

[76] E. Müller and K. Ley, Z. Naturforsch., 8b, 694 (1953); Chem. Ber., 87, 922 (1954).

[77] G. R. Yohe, D. R. Hill, J. E. Dunbar, and F. M. Scheidt, J. Am. Chem. Soc., 75, 2688 (1953).

Coppinger[78] have reported that 2,6-di-*t*-butylphenol is autoxidized in hot alkaline alcoholic solution (100°) forming 3,5,3',5'-tetra-*t*-butyldiphenoquinone (XIX) and hydrogen peroxide (85%). The intermediacy of a phenoxy radical was suggested.



XVII

XVIII

R = *t*-butyl

Kharasch and Joshi[79] have reaffirmed these results under

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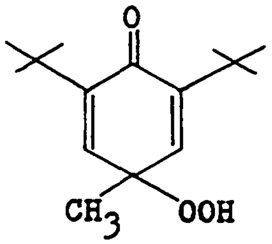
[78] T. W. Campbell and G. M. Coppinger, *ibid.*, *74*, 1439 (1952).

[79] M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, *22*, 1439 (1957).

relatively mild conditions (1 atmosphere oxygen at 40°). The legitimacy of the proposed reaction scheme received great support when these workers succeeded in isolating a substance corresponding to XVII by carrying out the oxidation with alkaline ferricyanide in the absence of oxygen.

Under these milder conditions DTBC absorbed one mole of oxygen yielding XIX (2,6-di-t-butyl-4-methyl-4-hydroperoxy-cyclohexa-3,5-dienone).



XIX

The alkaline autoxidation of 3,5,3',5'-tetra-t-butyl-4,4'-dihydroxydiphenylmethane (XX) is a dehydrogenation forming small amounts of the quinone methide (XXI). At higher temperatures (100°) and with extended contact times a complex spectrum of products have been isolated by Yohe and co-workers[77,80,81] in the alkaline oxidation of DTBC

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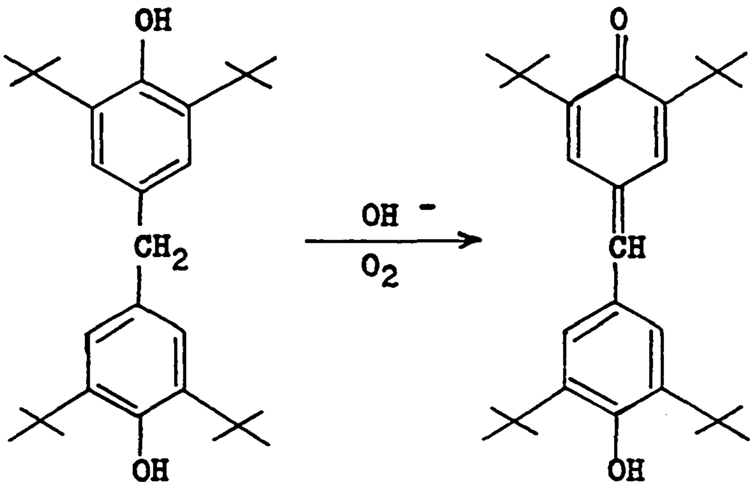
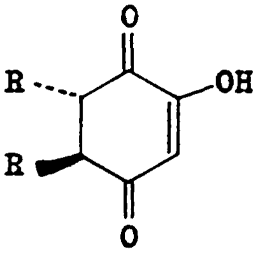
[80] G. R. Yohe, J. E. Dunbar, P. L. Pedrotti, F. M. Scheidt, F. G. H. Lee, and E. C. Smith, J. Org. Chem., 21, 1289 (1956).

[81] G. R. Yohe, J. E. Dunbar, M. W. Lansford, R. L. Pedrotti, F. M. Scheidt, F. G. H. Lee, and E. C. Smith, ibid., 24, 1251 (1959).



XX XXI

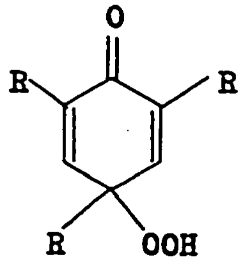
with molecular oxygen. In addition to the previously reported dimers (vide supra), pivalic acid was detected along with a $C_{14}H_{22}O_3$ acidic compound. The same compound was obtained by alkaline autoxidation of 3,5-di-t-butyl-4-hydroxybenzalehyde and from 3,5-di-t-butyl-4-hydroxybenzoic acid. The identity of this acid fraction has been ascertained as DL-trans-5,6-di-t-butyl-2-hydroxy-1,4-diketo-2-cyclohexene (XXII)[81].



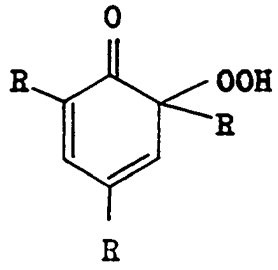
R = t-butyl

XXII

The highly hindered 2,4,6-tri-t-butylphenol undergoes alkaline autoxidation to a mixture of the ortho and the para cyclohexadienone hydroperoxides XXIII and XXIV[82].



XXIII



XXIV

R = t-butyl

In a kinetic study of the reaction it was found that the formation of hydroperoxides appeared to be autocatalytic, the catalyst being a decomposition product of 2,4,6-trialkyl-2-hydroperoxy-3,5-dienone (XXIV)[83]. The oxidation may also be catalyzed by quinones and aromatic polynitrocompounds. Since the addition of 9,10-dihydroanthracene, 2,4,6-tri-t-butylphenoxyl, or azo-bis-isobutyronitrile was without noticeable effect the reaction was assumed to be non-free radical. However, the catalytic effect of metal ions was noted.

To explain the observed catalytic effect of m-

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[82] A. F. Bickel and H. R. Gersmann, Proc. Chem. Soc., 1957, 231.

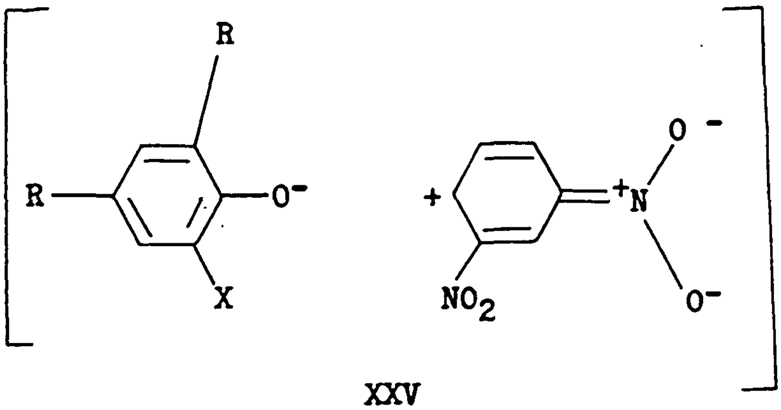
[83] H. R. Gersmann and A. F. Bickel, J. Chem. Soc., 1959, 2711.

dinitrobenzene (oxidation rate first order in phenol, dependent upon catalyst concentration, and independent of oxygen pressure) the following mechanism was suggested[83].

(29) $R:^- + \text{Catalyst} \rightleftharpoons (R, \text{Catalyst})^-$

(30) $(R, \text{Catalyst})^- + O_2 \longrightarrow RO_2:^- + \text{Catalyst}$

The reactive intermediate could be an electron donor-acceptor complex of structure XXV. In such a complex the phenol part of the molecule may develop free radical character, permitting rapid reaction with oxygen[83].



XXV

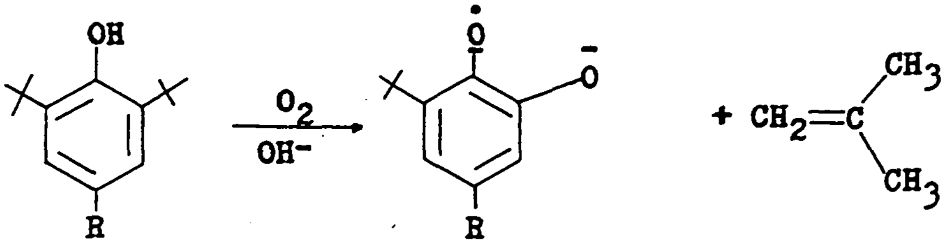
In the case of catalysis by quinones, the rate was found to be independent of catalyst concentration (from 5% onward) and proportional to the oxygen pressure. The experimental results were rationalized by the unique suggestion of an oxygen-anion complex that subsequently decomposes by interaction with the catalyst.

(31) $R:^- + O_2 \rightleftharpoons (R^-, O_2)$

(32) (R^-, O_2) + Catalyst $\longrightarrow$ $RO_2:^-$ + Catalyst

Among the unusual properties of the hydroperoxides XXIII and XXIV Gersmann and Bickel noted the interconversion of the 2- and the 4- isomers under the conditions of the reaction. For example, after two hours at 40° in the presence of oxygen, a solution of 2,4,6-tri-t-butyl-4 hydroperoxycyclohexadienone-1,3 yielded 19.5% of the 2-isomer and 30.5% of the 4-isomer, i.e., a ratio of 39/61. Under the same conditions the 2-isomer yielded a mixture of isomers in the ratio 42/58.

The suggestion that some sort of decomposition product of XXIV is responsible for the observed autocatalysis has received renewed support. Conradi and McLaren[84] have been able to detect intermediates formulated as XXVI on the basis of EPR measurements.



XXVI

Similar ortho semiquinones have been prepared by Ley and Müller[85]. The reduction of 2,4-di-t-butyl-1,2-benzoquinone

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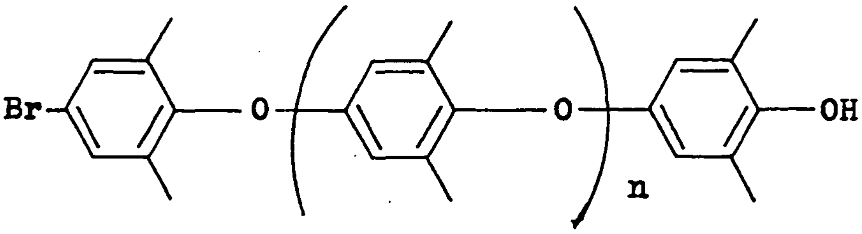
[84] J. J. Conradi and G. A. McLaren, *J. Am. Chem. Soc.*, *82*, 4745 (1960).

[85] K. Ley and E. Müller, *Angew. Chem.*, *30*, 469 (1958).

with lithium, sodium, or potassium. The sodium salt of DTBC yielded XXIII upon exposure to oxygen in ether. The product was accompanied by varying amounts of the corresponding carbinol[86].

Electron paramagnetic resonance studies of the oxidation of phenols have provided evidence for the presence of free radical intermediates[87,88,89]. However, the transient nature of many of these intermediates makes positive identification an extremely difficult task.

The preparation of polyethers (XXVII) via oxidation of halogen substituted phenolate ions has been recently described by Staffin and Price[90].



Poly-(2,6-dimethyl-1,4-phenylene oxide)

XXVII

Although chemical oxidizing agents are ordinarily preferred,

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[86] K. Ley, *ibid.*, *70*, 74 (1958).

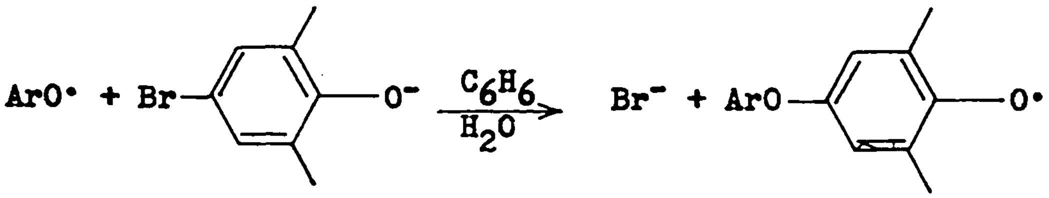
[87] J. K. Becconsall, S. Clough, and G. Scott, *Proc. Chem. Soc.*, *1959*, 308.

[88] A. Fairbourn and E. A. C. Lucken, *ibid.*, *1960*, 67.

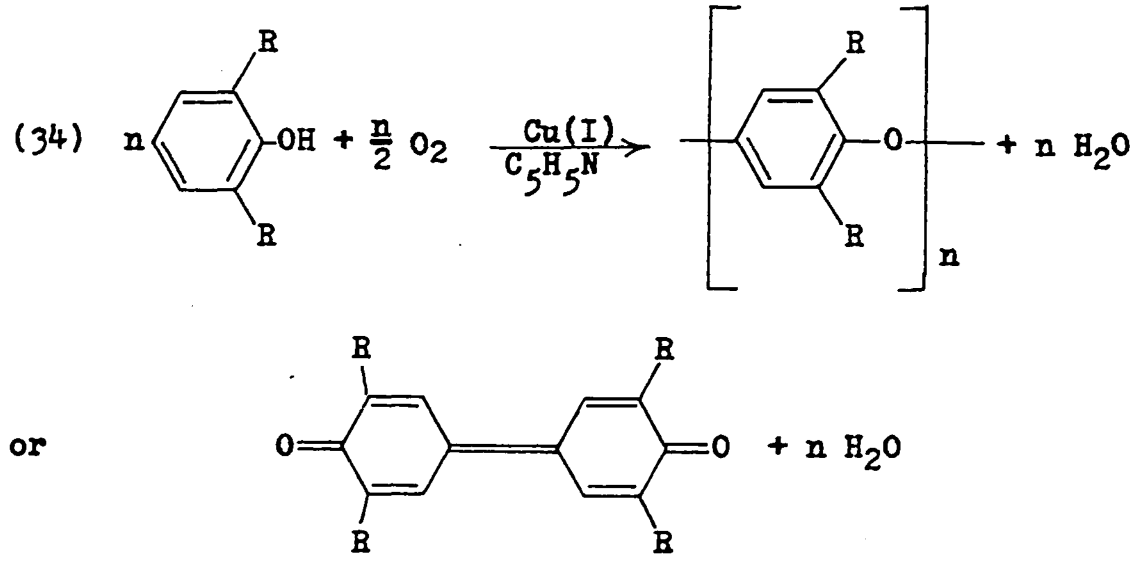
[89] J. E. Bennett, *Nature*, *186*, 385 (1960).

[90] G. D. Staffin and C. C. Price, *J. Am. Chem. Soc.*, *82*, 3632 (1960).

the reaction will take place through the agency of molecular oxygen. A key step in the polymerization process involves the displacement of bromide ion by an aroxyl radical.

(33)


Oxidative coupling of phenols to form polymeric materials also takes place in the presence of copper-amine catalysts[91].

(34)


R = CH_3, C-O coupling

R = t-Bu, C-C coupling

R = i-Pr, both

Brackman and Havinga have described the oxidation of a whole

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[91] A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, ibid., 81, 6335 (1960).

series of phenols catalyzed by copper-amine systems, as a model for the enzyme tyrosinase[92]. A comparable oxidation of aromatic amines such as aniline occurs under similar conditions (Cu(I) and pyridine)[93].

The absorption of oxygen by polyhydric phenols and its catalysis by metal ions, by alkali, and by various oxidases has been known for a long time[94]. The brown-colored compounds that result from these oxidations are known as humic acids and appear to be polymerized oxyquinones $(C_6H_4O_3)_x$[95,96]. The reported formation of hydroxyquinone (XXVIII) by reaction of quinone with hydrogen peroxide[97] and its isolation from the autoxidation of hydroquinone in sodium bicarbonate solution[98] tend to support this formulation. In a recent discussion of the constitution of humic acids,

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[92] W. Brackman and E. Havinga, <u>Rec. trav. chim.</u>, <u>74</u>, 937, 1021, 1070, 1100, 1107 (1955).

[93] A. P. Terentev and Y. D. Mogilyanskii, <u>Doklady Akad. Nauk S.S.S.R.</u>, <u>103</u>, 91 (1955).

[94] For a complete listing of the numerous early references see, for example, "Beilstein's Handbuch der Organischen Chemie", Bd. VI, Vierte Auflage, Springer, Berlin, 1923, pp. 838-841.

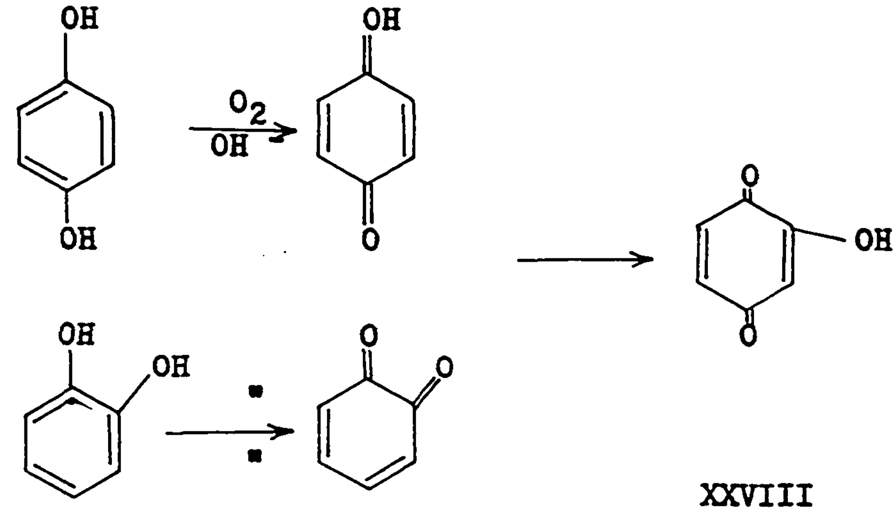
[95] W. Eller, <u>Brennstoffchem.</u>, <u>2</u>, 129 (1921); <u>ibid.</u>, <u>3</u>, 49 (1922); <u>Ann.</u>, <u>431</u>, 133, 162, 177 (1923).

[96] W. Eller and K. Koch, <u>Ber.</u>, <u>53</u>, 1469 (1920).

[97] W. Reinders and P. Dingemans, <u>Rec. trav. chim.</u>, <u>53</u>, 209, 231 (1934).

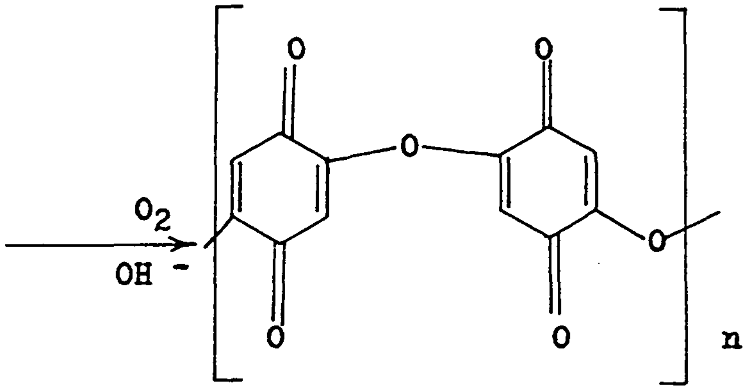
[98] W. Flaig and J. C. Salfeld, <u>Naturwiss.</u>, <u>47</u>, 516 (1960).

Flaig[99] has suggested a possible structure (XXIX).



XXVIII

XXVIII



XXIX

The overall primary reaction process was apparently suggested by Manchot[100] in 1901.

$$(35)\quad C_6H_4\,(OH)_2 + O_2 \xrightarrow{OH^-} C_6H_4O_2 + H_2O_2$$

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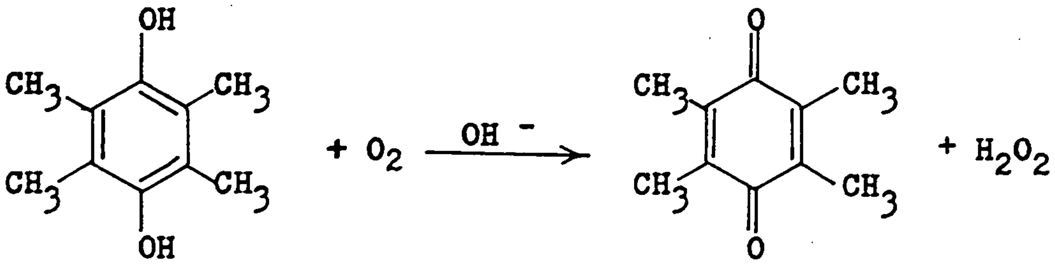
[99] W. Flaig, Z. Pflanzenernähr. Düngung Bodenkunde, 51, 193 (1950); [Original not available for examination, abstracted in C. A., 45, 10214 (1951).]

[100] W. Manchot, Ann., 314, 177 (1901).

Anthrahydroquinone was autoxidized to form equal amounts of the stable anthraquinone and hydrogen peroxide. The presence of hydrogen peroxide was subsequently also ascertained in other similar oxidations.

The kinetics of the reaction have been studied under a variety of conditions[101] but a detailed analysis of the reaction pathway has proved to be difficult, presumably because of further reactions of the initially formed quinone[102]. As an approach to a solution of this problem, James and Weissberger[103] selected durohydroquinone as the best model of the reaction. The products are quantitatively the stable duroquinone and hydrogen peroxide. The initial rate of the reaction follows the law

(36)



$$(36) \quad -d\,(O_2)\,/\,dt = k\,(O_2)\,(DHQ)\,(OH^-)^2$$

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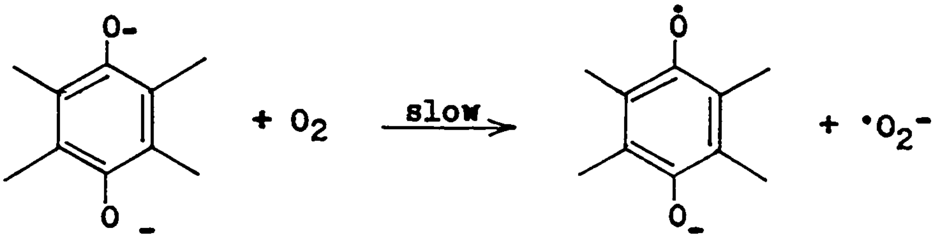
[101] V. K. LaMer and E. K. Rideal, J. Am. Chem. Soc., 46, 223 (1924); R. Dubrisay and A. Saint-Maxen, Compt. rend., 189, 694 (1929); J. R. Green and G. E. K. Branch, J. Am. Chem. Soc., 63, 3441 (1941).

[102] G. Kornfeld and A. Weissberger, ibid., 61, 360 (1939).

[103] T. H. James and A. H. Weissberger, ibid., 60, 98 (1938).

suggesting a direct reaction between oxygen and the durohydroquinone dianion. The reaction is autocatalytic (accelerated by duroquinone). The rate of the duroquinone-catalyzed process is independent of oxygen pressure. The scheme proposed to account for these observations is

(37)



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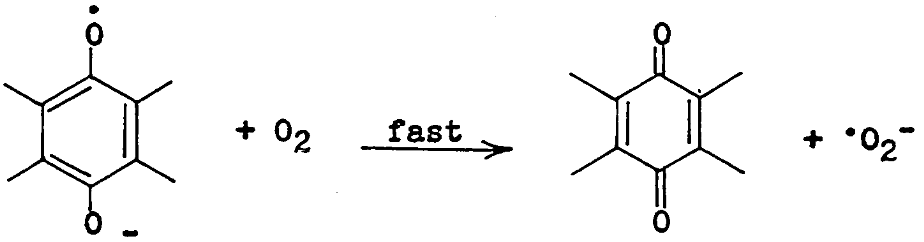

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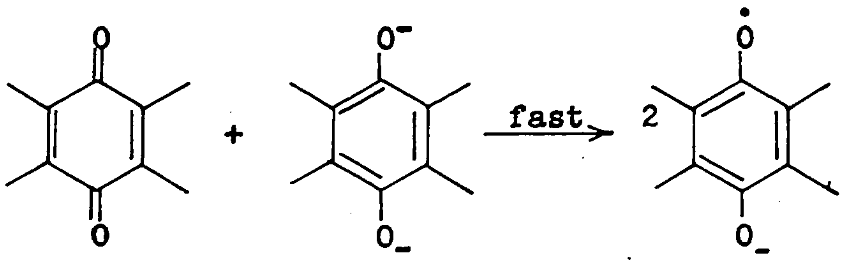

The autocatalysis occurs by virtue of reaction (39), wherein the semiquinone is generated. Since the reaction between oxygen and the dianion is slow, this semiquinone-forming process rapidly becomes rate determining (oxygen independent). The peroxy radical ions ("perhydroxyl" radicals) presumably react rapidly with any oxidizable species in the system to give H_2O_2.

With decreasing methyl substitution the kinetics become more complicated and extremely difficult to interpret[104,105]. Decreasing reaction rates make quinone catalysis hard to detect. This "saturation of catalysis" takes place very early in the reaction. Lu Valle and Weissberger[106] have derived a number of rate laws for the oxidation of compounds that form semiquinones as intermediates. On this basis a classification of the various reaction paths, along with their modifications, have been achieved. The mechanisms of these autoxidation reactions in the presence of foreign catalysts and inhibitors have also been discussed[107].

The autoxidation of catechol in the pH range from 6.5 to 10 was investigated by Joslyn and Branch[108]. The rate is first-order with respect to the reciprocal of the hydrogen ion concentration. The rate law is

$$(40)\quad -d(O_2)/dt \propto (\mathrm{Cat}^-)\,(O_2) \times \frac{C}{(C + A)}$$

where (Cat^-) is the concentration of the univalent catechol

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[104] T. H. James, J. M. Snell, and A. Weissberger, ibid., 60, 2084 (1938).

[105] J. E. Lu Valle and A. Weissberger, ibid., 69, 1576 (1947).

[106] J. E. Lu Valle and A. Weissberger, ibid., 69, 1567 (1947).

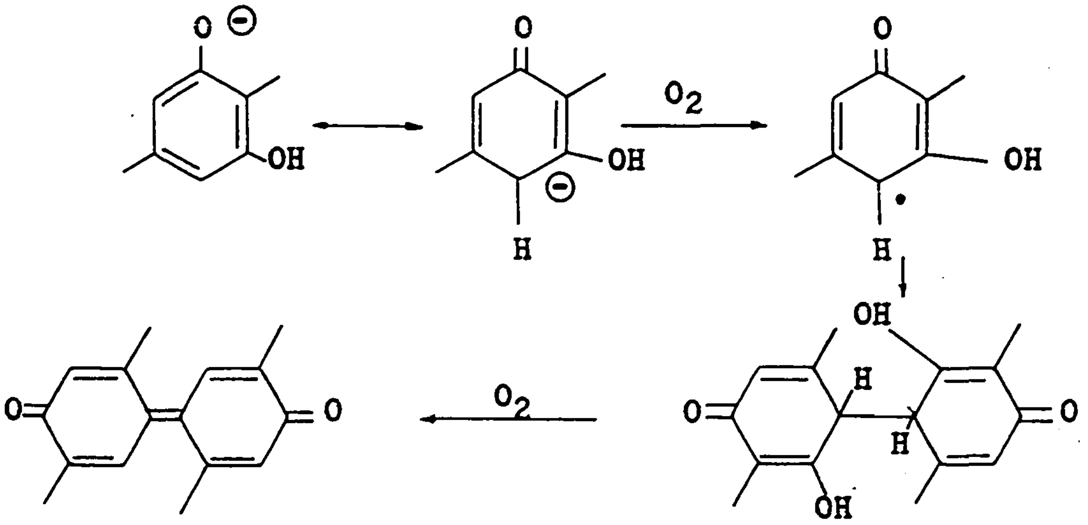
[107] J. E. Lu Valle and A. Weissberger, ibid., 69, 1821 (1947).

[108] M. A. Joslyn and G. E. K. Branch, ibid., 57, 1779 (1935).

ion, C is the total concentration of catechol, and A is a constant equal to 0.02. Above pH 10 the reaction rates are high due to oxidation of the divalent catechol anion.

The oxidation of phenanthrene-hydroquinone to phenanthroquinone has been noted[100,109]. The detection of an intermediate step ($HO_2\cdot$) in the alkaline autoxidation of hydroquinones has also been reported[110].

The autoxidation of orcinol (3,5-dihydroxytoluene) in the presence of alkali yields a product that, upon reduction, exhibits the properties of a pentahydroxy-ditolyl[111]. The formation of an analogous dimeric product from p-xylorcinol has evoked the following scheme as a rationalization[112].



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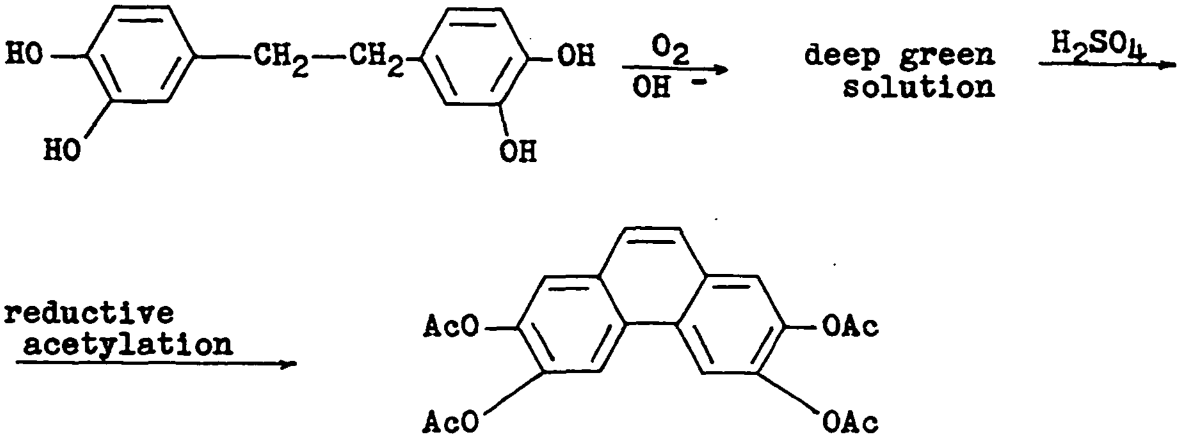
[109] A. Schonberg and R. Moubacher, J. Chem. Soc., 1939, 1430.

[110] T. H. James, J. Chem. Phys., 11, 183 (1943).

[111] F. Henrich, W. Schmidt, and F. Rossteutscher, Ber., 48, 483 (1915).

[112] F. Henrich, ibid., 71, 2049 (1938).

The formation of phenanthrene derivatives by alkaline oxidation of hydroxy bibenzyls probably takes place through a similar coupling mechanism[113].



The oxidation of resorcinol leads to 2,2'-dihydroxydiphenoquinone[114].

The reaction of pyrogallol with oxygen in alkaline solution has led to its extensive use as a scavenger for oxygen gas in solutions. The nature of this oxidation, however, is not amenable to careful investigation, since the primary product is a black, intractable tar. In several instances carbon monoxide has also been detected[115].

Harries[116] obtained the hexahydroxybiphenyl (XXX) by carrying out the oxidation under mild conditions in the

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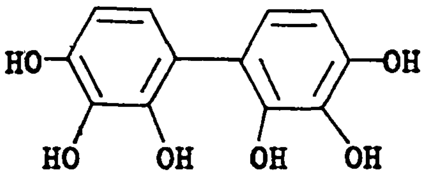
[113] H. Erdtmann, Ann., 505, 195 (1933).

[114] F. Henrich, Sitzber. physik.-med. Sozietat Erlangen, 71, 199 (1939); [Original not available for examination, abstracted in C. A., 35, 3997 (1941).]

[115] "Beilstein's Handbuch", op. cit., pp. 1071.

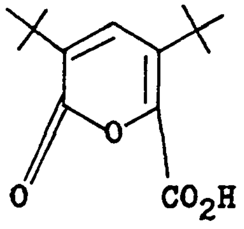
[116] C. Harries, Ber., 35, 2954 (1902).

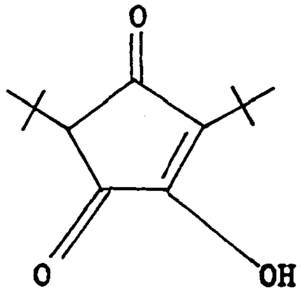
presence of barium hydroxide.

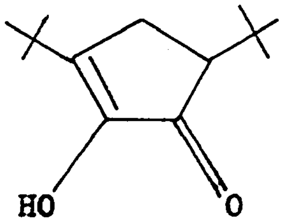


XXX

Using the conditions prescribed by Harries, Erdtmann[117] isolated a similar dimer from 4-ethyl-pyrogallol. However, 4,6-diethyl-pyrogallol led only to unidentified resins. The air oxidation of 4,6-t-butyl-pyrogallol gives an intensely purple intermediate and the following stable products[118]:







Purpurogallin (XXXI), a brick red solid, yields the substituted tropolone (XXXII) after prolonged (20 hr.) treatment with potassium hydroxide in the presence of air[119].

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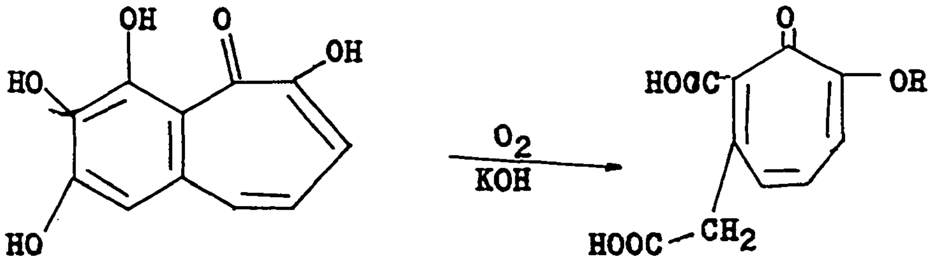
[117] H. Erdtmann, Ann., 513, 240 (1934).

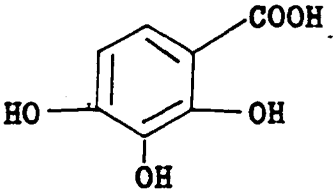
[118] T. W. Campbell, J. Am. Chem. Soc., 73, 4190 (1951). See however, H. Schulze and W. Flaig, Ann., 575, 231 (1952).

[119] R. D. Haworth, B. P. Moore, and P. L. Pauson, J. Chem. Soc., 1948, 1045.



XXXI XXXII

Dean and Nierenstein[120] have formulated this product as XXXIII,



XXXIII

however, the authenticity of their results is in doubt[121].

The application of electron paramagnetic resonance techniques to the study of the radical intermediates encountered in these oxidations has been summarized[122].

The autoxidation of alkyl substituted hydroquinones has been developed as a technical process for the manufacture of

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[120] H. F. Dean and M. Nierenstein, Ber., 46, 3868 (1913).

[121] J. A. Barltrop and J. S. Nicholson, J. Chem. Soc., 1948, 116.

[122] D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance", Butterworths Scientific Publications, London, 1958, Chapter 5. See also J. E. Wertz, Chem. Rev., 55, 921 (1955).

hydrogen peroxide[123]. The production of hydrogen peroxide in the oxidation of 2-ethylanthrahydroquinone has been studied by the use of deuterium isotopes[124].

Oxidation of Alcohols

The autoxidation behavior of hydroxy compounds has been studied under a variety of conditions. The platinum catalyzed oxidation proceeds under extremely mild conditions yielding ketones, aldehydes, or carboxylic acids depending on the nature of the alcohol[125]. Photosensitized autoxidation of several aliphatic alcohols has been reported to lead mainly to hydroxy-hydroperoxides along with hydroperoxy-peroxides[126]. Even so, under normal conditions, i.e., in the absence of catalysts or other sensitizers, alcohols are considered to be stable toward autoxidation.

The oxidative behavior of the alkali metal alcoholates is in marked contrast to the parent alcohols. As early as

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[123] W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, "Hydrogen Peroxide", Reinhold Publishing Corp., New York, 1955.

[124] A. I. Brodskii, V. I. Franchuk, M. M. Aleksankin, and V. A. Lunenok-Burmakina, Doklady Akad. Nauk S. S. S. R., **123**, 117 (1958).

[125] For a current assessment of this old reaction see K. Heyns and L. Blazejewicz, Tetrahedron, **9**, 67 (1960).

[126] G. O. Schenck and H. D. Becker, Angew. Chem., **70**, 504 (1958).

1891, Hemmelmayr reported that the sodium salts of methanol, ethanol, and amyl alcohol were labile to oxygen forming carboxylic acids and carbon-dioxide[127]. In his investigations concerning the nature and occurence of divalent carbon species Nef has confirmed and extended these results noting that sodium ethoxide burns "with considerable violence" in air or oxygen[128]. Sodium benzhydrolate reacts with oxygen to form benzophenone and a peroxidic solid formulated as Na_2O_2, the latter in 22% yield[129]. In the solid state oxidation takes place to form small amounts of benzoic acid along with the ketone and peroxide. More recently, Etienne and Fellion[130] have shown that while 9,9-diphenyl-9,10-dihydro-10-anthranol, 9-fluorenol, and benzhydrol are stable to oxygen in dry benzene solution, the addition of sodium or potassium causes the rapid absorption of oxygen. The corresponding ketones are formed in almost quantitative yield. The other product was presumably sodium peroxide (Na_2O_2). The reaction was postulated to proceed via a completely ionic process, the disodium complexes of ketones being key intermediates. Cornubert and Kondrachoff[131] have explained the observed isomerization

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[127] F. Hemmelmayr, Monats., 12, 151 (1891).

[128] J. U. Nef, Ann., 318, 177 (1901).

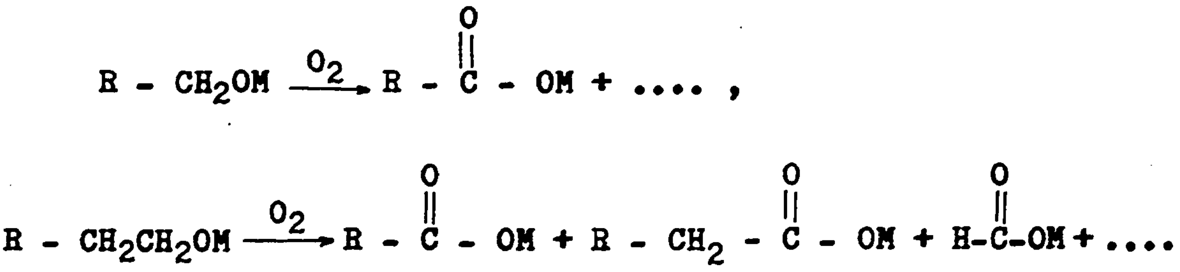
[129] R. F. Bacon, Am. Chem. J., 33, 68 (1905)

[130] A. Etienne and Y. Fellion, Compt. rend., 238, 1429 (1954).

[131] R. Cornubert and W. Kondrachoff, ibid., 245, 1362 (1954).

of axial to equatorial cyclohexanol in the presence of sodium and fluorenol-fluorenone as being due to the intervention of oxygen. Further studies[132] have confirmed and extended this thesis. The conversion of hydroxymethylene groups adjacent to aromatic rings in the presence of sodium methoxide treated alumina has been reported[69].

Etienne and Le Berre[133] have recently reassessed the problem of the autoxidation of alkali metal alcoholates from a more quantitative point of view. In general, aromatic alcohols react more rapidly than aliphatic, and, other things being equal, secondary more rapidly than primary. The organic reaction products resulting from the oxidation of primary alcohols are principally carboxylic acids accompanied by traces of aldehydes according to the overall reactions



$$R - CH_2OM \xrightarrow{O_2} R - \overset{\overset{O}{\|}}{C} - OM + \dots\dots ,$$

$$R - CH_2CH_2OM \xrightarrow{O_2} R - \overset{\overset{O}{\|}}{C} - OM + R - CH_2 - \overset{\overset{O}{\|}}{C} - OM + H\text{-}\overset{\overset{O}{\|}}{C}\text{-}OM + \dots\dots$$

Secondary alcohols absorb approximately one mole of oxygen and furnish the corresponding ketones and the hydroperoxide of the alkali metal utilized.

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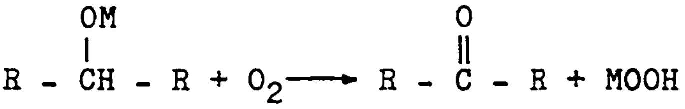
[132] B. Alexandre, R. Cornubert, Y. Fagnoni, and W. Kondrachoff, Bull. soc. chim. France, 1961, 661, 1332.

[133] A. Etienne and L. Le Berre, Compt. rend., 252, 1166 (1961).



$$R-\underset{}{\overset{\overset{\displaystyle OM}{|}}{C}H}-R+O_2\longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-R+MOOH$$

In spite of arguments to the contrary[134], the exact nature of the initial inorganic peroxide remains largely a mystery.

In a more complete presentation of his results, Le Berre[135] points out that the reaction rate seems to depend upon the quantity of base present, the structure of the alcohol, the nature of the alkali metal, and the presence or absence of free alcohol. Since the effect of additives on the reaction is inconclusive (sulfur compounds seem to inhibit reaction), Le Berre has hesitated to choose between a radical or an ionic pathway for the reaction. However, the appearance of a transient blue coloration when the oxygen supply of a previously autoxidizing solution of sodium benzhydrolate is interrupted, strongly suggests the intervention of ketyl (radical-ion) intermediates. This last view would seem to be in accord with recent EPR results wherein the metal ketyl of fluorenone has been detected in the autoxidation of fluorenol[136]. The preferred scheme, according to Le Berre, involves the following steps:

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[134] A. Le Berre, ibid., 252, 1341 (1961).

[135] A. Le Berre, Bull. soc. chim. France, 1961, 1198.

[136] G. A. Russell, Abstract of Papers, Seventeenth National Organic Chemistry Symposium, American Chemical Society, Bloomington, Indiana, June, 1961, Department of Chemistry, Iowa State University, Ames, Iowa, pp. 71-80.

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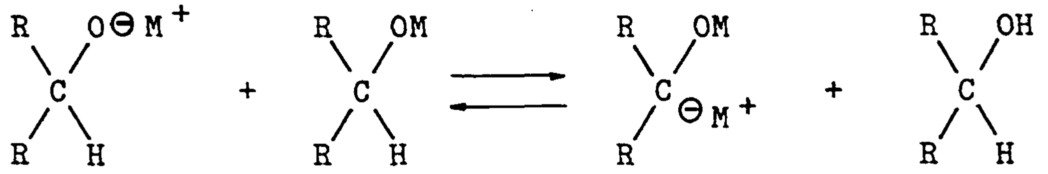

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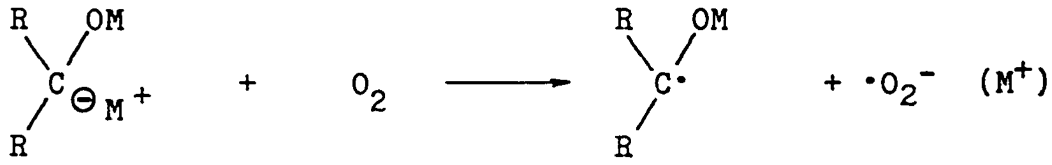

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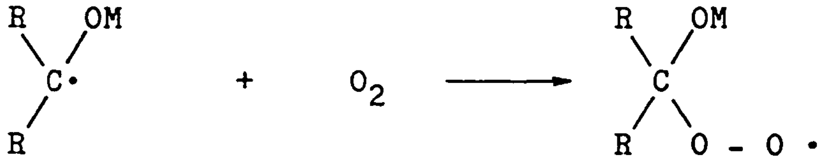

(44)


(45) $R_2\text{-C(OM)OOH} \longrightarrow R_2\text{-C(OM)OH} \longrightarrow R_2C{=}O \quad + \quad \text{MOOH}.$

Oxidation of Carbohydrates

The study of the action of molecular oxygen on alkaline solutions of simple sugars is of considerable chemical and biological interest from the standpoint of the mechanism of the in vivo oxidations of sugars. The reaction also has considerable value for the degradations of sugars to acids having shorter chains[137].

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[137] J. C. Sowden, "Occurrence, Properties and Synthesis of the Monosaccharides", in W. Pigman, ed., "The Carbohydrates", pp. 77-137, Academic Press, Inc., New York, N.Y., 1957, p. 122.

Although the alkaline autoxidation of simple sugars has been studied for half a century much of the work is of a semi-quantitative or preparative nature. Nef[138] demonstrated that the sugars are oxidized by air in alkaline solution with the formation of aldonic and other acids that have fewer carbons in the molecule. Other workers[139,140] obtained a number of additional products showing that extensive degradation and resin formation occurs. Nef proposed a theory of the formation of enediols to account for these phenomena. He postulated that the various enediols formed from the hexoses were split at the double bonds into fragments containing one to five carbon atoms. In the presence of oxidizing agents these fragments would yield a mixture of the corresponding acids[141].

Spengler and Pfannenstiel[142] found that yields could be increased and the reaction greatly simplified by the use of

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[138] J. U. Nef, Ann., 357, 294 (1907); ibid., 376, 1 (1910); ibid., 403, 204 (1914).

[139] J. W. Glattfield, Am. Chem. J., 50, 135 (1913).

[140] M. H. Powers and F. W. Upson, J. Am. Chem. Soc., 48, 195 (1926).

[141] A review of early developments of the progress of this theory can be found in W. L. Evans, Chem. Rev., 6, 281 (1929). Later modifications are summarized in W. L. Evans, ibid., 31, 537 (1942).

[142] O. Spengler and A. Pfannenstiel, Z. Wirtschaftsgruppe Zuckerind. Tech. Tl., 85, 546 (1935); [Original not available for examination, abstracted in C. A., 30, 4470 (1936).]

oxygen instead of air. For example, potassium D-arabonate has been obtained from D-glucose in yields of 60-75%. Ketoses react similarly, and in the case of L-sorbose, 2-keto-L-gulonic acid and L-xylonic acid are produced in good yield[143]. In addition to monosaccharides, the degradation has been applied successfully to the disaccharides cellobiose, maltose, and lactose[144]. The formation of tartaric acid in the reaction of 5-keto-D-gluconic acid with oxygen under alkaline conditions has been noted[145].

In addition to the work of Evans[141] a mechanism for the formation of saccharinic acids from glucose in modern terminology was given by Isbell[146].

The first quantitative kinetic experiments on the alkaline autoxidation of glucose are apparently due to Bamford and Collins[147]. These workers carried out a most elegant series of experiments with the object of developing a simple scheme relating the various degradation, interconver-

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[143] H. S. Isbell, J. Research Nat'l Bur. Standards, 29, 227 (1942).

[144] E. Hardegger, K. Kreis, and H. El Khadem, Helv. Chim. Acta, 35, 618 (1952).

[145] R. Pasternack and E. V. Brown, U. S. Patent 2,197,021 (Apr. 16, 1940); [Original not available for examination, abstracted in C. A., 34, 5468 (1940).]

[146] H. Isbell, J. Research Nat'l Bur. Standards, 32, 45 (1944).

[147] C. H. Bamford and J. R. Collins, Proc. Roy. Soc., A 204, 62 (1950).

sion, and autoxidation reactions of glucose in a quantitative manner. The overall stoichiometry observed was

$$(46)\quad C_6H_{12}O_6 + O_2 \xrightarrow{OH^-} CH_2OH\ (CHOH)_3\ COOH + HCOOH.$$

Arabonic and formic acids were formed in almost quantitative yield. The rate law observed was

$$(47)\quad \text{rate} = \frac{C\ (S_G)\ pO_2}{C' + pO_2}$$

where C depends on hydroxyl ion concentration and temperature, C' is nearly independent of alkali concentration, and S_G is the initial sugar concentration. The addition of benzoyl peroxide, sulfur, or hydroquinone had no noticeable effect on the reaction rate. Although cuprous, ferrous, and maganous ions were ineffective, cobaltous ions had a catalytic effect. This acceleration was explained as being due to the effect of cobalt on an initially formed peroxidic intermediate. A peroxidic intermediate was detected by the starch iodide test and its rate of formation was found equal to the rate of oxygen absorption (at (OH^-) greater than 1 M. On the basis of these results Bamford and Collins proposed the mechanism:

$$(48)\quad GH_2 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XH_2^- + H_2O$$

$$(49)\quad GH^- + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} XH^= + H_2O$$

(50) $XH_2^- + O_2 \xrightarrow{k_3} XH_2O_2^-$

(51) $XH^= + O_2 \xrightarrow{k_4} XHO_2^=$

(52) $XH_2O_2^- \xrightarrow{k_5}$ arabonic + formic acids

(53) $XHO_2^= \xrightarrow{k_6} P$

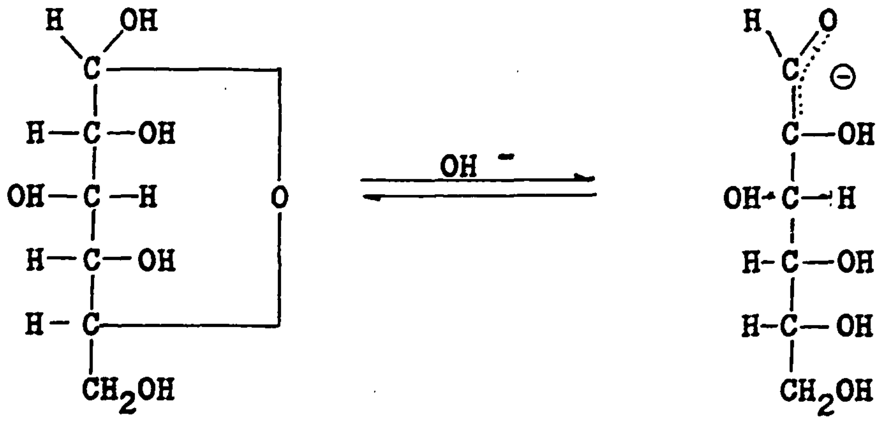
(54) $P \xrightarrow{k_7}$ arabonic and formic acids

At low base concentrations (less than 1 M) the reaction

(55) $XH_2^- + XH_2O_2^- \longrightarrow 2\ XH_2O^-$

is also important. Non-steady state experiments indicate that a plausible value for k_3 is 3.0×10^3 l/mole - sec. at 25°.

These intermediates may be pictured more clearly according to the following generalized scheme[148].



XXXV

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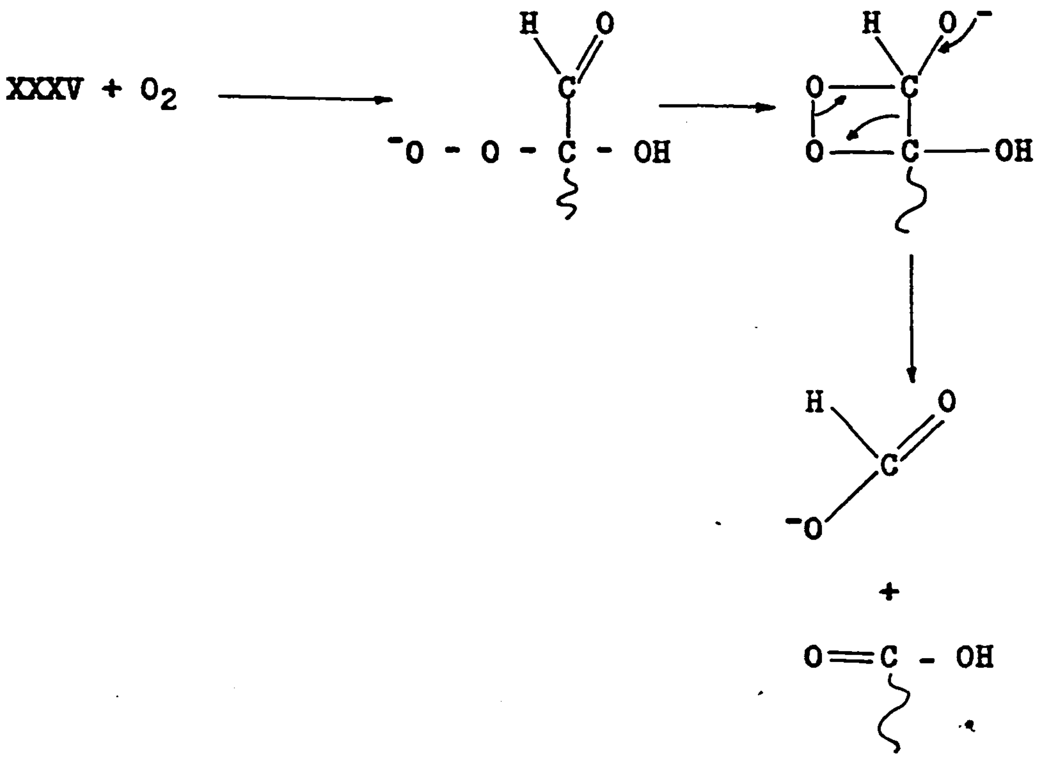
[148] C. H. Bamford, D. Bamford, and J. R. Collins, ibid., A 204, 85 (1950).



A quantitative study of the products from the action of potassium hydroxide and oxygen on glucose shows, in agreement with the previous reports, the main products to be D-arabonic and formic acid, with lactic, oxalic, and carbonic acids formed in minor amounts[149]. Recently, the best conditions for obtaining D-arabonic acid by alkaline oxidation of the hexoses D-glucose and D-fructose were summarized[150]. The acids formed after oxidation of D-glucose, D-fructose, and D-mannonse, i.e., arabonic, D-erythronic, D-glyceric, glycolic,

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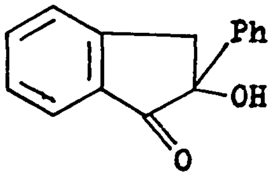
[149] B. Warshowsky and W. M. Sandstrom, Arch. Biochem. and Biophys., 37, 46 (1952).

[150] J. Dubourg and P. Naffa, Bull. soc. chim. France, 1959, 1353.

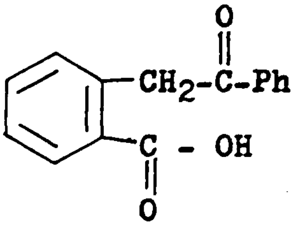
lactic, formic, oxalic, and carbonic were analyzed quantitatively. The kinetics were established and a mechanism based on the modified theories of Nef[141] and Bamford[147] was proposed.

Oxidation of Carbonyl Compounds

The seemingly catalytic effect of alkaline conditions upon the oxidative stability of ketones has been known for some time. Isolated reports in the literature contain references to the autoxidative cleavage of ketones. For example, Miller and Rohde[151] have found that β-phenylhydrindone is converted to a mixture of XXXVI and XXXVII after long standing in bicarbonate solution exposed to atmospheric oxygen. The corresponding β-methyl isomer yields a product analogous to XXXVII[152].



XXXVI



XXXVII

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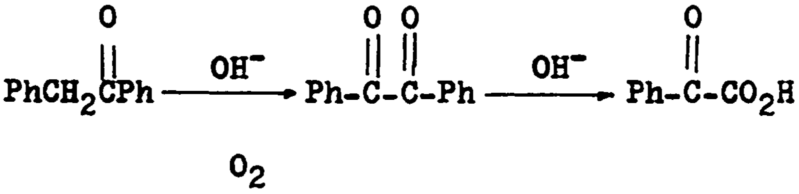
[151] W. Miller and Rohde, Ber. 25, 2095 (1892).

[152] A. H. Salway and E. S. Kipping, J. Chem. Soc., 95, 166 (1909).

Apparently, this compound undergoes further oxidation to form phthalic and acetic acids. In a similar manner, desoxybenzoin can readily be oxidized to benzil in basic solution[153]. If the basic treatment is extended, the benzil is isomerized to benzilic acid.



$$PhCH_2\overset{\overset{O}{\|}}{C}Ph \xrightarrow[O_2]{OH^-} Ph\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ph \xrightarrow{OH^-} Ph\text{-}\overset{\overset{O}{\|}}{C}\text{-}CO_2H$$

Analogously, phenyl benzyl glycolic acid was formed in poor yield when air was passed through a warm, aqueous, potassium hydroxide solution of dibenzyl ketone. Graebe[154] has reported the formation of naphthalic acid from acenaphthenone by the action of air on a hot alkaline alcoholic solution.

The observation that the terpene, carvone (XXXVIII) is readily autoxidized when shaken with air or oxygen in the presence of base was first made by Harries[155]. The product, according to Harries, is a yellow diketone identical with that obtained by the hydrolysis of carvonedioxime (XXXIX).

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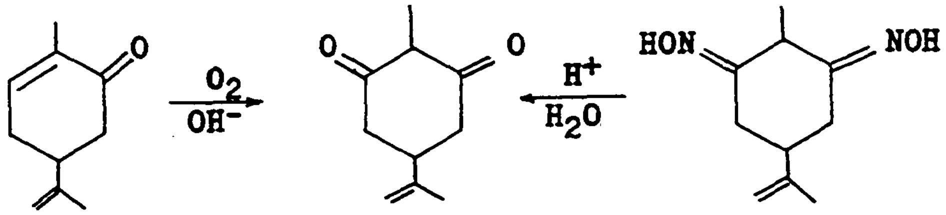
[153] V. Bogdanowska, Ber., 25, 1271 (1892).

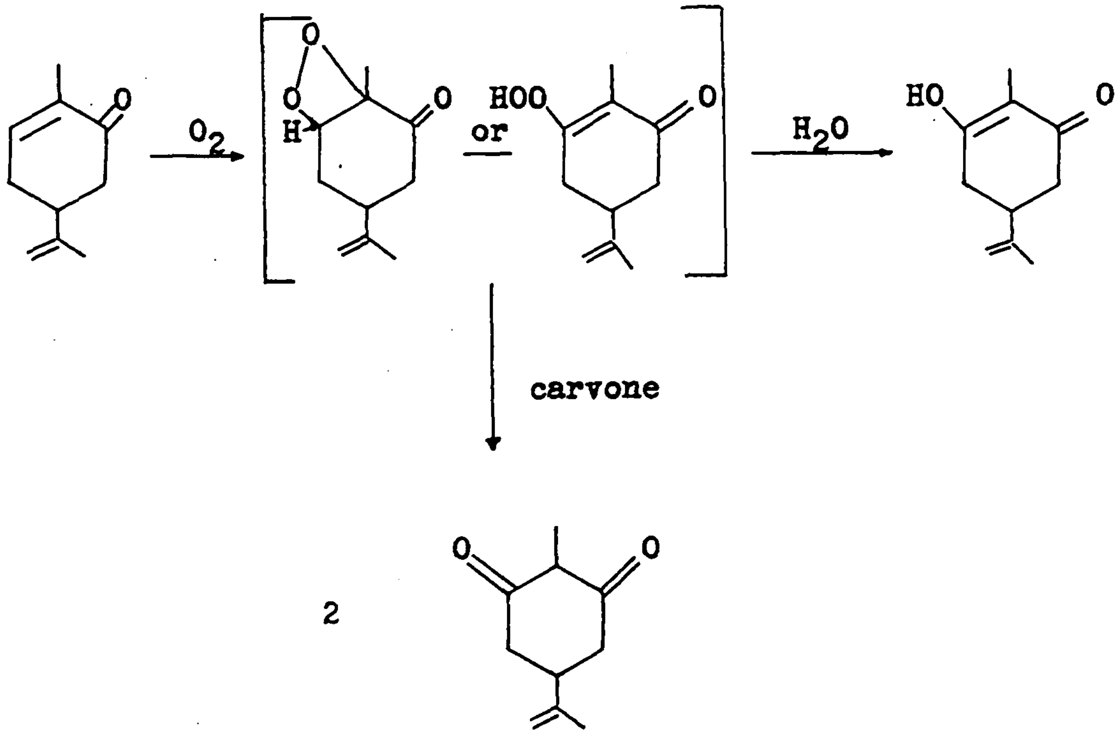
[154] C. Graebe and E. Gfeller, Ann., 276, 12 (1893); C. Graebe and J. Jequier, ibid., 290, 199 (1896).

[155] C. Harries, Ber., 34, 2105 (1901); C. Harries and A. Stähler, Ann., 330, 264 (1904).



XXXVIII XXXIX

This formation of the product has been rationalized in the following manner[156]:



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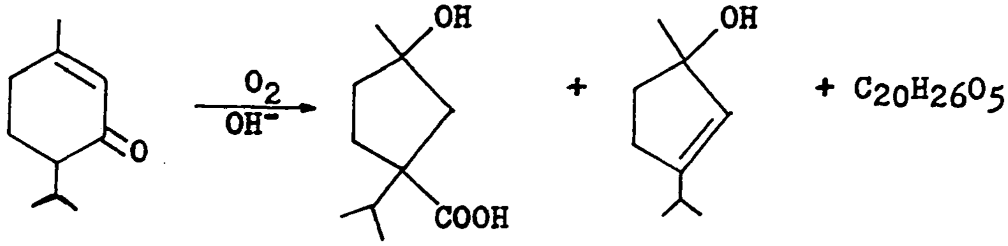
[156] C. Engler and J. Weissberg, "Kritische Studien über die Vorgänge der Autoxydation", Friedrich Viewig und Sohn, Braunschweig (Germany), 1904, p. 192.

The unstable intermediate "moloxide" or hydroperoxide can either decompose directly to the product or can react with starting material in an oxidative manner. It is important to note that the diketone product is obtained in yields of 3-5%, the remainder of the material being an intractable substance.

Treibs[157,158] has carried out an extensive study of the autoxidation of α,β -unsaturated ketones in the presence of alkali and of their oxidation with alkaline hydrogen peroxide and has concluded that the initial oxidation product of these compounds is almost certainly the keto-oxides. The autoxidation of piperitone (XL) yields a hydroxy acid, $C_{10}H_{18}O_3$, formulated as XLI (40-45%), an alkali soluble resin, $C_{20}H_{26}O_5$, and a small amount of tertiary alcohol[157,159,160].



XL XLI

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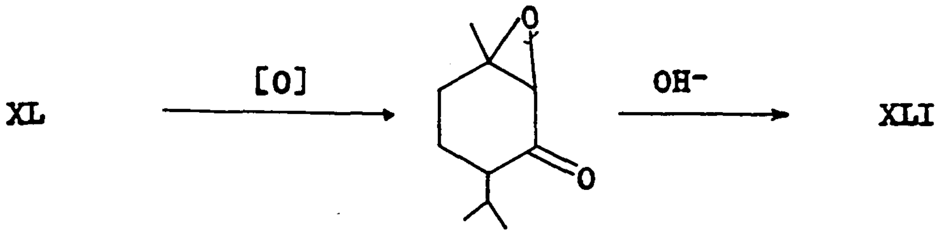
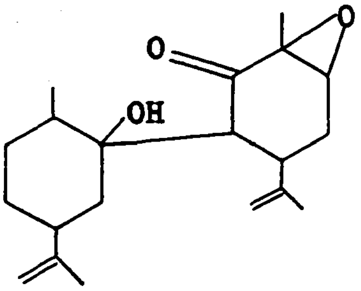
[157] W. Treibs, *Ber.*, *63*, 2473 (1930).
[158] W. Treibs, *ibid.*, *64*, 2178 (1931).
[159] W. Treibs, *ibid.*, *64*, 2545 (1931).
[160] W. Treibs, *ibid.*, *66*, 610 (1933).

A two stage reaction is assumed; the first stage consists in the reaction of the unsaturated ketone to form a "moloxide" or hydroperoxide that subsequently decomposes, leading to condensation products and hydrogen peroxide. The second stage consists in the reaction of this hydrogen peroxide with the original ketone to form a keto-oxide that subsequently rearranges to the observed reaction products under the influence of alkali. A re-investigation of

(56)


the oxidation of carvone yielded the original Harries product to the extent of 40% accompanied by considerable amounts of a resinous dimer, $C_{20}H_{28}O_3$, formulated as[161]



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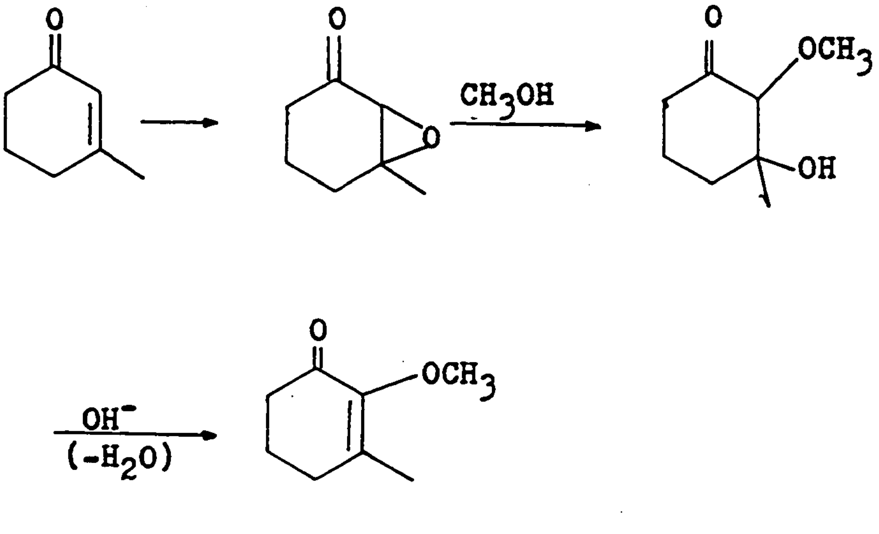
[161] W. Treibs, *ibid.*, *65*, 1314 (1932).

In subsequent publications Treibs has reported the alkaline autoxidation of carvenone[162], 3-methyl-cyclohexenone, 3,5-dimethylcyclohexenone, carvotanacetone, eucarvone, isophorone, and verbenone[163]. The validity of the epoxide intermediate has been conclusively demonstrated by the isolation of XLII from the autoxidation of 3-methyl-cyclohexeneone.



XLII

In a further study, Treibs[164] has been able to isolate the peroxidic intermediate compound by treatment of 3,5-dimethyl-cyclohexenone with an anhydrous alcoholic solution of hydrogen peroxide in the presence of ammonia. The peroxide is unstable and in water solution leads to the epoxide (50%) along with

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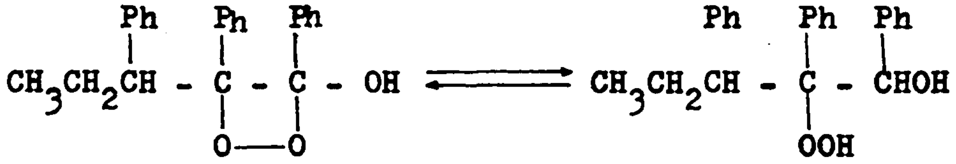
[162] W. Treibs, ibid., 65, 163 (1932).

[163] W. Treibs, ibid., 66, 1483 (1933).

[164] W. Treibs, ibid., 68, 1049 (1935).

some higher boiling material.

Many enols react rapidly with oxygen in moist etheral solution[165]. Typically, only the decomposition products of a peroxide or hydroperoxide can be isolated[165,166,167]. However, Kohler[165a] has isolated a stable crystalline peroxide, 1,2,3-triphenylpentene-1-ol peroxide (XLIII).



$$CH_3CH_2\overset{Ph}{CH} - \underset{O-}{\overset{Ph}{C}} - \underset{O}{\overset{Ph}{C}} - OH \rightleftharpoons CH_3CH_2\overset{Ph}{CH} - \underset{OOH}{\overset{Ph}{C}} - \overset{Ph}{C}HOH$$

XLIII

The nature of the peroxide is not perfectly clear, since it may be either the peroxide, the hydroperoxide, or a tautomeric mixture of the two. Spectroscopic evidence would tend to favor the hydroperoxide formulation[168]. The enol of 10-phenylanthrone reacts with oxygen to give the hydroperoxide[169].

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[165] (a) E. P. Kohler, *Am. Chem. J.*, *36*, 177 (1906); (b) E. P. Kohler and R. B. Thompson, *J. Am. Chem. Soc.*, *59*, 887 (1937).

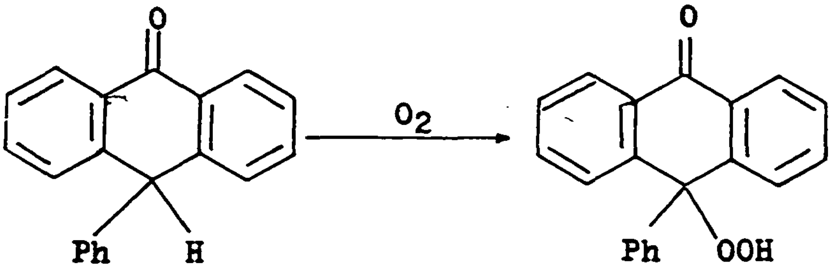
[166] R. C. Fuson, D. J. Byers, and N. Rabjohn, *ibid.*, *63*, 2639 (1941).

[167] R. C. Fuson, E. W. Maynert, and W. J. Shenk, Jr., *ibid.*, *67*, 1939 (1945).

[168] J. Rigaudy, *Compt. rend.*, *226*, 1993 (1948); R. C. Fuson and H. L. Jackson, *J. Am. Chem. Soc.*, *72*, 1637 (1950).

[169] J. Rigaudy, *Compt. rend.*, *226*, 1911 (1948); C. Dufraisse, A. Etienne, and J. Rigaudy, *Bull. soc. chim. France*, *1948*, 804.

Here, there is no tautomerization to the cyclic endo-peroxide.



The facile autoxidation of enolic 1,3-diketones substituted on the 2-carbon has been noted[170].

An extensive investigation into the mechanism of autoxidation of α - ketols was inaugurated by Weissberger, Mainz, and Strasser[171] in 1929. The oxidation of benzoin in alkaline solution in a deficiency of oxygen yields a violet intermediate that is destroyed by adding more oxygen. Experiments indicated that rates of autoxidation of α - ketols were identical with rates of racemization and were proportional to the concentrations of alkali in the reacting solutions[172]. This led to the conclusion that dissociation of the ketol was the first step in these processes.

Therefore the overall reaction

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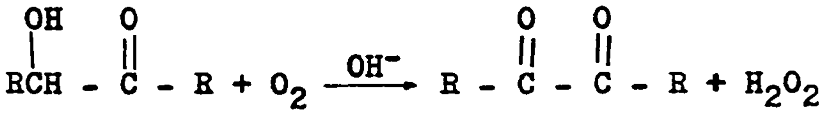
[170] R. B. Woodward and E. R. Blout, J. Am. Chem. Soc., 65, 562 (1943).

[171] A. Weissberger, H. Mainz, and E. Strasser, Ber., 62, 1942 (1929).

[172] A. Weissberger, E. Strasser, H. Mainz, and W. Schwarze, Ann., 478, 112 (1930).

(57) 

$$R\overset{OH}{\overset{|}{C}}H - \overset{O}{\overset{\|}{C}} - R + O_2 \xrightarrow{OH^-} R - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - R + H_2O_2$$

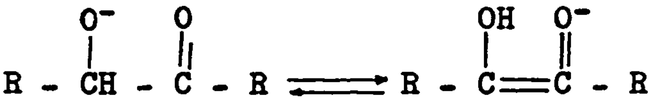
may be divided into the stages[173]:

(58) 

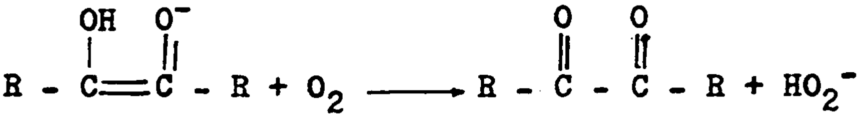
$$R - \overset{OH}{\overset{|}{C}}H - \overset{O}{\overset{\|}{C}} - R \xrightarrow{OH^-} R - \overset{O^-}{\overset{|}{C}}H - \overset{O}{\overset{|}{C}} - R + H_2O$$

(59) 

$$R - \overset{O^-}{\overset{|}{C}}H - \overset{O}{\overset{\|}{C}} - R + O_2 \longrightarrow R - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - R + HO_2^-$$

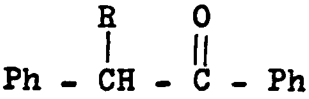
(60) 

$$R - \overset{O^-}{\overset{|}{C}}H - \overset{O}{\overset{\|}{C}} - R \rightleftharpoons R - \overset{OH}{\overset{|}{C}}{=}\overset{O^-}{\overset{\|}{C}} - R$$

(61) 

$$R - \overset{OH}{\overset{|}{C}}{=}\overset{O^-}{\overset{\|}{C}} - R + O_2 \longrightarrow R - \overset{O}{\overset{\|}{C}} - \overset{O}{\overset{\|}{C}} - R + HO_2^-$$

In comparing the oxidation of compounds of the type XLIV, many similarities were found[174].



$$Ph - \overset{R}{\overset{|}{C}}H - \overset{O}{\overset{\|}{C}} - Ph$$

XLIV

(a) R = NH_2

(b) R = OH

(c) R = OCH_3

Hydrogen peroxide was formed in all three cases and the

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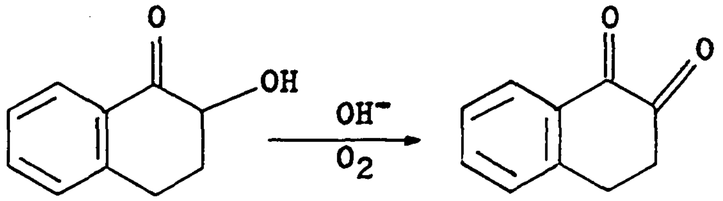
[173] A. Weissberger, W. Schwarze, and H. Mainz, *ibid*., **481**, 68 (1930); A. Weissberger, A. Dorken, and W. Schwarze, *Ber*., **64**, 1200 (1931); A. Weissberger and E. Dym, *Ann*., **502**, 74 (1932).

[174] T. H. James and A. Weissberger, *J. Am. Chem. Soc*., **59**, 2040 (1937).

reaction rates were directly proportional to the base concentration and independent of oxygen pressure. In each case the rate determining step is undoubtedly enolization. The rates varied considerably, being in the order 1.75, 1, 0.005 as written. Therefore, all three oxidations proceed by direct interaction of a monavalent anion with oxygen.

The α-ketol, 1-hydroxy-β-tetralone is oxidized in potassium hydroxide solution by atmospheric oxygen to give α-naphthohydroquinone, tetrahydrobinaphthyl, dinaphthylquinhydrone, and naphthalenic acid[175]. In a kinetic investigation, Weissberger and Schwarze[176] found the reaction to be first order with a rate constant similar to that for other α-ketols. The rate was proportional to the base concentration. The scheme postulated to account for these results is as follows

(61)



XLV

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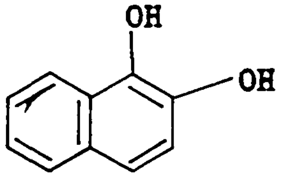
[175] F. Strauss, O. Bernoully, and P. Mautner, Ann., 444, 165 (1925).

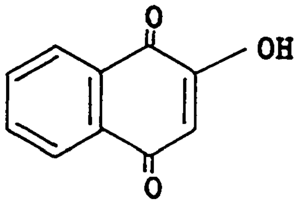
[176] A. Weissberger and W. Schwarze, ibid., 487, 53 (1931).

(62) XLV $\longrightarrow$

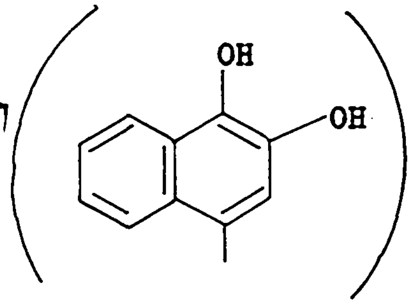


XLVI

(63) XLVI $\xrightarrow[O_2]{OH^-}$



(64) 2 XLVI $\xrightarrow[O_2]{OH^-}$



2 .

In a study of the effect of alkali on the autoxidation of tetralin at 120°, K. U. Ingold[177] encountered similar products. The paramagnetic nature of highly colored intermediates in these oxidations has been demonstrated[178].

The most important of the autoxidizable hydroxyketones or enediols is ascorbic acid. The overall reaction is

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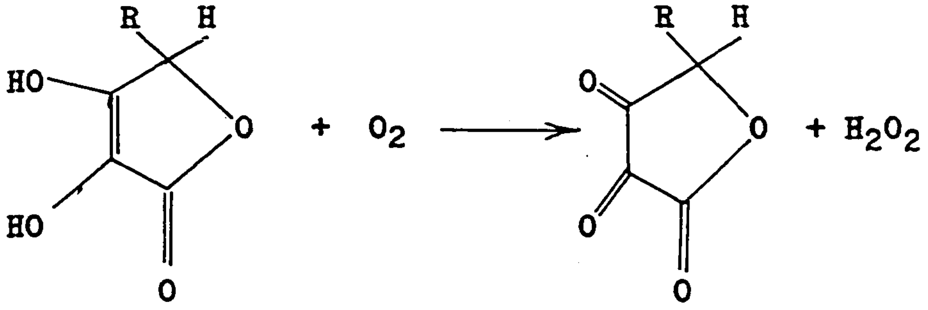
[177] K. U. Ingold, Can. J. Chem., 34, 601 (1956).

[178] J. L. Ihrig and R. G. Caldwell, J. Am. Chem. Soc., 78, 2097 (1956).

(65)



R = - $CHOHCH_2OH$

The reaction is first order with respect to ascorbic acid and is dependent upon pH showing that both mono and di-anions are involved in the reaction, although the latter reacts approximately 10^5 times as rapidly as the former[179]. The reaction is catalyzed by copper ion, although the mechanism appears to be more complicated in this instance[180,181]. Nord has developed a scheme wherein cupric ion is the actual oxidizing agent that reacts with the ascorbic acid anion and is in turn reoxidized by air. Nord's scheme is as follows:

(66) $H_2A \rightleftharpoons HA^- + H^+$

(67) $HA^- + 2\ Cu\ (II) \rightleftharpoons HA + 2\ Cu\ (I)$

(68) $HA^- \rightleftharpoons A^{=} + H^+$

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[179] A. Weissberger, J. E. La Valle, and D. S. Thomas, Jr., ibid., 65, 1934 (1943).

[180] A. Weissberger and J. E. Lu Valle, ibid., 66, 700 (1944).

[181] H. Nord, Acta Chem. Scand., 9, 442 (1955).

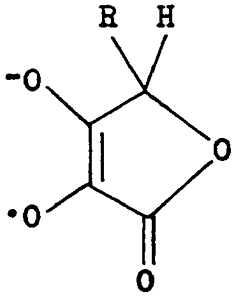
(69) $A^{=} + 2\ Cu\ (II) \longrightarrow A + 2\ Cu\ (I)$

(70) $2\ Cu\ (I) + 2\ H^{+} + \frac{1}{2}\ O_2 \longrightarrow 2\ Cu\ (II) + H_2O$

The overall reaction, the sum of these stages, thus becomes

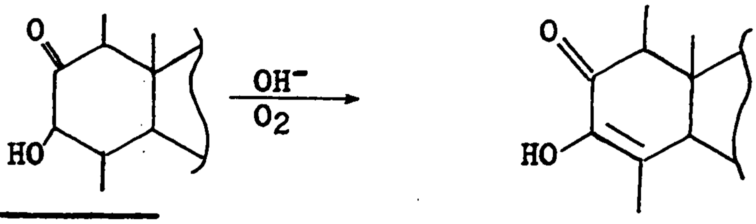
(71) $H_2A + \frac{1}{2}\ O_2 \longrightarrow A + H_2O$

The use of EPR spectroscopy along with a flow technique has allowed the detection of semi-quinone free radicals such as XLVII in this reaction[182].



XLVII

Further demonstration of the easy oxidizability of the ⍺-hydroxy-ketone system is provided by their facile dehydrogenations to diosphenols in the steroid series.



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[182] I. Yamazaki, H. S. Mason, and L. Piette, J. Biol. Chem., 235, 2444 (1960).

Recent examples of these reactions are provided by the compounds elatercin A[183], cevine[184], dihydroacetoxycurcurbitacin B[185], 2-α-hydroxytestosterone-2,17-diacetate[186].

The recurring phenomena of oxidative dehydrogenation is of considerable importance in the cyclic ketone series. Allen and Gilman[187] made use of such reactivity in their structure proof of the hydrocarbon rubrene. The intermediate tetrahydronaphthacenequinone (XLVIII) was dehydrogenated to XLIX by the action of molecular oxygen on an alkaline alcoholic solution. Similarly, tetrahydro-2,3-dimethylanthraquinone can be dehydrogenated by oxygen in basic solution[188].

The exposure of an alkaline alcoholic solution of a cyclic 1,4-diketone to air or oxygen causes rapid discoloration and the compound is transformed into the corresponding

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[183] D. Lavie and Y. Shvo, J. Am. Chem. Soc., 81, 3058 (1959).

[184] D. H. R. Barton and J. F. Eastham, J. Chem. Soc., 1953, 424.

[185] A. Melera and C. R. Noller, J. Org. Chem., 26, 1213 (1961).

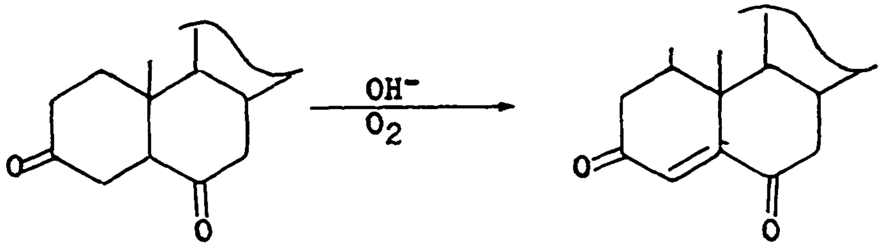
[186] P. N. Rao and L. R. Axelrod, J. Am. Chem. Soc., 82, 2830 (1960); R. L. Clarke, ibid., 82, 4629 (1960).

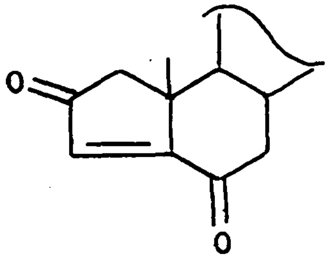
[187] C. F. Allen and L. Gilman, J. Am. Chem. Soc., 58, 937 (1936).

[188] C. F. H. Allen and A. Bell, Org. Synth., 22, 37 (1942).

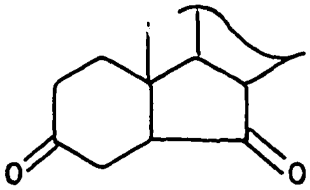
enedione in good yield[189]. Several examples of this peculiar behavior have been previously reported[190]. The difference in behavior of the A-norcoprostane-2,6-dione (L) type systems with the formally similar B-norcoprostane-3,6-dione (LI) structures is of interest.

(72)





L



LI

The product from L is the corresponding enedione, A-nor-3-cholestene-2,6-dione, LII. The isomer LI, however, yields no ketonic material; instead B-nor-2,4,6-cholestatriene-3,6-diol (LIII) is formed. The formation of tropone (LIV) from the autoxidation of 2,4-cycloheptadienone in alkaline

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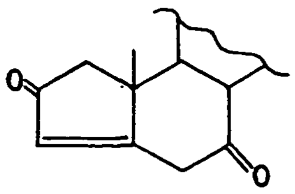
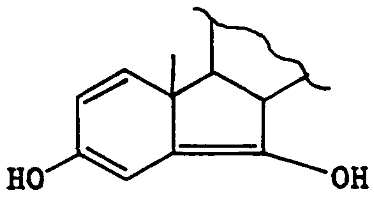
[189] W. E. Dauben, G. A. Boswell, and W. Templeton, *J. Org. Chem.*, *25*, 1853 (1960).

[190] D. H. R. Barton and P. de Mayo, *J. Chem. Soc.*, *1953*, 3111; D. H. R. Barton, J. F. McGhie, M. K. Pradhan, and S. A. Knight, *ibid.*, *1955*, 876.

solution is a further example of the reaction[191].

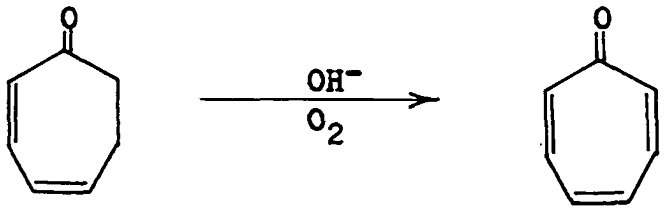


LII



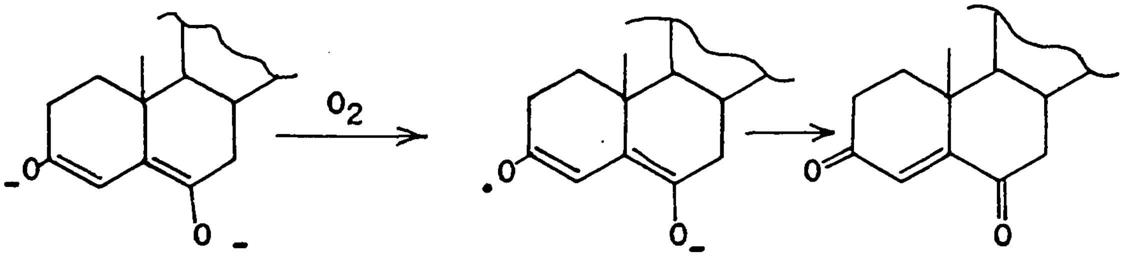
LIII

(73)



LIV

Dauben, Boswell, and Templeton[189] have suggested that the reaction proceeds through the dianion LV which is then oxidized to the anion-radical LVI and finally to the enedione.



LV

LVI

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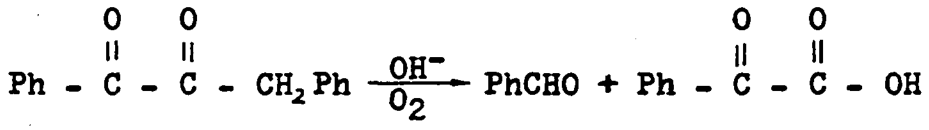
[191] E. E. Van Tamelen and G. T. Hildahl, *J. Am. Chem. Soc.*, *78*, 4405 (1956).

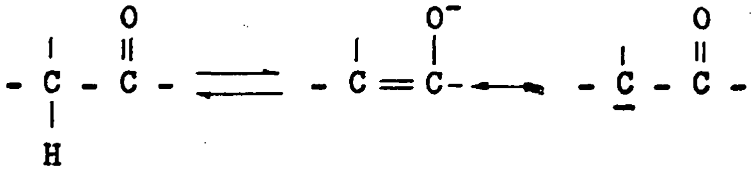
No mention is made of any peroxidic materials.

A more normal reaction series undergone by carbonyl containing compounds (ketones, esters, etc.) is that of oxidative cleavage. Kohler and Barnes[192] noted that alkaline solutions of α-oxido ketones, e.g., benzylphenyl diketone, absorb oxygen avidly yielding only cleavage products (no peroxides). The oxidation process probably involves the intervention of enolic species. Similarly,

(74) 

$$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_2Ph \xrightarrow[O_2]{OH^-} PhCHO + Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH}$$

diphenylpyruvic acid yields quantitative amounts of benzophenone and oxalic acid upon autoxidation in alkaline media[193]. Fluorenone is formed by the action of oxygen on 9-benzoyl fluorene. Rigaudy has proposed the scheme

(75) 

$$\mathrm{-\underset{H}{\underset{|}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}- \rightleftharpoons -\overset{|}{C}=\overset{O^-}{\overset{|}{C}}- \longleftrightarrow -\underset{-}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-}$$

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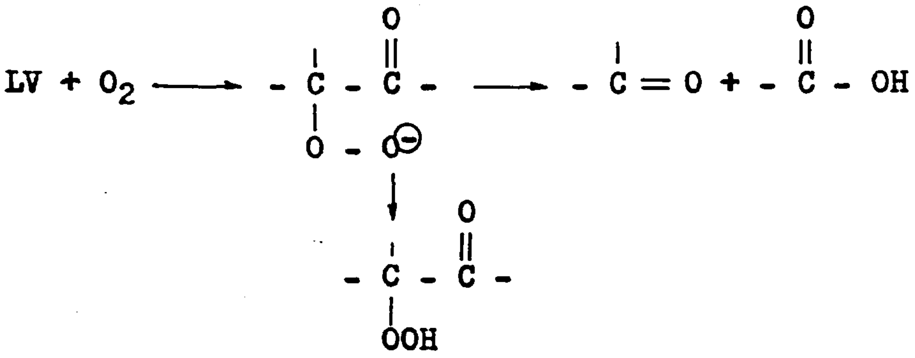
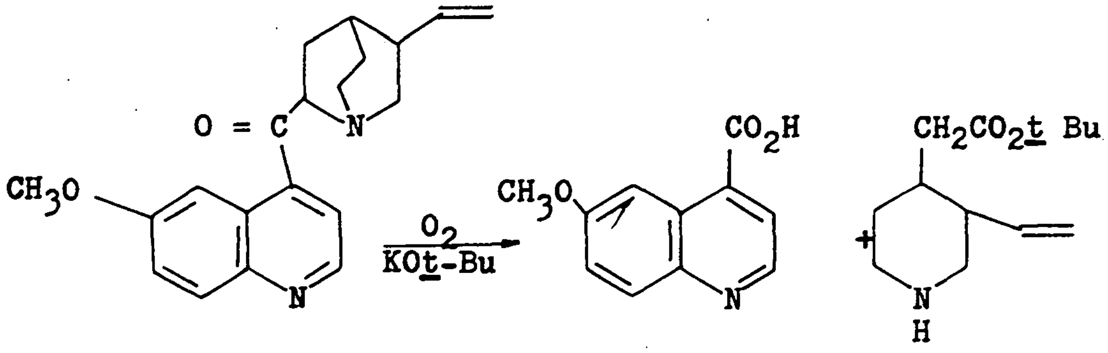
[192] E. P. Kohler and R. P. Barnes, *ibid.*, *56*, 211 (1934).

[193] J. Rigaudy, *Compt. rend.*, *228*, 253 (1949).

(76) 

The formation of quinic acid (LVII) in alkaline solutions of quininone (LVI) has been attributed to the action of air on the enolate ion[194]. Doering and Chanley[195] reported that the oxidative cleavage was very rapid and were able to isolate quinic acid in 92% yield along with 58% of the meroquinene t-butylester (LVIII).



LVI LVII LVIII

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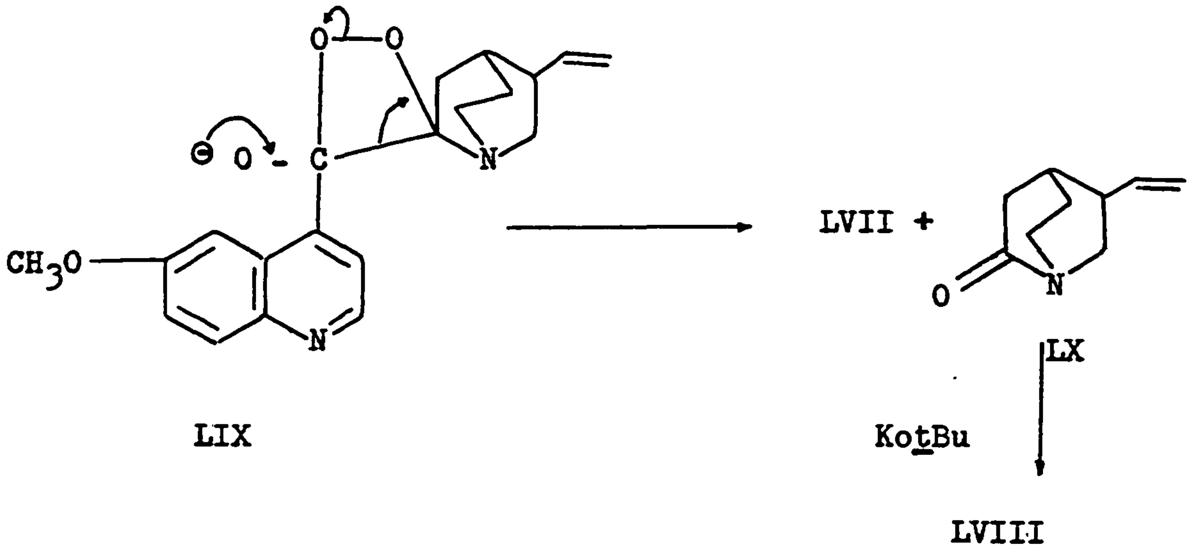
[194] R. B. Woodward, N. L. Wendler, and F. J. Brutschy, J. Am. Chem. Soc., 67, 1425 (1945).

[195] W. E. Doering and J. D. Chanley, ibid., 68, 586 (1946).

To account for these results Doering proposed the intermediate "moloxide"



LIX that decomposes to LVII and 2-keto-vinylquinuelidine (LX) which rapidly reacts with *t*-butoxy anion yielding LVIII.

In an effort to correlate structure of carbonyl compounds with ease of autoxidative cleavage Doering and Haines[196] investigated a large number of compounds. Oxidations were performed in potassium *t*-butoxide-*t*-butyl alcohol solutions at room temperature. Under these conditions propiophenone absorbed 1.5 equivalents of oxygen in 10 minutes, butyrophenone, 1.25 equivalents in 7 minutes, and acetophenone, 1.25 equivalents in 2.5 hours. No explanation for the anomalous behavior of acetophenone was put forward. In every

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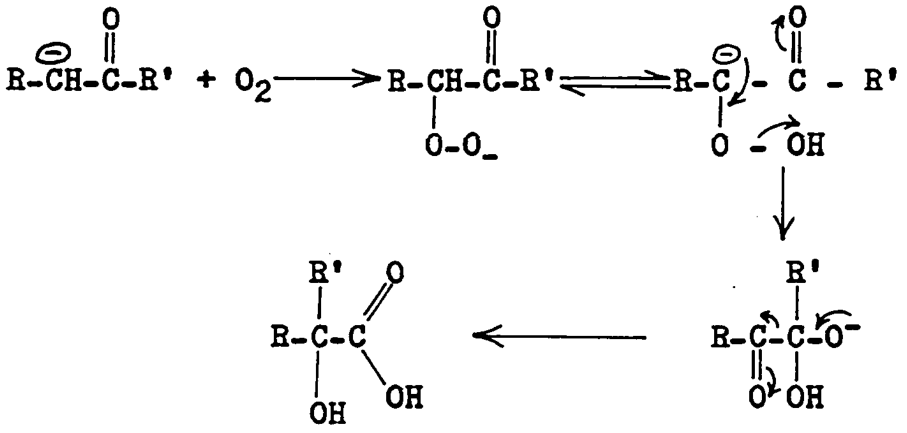
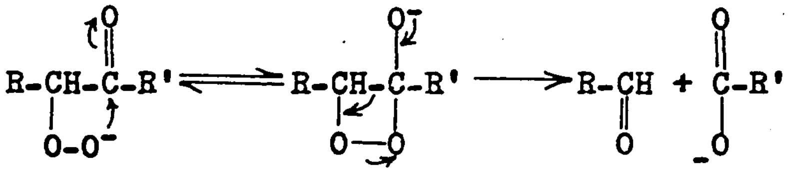
[196] W. E. Doering and R. M. Haines, *ibid.*, *76*, 482 (1954).

case cleavage products were isolated in high yields. A plausible reaction mechanism could either involve peroxidic intermediates similar to LIX or could involve the following steps:

(77)



(78)



R' = Ph

The autoxidation of sym-tetraphenylacetone leads to benzophenone (82.5%) diphenylacetic acid (82.5%) and a tertiary alcohol in 3.8% yield[197]. The isolation of the alcohol would appear to favor a hydroperoxide intermediate in the reaction.

Elkik in a study of the autoxidation of aldehydes and

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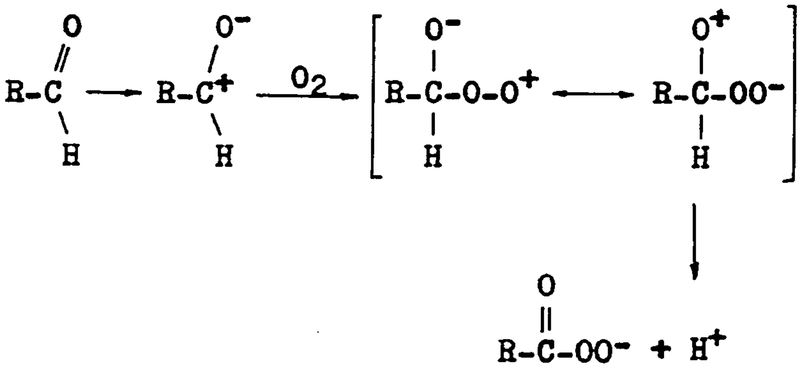
[197] D. O. Dean, W. B. Dickinson, G. B. Hoey, and C. T. Lester, ibid., 76, 4988 (1954).

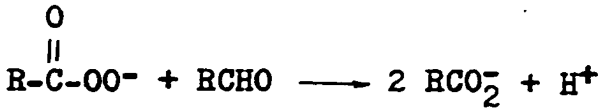
ketones in benzene solution under the influence of sodium *t*-amylate[198] has confirmed Doering's results for ketone oxidations. According to Elkik, aldehydes appear to be oxidized by two different mechanisms; the first leads to an acid with the same number of carbon atoms, the second by attack of oxygen on the α-carbon leads to a lower acid.

Scheme I

(79)



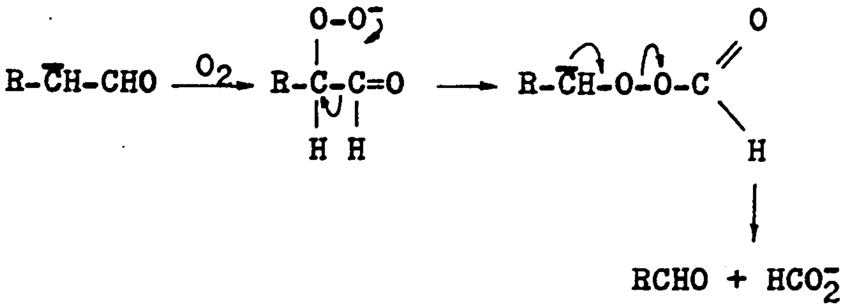
(80)



$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OO^- + RCHO \longrightarrow 2\ RCO_2^- + H^+$$

Scheme II

(81)



Interestingly, benzophenone, a non-enolizable ketone, gave, under the same conditions, small yields of benzoic acid and

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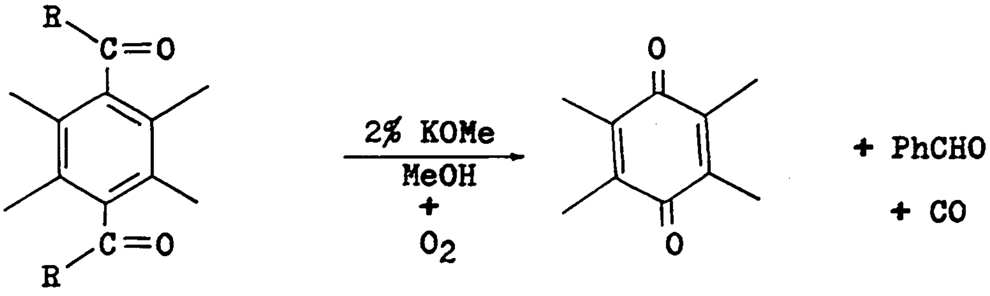
[198] E. Elkik, *Bull. soc. chim. France*, *1959*, 933.

phenol.

Under similar conditions the natural product limonin was oxidized to a diketone[199]. No cleavage products were reported. The isolation of 17-α-hydroperoxides in good yield from the alkali catalyzed autoxidation of specifically constructed steroidal molecules[200] seems a bit surprising in view of the preceding discussion of cleavage reactions. No explanation is offered at this time.

A novel autoxidative cleavage reaction of anthranyl ketones yields carbon monoxide as a gaseous product[201]. The 9,10-disubstituted anthracene (LX) yields anthraquinone (75%), benzaldehyde (50% based on two moles) and carbon monoxide (75% based on one mole) after reaction with oxygen in an alkaline alcoholic solution.

(83)



LX

$R = CH_2Ph$

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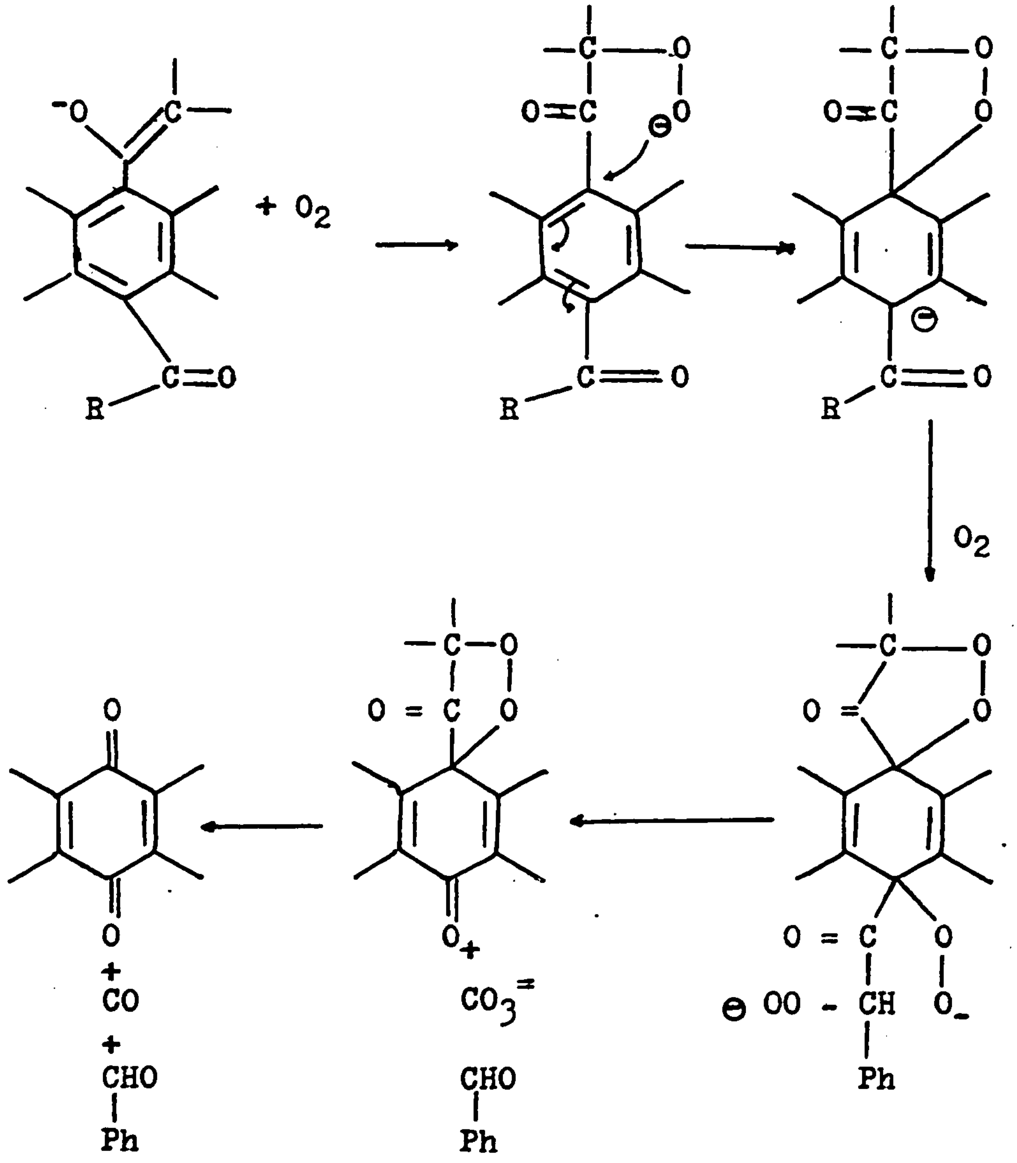
[199] D. Arigoni, D. H. R. Barton, E. J. Corey, and O. Jeger, *Experimentia*, **16**, 43 (1960); D. H. R. Barton, S. K. Pradhan, S. Sternhell, and J. F. Templeton, *J. Chem. Soc.*, **1961**, 255.

[200] E. J. Bailey, J. Elks, and D. H. Barton, *Proc. Chem. Soc.*, **1960**, 214.

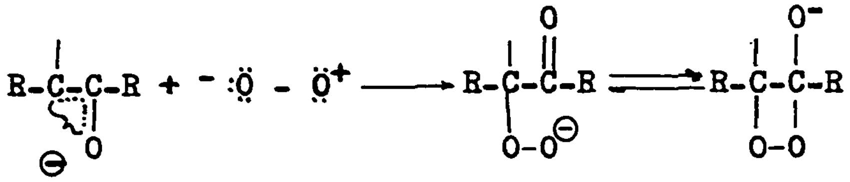
[201] G. Rio, P. J. Cornu, and R. Wagner, *Bull. soc. chim. France*, **1961**, 587.

The following mechanism is postulated:

(83)

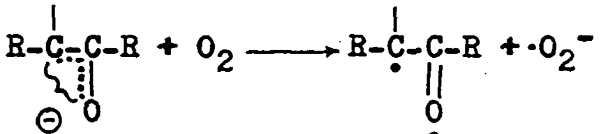


In summary of this section, the oxidation of carbonyl compounds usually proceeds via an enolate anion intermediate. Two likely reaction paths for the reaction of enolate anions with oxygen are possible. The first, as has been suggested, implies a reaction with oxygen in its dipolar form to yield the salt of a peroxide directly

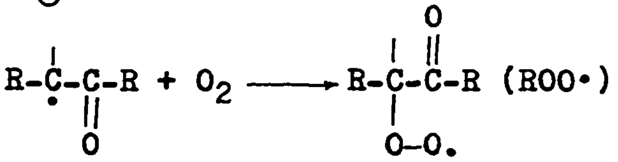
(84) 

$$R-\underset{\ominus\;\overset{\|}{O}}{\overset{|}{C}}-C-R + {}^{-}:\ddot{O}-\ddot{O}^{+} \longrightarrow R-\underset{O-O^{\ominus}}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-R \rightleftharpoons R-\underset{O-O}{\overset{|}{C}}-\overset{O^{-}}{\overset{|}{C}}-R$$

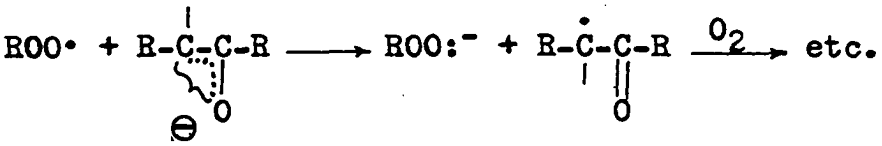
A second and possibly more inviting scheme would invoke a free radical chain mechanism,

(85) 

$$R-\underset{\ominus\;\overset{\|}{O}}{\overset{|}{C}}-C-R + O_2 \longrightarrow R-\overset{|}{\underset{\bullet}{C}}-\underset{O}{\underset{\|}{C}}-R + \cdot O_2^{-}$$

(86) 

$$R-\overset{|}{\underset{\bullet}{C}}-\underset{O}{\underset{\|}{C}}-R + O_2 \longrightarrow R-\underset{O-O.}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-R \; (ROO\cdot)$$

(87) 

$$ROO\cdot + R-\underset{\ominus\;\overset{\|}{O}}{\overset{|}{C}}-C-R \longrightarrow ROO:^{-} + R-\overset{\bullet}{\underset{|}{C}}-\underset{O}{\underset{\|}{C}}-R \xrightarrow{O_2} \text{etc.}$$

It is apparent that a satisfactory proof of either of these suggested reaction paths is not immediately forthcoming. Indications that the free radical scheme may be the correct one may lie in the discovery that the alkali catalyzed autoxidation of isobutyrophenone yields stable free radicals, as detected by EPR techniques[202].

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[202] C. E. Wintner, Dept. of Chemistry, Harvard University, Cambridge 38, Mass. Personal communication concerning EPR measurements in the autoxidation of ketones, June 1961.

Oxidation of Organometallic Compounds

Many metallic derivatives of organic compounds are extremely sensitive to attack by molecular oxygen[203,204]. Although this reactivity is not surprising in view of the generally labile nature of the carbon-metal bond, a complete understanding of the intrinsic basis of this property is not immediately forthcoming[205].

The autoxidation of armoatic Grignard reagents was first reported by Bodroux in 1903[206,207]. Passage of oxygen through an ethereal solution of various phenylmagnesium bromides followed by hydrolysis gave rise to the corresponding phenols in yields of 5-10%. At about the same time, Bouveault[208] obtained an 80% yield of benzyl alcohol from the oxidation

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[203] F. Runge, "Organo-Metallverbindungen", Wissenschaftliche Verlagsgesellschat M. B. H., Stuttgart (Germany), 1944.

[204] G. E. Coates, "Organo-Metallic Compounds", Methuen and Co., Ltd., London, Second edition, 1960.

[205] H. Hock, H. Kropf, and F. Ernst, Angew. Chem., 71, 541 (1959) present a review of current speculations concerning the mechanism of autoxidation of organometallic compounds.

[206] F. Bodroux, Compt. rend., 136, 158 (1903); Bull. soc. chim. France, [3] 31, 33 (1904).

[207] M. S. Kharasch and O. Reimmuth, "Grignard Reactions of Non-Metallic Substanus", Prentice-Hall, Inc., New York, 1954, pp. 1264-1274. A review of the action of oxygen on Grignard reagents with emphasis on synthetic utility.

[208] L. Bouveault, Bull. soc. chim. France, [3] 29, 1051 (1903).

of benzyl magnesium chloride. Similarly, Grignard[209] isolated α-phenethyl alcohol in 60% yield from the oxidation of α-phenethylmagnesium chromide.

The oxidation of phenylmagnesium bromide in ether solution was reinvestigated by Wuyts[210]. In addition to phenol he was able to identify benzene, biphenyl, α-phenylethanol, ethyl alcohol, and diphenyl ether among the products of the reaction. He suggested the probable intermediacy of peroxidic compounds and was able to confirm his suggestion by demonstrating the presence of peroxides via various color tests (e.g., with hydroquinone, diphenylamine, etc.). Schmidlin[211] had shown earlier that triphenylmethyl peroxide (LXI) is formed on oxidation of triphenylmethyl magnesium chloride. He had formulated the reaction as

$$(88) \quad 4\ Ph_3CMgCl + 3\ O_2 \longrightarrow 2\ \underset{\text{LXI}}{Ph_3COOCPh_3} + 2\ ClMgOMgCl$$

However, it is not unlikely that the occurrence of LXI is an artifact of the experiment since Bachmann and Cockerill[212]

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[209] V. Grignard, Compt. rend., 138, 1048 (1904).

[210] H. Wuyts, ibid., 148, 930 (1909).

[211] J. Schmidlin, Ber., 39, 631, 4183 (1906); ibid., 41, 423 (1908). See also J. Schmidlin, "Das Triphenylmethyl", Ferdinand Enke, Stuttgart (Germany), 1914, p. 127.

[212] W. E. Bachmann and R. F. Cockerill, J. Am. Chem. Soc., 55, 2932 (1933).

have found the major product of this reaction to be the carbinol (54%) accompanied by small amounts ($<$10%) of LXI.

Porter and Steel[213] studied the effect of temperature on the yield of phenol available from the oxidation of phenylmagnesium bromide in ethereal solution. They found that the phenol yield was lowest at higher temperatures. In addition to the previously reported[210] products of this reaction they succeeded in isolating and identifying *p*-terphenyl, *p*-quinone, and *p*,*p'*-dihydroxybiphenyl. The occurrence of diphenyl among the products was attributed to the intervention of the Wurtz coupling reaction (probably not so). To account for these results, Porter and Steel proposed a two stage reaction sequence. The organo-metallic compound is first oxidized to a transient peroxidic intermediate by means of molecular oxygen; this intermediate is then reduced to a phenolate by further combination with unreacted Grignard reagent.

$$(89)\quad C_6H_5MgBr + O_2 \longrightarrow C_6H_5O_2MgBr$$

$$(90)\quad C_6H_5O_2MgBr + C_6H_5MgBr \longrightarrow 2\ C_6H_5OMgBr$$

The formation of ethanol and α-phenethyl alcohol is attributed to a side reaction of the peroxidic intermediate with ether.

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[213] C. W. Porter and C. Steel, *J. Am. Chem. Soc.*, *42*, 2650 (1920).

Although the yield of phenols from the oxidation of aryl Grignards is not appreciably affected by lowering the reaction temperature (down to -50°C), Ivanoff[214] found that the addition of equimolar amounts of alkylmagnesium halides effects a doubling of the yield of phenolic product. He proposed that the increased yields were the result of a process whereby the alkyl Grignard reagent in the "mixed" reaction was oxidized first to an alkyl hydroperoxide that was subsequently reduced by the aryl Grignard. Alternatively, Wuyts[215] has suggested the reverse explanation, i.e., the aryl Grignard is peroxidized initially to an aryl hydroperoxide that is later reduced by the "more reductive" alkyl Grignard. Addition of cobaltous halides has little or no effect on the oxidation of alkyl Grignards while with aryl Grignard reagents the normal oxidation leading to phenol is suppressed and increased amounts of coupling products are formed[216]. Müller and Töpel[217] found that yields of phenol up to 45% could be obtained from the oxidation of aryl magnesium halides in non-oxidizable solvents, e.g., phenetole.

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[214] D. Ivanoff, Bull. soc. chim. France, [4] 39, 47 (1926).

[215] H. Wuyts, Bull. soc. chim. Belg., 36, 222 (1927).

[216] M. S. Kharasch and W. B. Reynolds, J. Am. Chem. Soc., 65, 501 (1943).

[217] E. Müller and T. Töpel, Ber., 72, 273 (1939).

The first step of the Porter and Steel scheme has been confirmed by Walling and Buckler[218,219]. These investigators carried out the oxidation of t-butyl magnesium chloride at -75°C by an inverse addition procedure. In this manner a 35% yield of t-butyl hydroperoxide was obtained. By using dilute solutions, low temperatures, and the inverse addition procedure yields of t-butyl hydroperoxide of 91% were consistently obtained. The procedure has been successfully applied to the preparation of a number of aliphatic hydroperoxides. Although no hydroperoxides were isolated from the oxidation of aryl Grignard reagents even at -78°C, peroxides (5-9%) were detected by the liberation of iodine from potassium iodide. Acetylenic Grignard reagents were stable toward oxidation. Extensive studies as to the effect of various reaction variables on the yield of hydroperoxides as well as the preparation of several unusual hydroperoxides have been reported[220,221].

In view of the fact that typical free radical inhibitors appeared to have no effect on the reaction rate and/or products Walling and Buckler[218] have suggested that the

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[218] C. Walling and S. A. Buckler, J. Am. Chem. Soc., 75, 4372 (1953); ibid., 77, 6032 (1955).

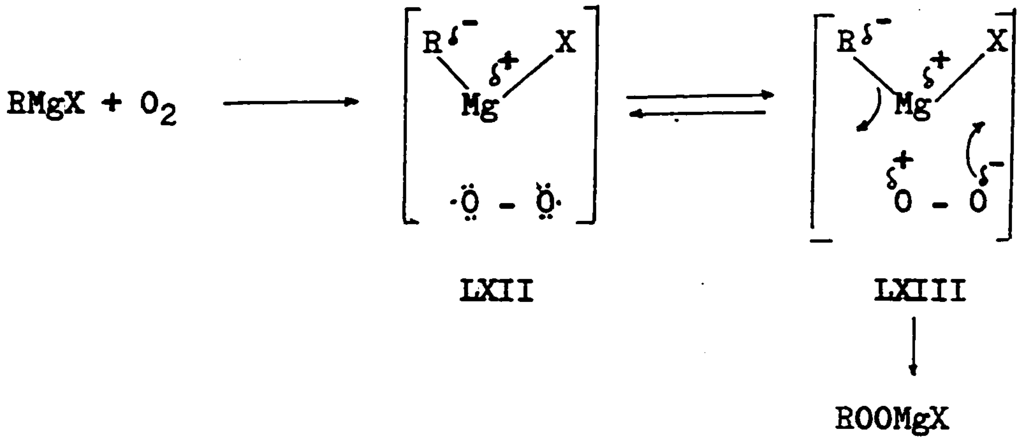
[219] C. Walling and S. A. Buckler, ibid., 77, 6039 (1955).

[220] H. Hock and F. Ernst, Chem. Ber., 92, 2712 (1959).

[221] H. Hock and F. Ernst, ibid., 92, 2723 (1959).

reaction proceeds through an initial bimolecular association of oxygen and Grignard reagent, followed by rearrangement.

(91)



Hock and Ernst[205,220] have concurred in this view. The prevalence of by-products in the oxidation of aryl Grignard reagents is accounted for on the basis of the ready decomposition of phenyl hydroperoxides into phenoxy radicals[218]. However, the possibility that a competing radical reaction may occur has also been considered[205].

(92) $\text{LXII} \longrightarrow R\cdot + XMgOO\cdot$

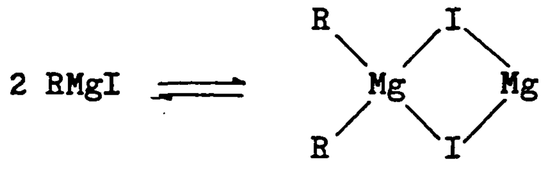
(93) $2\,R\cdot \longrightarrow R - R$

(94) $R\cdot + \text{solvent} \longrightarrow \text{etc.}$

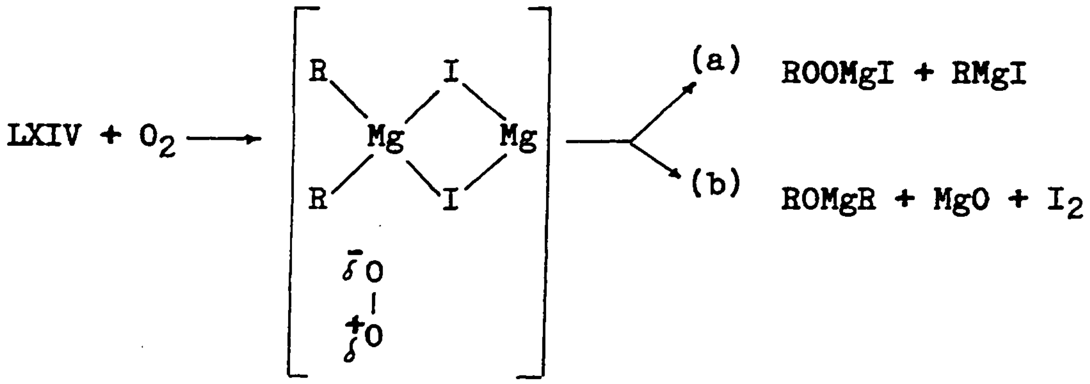
This model is sufficient to rationalize the initial peroxide formation from alkyl or aryl magnesium chlorides or bromides. In the case of alkyl or aryl magnesium iodides the autoxidation takes a different path. The products of the autoxidation are alkyl or aryl iodides[222]. The reaction has been formulated as

(95) $2\ C_2H_5MgI + O_2 \longrightarrow 2\ C_2H_5I + 2\ MgO$

Although the detailed reaction path is obscure, Hock[205] has suggested that the differing reactivity may be due to the particular structure of the Grignard compound, e.g., LXIV

(96)


LXIV

(97)


LXV

The complex, LXV, may decompose by two paths (97 a and b): the iodine formed in (97b) can then react further to form alkyl iodides and magnesium iodide.

The second step in the Porter and Steel scheme, reaction

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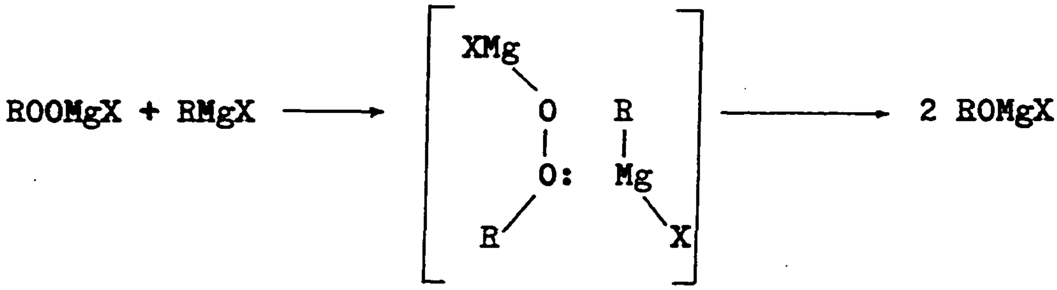
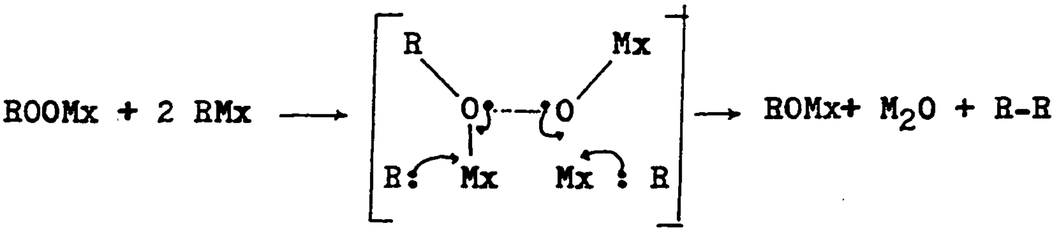
[222] J. Meisenheimer and W. Schlichenmaier, <u>Ber</u>., <u>61</u>, 2029 (1928).

(90), the reduction of the hydroperoxide, has been studied independently[217,218,219,223]. The reaction is postulated as proceeding through an initial complex, LXVI,

(98)


LXVI

and is considered to be a completely polar reaction. However, an alternative possibility has been suggested[205]

(99)


A comparative study of the physical and chemical properties of methyl compounds of the elements, $M(CH_3)_n$, leads to the conclusion that a rapid reaction of these compounds with oxygen appears to be related to atomic charges and also to the availability of unoccupied low energy orbitals[224]. Within any one sub-group of the periodic table

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[223] T. W. Campbell, W. Burney, and T. L. Jacobs, *J. Am. Chem. Soc.*, *72*, 2735 (1950); W. Treibs, *Chem. Ber.*, *84*, 438 (1951); S. O. Lawesson and N. C. Yang, *J. Am. Chem. Soc.*, *81*, 4230 (1959).

[224] R. T. Sanderson, *ibid.*, *77*, 4531 (1955).

the reactivity toward oxygen can be correlated with the Pauling values of electronegativity of the elements[205,224].

Tri-alkyl boranes are autoxidized very rapidly; the lower members of the series are spontaneously inflammable. Under controlled conditions the slow autoxidation of triethylboron produces the diethyl ester of ethyl boronic acid[225]. After hydrolysis boronic acid and ethyl alcohol

$$(CH_3CH_2)_3B + O_2 \longrightarrow CH_3CH_2B(OCH_2CH_3)_2$$

$$CH_3CH_2B(OCH_2CH_3)_2 + H_2O \longrightarrow CH_3CH_2OH + (HO)_3B$$

were isolated. In this initial publication, Frankland also reported that the ammonate of trimethylboron is stable to oxygen. The formation of boronic esters was confirmed by Krause and his co-workers[226] for a number of alkyl boranes. Johnson and Van Campen[227] showed that the presence of water exerted an inhibiting effect on the autoxidation reaction. In the oxidation of tri-_n_-butyl borane in moist air one half mole of oxygen is absorbed and LXVII is formed. Under anhydrous conditions one mole of oxygen is absorbed and

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[225] E. Frankland, _J. Chem. Soc._, _15_, 363 (1862).

[226] E. Krause and R. Nitsche, _Ber._, _54_, 2784 (1921); E. Krause and H. Polack, _ibid._, _61_, 278 (1928); E. Krause and P. Nobbe, _ibid._, _63_, 294 (1930); E. Krause and P. Nobbe, _ibid._, _64_, 2112 (1931).

[227] J. R. Johnson and M. G. Van Campen, Jr., _J. Am. Chem. Soc._, _60_, 121 (1938).

LXVIII is obtained.

$\underline{n}$-$Bu_2B(O_2\text{-}Bu)$ LXVII

$(\underline{n}Bu)\,B\,(O_2\text{-}Bu)_2$ LXVIII

Johnson and Van Campen conclude that the anhydrous autoxidation is a stepwise process in which the dialkyl boronic acid is an intermediate. The addition of moisture inhibits further oxidation through the formation of a stable hydrate. They propose an oxidation process involving the initial formation of a "borine peroxide" intermediate, followed by further reaction with a second mole of trialkyl borane.

(100) $R_3B + O_2 \longrightarrow R_3B{\cdot}O_2$

(101) $R_3B{\cdot}O_2 + R_3B \longrightarrow 2\ R_2BOR$

In the gas phase trimethylboron reacts with one mole of oxygen to form a product formulated[228] as $CH_3B\,(OCH_3)_2$. Similarly, tri-*iso*-propylboron forms the corresponding boronate ester that is slowly oxidized further to borate. That one of the early steps in the autoxidation reaction is the formation of a peroxide has been confirmed in the case of trimethyl borane[229]. Oxidation of trimethyl borane

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[228] C. H. Bamford and D. M. Newitt, *J. Chem. Soc.*, *1946*, 695.

[229] R. C. Petry and F. H. Verhoek, *J. Am. Chem. Soc.*, *78*, 6416 (1956).

in a flow system (room temperature, contact time 2-3 min., 10-15 mm. pressure) yields an explosive product (LXIX).

Me_2BOOMe

LXIX

Dialkyl boron compounds of the type R_2BCl and R_2BOBR_2 are also rapidly oxidized by oxygen[230]. The controlled autoxidation of boronous acids[231], alkyl boronites[231], and boronic acids[232] has also been investigated. Secondary and tertiary alkyl boronic acids are especially rapidly oxidized, but water completely inhibits the reaction of primary and secondary compounds[232]. Monoalkyl boron compounds are stable to oxygen[233]. The trimeric tri-n-butyl boronic anhydride $(n\text{-}BuBO)_3$[234] rapidly combines with oxygen to form the n-butyl ester of metaboric acid. A peroxidic intermediate is indicated since iodine is liberated from potassium iodide by the oxidized solution. Grummitt has proposed the process:

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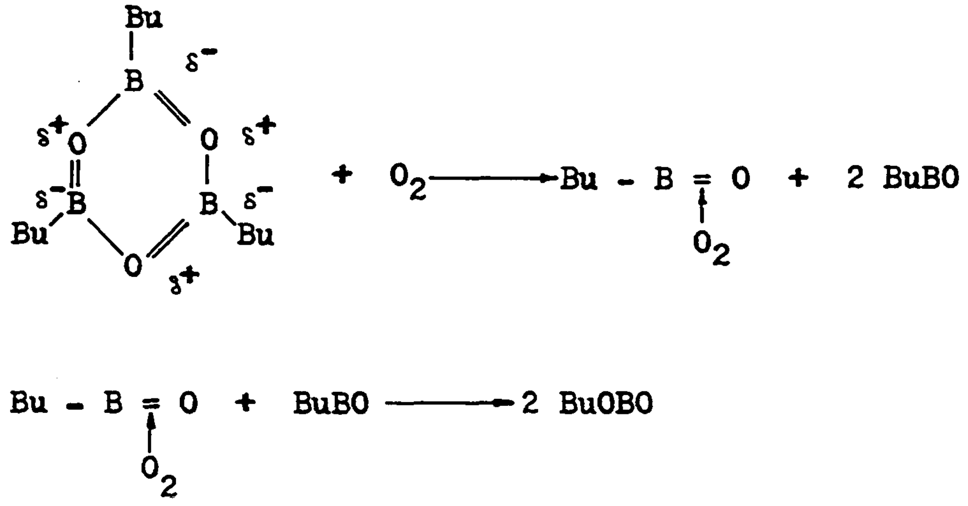
[230] J. R. Johnson, H. R. Snyder, and M. G. Van Campen, Jr., J. Am. Chem. Soc., 60, 115 (1938).

[231] E. Frankland, Proc. Roy. Soc., 25, 165 (1877).

[232] H. R. Snyder, J. A. Kuck and J. R. Johnson, J. Am. Chem. Soc., 60, 105 (1938); J. R. Johnson, M. G. Van Campen, Jr., and O. Grummitt, ibid., 60, 111 (1938).

[233] P. A. McCusker and L. J. Glunz, ibid., 77, 4253 (1955).

[234] O. Grummitt, ibid., 65, 1811 (1942).



The peroxide intermediate initiated the rapid polymerization of vinyl acetate. Aryl boron compounds are increasingly stable to oxygen. Tri-phenylboron is completely oxidized after one hour at 25°[235]. Under identical conditions tri-1-naphthylboron is much less reactive (50 days for complete reaction at 25°). Trimesitylboron is inert. Although trivinylboron does not react with oxygen at room temperature, methyl divinylboron is more reactive[236].

Abraham and Davies[237] found that neat tri-*n*-butylboron absorbed 1.01 mole of oxygen, giving dibutyl butylboronate and a trace (0.02 mole) of peroxide (iodometrically). In dilute cyclohexane solution 1.2 moles of oxygen were absorbed

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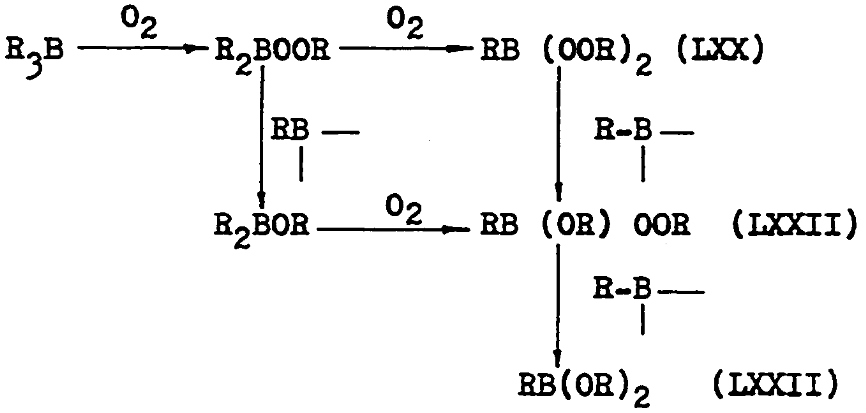
[235] H. C. Brown and V. H. Dodson, *ibid.*, *79*, 2303 (1957).

[236] T. D. Parsons, M. B. Silverman, and D. M. Ritter, *ibid.*, *79*, 5091 (1957).

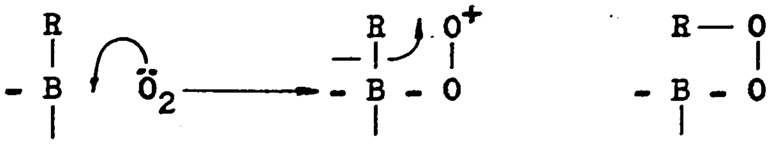
[237] M. H. Abraham and A. G. Davies, *J. Chem. Soc.*, *1959*, 429.

yielding a product containing 1.06 mole peroxide. Addition of tri-*n*-butylboron at the end of the oxidation brought about the reduction of the oxidizing agent to dibutyl butylboronate. These facts have been interpreted on the basis of the following scheme:



The initial product of the oxidation is a peroxide, R_2BOOR, that can be reduced to R_2BOR or further oxidized to LXX. The sequence of reactions can thus lead to the formation of LXX, LXXI, and LXXII, either singly or in mixture according to reaction conditions.

The initial step is presumably analogous to that pictured earlier for the alkyl magnesium compounds, i.e., an initial coordination of oxygen on to the boron atom followed

(102)


by, or concurrent with, a 1,3 shift of the alkyl group from boron to oxygen. On this basis Abraham and Davies suggest that the ease of autoxidation of organoboron compounds is related to the ability of the substituent groups to donate electrons to the unfilled shell of the boron atom. For example, the reactivity series

$$\text{Alkyl} - \text{B}\langle \quad > \quad \text{Vinyl} - \text{B}\langle \quad \sim \quad \text{Aryl} - \text{B}\langle$$

can be accounted for by the occurrence of $p_{\pi}-p_{\pi}$ overlap from the organic group to boron. Similarly, the series

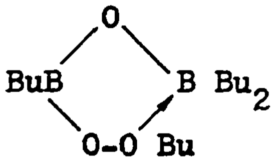
$R_3B > R_2BOR > RB(OR)_2$

$R_2BOH > R_2BOR > R_2BO^-Na^+$

$R_3B > R_2BCl > RBCl_2$

from similar overlap of the oxygen or halogen atoms.

The observation that sec-butylboronous anhydride in ether absorbs only 1 mole of oxygen and in water 1.70 moles has been interpreted as being due to intramolecular association (LXXIII), thereby inhibiting autoxidation of the second sec-butyl group[238].



LXXIII

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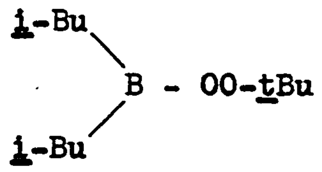
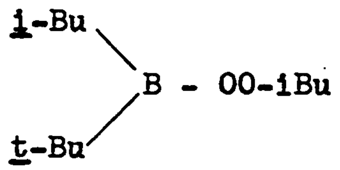
[238] A. G. Davies and D. G. Hare, ibid., 1959, 438.

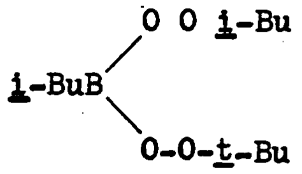
As a test for the proposed reaction mechanism for autoxidation of organoboron compounds Davies, Hare, and White[239] determined the relative reactivity of the *t*-butyl group and the *iso*-butyl group in the autoxidation of di-*iso*-butyl-*t*-butylboron. The absorption of the first mole of oxygen gives a product equivalent to 69% (LXXIV) and 31% (LXXV). The selectivity during the absorption of the second mole of oxygen is approximately 45:1 and the ultimate product consists of 99% (LXXVI) and 1% (LXXVII).



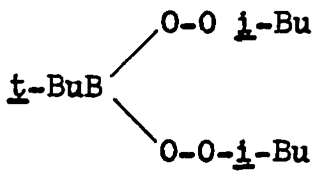
LXXIV



LXXV



LXXVI



LXXVII

The *iso*-butyl-*iso*-butylperoxy-*t*-butylperoxyboron (LXXVI) rapidly decomposes at room temperature via the process

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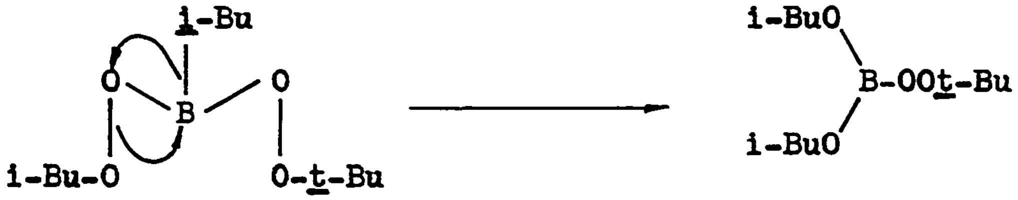
[239] A. G. Davies, D. G. Hare, and R. F. M. White, *ibid.*, *1961*, 341.



It is interesting to note that when the oxidation was carried out in carbon tetrachloride the product was the compound i-BuB(O-t-Bu)(O-i-Bu), and t-butyl chloride and carbonyl chloride were detected. The fact that polymerization of acrylonitrile is induced by the oxidizing mixture was also noted. These data tend to cast some doubt as to the validity of the previously suggested mechanism.

The oxidation of dialkyl zinc compounds has been pictured as proceeding via the usual coordination-rearrangement scheme[205,220,240]. However, Coates[241] has disagreed and postulates the alternative electron transfer process

(103) $$\mathrm{RZnR} \overset{e^{-}}{\curvearrowright} + \mathrm{O_2} \longrightarrow \mathrm{RZn^{+}}\} \; \mathrm{RO_2^{-}} \longrightarrow \mathrm{RZnOOR}$$

since the zinc alkyls are weak acceptors to oxygen donors.

The facile autoxidation of aluminum alkyls has been proposed as a synthetic process for the preparation of

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[240] M. H. Abraham, *ibid.*, *1960*, 4130.

[241] Coates, *op. cit.*, p. 67.

primary alcohols from terminal olefins[242,243,244]. The aluminum alkyls are most conveniently prepared from commercially available terminal olefins. The aluminum alkyl is then oxidized according to the overall reaction

$$(104) \quad AlR_3 + 1.50O_2 \longrightarrow Al(OR)_3$$

and the alkoxide obtained is hydrolyzed to aluminum hydroxide and the corresponding primary alcohol. The mechanism of the oxidation is apparently similar to that discussed above[205]. Peroxides have been isolated from the autoxidation of organo-aluminum compounds[205,220].

The oxidation of dicyclohexyl mercury in *iso*-propyl alcohol at 60° gives rise to a number of products including acetone (20%), cyclohexanol (44%), cyclohexanone (43%), and mercury (64%)[245]. The authors suggest an unstable peroxide intermediate that decomposes to form the observed reaction products.

The organic derivatives of the alkali metals possess a

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[242] K. Ziegler, *International Congress of Pure and Applied Chemistry*, *Zurich*, *July 21-27, 1955*, *14*, 274 (1955).

[243] A. M. Sladkov, V. A. Markevich, I. A. Yavich, L. K. Luneva, and V. N. Chernov, *Doklady Akad. Nauk SSSR*, *119*, 1159 (1958).

[244] K. Ziegler, F. Krupp, and K. Zosel, *Ann.*, *629*, 241 (1960).

[245] G. A. Razuvaev, G. G. Petukhov, S. F. Zhil'tsov, and L. F. Kudryartsev, *Doklady Akad. Nauk, SSSR*, *135*, 87 (1960).

highly polarized carbon-metal bond ($\overset{\delta-}{C}\text{—}\overset{\delta+}{M}$) and thus are more nearly ionic in character as evidenced by their conductivity. The organo-lithium compounds may prove an exception to this generalization, the metal-carbon bond in such substances approaching more nearly a covalent nature. Accordingly, the reactions are more liable to proceed via electron transfer and radical pathways yielding dimeric products in addition to the usual peroxides and alcoholates.

Schlenk and Marcus[246] report that the red color of triphenylmethyl-sodium is rapidly destroyed on contact of an ethereal solution with air. Although no experimental details are presented, the fleeting appearance of the yellow triphenylmethyl color encouraged Schlenk and Marcus to propose the rationale:

(105) $2\ Ph_3C^-Na^+ + O_2 \longrightarrow 2\ Ph_3C\cdot + Na_2O_2$

(106) $2\ Ph_3C + O_2 \longrightarrow Ph_3COOCPh_3$

Coates[247] has presented a more logical sequence:

(107) $Ph_3C^-Na^+ + O_2 \longrightarrow Ph_3C\cdot + Na^+O_2^-$

(108) $Ph_3C^-Na^+ + Na^+O_2 \longrightarrow Ph_3C\cdot + Na_2O_2$

(109) $2\ Ph_3C\cdot \rightleftharpoons Ph_3C - CPh_3$

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[246] W. Schlenk and E. Marcus, Ber., 47, 1666 (1914).

[247] Coates, op. cit., p. 31.

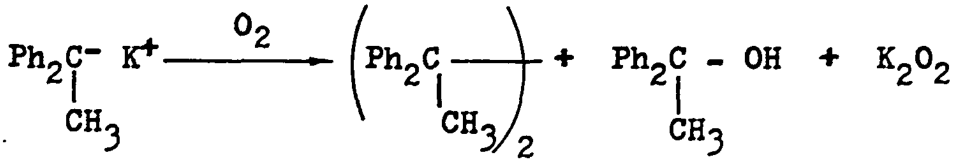
(110) $Ph_3C\cdot + O_2 \longrightarrow Ph_3COO\cdot$

(111) $Ph_3COO\cdot + \cdot CPh_3 \longrightarrow Ph_3COOCPh_3$

Although the previous results seem to have been duplicated[248], Bachmann and Wiselogle[249] find that the peroxide is actually a side product; the carbinol is isolated in good yield.

$$Ph_3C^-Na^+ + O_2 \longrightarrow \underset{67\%}{Ph_3COH} + \underset{4\%}{(Ph_3CO)_2} + \underset{(?)}{Ph_3COOH}$$

In apparent agreement with these results is the report of Ziegler and Schnell[250] concerning the oxidation of diphenylmethyl potassium wherein the dimeric product is formed in <u>low</u> (unspecified) yield along with the corresponding carbinol.



$$Ph_2\underset{CH_3}{\underset{|}{C}}{}^- K^+ \xrightarrow{O_2} \underset{\text{low yield}}{\left(Ph_2\underset{CH_3}{\underset{|}{C}}-\right)_2} + Ph_2\underset{CH_3}{\underset{|}{C}} - OH + K_2O_2$$

Similarly, Wooster[251] mentions that diphenylmethyl sodium is

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[248] C. A. Kraus and R. Rosen, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>47</u>, 2739 (1925).

[249] W. E. Bachmann and F. Y. Wiselogle, <u>ibid</u>., <u>58</u>, 1943 (1936).

[250] K. Ziegler and B. Schnell, <u>Ann</u>., <u>437</u>, 231 (1924).

[251] C. B. Wooster, <u>Chem</u>. <u>Rev</u>., <u>11</u>, 21 (1932).

"smoothly oxidized" in liquid ammonia to the hydrocarbon and sodium peroxide. No experimental details concerning this reaction are available.

The oxidation of a benzene solution of phenyllithium gives phenol (22-26%), diphenyl (25%), and a trace of _p_-phenylphenol[252]. The results of an exhaustive investigation with regard to the influence of structure of the aromatic portion of lithium aryls on the yield of dimeric products in the autoxidation have been reported[217]. In no case has an aryl peroxide or hydroperoxide been isolated. The oxidation of 9-benzyl fluorenyl lithium has been reported to yield dimer quantitatively[253] while fluorenyl lithium compounds not possessing the substituent in the 9-position form ketones exclusively[254]. The oxidation of aliphatic organolithium compounds leads to isolable hydroperoxides under appropriate con ditions[205,218,220,221]. Triphenylsilyllithium apparently undergoes autoxidation in a manner similar to the carbon anlog[255]. The oxidation of rubidium compounds is in accord with the foregoing scheme, i.e., (107)

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[252] H. Gilman and H. A. Pacevitz, _J. Am. Chem. Soc._, _61_, 1603 (1939).

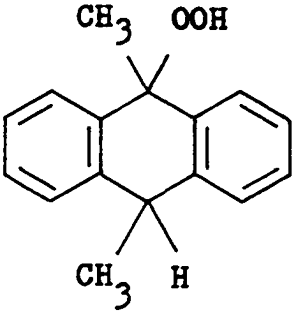
[253] D. Lavie and E. D. Bergmann, _Bull. soc. chim. France_, _1951_, 250.

[254] E. D. Bergmann, Y. Hirshberg, D. Lavie, Y. Sprinzak, and J. Szmuszkovicz, _ibid._, _1952_, 703.

[255] M. V. George and H. Gilman, _J. Am. Chem. Soc._, _81_, 3288 (1959).

to (111)[256].

The autoxidation of alkali metal adducts of stilbene or of benzophenone (metal ketyl) usually furnish the original parent compound along with alkali peroxide[257]. Similarly, the adduct of sodium and naphthalene (radical ion?) yields the original hydrocarbon on low temperature autoxidation along with sodium peroxide[258]. In the case of 9,10-dimethylanthracene, the hydroperoxide LXXVI is obtained on autoxidation[258].



LXXVI

Oxidation of Hydroxylamines

The instability of hydroxylamines in the presence of air or oxygen is well known. The autoxidation of aliphatic hydroxylamines, in particular benzylhydroxylamine, has been

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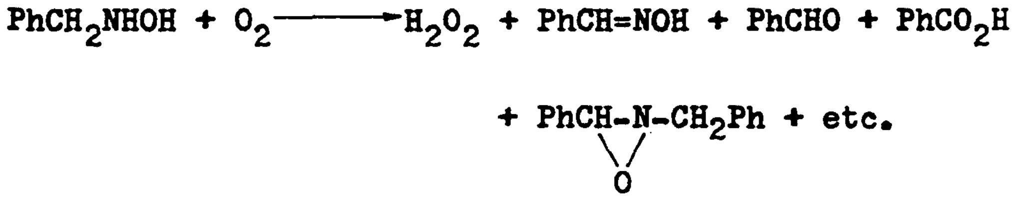
[256] H. Erdmann and P. Kothner, Ann., 294, 66 (1897).

[257] W. Schlenk, J. Appenrodt, A. Michael, and A. Thal., Ber., 47, 473 (1914).

[258] H. Hock and F. Ernst, ibid., 92, 2732 (1959).

studied and found to lead to a variety of products[259,260], e.g. benzaldoxime, benzaldehyde, benzoic acid, benzyl-*iso*-benzaldoxime, along with a number of other condensation products. The presence of hydrogen peroxide was inferred by positive results to several color tests.

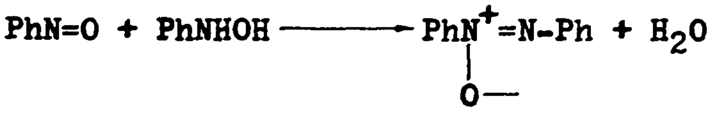


$$\mathrm{PhCH_2NHOH + O_2 \longrightarrow H_2O_2 + PhCH{=}NOH + PhCHO + PhCO_2H}$$
$$\mathrm{+\ \underset{\diagdown\,O\,\diagup}{PhCH\text{-}N}\text{-}CH_2Ph + etc.}$$

Arylhydroxylamines are readily autoxidized in solution to form nitrosobenzenes as primary products[261]. In neutral solution, phenylhydroxylamine yields azoxybenzene as the main product, along with hydrogen peroxide. The azoxybenzene is formed by condensation of nitrosobenzene with unchanged phenylhydroxylamine.

Neutral solution

$$\mathrm{PhNHOH + O_2 \longrightarrow PhN{=}O + H_2O_2}$$



$$\mathrm{PhN{=}O + PhNHOH \longrightarrow \underset{O^{-}}{\underset{|}{PhN^{+}}}{=}N\text{-}Ph + H_2O}$$

In alkaline solution the products of atmospheric oxidation

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[259] R. Behrend and E. König, Ann., 263, 210 (1891).

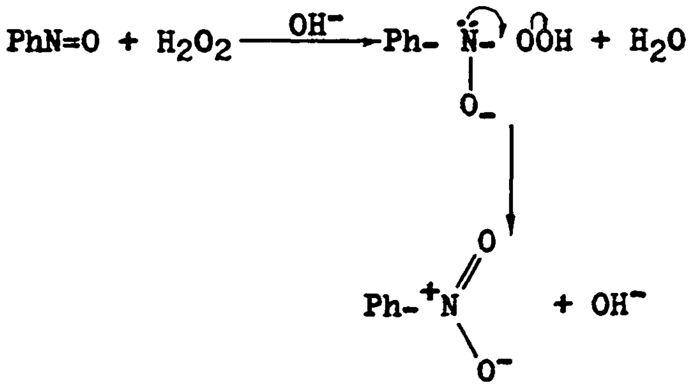
[260] E. Bamberger and B. Szolayski, Ber., 33, 3193 (1900).

[261] E. Bamberger, *ibid.*, 33, 113 (1900).

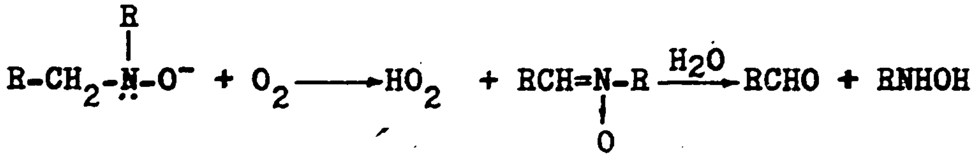
are mainly azoxybenzene and nitrobenzene, but no hydrogen peroxide. The nitrobenzene is presumably due to the further oxidation of the initially formed nitrosobenzene by the alkaline hydrogen peroxide.

Alkaline solution

$$\text{PhNHOH} + O_2 \xrightarrow{OH^-} \text{PhN=O} + H_2O_2$$



More recent studies on the autoxidation of N,N-dialkylhydroxylamines in aqueous alkaline solution have again demonstrated the occurrence of an oxidative dehydrogenation[262]. The dehydrogenation products are not stable and are further hydrolyzed.

(112) 

$$R\text{-}CH_2\text{-}\overset{R}{\underset{\cdot\cdot}{N}}\text{-}O^- + O_2 \longrightarrow HO_2 + RCH{=}\underset{O}{N}\text{-}R \xrightarrow{H_2O} RCHO + RNHOH$$

The rate of autoxidation is a function of pH, being most rapid in the presence of sodium hydroxide. Positive catalysis

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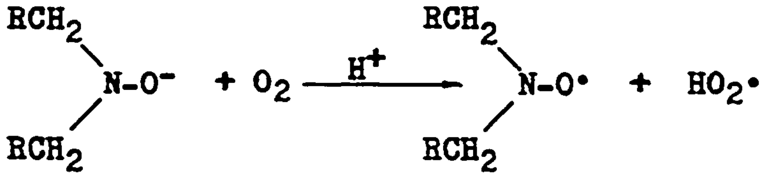
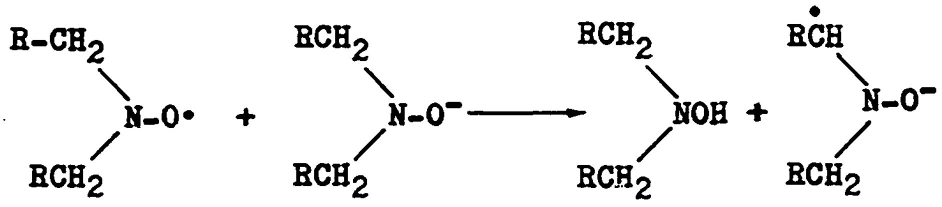
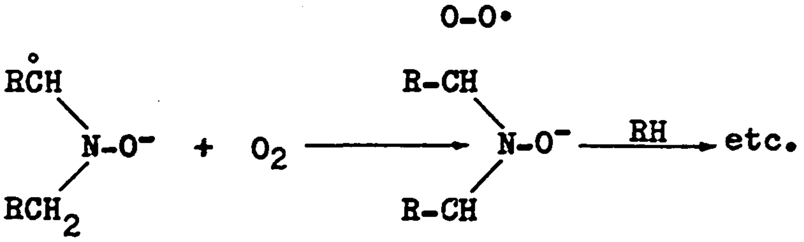
[262] D. H. Johnson, M. A. Thorold-Rogers, and G. Trappe, J. Chem. Soc., 1956, 1093.

by cupric ion and by 2-naphthol was observed. A mechanism involving the following steps has been proposed:

(113) 

(114) 

(115) 

The presence of an organic peroxide in addition to the hydrogen peroxide was demonstrated by polarographic measurements.

Chemiluminescent Oxidations

A number of chemical substances emit visible light upon oxidation in alkaline solution with molecular oxygen. For example, the autoxidation of aryl Grignard reagents is often strongly chemiluminescent[263]. One of the earliest observa-

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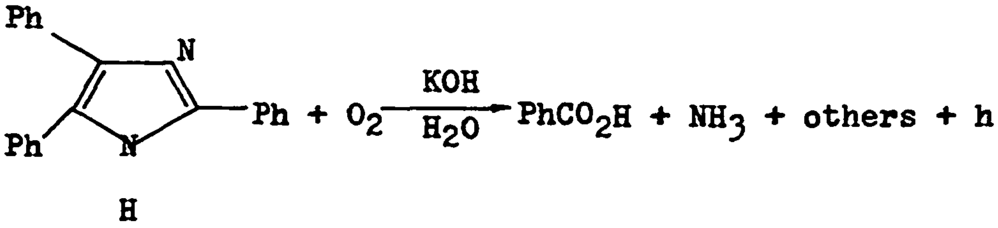
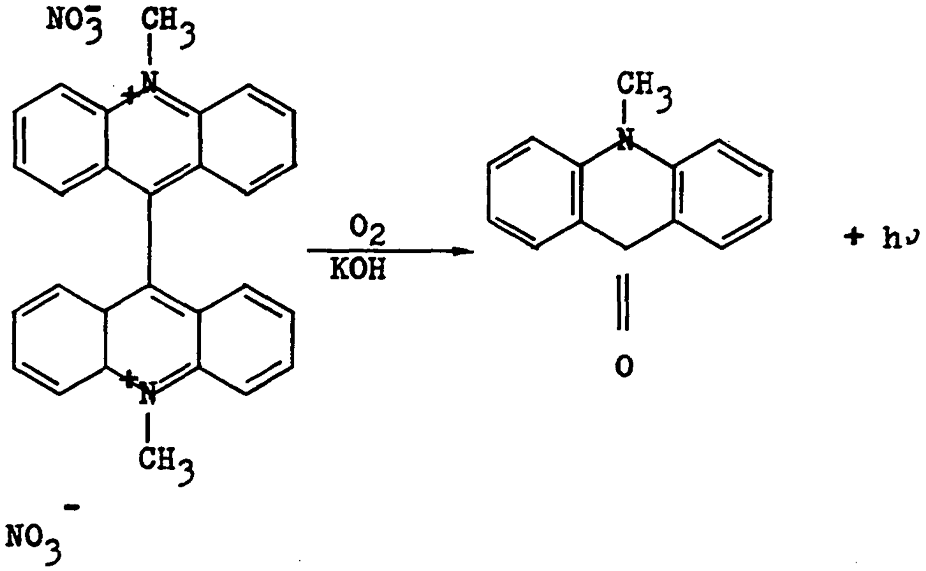
[263] R. T. Dufford, D. Nightingale, and S. Calvert, J. Am. Chem. Soc., 47, 95 (1925).

tions of this phenomena was made in connection with the compound lophine (LXXVII) in 1877[264].



LXXVII

Analogously, the compound lucigenin (10,10'-dimethyl-9,9'-biacridinium nitrate (LXXVII) undergoes oxidation in alkaline solution with simultaneous emission of light[265].



LXXVIII

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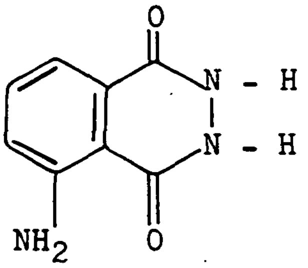
[264] B. Radziszewski, Ber., 10, 70 (1877).

[265] K. Gleu and W. Petsch, Angew. Chem., 48, 57 (1935).

The origin of this interesting phenomenon is far from completely understood. In this respect, the compound 3-amino-phthalhydrazide (luminol, LXXIX) has received the most study from a mechanistic viewpoint[266,267].



LXXIX

In view of the existence of several excellent compilations[266,267] we shall neglect any historical presentation of this problem. Suffice to note that the reaction is undoubtedly of a radical nature (chemiluminescence is inhibited by radical chain stoppers) and of somewhat different nature in water than in organic solvents. In dimethyl-sulfoxide (potassium t-butoxide base) the oxidation proceeds by way of the dianion of luminol and the following pathway has been

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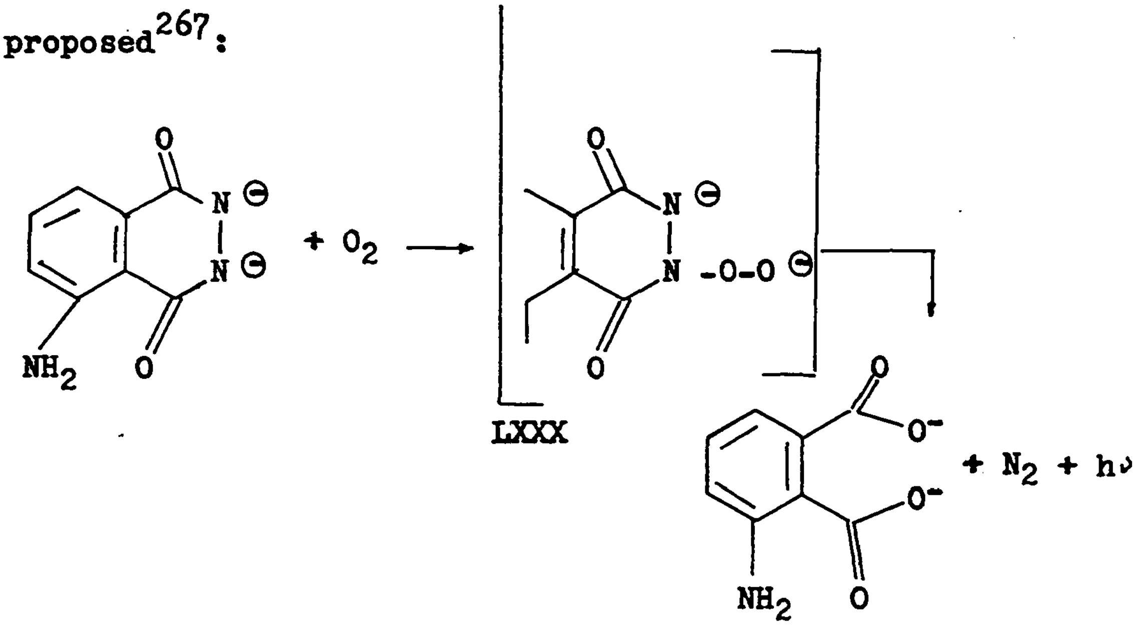
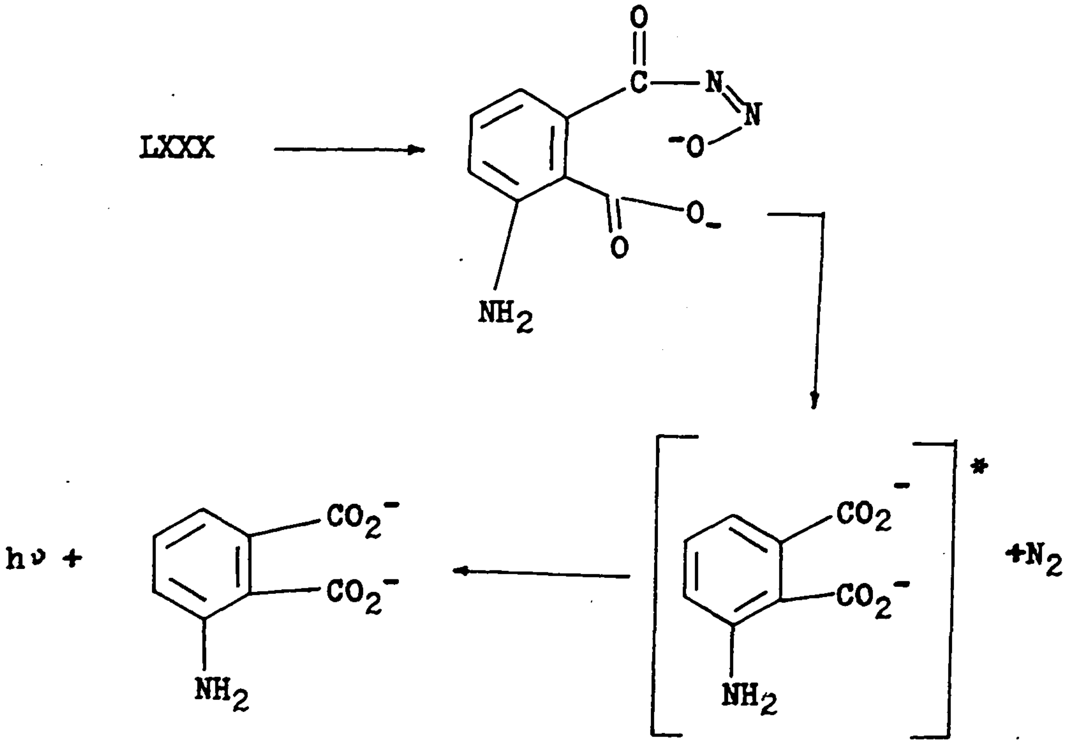
[266] T. Bremer, Bull. soc. chim. Belges, 62, 569 (1953). This reference presents a review of existing mechanistic speculations concerning the origin and nature of chemiluminescence in addition to a critical discussion of the luminol problem.

[267] E. H. White, "The Chemiluminescence of Luminol", in W. D. McElroy and B. Glass, eds., "Light and Life", pp. 183-196, Johns Hopkins Press, Baltimore, 1961. A discussion of various suggested mechanisms for luminol chemiluminescence along with a new mechanistic postulate.

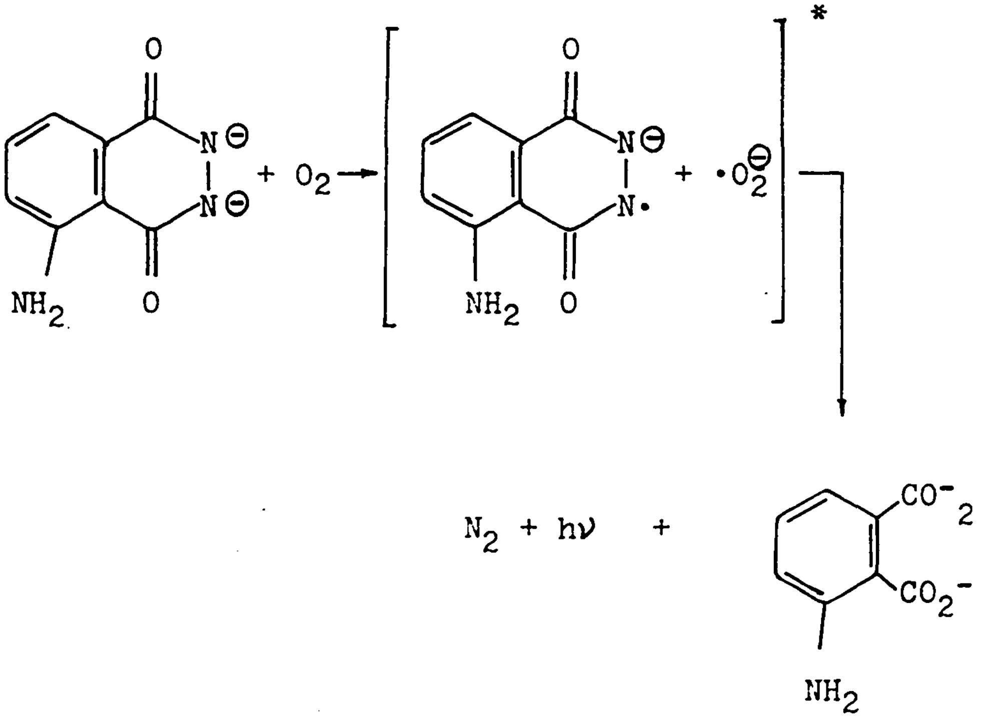
proposed[267]:



Since hydrogen peroxide is <u>apparently</u> not observed in the reaction in dimethyl-sulfoxide, an intramolecular decomposition for the intermediate LXXX is imagined.



In spite of the many speculations concerning the mechanism of this reaction much additional data are necessary to effect anywhere near a complete understanding. For example, a possible source of chemiluminescence from the oxidation of luminal would appear to be



The likelihood of an initial complex between oxygen and the dianion that could decay with the emission of light has not been seriously considered, but may be a possibility.

Oxidation of Hydrazobenzene

The detection of hydrogen peroxide along with a azobenzene as a product of the autoxidation of hydrazobenzene in alkaline alcoholic solution was first reported by Manchot in 1900[100]. However, no substantial amounts of the peroxide were actually isolated until the work of Walton and Filson[268] in 1932. They discovered that hydrazobenzene in an alcohol or benzene solution absorbed oxygen to form hydrogen peroxide (quantitative) and azobenzene with negligible occurrence of side reaction. The reaction in basic solution has been described in the patent literature[269] as a commercial source of hydrogen peroxide[270].

In spite of the proved utility of the reaction, apparently only one serious attempt at establishing a mechanism has been made. Blackadder and Hinshelwood[271] have presented the results of a kinetic study of the oxidation of hydrazobenzene in alkaline alcoholic solution and have concluded that the reaction follows the rate law (116), first order in hydrazobenzene, and independent of oxygen pressure.

$$(116)\quad d(\mathrm{PhNHNHPh})/dt = \frac{K_1k_2[\mathrm{PhNHNHPh}]}{[\mathrm{H}^+]}$$

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[268] J. H. Walton and G. W. Filson, *J. Am. Chem. Soc.*, *54*, 3228 (1932).

[269] See, *inter alia*, E. C. Soule, U. S. Patent 2,035,101, March 24, 1936; abstracted in *C. A.*, *30*, 3180 (1936); G. L. Cunningham, U. S. Patent 2,083,691, June 15, 1937; abstracted in *C. A.*, *31*, 5520 (1937); G. L. Cunningham and F. E. Romesberg, U. S. Patent 2,908,552, Oct. 13, 1959; abstracted in *C. A.*, *54*, 3882 (1960).

[270] See *Chem. Week*, *73*, 78 (1953).

[271] D. A. Blackadder and C. Hinshelwood, *J. Chem. Soc.*, *1957*, 2898.

The following mechanism has been proposed to account for these results:

$$(117)\quad \text{PhNH-NHPh} \underset{k\text{-}1}{\overset{k_1}{\rightleftharpoons}} \text{Ph-}\bar{\text{N}}\text{-NH-Ph} + \text{H}^+ \qquad K_1 = k_1/k\text{-}1$$

$$(118)\quad \text{Ph-}\bar{\text{N}}\text{-NH-Ph} \underset{k\text{-}2}{\overset{k_2}{\rightleftharpoons}} \text{Ph-}\bar{\text{N}}\text{-}\bar{\text{N}}\text{-Ph} + \text{H}^+ \qquad K_2 = k_2/k\text{-}2$$

$$(119)\quad \text{Ph-}\bar{\text{N}}\text{-}\bar{\text{N}}\text{-Ph} + \text{O}_2 \xrightarrow{k_3} \text{Ph-N=N-Ph} + \text{O}_2^{=}$$

The formation of the dianion (reaction 118) was assumed to be rate determining on the seemingly tenuous reasoning that it involved charge redistribution (participation of phenyl group in stabilizing negative charge).

In a subsequent publication[272], these authors reported the effect of cupric ion on the reaction. The observed catalysis was rationalized on the basis of the rate determining step,

$$(120)\quad \text{Ph}\bar{\text{N}}\text{-NHPh} + \text{Cu(II)} \longrightarrow \text{Ph-}\dot{\text{N}}\text{-NHPh} + \text{Cu(I)}.$$

followed by the steps,

$$(121)\quad \text{Ph-}\dot{\text{N}}\text{-NH-Ph} + \text{Cu(II)} \longrightarrow \text{Ph-N=N-Ph} + \text{Cu(I)} + \text{H}^+$$

$$(122)\quad \text{Cu(I)} + \text{O}_2 \longrightarrow \text{Cu(II)} + \cdot\text{O}_2^{-}$$

A great deal of additional data are necessary before this mechanism can be considered established. The observation

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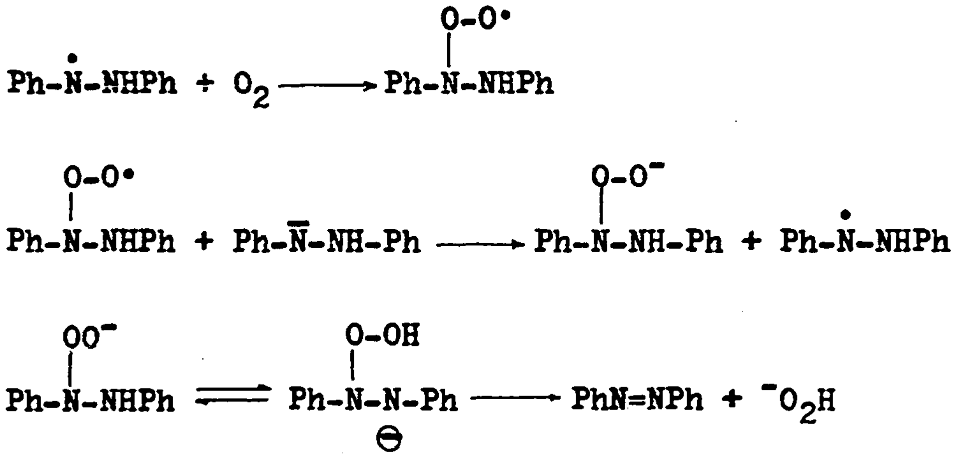
[272] D. A. Blackadder and C. Hinshelwood, *ibid.*, *1957*, 2904.

that diphenylamine undergoes a one-electron transfer reaction with oxygen in basic solution[273] appears to favor a radical mechanism, e.g.,

$$\mathrm{Ph{-}\bar{N}{-}NH{-}Ph} + O_2 \longrightarrow \mathrm{Ph{-}\dot{N}{-}NH{-}Ph} + \bullet O_2^-$$

$$\mathrm{Ph{-}\dot{N}{-}NHPh} + \bullet O_2^- \longrightarrow \mathrm{Ph{-}N{=}N{-}Ph} + HO_2^-$$

or



$$\mathrm{Ph{-}\dot{N}{-}NHPh} + O_2 \longrightarrow \mathrm{Ph{-}\overset{\overset{O-O\bullet}{|}}{N}{-}NHPh}$$

$$\mathrm{Ph{-}\overset{\overset{O-O\bullet}{|}}{N}{-}NHPh} + \mathrm{Ph{-}\bar{N}{-}NH{-}Ph} \longrightarrow \mathrm{Ph{-}\overset{\overset{O-O^-}{|}}{N}{-}NH{-}Ph} + \mathrm{Ph{-}\dot{N}{-}NHPh}$$

$$\mathrm{Ph{-}\overset{\overset{OO^-}{|}}{N}{-}NHPh} \rightleftharpoons \mathrm{Ph{-}\overset{\overset{O-OH}{|}}{N}{-}\underset{\ominus}{N}{-}Ph} \longrightarrow \mathrm{PhN{=}NPh} + {}^-O_2H$$

Oxidation of Heterocyclic Compounds

Hydantoins

The initial observation of autoxidation in alkaline solution in the hydantoin series appears to be that of Pinner[274] who heated 5-phenyl-hydantoin in alcoholic potassium hydroxide and obtained diphenylhydantil

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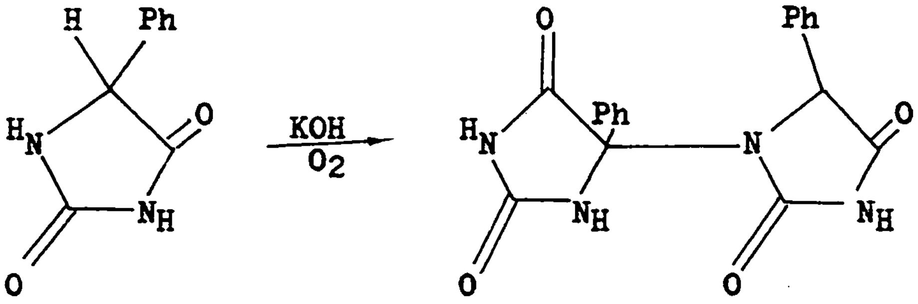
[273] R. Hoskins, *J. Chem. Phys.*, *25*, 788 (1956).

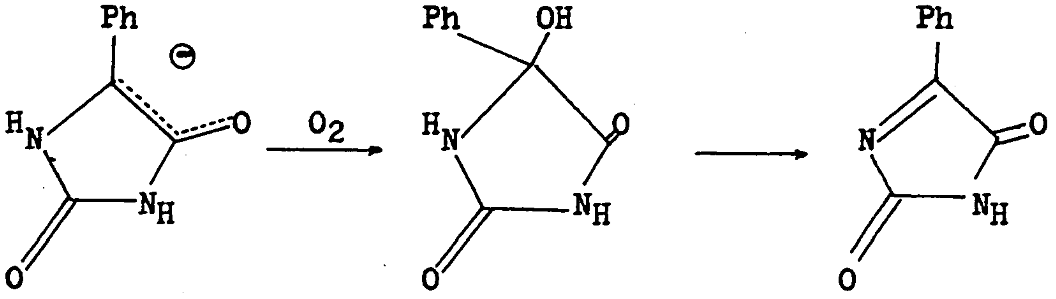
[274] A. Pinner, *Ann.*, *350*, 135 (1906).

(octahydro-2,4,2',4'-tetraoxo-5,5'-diphenyl-1,5'-diglyoxalinyl, LXXXI).



LXXXI

He attributed the result to oxidation by air. This result has recently been confirmed and extended[275]. Edwards and Nielsen found that 5-alkyl hydantoins were not oxidized and concluded that the oxidation involved an anion, possibly LXXXII.



LXXXII

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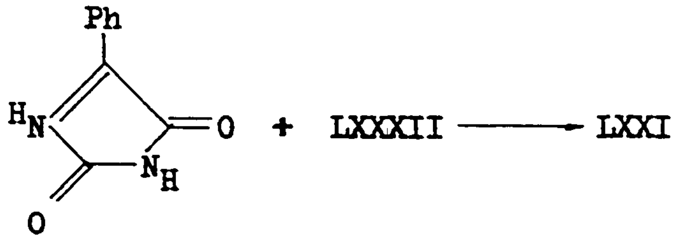
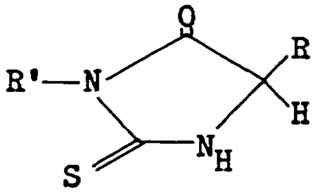
[275] J. T. Edwards and S. Nielsen, J. Chem. Soc., 1959, 2327.



The reaction was extended to a series of substituted 2-thiohydantoins (LXXXIII), wherein similar products were obtained

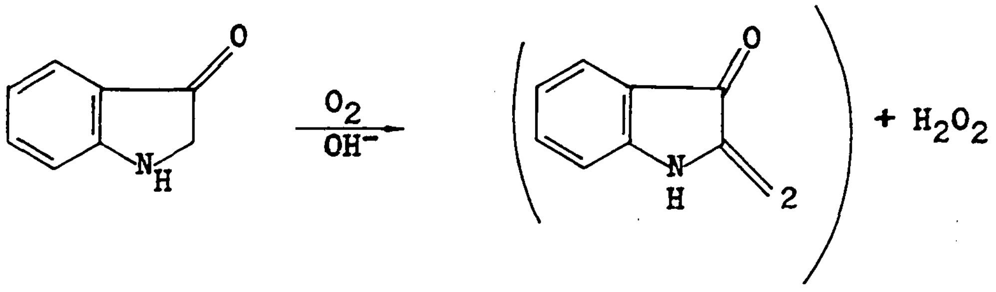


LXXXIII

Again, it is not unlikely that the reaction may involve radical intermediates.

Indoxyls

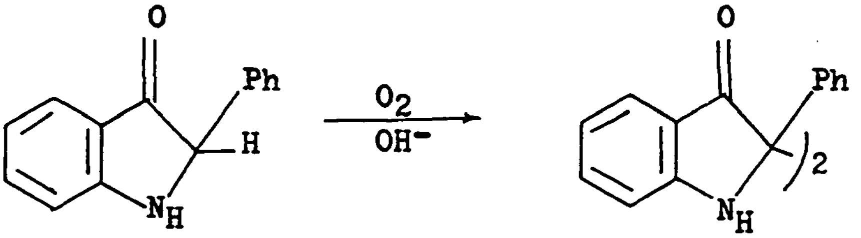
The formation of indigo (LXXV) from indoxyl (LXXIV) via an oxidative dimerization in alkaline solution is a well established reaction in the dye industry.



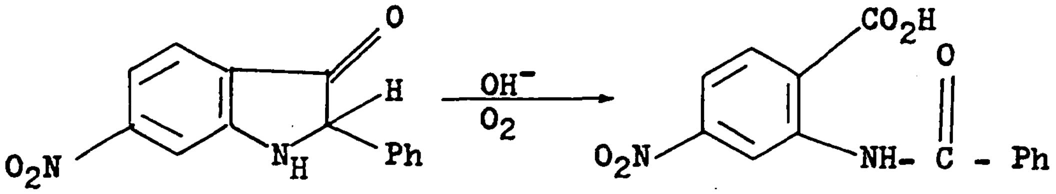
LXXXIV

LXXXV

The reaction has been the subject of considerable study[276,277] and undoubtedly proceeds through initial dimerization to the leuco form followed by oxidative dehydrogenation of the type previously described. The reaction stops at the dimerization stage if 2-phenylindoxyl is subjected to similar conditions[276].



In aqueous alkali under controlled conditions, indoxyls substituted in the benzene ring give ring opening reactions, e.g.[278],



(80%)

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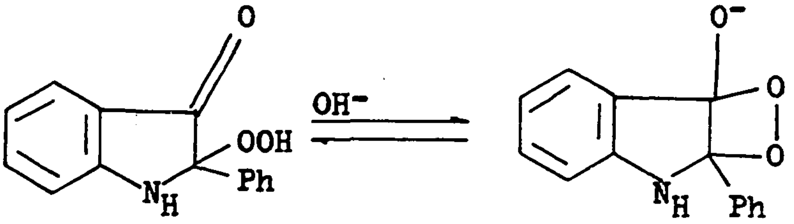
[276] L. Kalb and J. Bayer, Ber., 45, 2150 (1912); ibid., 46, 3879, 3881 (1913).

[277] L. Ettinger and P. Friedländer, ibid., 45, 2074 (1912); P. Friedländer and K. Kunz, ibid., 55B, 1597 (1922).

[278] P. Ruggli, A. Zimmerman, and O. Schmid, Helv. Chim. Acta, 16, 1249 (1933).

Similarly, 2-phenyl-5-styryl-6-nitroindoxyl gives an analogous product. The different products formed from similar starting materials may be due to (a) the nitro compound being more acidic, hence reacting more slowly and forming less dimer, (b) the possibility that the dimer may be dissociated in the case of the nitro compound and hence react further with oxygen, or (c) difference in reaction conditions (rate of stirring, etc.). The ring opened product could arise in a manner similar to that presented earlier to account for the oxidative cleavage of ketones (*vide supra*).



Tetrahydrocarbazole

The ready autoxidation to a hydroperoxide of tetrahydrocarbazole and related compounds was first reported in 1949[279]. The reaction can be formulated simply as involving the radical LXXXVI with attack of oxygen occurring at carbon.

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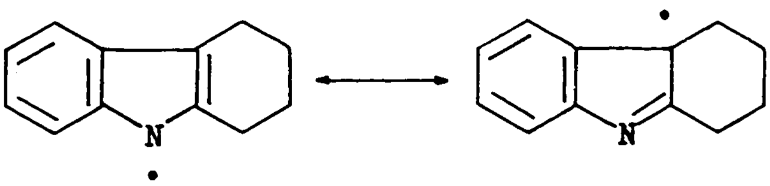
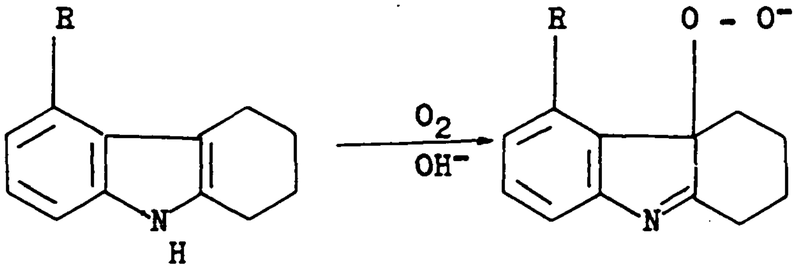
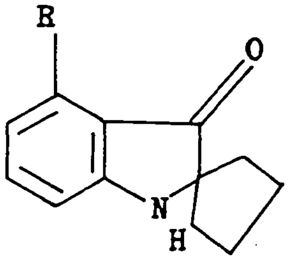
[279] R. J. S. Beer, L. McGrath, A. Robertson, and A. B. Woodier, *Nature*, *164*, 362 (1949); R. J. S. Beer, L. McGrath, and A. Robertson, *J. Chem. Soc.*, *1950*, 2118.



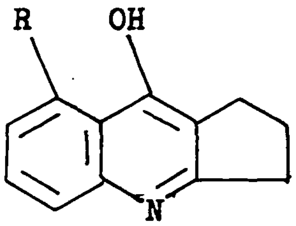
LXXXVI

A similar reaction occurs in alkaline alcoholic solution[280], forming the products LXXXVII and LXXXVIII.





+



LXXXVII LXXXVIII

Although the tetrahydrocarbuzole hydroperoxide was not isolated, independent experiments showed that it rapidly

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[280] R. J. S. Beer, T. Broadhurst, and A. Robertson, *ibid.*, *1952*, 4946.

rearranged to the isolated products. Substituent effects were in accord with those expected for a reaction involving radical intermediates.

Conclusions

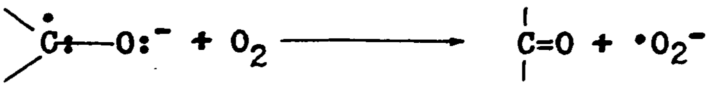
Although the products of the reaction of oxygen with organic materials in alkaline solution are numerous and the overall reactions involved are often complex, the specific reactions involving molecular oxygen are few and relatively simple. In general, the most important reaction involving molecular oxygen is the combination of an alkyl radical with oxygen

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

forming a peroxy radical.

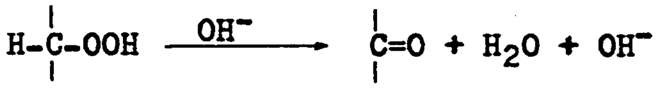
Oxygen reacts readily with a variety of anions and carbanions, but many of these reactions can be explained by free radical chain reactions. Oxygen can remove one electron from various carbanions and anions, particularly those of the hydroquinone type (see also perylene, fluoradene, etc.).

$$-\overset{|}{\underset{|}{C}}: + O_2 \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + \cdot O_2^-$$

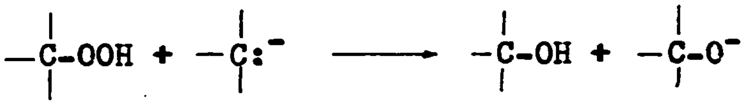


Reactions of this type are often of importance in oxidative dehydrogenation performed in alkaline media.

Also, in basic solution, the hydroperoxides formed are usually not stable and can decompose by various paths



$$H-\overset{|}{\underset{|}{C}}-OOH \xrightarrow{OH^-} \overset{|}{\underset{|}{C}}=O + H_2O + OH^-$$



$$-\overset{|}{\underset{|}{C}}-OOH + -\overset{|}{\underset{|}{C}}:^- \longrightarrow -\overset{|}{\underset{|}{C}}-OH + -\overset{|}{\underset{|}{C}}-O^-$$

Thus, the variety of products obtained is not due to any exceptional reactivity of molecular oxygen, but rather to the instability and further reaction of the initially formed peroxidic intermediates.

EXPERIMENTAL

Chemicals

Benzhydrol

Benzhydrol (Matheson, Coleman, and Bell) was recrystallized from alcohol-water, m.p. 69°.

Benzyl alcohol

Benzyl alcohol (Matheson, Coleman, and Bell) was distilled *in vacuo* through a one foot silvered Vigreux column. A sharp center fraction (b.p. 58.2 to 59°, $n_D^{20} = 1.5406$) was collected and retained for further use.

tert.-Butyl alcohol

tert.-Butyl alcohol (Eastman, White Label) was stored over calcium hydride. Immediately prior to use, the alcohol was distilled from fresh calcium hydride, b.p. 82.2°.

Cumene

Cumene (Matheson, Coleman, and Bell) was distilled, under nitrogen, through a three foot packed column. The fore-run was discarded and the fraction boiling at 152.5 - 153° was collected and stored under nitrogen. This material was used within 24 hours after the distillation.

2,4-Dinitrocumene

2,4-Dinitrocumene was prepared by the mixed acid nitration of pure cumene at 80° according to the method of

Hansch and Helmkamp[281]. After a preliminary distillation the material was carefully fractionated *in vacuo* through a 30 inch spinning band column at a reflux ratio of 15:1. Physical constants were b.p. 134-6° (0.5 mm.), $n_D^{20} = 1.5548$; lit.[282] b.p. 169-71° (11 mm.), $n_D^{25} = 1.5523$.

2,4-Dinitrotoluene

2,4-Dinitrotoluene (Eastman, White Label) was used as received, m.p. 69-70°.

Diphenylacetonitrile

Diphenylacetonitrile (Eastman, Practical) was twice recrystallized from *iso*-propyl alcohol, m.p. 72-73°.

meso-2,3-Diphenylbutane

meso-2,3-Diphenylbutane was prepared by the method of Conant and Blatt[283]. The Grignard reagent from -phenethylbromide was treated with anhydrous cupric chloride. The solid *meso* isomer obtained in 20% yield was easily separated from the oily d,l isomers. Upon recrystallization from alcohol the m.p. was 126-7°.

Ethylbenzene

Ethylbenzene (Matheson, Coleman, and Bell) was distilled,

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[281] C. Hansch and G. Helmkamp, *J. Am. Chem. Soc.*, *73*, 3080 (1951).

[282] B. M. Wepster, *Rec. trav. chim.*, *76*, 335 (1957).

[283] J. B. Conant and A. H. Blatt, *J. Am. Chem. Soc.*, *50*, 551 (1928).

under nitrogen, through a three foot packed column. A center fraction, b.p. 135-6°, $n_D^{25} = 1.4937$, was collected and stored under nitrogen until used.

Fluorene

Fluorene was a crude, industrial material, used in the undergraduate organic laboratories. It was recrystallized several times from alcohol yielding white plates, m.p. 116.4-117°.

9-Fluorenol

9-Fluorenol was obtained by the lithium aluminum hydride reduction of fluorenone in ether solvent[284]. The yield was nearly quantitative and after recrystallization from alcohol-water yielded crystals, m.p. 155-6°.

Fluorenone

Fluorenone (Eastman, White Label) was used as received, m.p. 83-83.5°.

p-Nitroacetophenone

p-Nitroacetophenone (Eastman, Practical) was recrystallized from ethanol, m.p. 79-80°.

p-Nitrobenzyl alcohol

p-Nitrobenzyl alcohol (Eastman, White Label) was used as received, m.p. 92.5-93°.

p-Nitrobenzyl iodide

p-Nitrobenzyl iodide was prepared by the method of

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[284] W. G. Brown, *Organic Reactions*, *6*, 469 (1951).

Finkelstein[285]. The compound was recrystallized from anhydrous acetone, m.p. 127.2-128°; lit.[286] 127.2-127.9°.

p-Nitrocumene

p-Nitrocumene was prepared by the mixed acid nitration of cumene at 45°[287]. The compound was distilled *in vacuo* through a 30 inch spinning-band column at a reflux ratio of 15:1. The fraction of b.p. 132° (13 mm.), $n_D^{20} = 1.5363$, was collected and stored under nitrogen until used. (Lit.[288] b.p. 134° (13 mm.), $n_D^{20} = 1.5369$).

p-Nitroethylbenzene

p-Nitroethylbenzene was prepared by the mixed acid nitration of ethylbenzene[287]. The compound was fractionally distilled *in vacuo* through a 30 inch spinning bank column at a reflux ratio of 15:1. The fraction of b.p. 125-125.4° (13 mm.), $n_D^{20} = 1.5458$ was collected and stored under nitrogen until used. (Lit.[288] b.p. 126°, $n_D^{20} = 1.5459$).

2-Nitrofluorene

2-Nitrofluorene was prepared by the nitration of fluorene in glacial acetic acid as per the procedure of Kuhn[289]. The

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[285] H. Filkelstein, *Ber.*, *43*, 1528 (1910).

[286] I. J. Gardner and R. M. Noyes, *J. Am. Chem. Soc.*, *83*, 2409 (1961).

[287] K. L. Nelson and H. C. Brown, *ibid.*, *73*, 5605 (1951).

[288] H. C. Brown and W. H. Bonner, *ibid.*, *76*, 605 (1954).

[289] W. E. Kuhn, "2-Nitrofluorene and 2-Aminofluorene", in A. H. Blatt, ed., "Organic Syntheses", Coll. Vol. 2, p. 447, John Wiley and Sons, Inc., New York, 1943.

compound was twice crystallized from glacial acetic acid yielding fine yellow needles, m.p. 157-158°.

p-Nitrophenylacetonitrile

p-Nitrophenylacetonitrile (Eastman, White Label) was recrystallized from alcohol-water, m.p. 116-117°.

4-Nitrodiphenylmethane

4-Nitrodiphenylmethane was prepared by the condensation of *p*-nitrobenzyl alcohol with benzene through the agency of sulfuric acid according to the method of Basler[290]. The compound was recrystallized from cold absolute ethanol, m.p. 31-2°. Alternatively, the compound may be prepared by the aluminum chloride catalyzed Friedel-Crafts reaction of *p*-nitrobenzyl chloride and benzene[291].

Bis-(p-nitrophenyl)methane

Bis-(*p*-nitrophenyl)methane was prepared by the mixed acid nitration of diphenylmethane according to the method of Parkes and Morley[292]. After several recrystallizations from glacial acetic acid pale orange needles were obtained, m.p. 186-187°.

Bis-(2,4-dinitrophenyl)methane

Bis-(2,4-dinitrophenyl)methane was prepared via the

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[290] A. Basler, *Ber.*, *16*, 2714 (1883).

[291] W. Staedel, *Ann.*, *283*, 160 (1894).

[292] G. D. Parkes and R. H. A. Morley, *J. Chem. Soc.*, *1936*, 1478.

nitration of diphenylmethane using potassium nitrate as the nitrating agent[293]. The compound was recrystallized from glacial acetic acids yellow platelets, m.p. 173.5-175°.

Mono-p-nitrotriphenylmethane

Mono-p-nitrotriphenylmethane was prepared using a recently published modification of Baeyer and Lohr's method[294,295]. The compound was recrystallized from hexane, m.p. 92-93°.

Tris-(p-nitrophenyl)methane

Tris-(p-nitrophenyl)methane was prepared by the mixed acid nitration of triphenylmethane at 0° according to a published procedure[296]. The compound was recrystallized from chloroform-ether, m.p. 212.5-214°.

Meso-(2,3-p-nitrophenyl)-butane

Meso-(2,3-p-nitrophenyl)-butane was prepared by the nitration of meso-2,3-diphenylbutane with nitric acid in acetic anhydride[297]. After recrystallization from glacial acetic acid it had a m.p. 254-6°.

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[293] K. Matsumura, J. Am. Chem. Soc., 51, 817 (1929).

[294] A. Baeyer and R. Lohr, Ber., 23, 1621 (1890).

[295] D. Y. Curtin and J. C. Kauer, J. Org. Chem., 25, 880 (1960).

[296] J. B. Shoesmith, C. E. Sosson, and A. C. Hetherington, J. Chem. Soc., 1927, 2227.

[297] S. F. Torf and N. V. Khromov-Borisov, J. Gen. Chem., U.S.S.R., 24, 1653 (1954).

2-Nitropropane

2-Nitropropane (Eastman, Practical) was distilled through a one foot Vigreux column under nitrogen, b.p. 120-120.8°, n_D^{20} = 1.3946.

p-Nitrotoluene

p-Nitrotoluene (Eastman, Practical) was twice recrystallized from alcohol, m.p. 52.8-53.6°.

o-Nitrotoluene

o-Nitrotoluene (Eastman, White Label) was used as received.

p-Nitrosotoluene

p-Nitrosotoluene was prepared by the procedure of Lutz and Lytton[298]. The compound was recrystallized from methanol, m.p. 48-49°.

Phenylacetonitrile

Phenylacetonitrile (Eastman, White Label) was distilled *in vacuo* through a 30 inch spinning band column. A center fraction was collected for use, b.p. 60° (1 mm.), n_D^{25} = 1.5211.

9-Phenylfluorene

9-Phenylfluorene, prepared from fluorenone by the method of Ullman and von Wurstemberger[299], was sublimed and

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[298] R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, *2*, 68 (1937).

[299] F. Ullman and R. von Wurstemberger, *Ber.*, *37*, 73 (1904).

recrystallized from alcohol, m.p. 147.5-148°. The ultraviolet spectrum in 95% ethanol showed maxima at 265 μ (ϵ 20,000), 293 μ (ϵ 5,980), and 304 μ (ϵ 9,400)[300].

Phenylnitromethane

Phenylnitromethane was prepared by the procedure of Black and Babers[301]. The compound was distilled through a small Vigreux column in vacuo, b.p. 76° (2 mm.), n_D^{20} = 1.5316[302].

Potassium t-butoxide

Potassium t-butoxide solutions were prepared by weighing the requisite amount of freshly cleaned potassium into anhydrous t-butyl alcohol in a dry 3-necked flask. The solution was heated gently, under nitrogen, until all of the potassium had dissolved. The solutions were standardized by potentiometric titration with standard aqueous perchloric acid. The base was made in one liter batches and stored in a polyethylene bottle. The solutions gradually turned light yellow and lost titer at the rate of approximately 2% per week.

Sym-trinitrobenzene

Sym-trinitrobenzene (Eastman, White Label) was

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[300] H. Rapoport and G. Smolinsky, J. Am. Chem. Soc., 82, 441 (1960).

[301] A. P. Black and F. H. Babers, "Methyl Nitrate", in A. H. Blatt, ed., "Organic Syntheses", Coll. Vol. 2, pp. 412-413, John Wiley and Sons, Inc., New York, 1943, p. 412.

[302] N. Kornblum, H. O. Larsen, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, J. Am. Chem. Soc., 78, 1497 (1956).

recrystallized from glacial acetic acid, m.p. 122-123°.

2,4,6-Trinitrotoluene

2,4,6-Trinitrotoluene (Eastman, Practical) was recrystallized five times from absolute alcohol, m.p. 81-81.7°.

Apparatus

Oxidation apparatus and procedure

Oxidation rates and products were determined by weighing an appropriate amount of substrate into a 25 ml. standard taper (19/38) Erlenmeyer flask, pipetting 25 ml. of a standardized solution of potassium t-butoxide in t-butanol. The flask was then attached to an all glass manifold system equipped with a mercury manometer, a 50 ml. gas buret, and connections for establishing a vacuum. The system was alternately evacuated and flushed with dry, carbon dioxide free, oxygen several times. Finally, the system was filled with oxygen at a pressure of 700 ± 5 mm. as indicated on the mercury manometer. Magnetic stirring was commenced and oxygen uptake at room temperature (27 ± 3°C) was followed at constant pressure by manually adjusting the height of a mercury filled bulb.

The magnetic stirring was provided by a 20 mm. x 8 mm. glass covered iron nail, placed in the reaction medium. The magnetic bar was turned by Alnico magnet mounted on an inverted Waco stirrer rated at 600 rpm. These conditions are referred to throughout this thesis as "diffusion controlled". In actual fact however, the region of diffusion control was established only for the particular reaction of p-nitrotoluene. It is evident that the region of diffusion control must be established separately for each individual case and will depend upon a host of empirical parameters. Still, no confusion should arise over the application of the description "diffusion controlled" as implying no more than the above described experimental conditions. The one case wherein the terminology is rigorously appropriate will be referred to without the quotation marks.

Experiments at 200 mm. were performed by passing dry, CO_2 free, compressed air over a magnetically stirred solution of the substrate in a suitable solvent. Non-diffusion controlled experiments were performed on a Parr Hydrogenation Apparatus at various appropriate pressures and shaking speeds using 50 ml. of t-butoxide/t-butanol solution in a 250 ml. heavy-walled pressure bottle.

Potentiometer and electrodes

A Beckman Model G pH meter, equipped with glass and standard calomel electrodes was employed for the potentiometric titrations.

Isolation of Oxidation Products

Yields of products in the oxidation of p-nitrotoluene were determined at the conclusion of each oxidation by treating the reaction mixture with iced water, filtering the resulting solution through a weighed sintered glass crucible and titrating the filtrate potentiometrically with standard acid. The contents of the crucible were washed with cold absolute methanol to remove any unreacted nitro compound followed by several washings with hot water. The crucible was dried overnight (usually 12 to 15 hours) in an oven at 110°, cooled to room temperature in a dessicator and weighed. This procedure permitted quantitative recovery of products on the basis of starting material for reactions that had gone to completion. For the shorter experiments (< 2 hours, $< 0.5M$ base) the p,p'-dinitrobibenzyl melted sharply at 182 - 184° (uncorr.). At longer times, and at high base concentrations, the yellow bibenzyl was contaminated with pale green p,p'-dinitrostilbene. (The green color of the stilbene underwent an irreversible thermochromic change when heated above 80°). p-Nitrobenzoic acid was isolated by filtering the aqueous filtrate after the potentiometric titration. The acid so isolated melted at 233-237° and after recrystallization showed no melting point depression with an authentic sample.

The oxidation products of benzhydrol, 9-fluorenol, and fluorene were treated with iced water and acidified with dilute hydrochloric acid. Fluorenone was precipitated quantitatively by this procedure (yields $> 93\%$). In the case of benzhydrol it was convenient to extract the acidied solution several times with ether, and to finally determine the yield of benzophenone by the formation, drying, and weighing of its 2,4-dinitrophenylhydrazone.

The products of the autoxidation of other nitro compounds and hydrocarbons were not determined quantitatively. In these cases qualitative identification was ascertained by treating the reaction solution with iced water, acidification, and ether extraction. After evaporation of the ether the compounds were recrystallized and identified by melting point, mixed melting point, and infra-red spectra. These products will be discussed in the Results section of this thesis.

In the case of the oxidation of 9-phenylfluorene it is of interest to point out that one product isolated in low yields proved to be the *bis*-(9-phenylfluorenyl)-peroxide.

RESULTS

Oxidation of p-Nitrotoluene

Although many speculations as to the probable mechanism of the oxidative dimerization of p-nitrotoluene in basic media have been put forward[7,20,23,24], none seem to be completely satisfactory nor to fit all of the available data. In the present work, the problem of devising a rational mechanistic pathway for this autoxidation process has been approached primarily from a stoichiometric rather than a kinetic point of view. The oxidation reactions were carried out in a solvent system consisting of potassium t-butoxide/ t-butanol at ambient temperatures. Such a solvent possesses the advantage of being exceptionally stable to oxidation while supplying sufficient base strength to ionize many weakly acidic organic compounds. The rates and products of the reaction were determined under a variety of conditions.

In t-butyl alcohol solution containing potassium t-butoxide p-nitrotoluene absorbs oxygen rapidly at an initial rate dependent upon the concentration of t-butoxide ion (Figure 1, Tables 8 to 11). However, above a base concentration of approximately twice that of the p-nitrotoluene, the initial rate appears to be independent of further increase in the concentration of potassium t-butoxide.

An investigation of the stoichiometry of the reaction of oxygen with p-nitrotoluene in t-butyl alcohol containing an excess of potassium t-butoxide revealed that the rate (Figure 2, Table 12) and products of the reaction as ordinarily conducted are a function of the rate of diffusion of oxygen into the system. When the supply of oxygen is increased by more vigorous stirring so that the reaction is no longer dependent upon the rate of diffusion of oxygen, the coupling product (p,p'-dinitrobibenzyl) decreases in importance and p-nitrobenzoic acid is found instead. The products of the oxidation are summarized in Table 2 as a function of the oxygen pressure and the shaking rate.

The results tabulated in Table 2 demonstrate that at the faster shaking speeds the products of oxidation are independent of the rate of agitation. Even under these conditions some bibenzyl is formed. Moreover, the amount of bibenzyl formed decreases with increasing oxygen pressure thus giving an indication that bibenzyl results from some intermediate that can be trapped by oxygen and oxidized to p-nitrobenzoic acid. It is possible that at sufficiently high oxygen pressures the yield of coupling product will approach zero. It thus appears likely that the bibenzyl is formed by a reaction of benzyl radicals and that this reaction decreases in importance as the concentration of oxygen is increased.

The mode of formation of p-nitrobenzyl radicals was investigated by studying the oxidation under a set of conditions wherein the rate and products of the reaction were determined by the rate of diffusion of oxygen. The data in Table 3, presented in Figures 3 and 4, show that the p-nitrobenzoic acid formed (as the minor product under these experimental conditions) does not result from further oxidation of the bibenzyl. In fact, upon continued oxidation the p,p'-dinitrobibenzyl is dehydrogenated to form exclusively p,p'-dinitrostilbene, a product stable to molecular oxygen in basic solution. When the data on the yield of bibenzyl and acid as a function of time and oxygen absorption are plotted as in Figure 5, several important conclusions may be derived. First, it becomes obvious that p-nitrobenzoic acid is not an initial oxidation product but must be formed by further oxidation of some intermediate. Second, the p,p'-dinitrobibenzyl is indeed an initial product of oxidation, and is formed at the beginning of the reaction in a ratio of one mole of dimer to one mole of oxygen absorbed.

At the beginning of the reaction one molecule of oxygen serves to generate two p-nitrobenzyl radicals:

(123) $RCH_2{:}^- + \cdot O\text{-}O\cdot \longrightarrow RCH_2\cdot + \overset{\ominus}{:}O\text{-}O\cdot$

(124) $RCH_2{:}^- + \cdot O\text{-}O{:}^- \longrightarrow RCH_2\cdot + O_2^{=}$

(125) $2RCH_2\cdot \longrightarrow RCH_2CH_2R$

R = p-nitrophenyl

As the concentration of nitro compound becomes lower the rate of oxygen consumption will decrease and the oxygen concentration in solution will increase. At this stage in the reaction p-nitrobenzyl radicals will compete with p-nitrobenzyl carbanions for oxygen:

(126) $RCH_2\cdot + O_2 \longrightarrow RCH_2OO\cdot$

Under conditions of more vigorous stirring wherein oxygen is present in solution at its equilibrium concentration, reaction (126) competes more favorably with reaction (125). However, some bibenzyl is still produced even when oxygen is present at an equilibrium concentration of 4 atmospheres.

A number of reactions can be formulated leading to the formation of p-nitrobenzoic acid from the p-nitrobenzyl peroxy radical via the alcohol and aldehyde:

(127) $RCH_2OO\cdot + RCH_2\overset{-}{:} \longrightarrow RCH_2\cdot + RCH_2OO:^-$

(128) $RCH_2OOH + RCH_2OO:^- \longrightarrow RCH_2O:^- + RCH_2OH + O_2$

(129) $2\ RCH_2OO\cdot \longrightarrow RCH_2OH + RCHO + O_2$

(130) $RCH_2OOH + \overset{-}{:}OR \longrightarrow HOR + RCHO + \overset{-}{:}OH$

(131) $RCH_2OOH + R:^- \longrightarrow RCH_2OH + RCH_2O^-$

(132) $RCH_2\cdot + RCH_2OO\cdot \longrightarrow RCH_2OOCH_2R$

(133) $RCH_2OOCH_2R \xrightarrow{^-OR} RCHO + RCH_2OH$

R = p-nitrophenol

Independent experiments have shown that under the reaction conditions both p-nitrobenzyl alcohol and p-nitrobenzaldehyde are subject to rapid oxidation giving quantitative yields of p-nitrobenzoic acid.

Support for the above interpretation was also obtained by working at very low base concentrations wherein the p-nitrotoluene would not be completely ionized. In the presence of dilute base where the carbanion concentration is lower and the oxygen concentration proportionally higher, the yield of bibenzyl is decreased and the yield of acid increased (see Tables 3 and 4). The reaction will not proceed to completion when the p-nitrotoluene concentration greatly exceeds the concentration of base since the acid formed will neutralize the base present. As shown in Tables 3 and 4 the ratio of coupling product to acid is roughly independent of base concentration from 0.3 to 0.9 M when the base is present in a large excess over the nitro compound (see also Figure 4). It is believed that in this concentration range the nitro compound is essentially completely ionized.

Additional evidence for a competition of the type discussed above is provided by the data of Table 5, presented graphically in Figure 6. As the concentration of p-nitrotoluene decreases at constant base concentration the amount of coupling product also decreases. This is to be expected since the concentration of oxygen remains constant as the quantity of carbanion is decreased thereby favoring reaction (126) at the expense of the bimolecular process, reaction (125).

Although acidic potassium iodide solution did not release iodine upon addition of a freshly oxidized aliquot of p-nitrotoluene, the presence of hydrogen peroxide was inferred by a positive response to the exceedingly sensitive peroxychromic acid test[303]. Quantitative analysis for the potassium peroxide by the method of James and Weissberger[103] has yielded inconclusive results that were not reproducible. The failure of this method may be due to the instability of hydrogen peroxide in strongly basic media[123]. The yield of potassium peroxide has been estimated from a consideration of oxygen balance in the reaction and the effect of trace quantities of metal ions capable of destroying hydrogen peroxide during the course of the oxidation. The assumption that one mole of potassium peroxide is formed per mole of bibenzyl seems justified on the basis of experiments containing lead ion, a potent heterogeneous catalyst for the decomposition of hydrogen peroxide in basic media[304]. The same oxidation products were formed in the absence and presence of lead ion in 0.335 M base (cf. Table 4), and no effect on initial rate was evident (Figure 7, Tables 13 and

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[303] L. N. Lapin, Z. Anal. Chem., 102, 418 (1935).

[304] Schumb, Satterfield, and Wentworth, op. cit., p. 480.

and 14). However, in the presence of lead ion the oxygen consumption was 0.19 mole lower, consistent with the fact that 0.37 mole of potassium peroxide (equal to the quantity of bibenzyl) had been destroyed.

(134) $2\ K_2O_2 \xrightarrow{PbO} O_2 + 2\ K_2O$

On the basis of equation (134) the presence of lead ion would be expected to decrease oxygen consumption by 0.37/2 mole. In some of the longer experiments summarized in Table 4 the bibenzyl was contaminated with stilbene, an observation consistent with the fact that the oxygen balance based on _p_-nitrobenzoic acid and _p_,_p_'-dinitrobibenzyl is consistently low in oxidations performed in the presence of excess base.

The isomer, _o_-nitrotoluene oxidizes at an initial rate somewhat faster than _p_-nitrotoluene (Figure 8, Table 15). The products of the oxidation are more complicated in this case, the only positive identification being _o_-nitrobenzoic acid. In addition a complex mixture of dark colored oils was obtained that defied chromatographic separation. No further attempts were made at identification, although it is most likely that the products are derived from anthranil or similar derivatives as discussed in the opening section of this thesis. The rate difference may be attributed to the difference in acidity of the _ortho_ and _para_ isomers, the _ortho_ isomer forming the _least_ stable carbanion due to steric inhibition of resonance.

Table 2. Reaction of oxygen with p-nitrotoluene at 27°C[a]

Shaking rate (per minute)	PNT x 10^3	$\frac{\text{Base}}{\text{PNT}}$	Time (minutes)	% dimer[b]	$\frac{\text{Dimer}}{\text{acid}^c}$
Oxygen pressure = 150 mm. Hg[d]					
MS[e]	7.57	3.4	390	91.2	5.15
MS[e]	4.48	3.2	60	88.5	3.91
MS[e]	4.45	3.2	120	87.6	3.48
MS[e]	7.00	3.1	360	88.3	3.77
MS[f]	4.28	1.7	120	77.2	1.68
MS[f]	4.31	1.7	120	76.2	1.59
MS[f]	4.45	1.6	120	75.0	1.50
220	4.35	3.8	120	60.3	0.76
Oxygen pressure = 700 mm. Hg					
220	8.13	2.2	120	51.4	0.53
220	8.15	2.2	130	47.9	0.46

---

[a] Weighed amount of p-nitrotoluene in 50 ml. of potassium t-butoxide/t-butanol on Parr Hydrogenation Apparatus unless specified otherwise.

[b] At completion of reaction. Under the conditions described here (particularly at longer reaction times) the dimeric product was a mixture of p,p'-dinitrobibenzyl and p,p'-dinitrostilbene, the latter predominating.

[c] Acid = p-nitrobenzoic acid.

[d] Experiments at 150 mm. Hg performed by passing a slow stream of dry, carbon-dioxide free, t-butyl alcohol saturated, compressed air over the surface of the solution.

[e] MS refers to magnetic stirring effected by a Teflon covered bar impelled by a variable speed magnetic stirrer (A. H. Thomas Co.) set at slowest rate of revolution (i.e., no vortices apparent).

[f] Conditions same as in e above except that stirrer set at maximum rate of revolution.

Table 2 (Continued)

Shaking rate (per minute)	PNT x 10^3	Base / PNT	Time (minutes)	% dimer[b]	Dimer / acid[c]
Oxygen pressure = 755 mm. Hg[g]					
300	3.65	14.3[h]	437	23.0	0.15
300	3.65	26.4[h]	1123	71.7	1.27
300	3.65	2.6[i]	333	43.8	0.39
300	3.65	2.6[j]	1080	NR	----
Oxygen pressure = 860 mm. Hg					
138	4.47	3.0	120	37.8	0.30
224	4.53	3.0	120	33.2	0.24
160	3.56	*ca.* 50[k]	270	32.6	0.24
220	4.47	*ca.* 50[k]	660	28.2	0.20
Oxygen pressure = 2050 mm. Hg					
220	4.69	3.0	5	25.1	----
220	4.50	3.0	10	28.0	----
220	4.51	3.0	20	31.6	----
220	4.47	3.0	40	33.1	----
220	2.40	6.0	120	17.6	0.11
220	4.60	3.0	120	20.8	0.13
220	8.40	1.7	120	22.1	0.14
138	4.17	4.0	150	29.8	0.21
220	4.39	3.8	150	25.6	0.17

---

[g] These experiments performed under kinetic controlled conditions in an apparatus immersed in an oil bath and agitated by an eccentric wheel driven by an electric motor.

[h] Solvent in this experiment was methanolic potassium hydroxide (15 ml.).

[i] Solvent in this experiment was 15 ml. of potassium *t*-butoxide/*t*-butanol.

[j] Solvent mixture consisted of 67% *t*-butanol/33% methanol (v/v), potassium *t*-butoxide base.

[k] Solvent was 50 ml. of 30% methanolic potassium hydroxide solution.

Table 2 (Continued)

Shaking rate (per minute)	PNT x 10^3	$\frac{\text{Base}}{\text{PNT}}$	Time (minutes)	% dimer[b]	$\frac{\text{Dimer}}{\text{acid}^c}$
Oxygen pressure = 3040 mm. Hg					
160	9.04	1.6	180	21.2	0.13
160	4.80	3.1	60	21.6	0.14
160	2.46	6.0	60	21.2	0.13
220	4.76	3.1	60	22.2	0.14
220	4.73	3.0	180	21.8	0.14
220	9.03	1.6	120	21.7	0.14

Figure 1. Rates of oxidation of p-nitrotoluene as a function of concentration of base (oxidations performed in 25 ml. of potassium t-butoxide/t-butanol at 27°C and 700 mm. oxygen pressure)

☐ 0.123 M base; molar ratio of base to p-nitrotoluene = 0.64

● 0.354 M base; molar ratio = 1.85

△ 0.514 M base; molar ratio = 2.89

○ 0.933 M base; molar ratio = 4.29

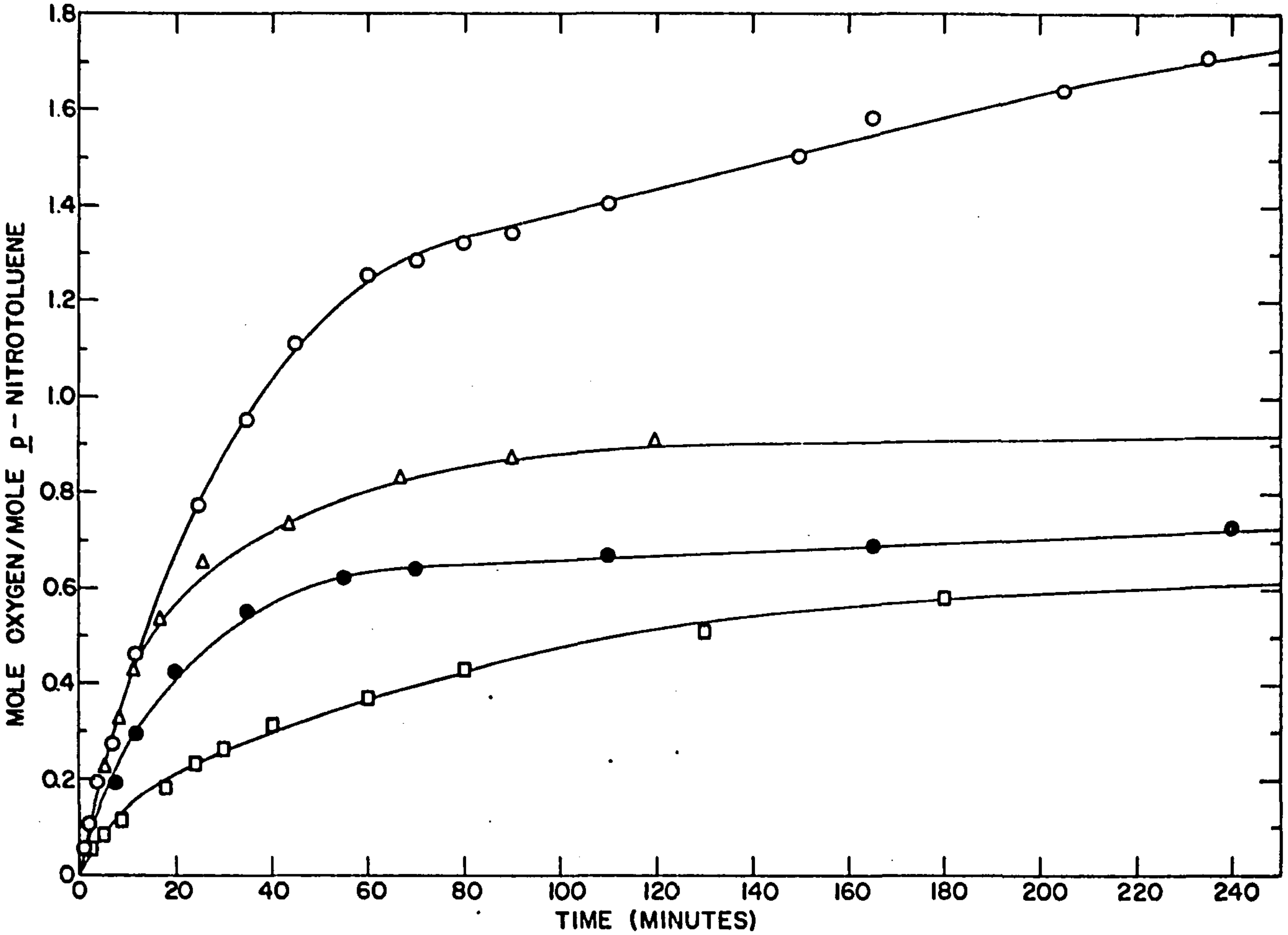

MOLE OXYGEN/MOLE p-NITROTOLUENE
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
TIME (MINUTES)
0
20
40
60
80
100
120
140
160
180
200
220
240

Figure 2. Effect of agitation on rate of oxidation of p-nitrotoluene (8.15×10^{-3} mole in 50 ml. of 0.352 M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure)

○ Rapid shaking (i.e., 220 shakes/min.) in 250 ml. heavy-walled pressure bottle on Parr Hydrogenation Apparatus (molar ratio = 2.16)

.... 4.78×10^{-3} mole p-nitrotoluene in 25 ml. of 0.354 M potassium *t*-butoxide/*t*-butanol under "diffusion controlled" conditions

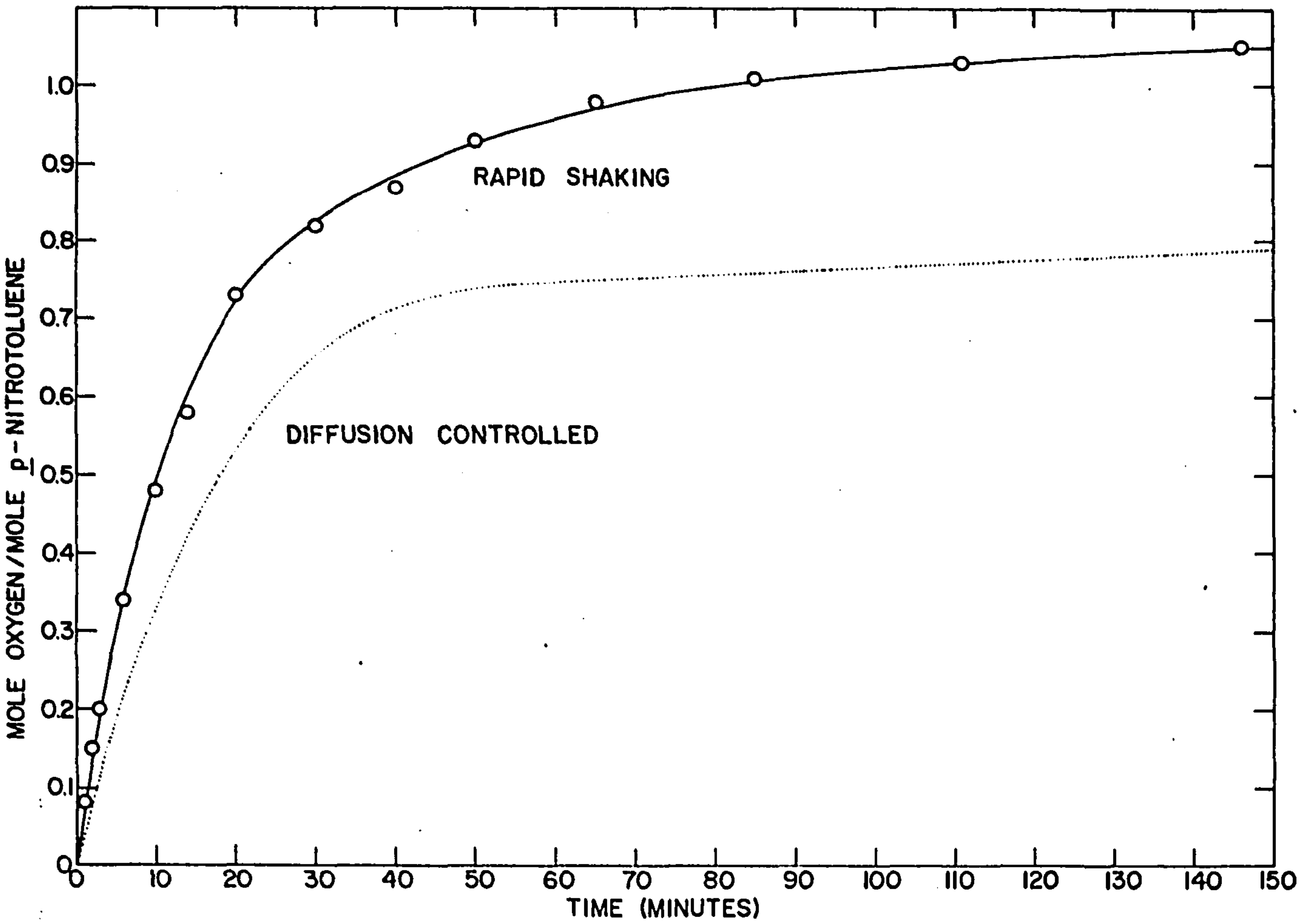

RAPID SHAKING
DIFFUSION CONTROLLED
MOLE OXYGEN/MOLE p-NITROTOLUENE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
TIME (MINUTES)

Table 3. Products of the oxidation of *p*-nitrotoluene[a]

Concentration of base[b]	Time (minutes)	Oxygen absorbed[c]	Coupling product[c]	Acid[c]
0.12 M	6	0.09	0.03	----
	12	0.15	0.05	----
	18	0.22	0.09	----
	30	0.28	0.10	0.10
	60	0.33	0.12	0.18
	120	0.48	0.13	0.27
	180	0.58	0.14	0.34
	240	0.57	0.15	0.35
	300	0.55	0.15	0.33
	330	0.60	0.15	0.38
0.35 M	4	0.11	0.14	----
	6	0.16	0.16	----
	10	0.29	0.32	0.05
	14	0.37	0.33	----
	20	0.51	0.37	0.07
	30	0.50	0.40	0.10
	40	0.65	0.40	0.17
	60	0.71	0.39	0.21
	120	0.75	0.40	0.20
	180	0.76	0.44	0.20
	240	0.73	0.39	0.22
0.51 M	5	0.17	0.18	0.03
	10	0.34	0.33	0.05
	20	0.56	0.40	0.08
	44	0.71	0.40	0.15
	67	0.83	0.41	0.20
0.93	330	1.75	0.41	0.19

[a] Products of oxidation are *p*,*p*'dinitrobibenzyl and *p*-nitrobenzoic acid. At longer reaction times (> 60 minutes; >0.35 M base) coupling product is a mixture of bibenzyl and stilbene, the latter predominating.

[b] 25 ml. of potassium *t*-butoxide/*t*-butanol added to 4.2 to 4.7 x 10^{-3} mole of *p*-nitrotoluene. Reactions run under diffusion controlled conditions.

[c] Mole/mole *p*-nitrotoluene.

Figure 3. Products of oxidation of *p*-nitrotoluene as a function of time (diffusion controlled reaction of oxygen (700 mm.) with p-nitrotoluene (4.75×10^{-3} mole) in 25 ml. of 0.123 M potassium *t*-butoxide/*t*-butanol at 26°C)

○ Dimer (*p*,*p*'-dinitrobibenzyl)

⊗ Acid (*p*-nitrobenzoic)

Molar ratio of base to *p*-nitrotoluene = 0.65

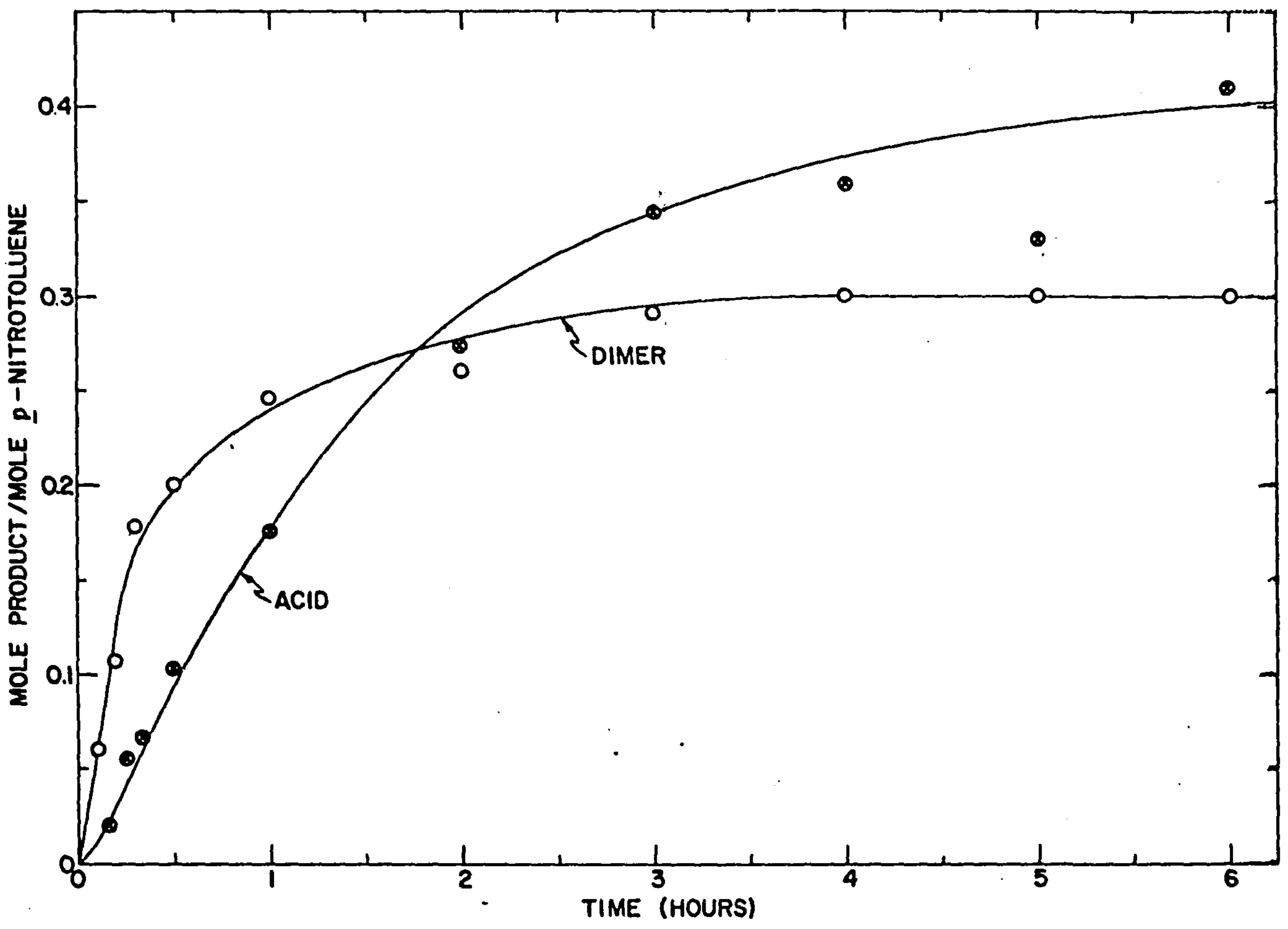

MOLE PRODUCT/MOLE p-NITROTOLUENE
0
0.1
0.2
0.3
0.4
0
1
2
3
4
5
6
TIME (HOURS)
ACID
DIMER

Figure 4. Products of the oxidation of *p*-nitrotoluene as a function of time (diffusion controlled reaction of oxygen (700 mm.) with *p*-nitrotoluene (*ca*. 4.3 x 10^{-3} mole) in 25 ml. of potassium *t*-butoxide/*t*-butanol at 26°C)

○ Molar ratio of base to *p*-nitrotoluene = 2.10

△ Molar ratio of base to *p*-nitrotoluene = 3.02

Dimer = *p*,*p*'-dinitrobibenzyl

Acid = *p*-nitrobenzoic

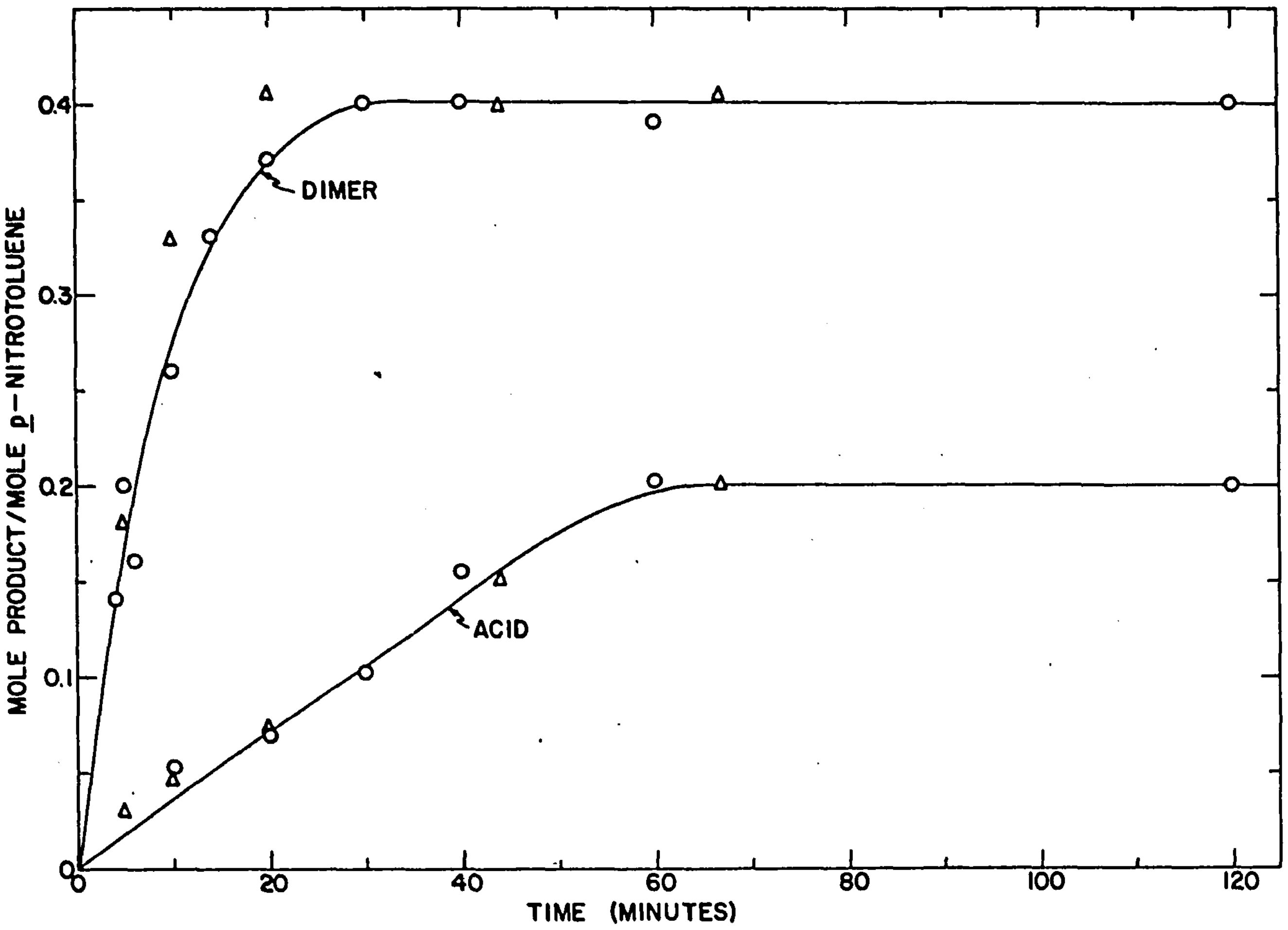

0.4
0.3
0.2
0.1
0
MOLE PRODUCT/MOLE p-NITROTOLUENE
0
20
40
60
80
100
120
TIME (MINUTES)
DIMER
ACID

Figure 5. Products of the oxidation of p-nitrotoluene as a function of oxygen absorbed and time

○ Molar ratio of base to p-nitrotoluene = 2.10

⊗ Molar ratio of base to p-nitrotoluene = 3.02

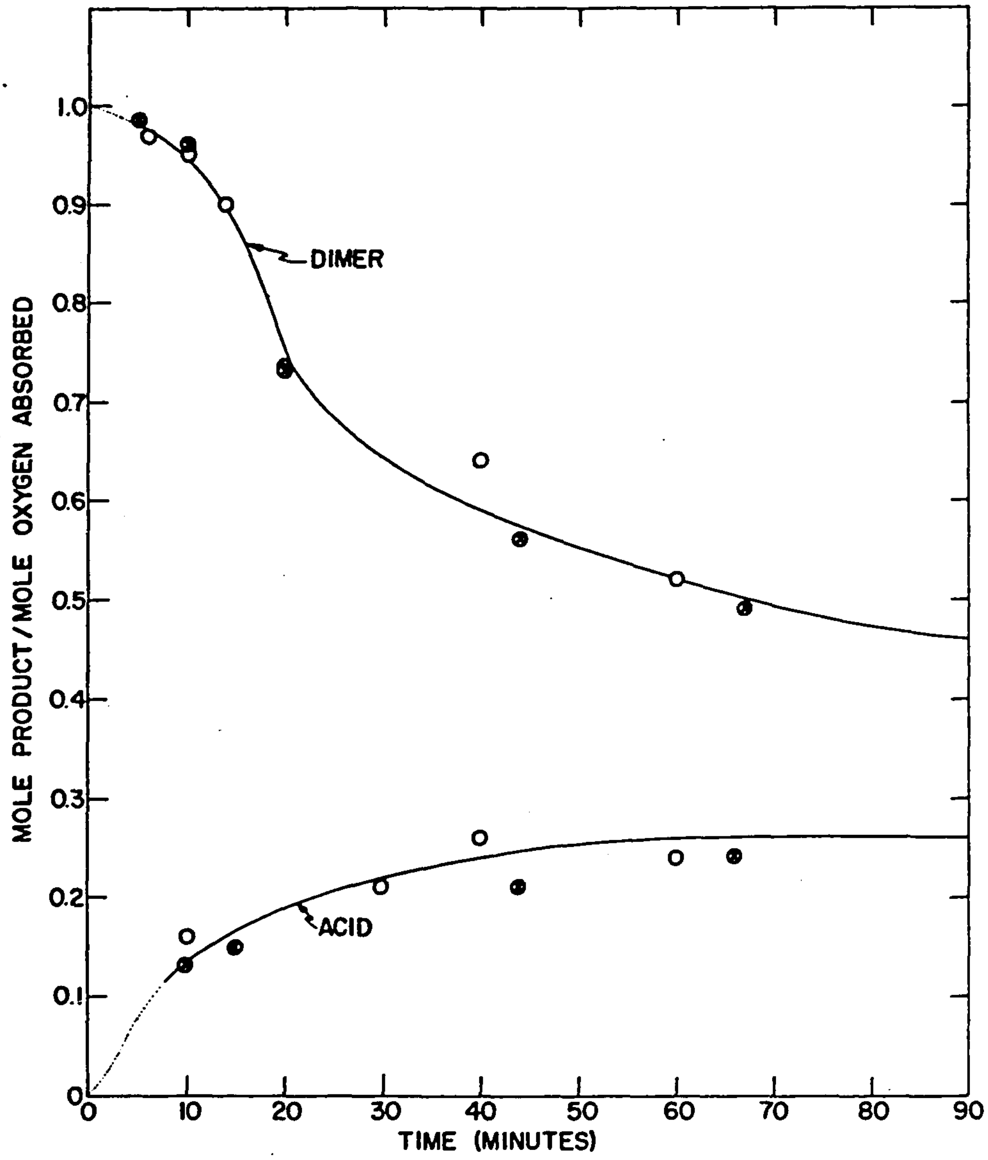

MOLE PRODUCT/MOLE OXYGEN ABSORBED
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
DIMER
ACID
TIME (MINUTES)
0
10
20
30
40
50
60
70
80
90

Table 4. Material balance in oxidation of *p*-nitrotoluene[a]

Base/PNT	Time (minutes)	Oxygen absorbed[b]	Dimer[b]	Acid[b]	Oxygen absorption (theory)[c]
0.68[d]	120	0.48	0.13	0.27	0.54
	180	0.58	0.14	0.34	0.65
	240	0.57	0.15	0.35	0.66
	300	0.55	0.15	0.33	0.64
	360	0.60	0.15	0.38	0.72
2.46	180	0.85	0.37	0.26	0.76
2.46[e]	180[e]	0.66[e]	0.36[e]	0.27[e]	0.59[e,f]
1.85	30	0.50	0.40	0.10	0.55
	40	0.65	0.40	0.17	0.65
	60	0.71	0.39	0.21	0.71
	120	0.75	0.40	0.20	0.70
	240	0.73	0.39	0.22	0.72

---

[a] Diffusion controlled conditions; *p*-nitrotoluene = 4.2 to 5.2×10^{-3} mole in 25 ml. of potassium *t*-butoxide/*t*-butanol.

[b] Mole/mole *p*-nitrotoluene

[c] Based on $2\ RCH_2{:}^- + O_2 \longrightarrow RCH_2CH_2R + O_2^{=}$

$$RCH_2{:}^- + 3/2\ O_2 \longrightarrow RCO_2^- + H_2O$$

(R = *p*-nitrophenyl)

[d] Oxidations did not proceed to completion.

[e] One mole per cent lead sub-acetate added at beginning of reaction.

[f] Assuming that $2\ K_2O_2 \xrightarrow{Pb^{\#}} 2\ K_2O + O_2$.

Table 4 (Continued)

$\frac{\text{Base}}{\text{PNT}}$	Time (minutes)	Oxygen absorbed[b]	Dimer[b]	Acid[b]	Oxygen absorption (theory)[c]
1.47[g]	240	1.00	----	0.51	1.02[h]
4.46[g]	115	1.98	----	1.01	2.02[h]
2.89	44	0.71	0.40	0.15	0.63
	67	0.83	0.41	0.20	0.71
4.29[i]	330	1.75	0.41	0.19	0.70

[g] Substrate = p-nitroethylbenzene; no dimer formed.

[h] Based on the reaction

$$R(CH_3)CH:^- + 2\ O_2 \longrightarrow RCO_2^- + H_2O + CH_2O$$

[i] Product predominantly p,p'-dinitrostilbene.

Table 5. Yield of dimer as a function of initial concentration of p-nitrotoluene[a]

Concentration PNT (x 10^3)	$\frac{\text{Base}}{\text{PNT}}$	Oxygen absorbed[b]	Dimer[b]
5.53	1.59	0.71	0.39
4.20	2.10	0.97	0.32
3.31	2.66	1.10	0.31
1.99	4.42	1.26	0.26
1.18	7.46	1.48	0.22

[a] Oxidations performed under diffusion controlled conditions in 25 ml. of 0.352 M potassium t-butoxide/t-butanol for a duration of 180 minutes (T = 26°C.).

[b] Moles/mole p-nitrotoluene.

Table 6. Yield of dimer *vs.* time[a]

Time (minutes)	$\frac{\text{Base}}{\text{PNT}}$	Oxygen absorbed[b]	Dimer[b]
15	4.53	0.81	0.21
60	4.53	1.28	0.25
218	4.53	1.39	0.25

[a] Diffusion controlled conditions at 26°C. Base = 0.352 M.

[b] Moles/mole *p*-nitrotoluene.

Figure 6. Yield of *p,p'*-dinitrobibenzyl as a function initial concentration of p-nitrotoluene (Oxidations performed in 25 ml. 0.352 M *t*-butoxide/*t*-butanol at 25°C and 700 mm. oxygen pressure at a duration of 180 minutes. Diffusion controlled conditions.)

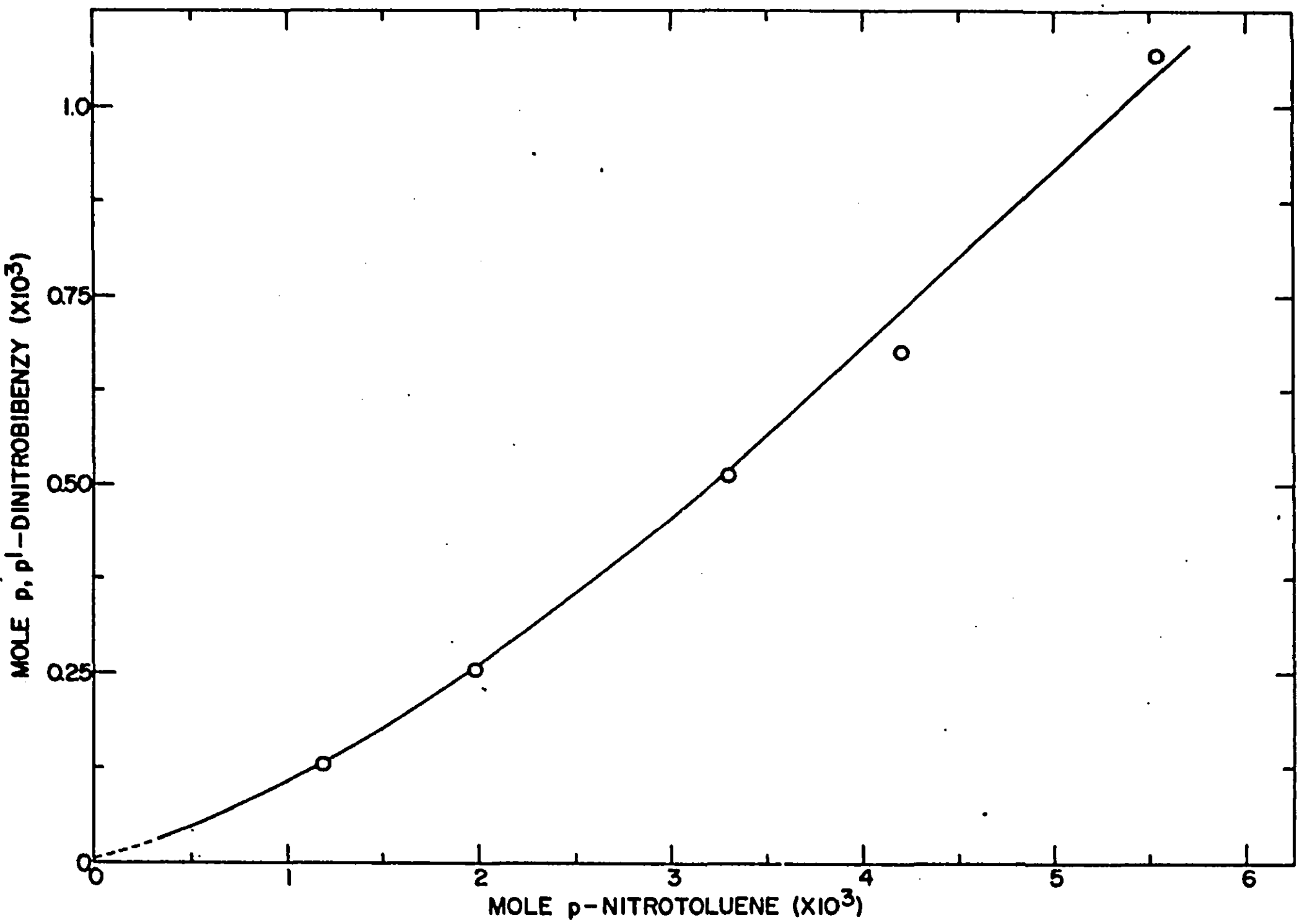

MOLE p, p|-DINITROBIBENZY (X10^3)
0
0.25
0.50
0.75
1.0
0
1
2
3
4
5
6
MOLE p-NITROTOLUENE (X10^3)

Figure 7. Effect of addition of lead sub-acetate (*ca.* 2 mole per cent) on the oxidation of p-nitrotoluene (25 ml. of 0.335 M potassium *t*-butoxide/*t*-butanol at 27°C and 700 mm. oxygen pressure. Diffusion controlled conditions.)

● *p*-nitrotoluene (4.31 x 10^{-3} mole)--no additive

○ *p*-nitrotoluene (4.28 x 10^{-3} mole)--lead sub-acetate added

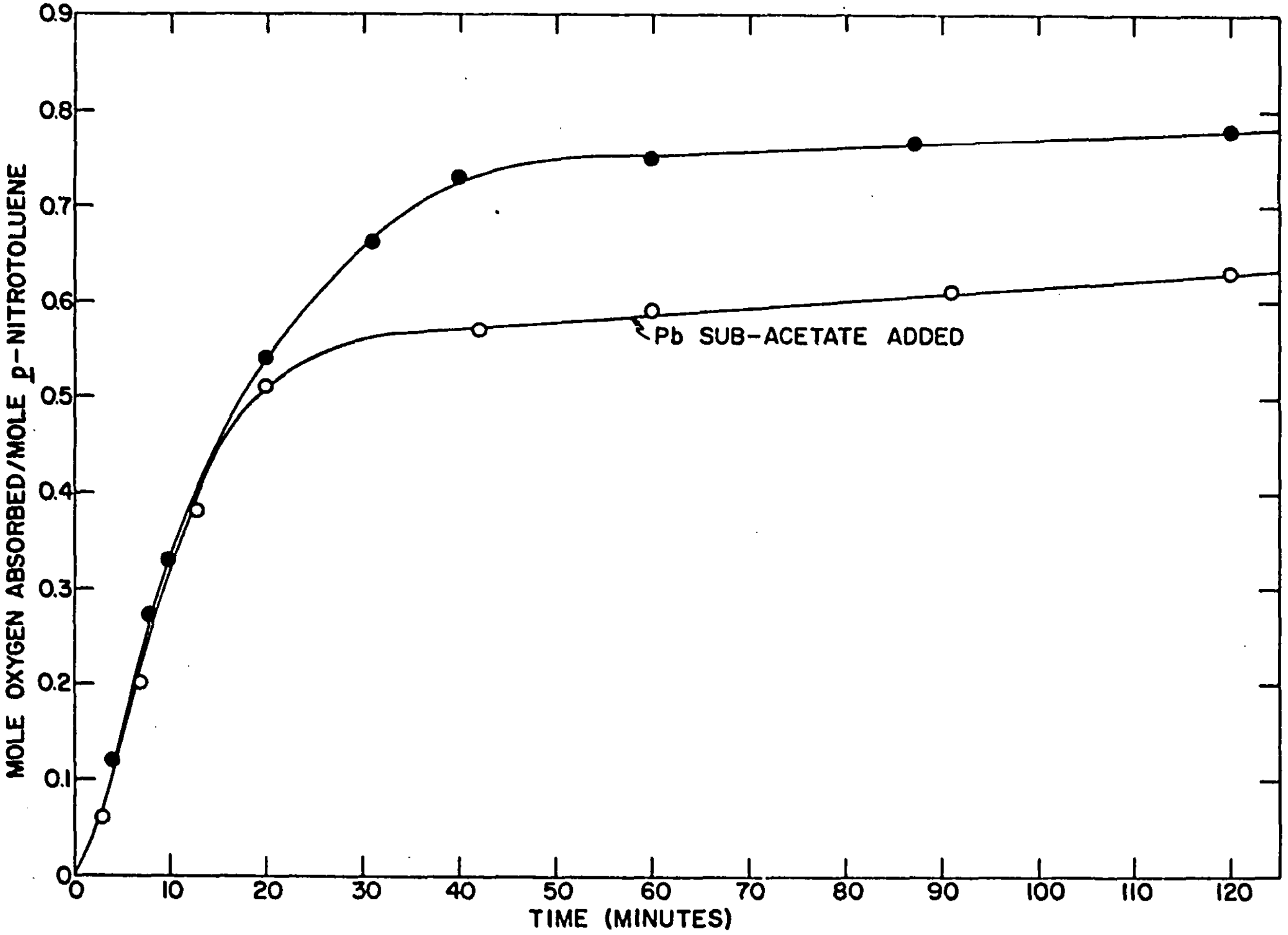
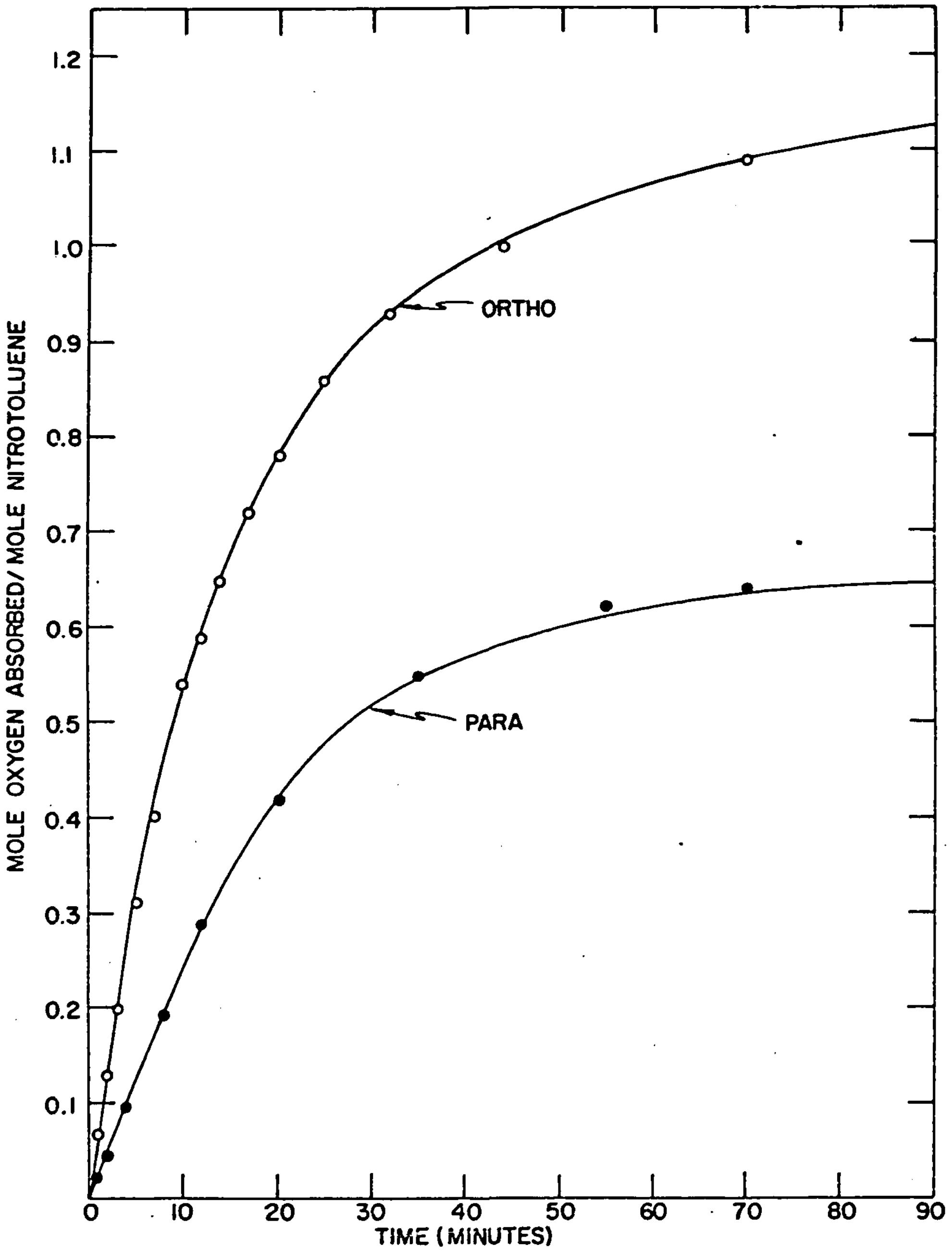

MOLE OXYGEN ABSORBED/MOLE p-NITROTOLUENE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME (MINUTES)
Pb SUB-ACETATE ADDED

Figure 8. Rate of oxidation of nitrotoluene isomers in 25 ml. of 0.352 M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure

○ 3.33×10^{-3} mole ortho-nitrotoluene

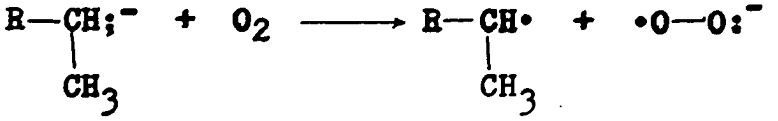
● 4.78×10^{-3} mole para-nitrotoluene


MOLE OXYGEN ABSORBED/ MOLE NITROTOLUENE
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)
ORTHO
PARA

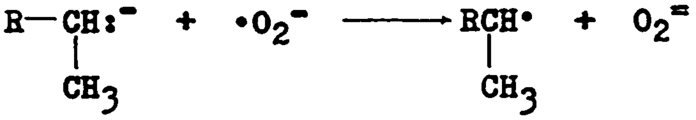
Oxidation of *p*-Nitrotoluene Homologs

The oxidations of *p*-nitroethylbenzene and *p*-nitrocumene in 0.289 M potassium *t*-butoxide/*t*-butanol solution form the basis for an interesting comparison with the oxidation of *p*-nitrotoluene. The relative rates of oxidation of these compounds are shown in Figure 9 (Tables 19 and 22). The initial rate of oxygen absorption is slower in the case of *p*-nitroethylbenzene, while *p*-nitrocumene did not absorb any appreciable amounts of oxygen over extended periods of time. The addition of traces of potassium ferricyanide or small amounts (approximately 10 mole per cent) of *p*-nitrotoluene had no discernible effect on the oxidation of *p*-nitrocumene.

The oxidation of *p*-nitroethylbenzene yielded only a single isolated product, *p*-nitrobenzoic acid. No dimer was isolated although *meso*-2,3-diphenylbutane is almost completely insoluble in this medium. That the acid was not formed by oxidation of dimer at all was shown by the fact that the expected dimer, *meso*-2,3-diphenylbutane does not absorb any oxygen under the reaction conditions. The acid undoubtedly arises from further oxidation of *p*-nitrophenylacetophenone, a reasonable reaction intermediate.

(135)


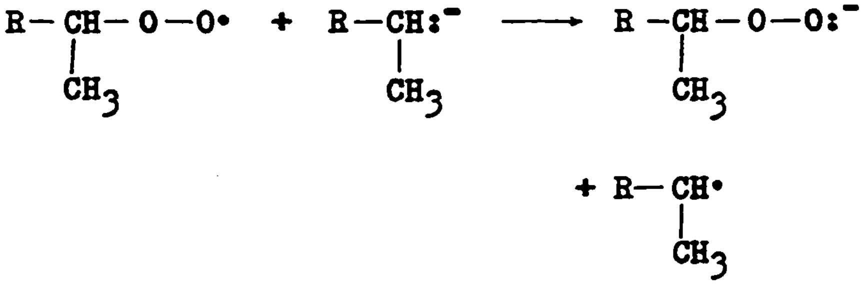
$$R-\underset{\displaystyle CH_3}{\underset{|}{CH}}:^- + O_2 \longrightarrow R-\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot + \cdot O-O:^-$$

(136) 

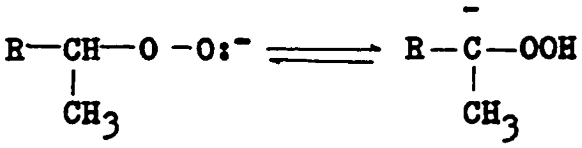
$$R-\underset{\substack{|\\CH_3}}{CH}{:}^- + \cdot O_2^- \longrightarrow R\underset{\substack{|\\CH_3}}{CH}\cdot + O_2^{=}$$

(137) 

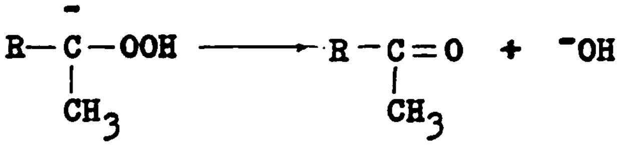
$$R\underset{\substack{|\\CH_3}}{CH}\cdot + O_2 \longrightarrow R\underset{\substack{|\\CH_3}}{CH}-O-O\cdot$$

(138) 

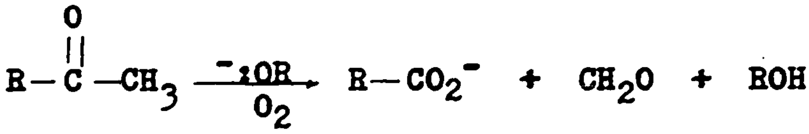
$$R-\underset{\substack{|\\CH_3}}{CH}-O-O\cdot + R-\underset{\substack{|\\CH_3}}{CH}{:}^- \longrightarrow R-\underset{\substack{|\\CH_3}}{CH}-O-O{:}^- + R-\underset{\substack{|\\CH_3}}{CH}\cdot$$

(139) 

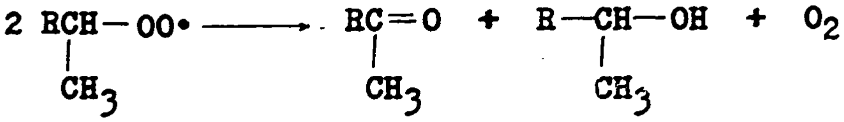
$$R-\underset{\substack{|\\CH_3}}{CH}-O-O{:}^- \rightleftharpoons R-\overset{-}{\underset{\substack{|\\CH_3}}{C}}-OOH$$

(140) 

$$R-\overset{-}{\underset{\substack{|\\CH_3}}{C}}-OOH \longrightarrow R-\underset{\substack{|\\CH_3}}{C}=O + {}^-OH$$

(141) 

$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[O_2]{^-{:}OR} R-CO_2^- + CH_2O + ROH$$

(142) 

$$2\ R\underset{\substack{|\\CH_3}}{CH}-OO\cdot \longrightarrow R\underset{\substack{|\\CH_3}}{C}=O + R-\underset{\substack{|\\CH_3}}{CH}-OH + O_2$$

Independent experiments show that p-nitroacetophenone is susceptible to autoxidation under the reaction conditions, rapidly forming quantitative amounts of p-nitrobenzoic acid (Figure 10, Table 21). The order of reactivity of these three compounds follows the expected order of acidity (p-nitrocumene being the weakest acid, i.e., leading to least stable tertiary carbanion). It appears, therefore, that the relative rates of oxidation reflect the relative concentrations of anion present. Support for this view is presented in Figure 11 (Tables 19 and 20) wherein the rate of oxidation of p-nitroethylbenzene is presented as a function of base concentration. In the more highly basic solutions a higher initial concentration of carbanion is available and the initial rate approaches that of p-nitrotoluene.

Figure 9. Rate of oxidation of p-nitrotoluene homologs in 25 ml. of 0.289 M potassium t-butoxide/t-butanol at 27°C and 700 mm. oxygen pressure

☐ p-nitrotoluene (4.31 x 10^{-3} mole)

○ p-nitroethylbenzene (4.90 x 10^{-3} mole)

● p-nitrocumene (4.17 x 10^{-3} mole)

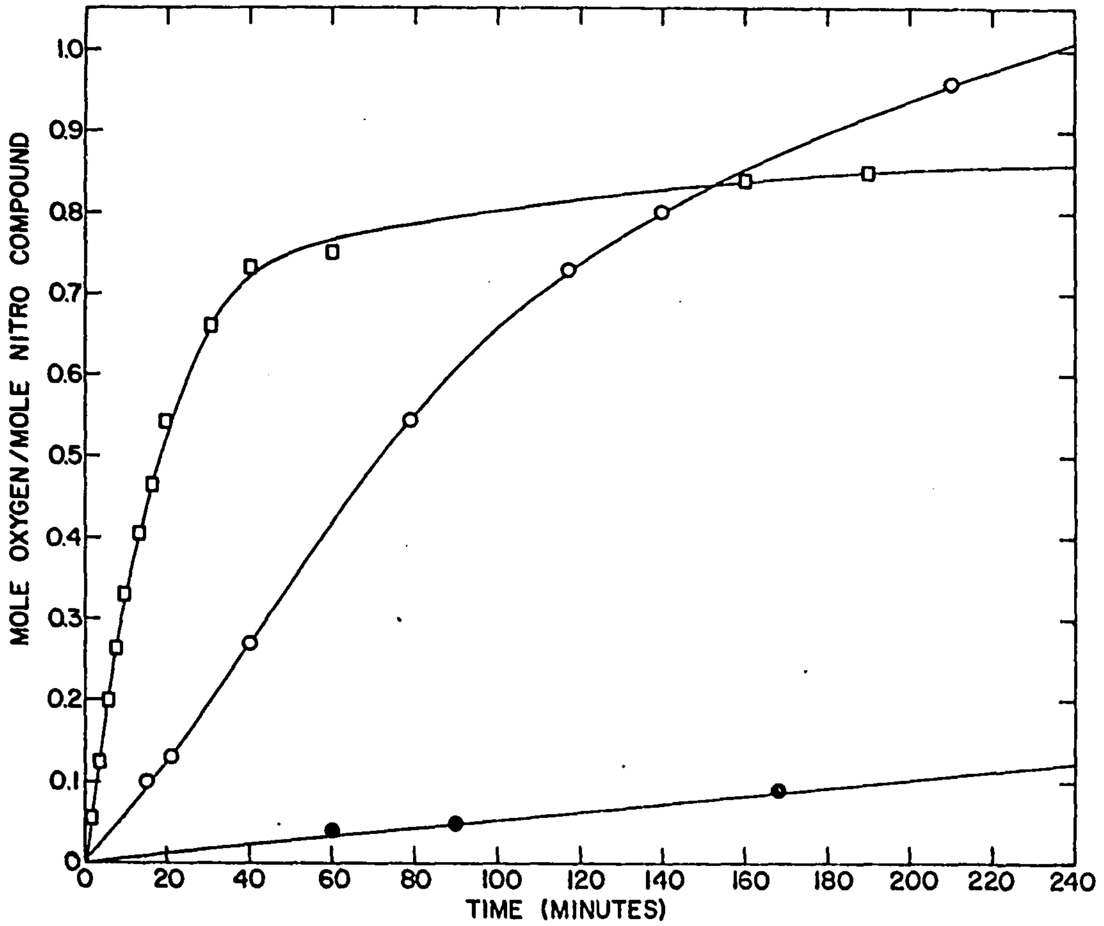

MOLE OXYGEN/MOLE NITRO COMPOUND
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
20
40
60
80
100
120
140
160
180
200
220
240
TIME (MINUTES)

Figure 10. Rate of oxidation of p-nitroacetophenone (4.02×10^{-3} mole) in 25 ml. of 0.289 M potassium t-butoxide/t-butanol at 25°C and 700 mm. oxygen pressure

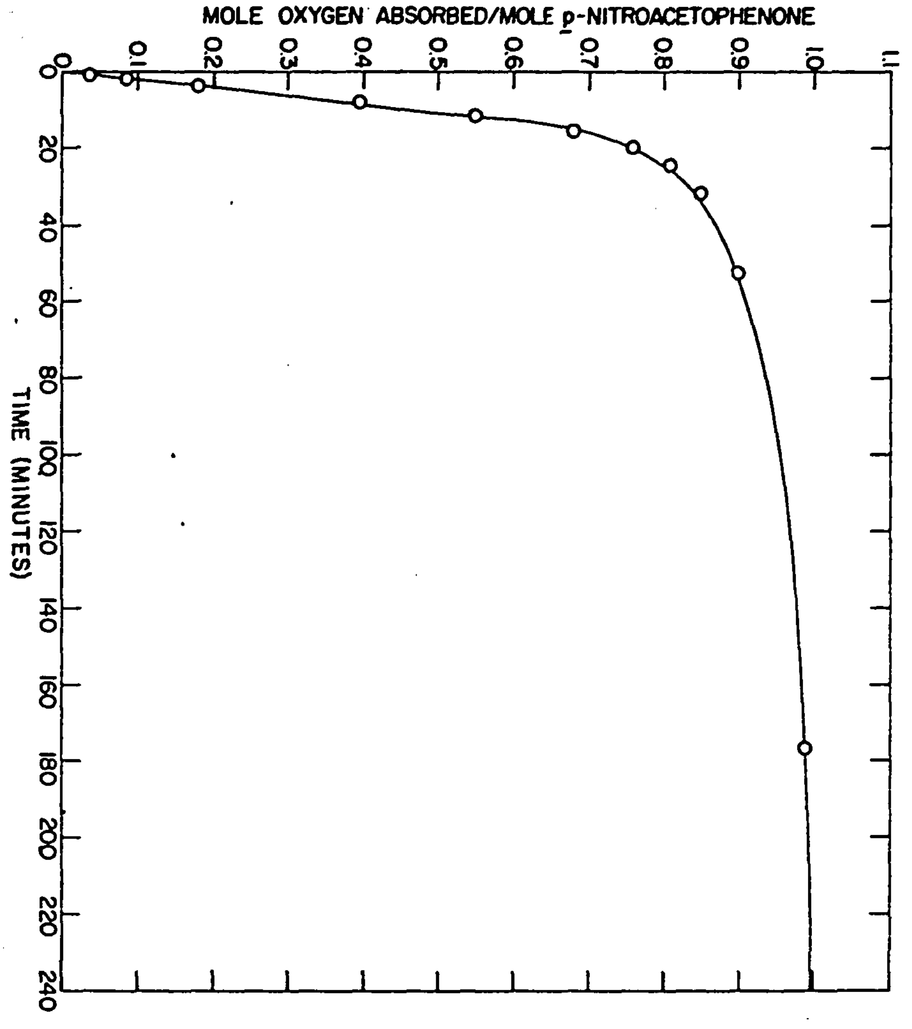
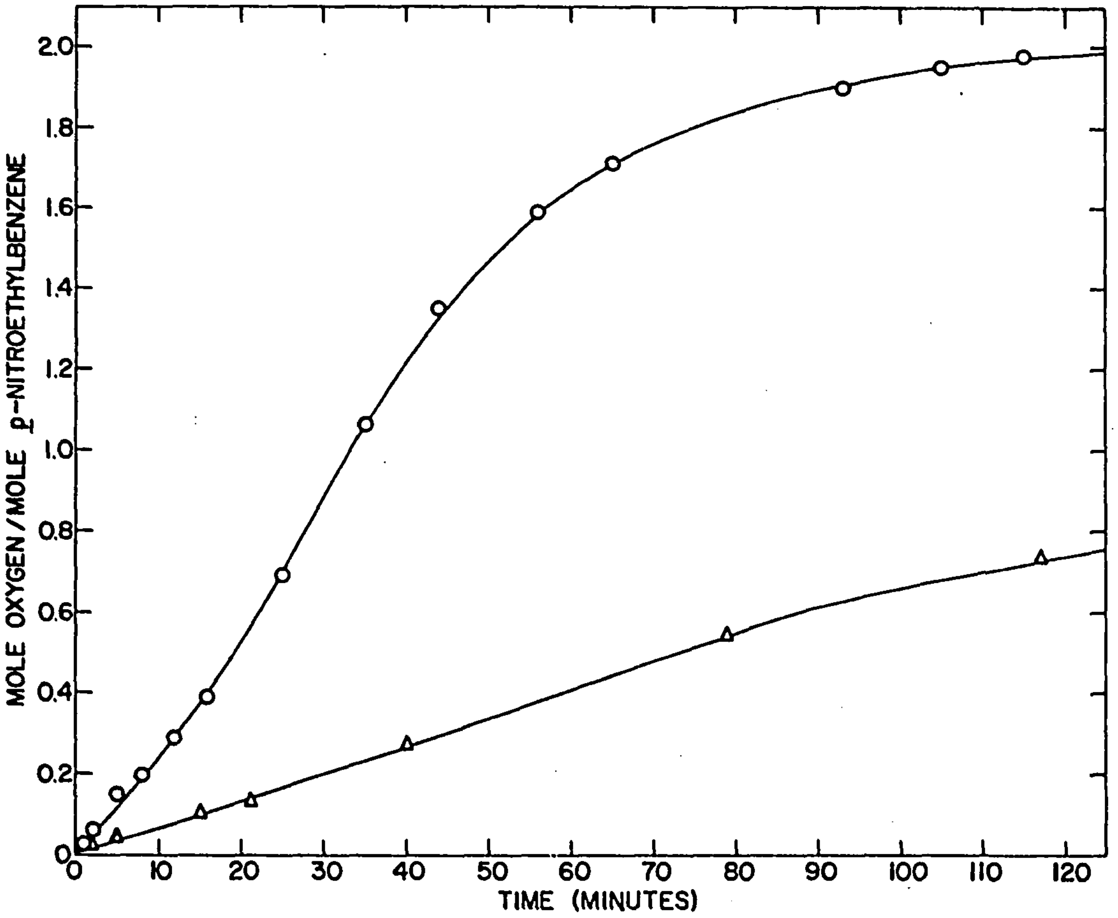

MOLE OXYGEN ABSORBED/MOLE p-NITROACETOPHENONE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
TIME (MINUTES)
0
20
40
60
80
100
120
140
160
180
200
220
240

Figure 11. Rate of oxidation of p-nitroethylbenzene in 25 ml. of potassium t-butoxide/t-butanol at 25-27°C and 700 mm. oxygen pressure

△ 4.90×10^{-3} mole substrate in 0.289 M base (Molar ratio = 1.47)

○ 4.48×10^{-3} mole substrate in 0.80 M base (Molar ratio = 4.46)


MOLE OXYGEN / MOLE p-NITROETHYLBENZENE
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME (MINUTES)

Oxidation of Polynitrotoluenes

The factors affecting the rate of autoxidation of a particular hydrocarbon in basic solution are several and are frequently complex. Among these factors it is reasonable to expect that the acidity of a particular hydrocarbon is of extreme importance. For example, in order for autoxidation to occur conveniently a sufficient supply of carbanion must be available. This implies that a minimum level of acidity (i.e., ability to form carbanion) is a requirement for oxidation. In addition, a maximum level of acidity must also be a requirement for oxidation. Since the initiation step involves an electron transfer to oxygen, the thermodynamic stability of each carbanion must be considered. For those carbanions of particular stability this process may be distinctly unfavored and therefore lead to slow oxidation rates.

The oxidation of the compounds 2,4-dinitrotoluene and 2,4,6-trinitrotoluene are examples of such behavior. Although the 2,4-dinitro compound is distinctly acidic and forms appreciable carbanion concentrations in basic media, it autoxidizes at somewhat slower initial rate than does the weaker acid p-nitrotoluene. The even more acidic compound 2,4,6-trinitrotoluene absorbs very little oxygen over extended periods of time (Figure 12, Tables 23 and 25). No coupling products were formed in either case. With 2,4-dinitrotoluene trace amounts of 2,4-dinitrophenol were detected among the oxidation products by its distinctive reversible indicator behavior as a function of pH.

Substitution of an additional nitro group on the p-nitrocumene nucleus leads to an appreciable initial rate of oxidation for the 2,4-dinitro isomer. The oxidation rates were identical in both ethyl and t-butyl alcohols (Figure 13, Tables 26 and 27), however the base concentration in ethanol is 10-12 times greater than in t-butanol. Again no products were isolated although 2,4-dinitrophenol was detected by its distinctive color behavior.

Oxidation of Di- and Tri-phenylmethane Derivatives

The rates of oxidation of 4-nitrodiphenylmethane, bis-(4-nitrophenyl)-methane, and bis-(2,4-dinitrophenyl)-methane are in inverse order of their acidities, the first named compound being least acidic (Figure 14, Tables 28 to 30). Although appreciable quantities of carbanion are present in 0.3 M potassium t-butoxide solutions of bis-(2,4-dinitrophenyl)-methane, oxidation proceeds at a negligible rate in this medium. No coupling products were formed on any of these oxidations, the isolated products being exclusively the ketones.

In the triphenyl methane series, both mono-p-nitrotriphenylmethane and _tris_-(_p_-nitrophenyl)-methane were studied. The former compound oxidizes rapidly in 0.39 M potassium _t_-butoxide/_t_-butanol absorbing a total of one mole of oxygen per mole of nitro compound (Figure 15, Table 31). The product in this instance was mono-_p_-nitrotriphenyl carbinol. The corresponding hydroperoxide could have been present but a careful search was not made.

More interesting behavior was exhibited by the _tris_-(_p_-nitrophenyl)-methane. In this instance very little oxygen was absorbed even after long periods of exposure (Figure 16, Tables 32 and 33). The addition of ferric ion had only a small effect on the rate of oxidation. However, in a medium of ethanolic potassium hydroxide oxidation takes place at a rapid initial rate (Figure 17, Tables 34 to 36). Here, increasing the strength of the basic medium has the effect of slowing considerably the initial oxidation rate. Again ferric ion has negligible effect on the initial rate of oxygen absorption but serves only to prolong the period of rapid oxidation.

The dramatic difference in oxidation behavior between two such similar compounds is especially striking. Apparently, the _tris_-(_p_-nitrophenyl)-methane is a compound that forms an anion of considerable stability in potassium _t_-butoxide/_t_-butanol solution.

Figure 12. Rates of oxidation of polynitrotoluenes in 25 ml. of 0.389 M potassium t-butoxide/t-butanol at 30°C and 700 mm. oxygen pressure

○ 2,4-dinitrotoluene (2.88 x 10^{-3} mole)

△ 2,4,6-trinitrotoluene (2 .27 x 10^{-3} mole)

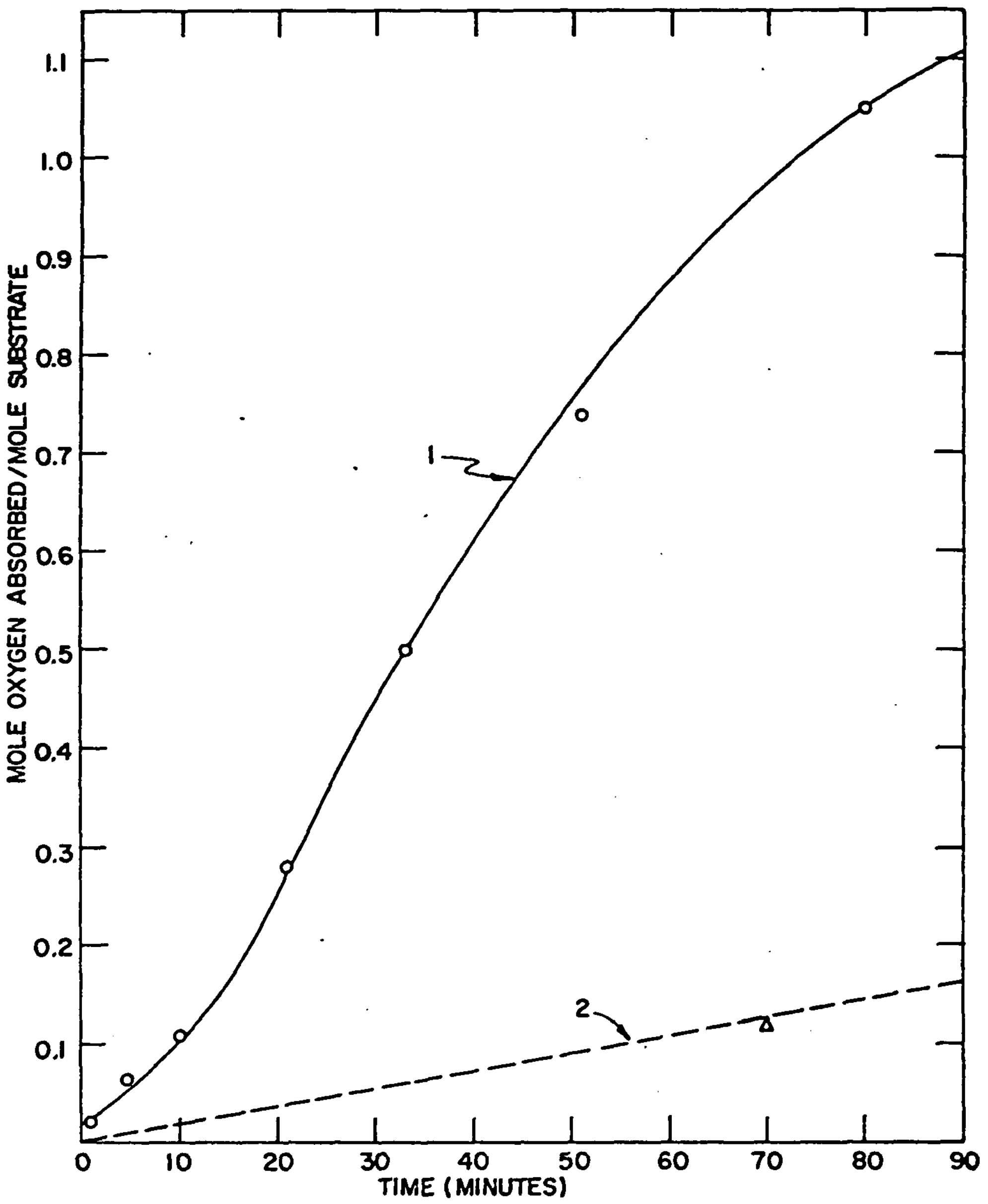

MOLE OXYGEN ABSORBED/MOLE SUBSTRATE
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)
1
2

Figure 13. Rates of oxidation of 2,4-dinitrocumene in basic medium at 700 mm. oxygen pressure

△ 3.05×10^{-3} mole substrate in 25 ml. of 30% ethanolic potassium hydroxide (27°C)

○ 2.80×10^{-3} mole substrate in 25 ml. of 0.389 M potassium *t*-butoxide/*t*-butanol (30°C)

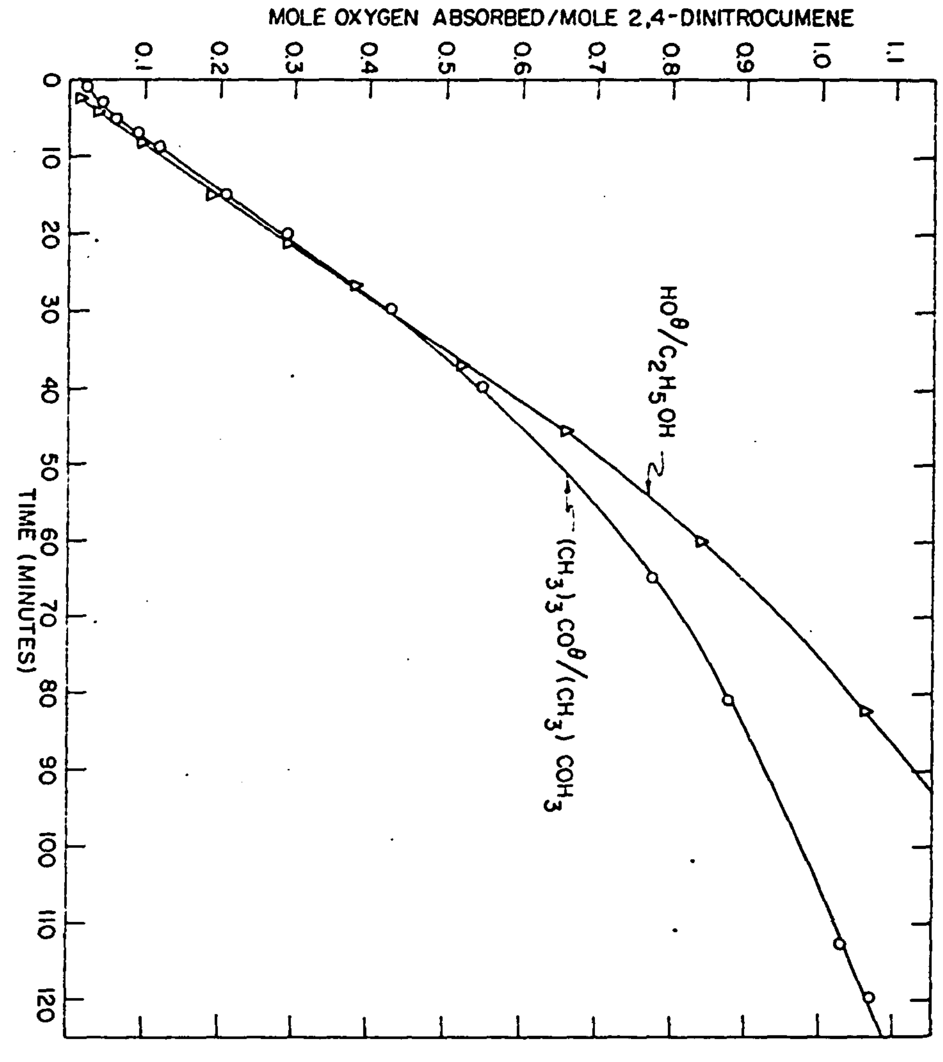
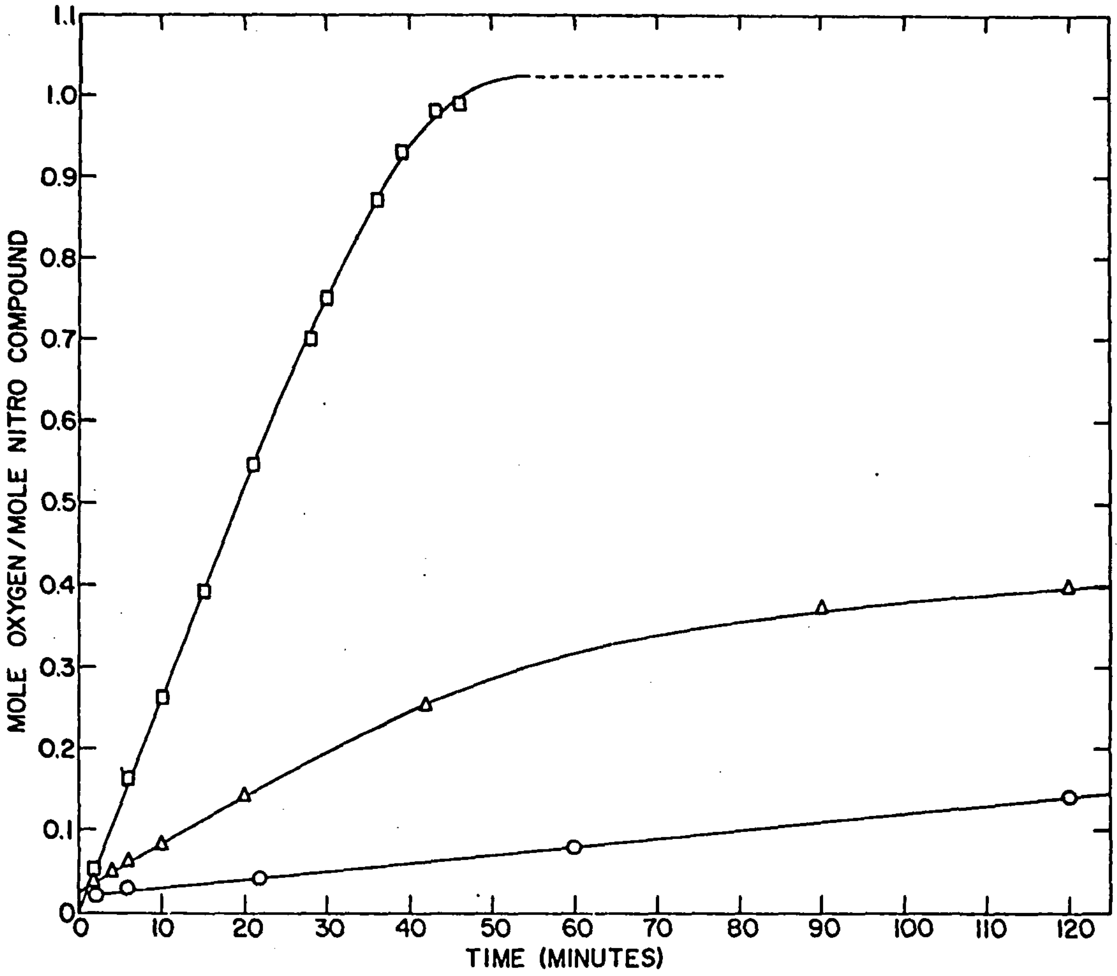

MOLE OXYGEN ABSORBED/MOLE 2,4-DINITROCUMENE
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME (MINUTES)
HO^{θ}/C_2H_5OH
$(CH_3)_3CO^{\theta}/(CH_3)COH_3$

Figure 14. Rates of oxidation of diphenylmethane derivatives in 25 ml. potassium *t*-butoxide/*t*-butanol at 25°C and 700 mm. oxygen pressure

□ 4-nitrodiphenylmethane (3.75×10^{-3} mole); 0.352 M *t*-butoxide

△ *bis*-(4-nitrophenyl)-methane (2.84×10^{-3} mole); 0.289 M *t*-butoxide

○ *bis*-(2,4-dinitrophenyl)-methane (3.25×10^{-3} mole); 0.289 M *t*-butoxide


MOLE OXYGEN/MOLE NITRO COMPOUND
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME (MINUTES)

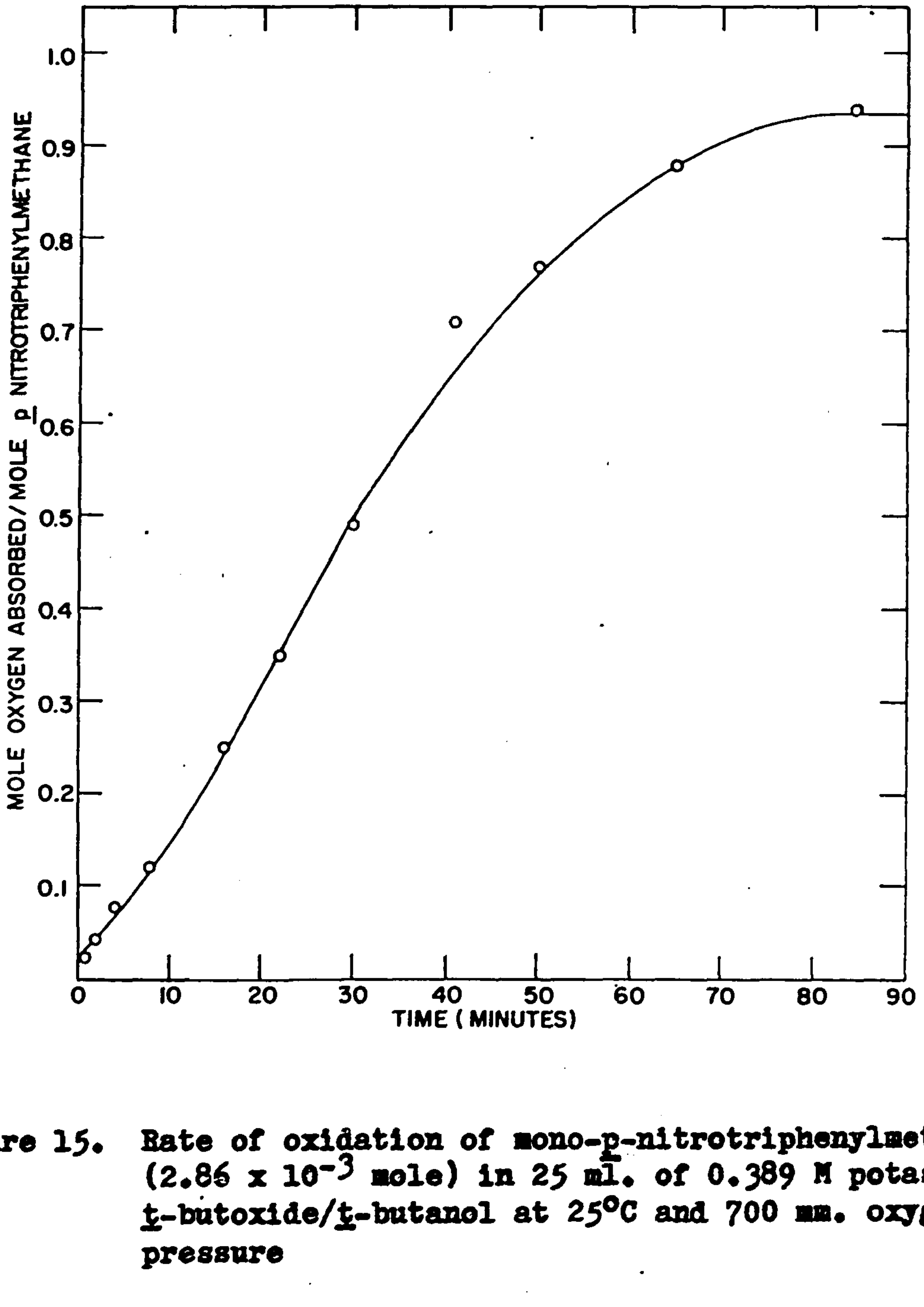


Figure 15. Rate of oxidation of mono-p-nitrotriphenylmethane (2.86×10^{-3} mole) in 25 ml. of 0.389 M potassium t-butoxide/t-butanol at 25°C and 700 mm. oxygen pressure

Figure 16. Effect of ferric chloride on the rate of autoxidation of *tris*-nitrophenyl)-methane in 25 ml. of 0.352 M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure

Curve 1 *tris*-(*p*-nitrophenyl)-methane (2.51×10^{-3} mole) + *ca*. one mole per cent $FeCl_3$

Curve 2 *tris*-(*p*-nitrophenyl)-methane (3.01×10^{-3} mole); slow oxygen absorption attains 0.30 mole/mole substrate after 10.5 hours

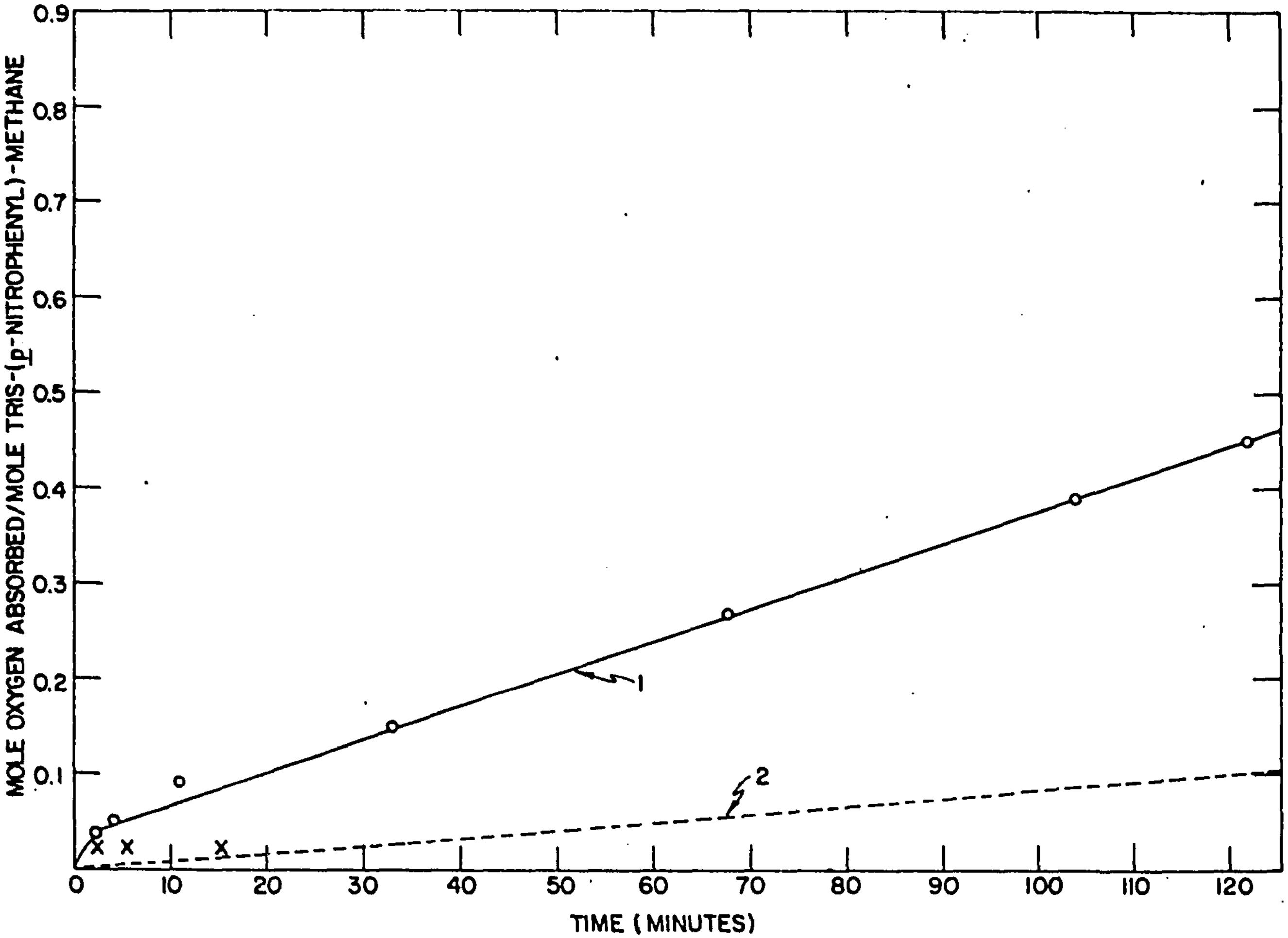
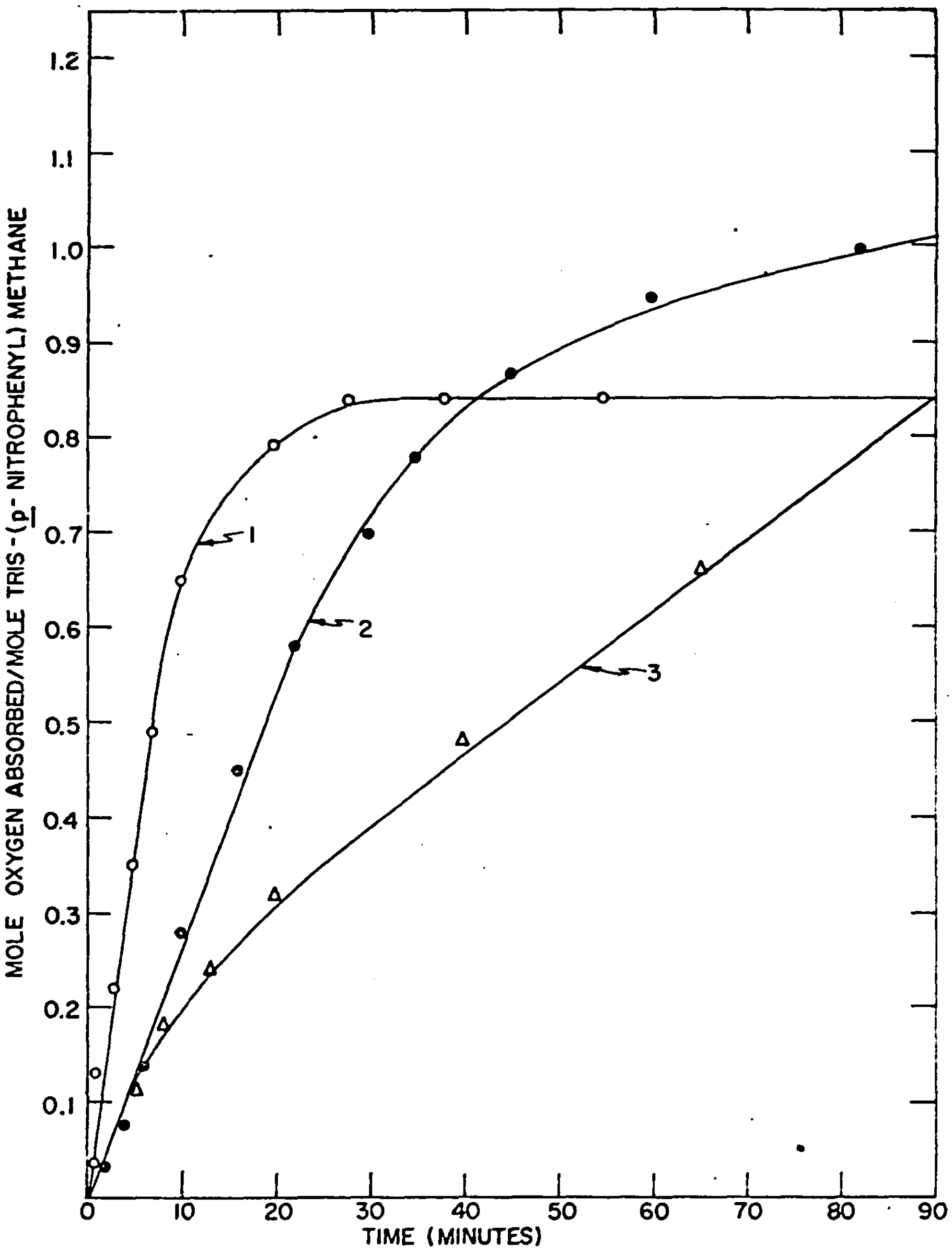

MOLE OXYGEN ABSORBED/MOLE TRIS-(p-NITROPHENYL)-METHANE
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME (MINUTES)
1
2

Figure 17. Rates of oxidation of <u>tris</u>-(<u>p</u>-nitrophenyl)-methane in 25 ml. potassium hydroxide/absolute ethanol at 26°C and 700 mm. oxygen pressure

Curve 1 5.09×10^{-4} mole substrate in 0.35 M base (molar ratio = 5.84)

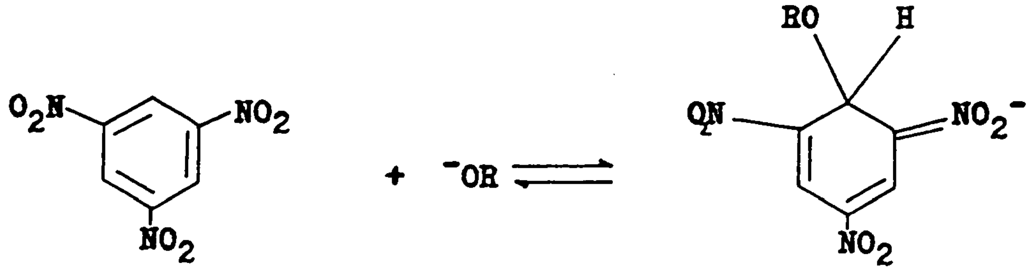
Curve 2 2.49×10^{-3} mole substrate in 0.70 M base (ferric chloride added)

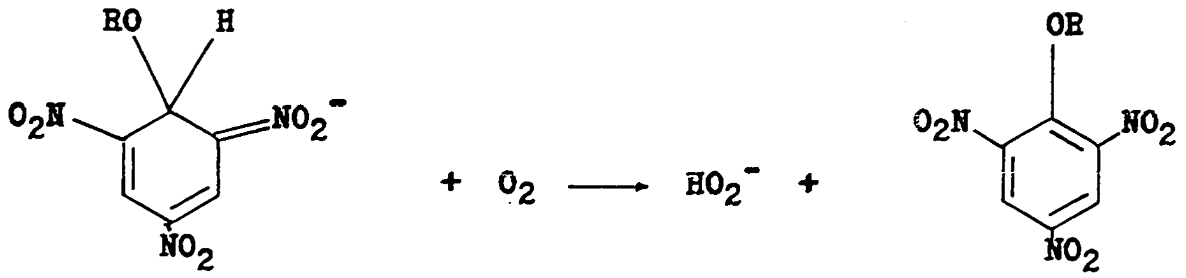
Curve 3 2.07×10^{-3} mole substrate in 0.70 M base (molar ratio = 11.8)


MOLE OXYGEN ABSORBED/MOLE TRIS-(p- NITROPHENYL) METHANE
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)
1
2
3

Oxidation of Other Nitro Compounds

Although *sym*-trinitrobenzene does not ionize, even in strongly basic medium, oxidation occurs after a long, variable induction period (Figure 18, Tables 37 to 40). The addition of various metal ions seems to have little consistent effect. The only product identified was picric acid which was formed along with considerable amounts of intractable oils and amorphous materials. Presumably the oxidation occurs by abstraction of a hydride ion by an unknown process, similar to the ferricyanide oxidation of similar compounds[305].





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[305] P. Hepp, Ann., 215, 344 (1882).

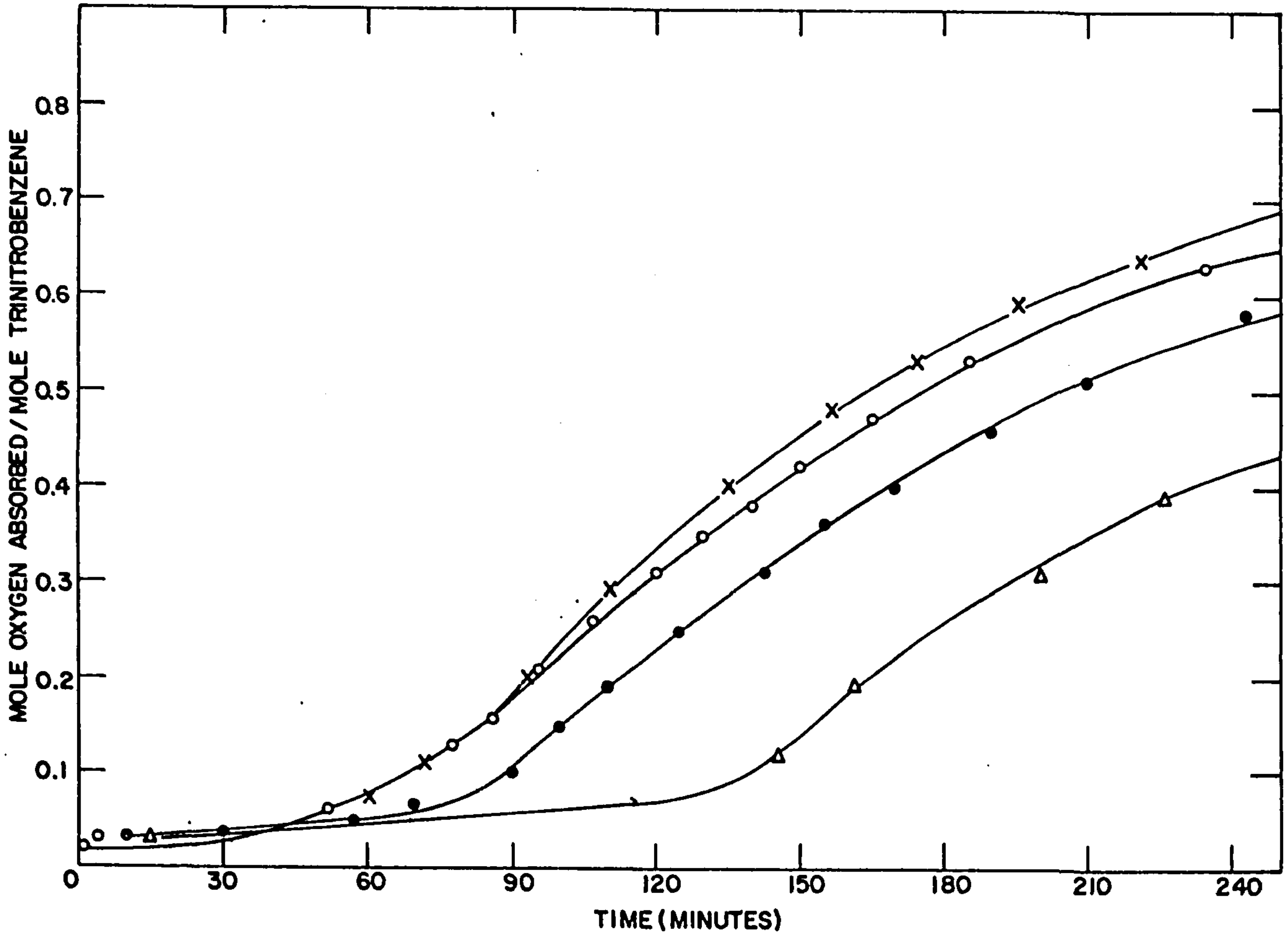
Figure 18. Effect of additives on rate of oxidation of *sym*-trinitrobenzene in 25 ml. of 0.389 M potassium *t*-butoxide/*t*-butanol at 30°C and 700 mm. oxygen pressure

● 3.76×10^{-3} mole substrate; no additive

△ 3.88×10^{-3} mole substrate; 0.1 ml. *t*-butylhydroperoxide added

○ 3.77×10^{-3} mole substrate; $HAuCl_4 \cdot 3\ H_2O$ added (*ca*. one mole per cent)

× 3.62×10^{-3} mole substrate; ferric chloride added (*ca*. one mole per cent)


MOLE OXYGEN ABSORBED / MOLE TRINITROBENZENE
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
30
60
90
120
150
180
210
240
TIME (MINUTES)

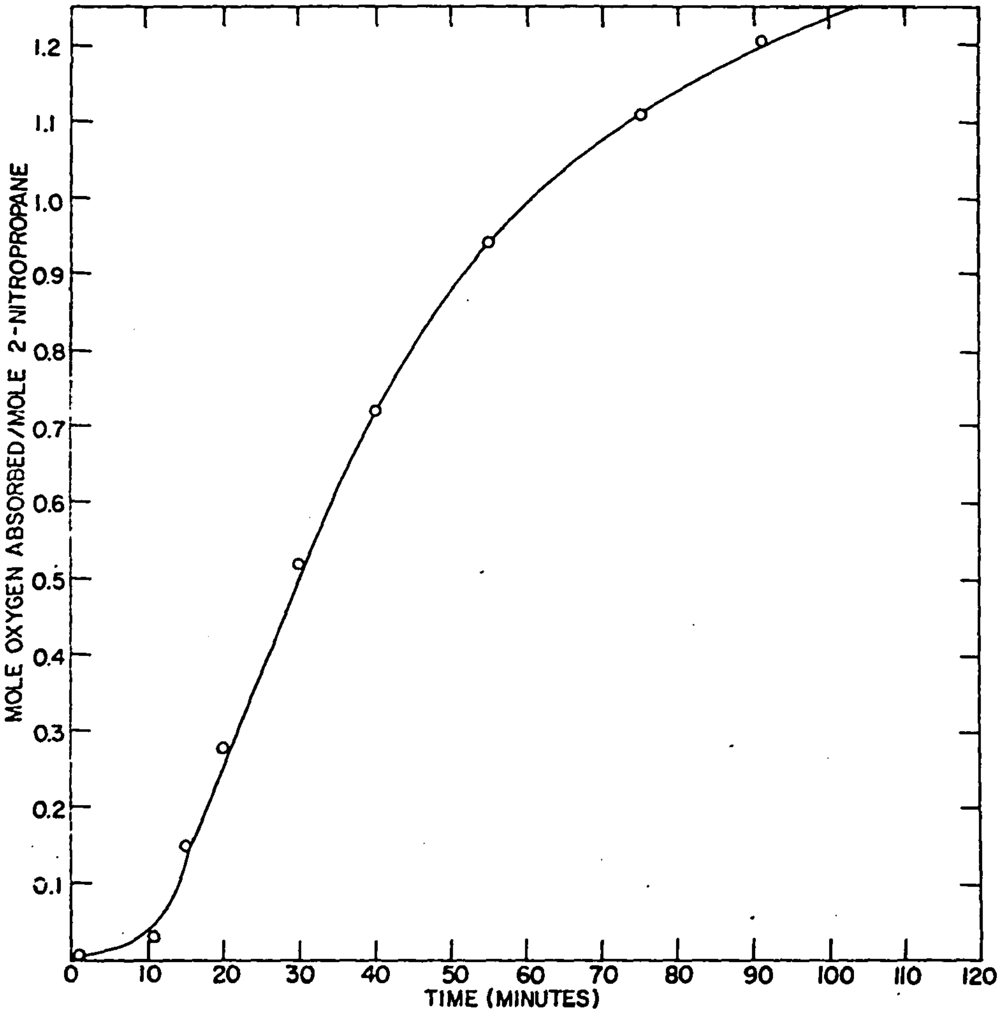


Figure 19. Rate of oxidation of 2-nitropropane (3.23×10^{-3} mole in 25 ml. of 0.389 M potassium _t_-butoxide/ _t_-butanol at 23°C and 700 mm. oxygen pressure

The oxidation of 2-nitropropane in 0.39 M potassium t-butoxide/t-butanol proceeds normally after a short induction period (Figure 19, Table 41). The oxidation behavior of this compound has been discussed above (pp. 17-18). Phenylnitromethane does not absorb any oxygen in 0.3 M potassium t-butoxide at periods up to 24 hours.

Oxidation of Acetonitrile Derivatives

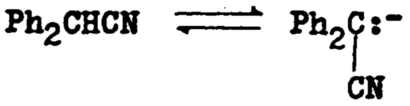
Solutions of phenylacetonitrile and of diphenylacetonitrile in 0.39 M potassium t-butoxide/t-butanol rapidly absorb one mole of oxygen per mole of nitrile to form benzoic acid and benzophenone, respectively, in quantitative amounts (Figures 20 and 21, Tables 42 to 52). In the case of diphenylacetonitrile the nitrile portion of the molecule ultimately forms cyanate ion[60]. The fate of the nitrile portion of the molecule has not been ascertained for phenylacetonitrile. The addition of ferric chloride to the solutions appears to have a slight accelerating effect on the initial rate of oxidation in the potassium t-butoxide/t-butanol solvent system. Under these conditions p-nitrophenylacetonitrile absorbs oxygen slowly or not at all (Figure 21, Tables 44 and 45). Addition of potassium ferricyanide appears to have no appreciable effect on the oxidation rate (Table 45).

In piperidine solution diphenylacetonitrile is rapidly autoxidized in the presence of added base (Figure 22, Table

46). When the base is present in a deficient amount, oxidation ceases as soon as an amount of oxygen equivalent to the base present is used up in agreement with the overall reaction:

$$\mathrm{Ph_2CHCN} + \mathrm{OH^-} + \mathrm{O_2} \longrightarrow \mathrm{H_2O} + \mathrm{Ph_2C{=}O} + \mathrm{^-OCN}$$

In the presence of catalytic amounts of cupric ion the oxidation proceeds at a rapid initial rate, ultimately absorbing 1.5 moles of oxygen per mole of nitrile. The addition of ferric ion also serves to catalyze the oxidation of diphenylacetonitrile in piperidine in the absence of any added base. The stoichiometry in the copper catalyzed reaction can be satisfactorily accounted for on the basis of a scheme such as the following:

(143) 

$$\mathrm{Ph_2CHCN} \rightleftharpoons \mathrm{Ph_2}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{:^-}$$

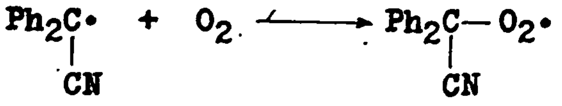
(144) 

$$\mathrm{PH_2}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{:^-} + \mathrm{Cu(II)} \longrightarrow \mathrm{Ph_2}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{\cdot} + \mathrm{Cu(I)}$$

(145) $\mathrm{Cu(I)} + \mathrm{O_2} \longrightarrow \mathrm{Cu(II)} + \mathrm{\cdot O_2^-}$

(146) 

$$\mathrm{Ph_2}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{:^-} + \mathrm{\cdot O_2^-} \longrightarrow \mathrm{Ph_2}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{\cdot} + \mathrm{O_2^=}$$

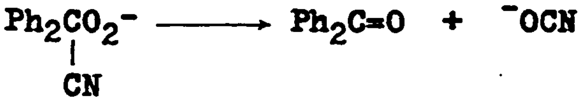
(147) 

$$\mathrm{Ph_2}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{\cdot} + \mathrm{O_2} \rightleftharpoons \mathrm{Ph_2}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{-O_2\cdot}$$

(148)

$$\underset{\mathrm{CN}}{\underset{|}{\mathrm{Ph_2C}}}{-}\mathrm{O_2}\cdot \;+\; \underset{\mathrm{CN}}{\underset{|}{\mathrm{Ph_2C}}}\mathrm{:^-} \longrightarrow \underset{\mathrm{CN}}{\underset{|}{\mathrm{Ph_2C}}}{-}\mathrm{O:^-} \;+\; \underset{\mathrm{CN}}{\underset{|}{\mathrm{Ph_2C}}}\cdot$$

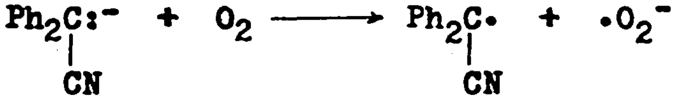
(149)



$$\underset{\mathrm{CN}}{\underset{|}{\mathrm{Ph_2CO_2^-}}} \longrightarrow \mathrm{Ph_2C{=}O} \;+\; {}^-\mathrm{OCN}$$

In the absence of added metallic catalysts, the preferred initiation step is

(150)



$$\underset{\mathrm{CN}}{\underset{|}{\mathrm{Ph_2C}}}\mathrm{:^-} \;+\; \mathrm{O_2} \longrightarrow \underset{\mathrm{CN}}{\underset{|}{\mathrm{Ph_2C}}}\cdot \;+\; \cdot\mathrm{O_2^-}$$

Under these conditions (strongly basic) the peroxide formed in reaction (143) can itself serve as an oxidizing agent, attacking the carbanion to form the observed products of the reaction. It is important to note that in no case were dimeric products detected in the autoxidation of acetonitrile derivatives.

Figure 20. Rates of oxidation of phenylacetonitriles in 25 ml. of potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure

○ phenylacetonitrile (3.46×10^{-3} mole) in 0.389 M base--no additive

× phenylacetonitrile (3.68×10^{-3} mole) in 0.389 M base--ferric chloride added

△ *p*-nitrophenylacetonitrile (3.92×10^{-3} mole) in 0.289 M base

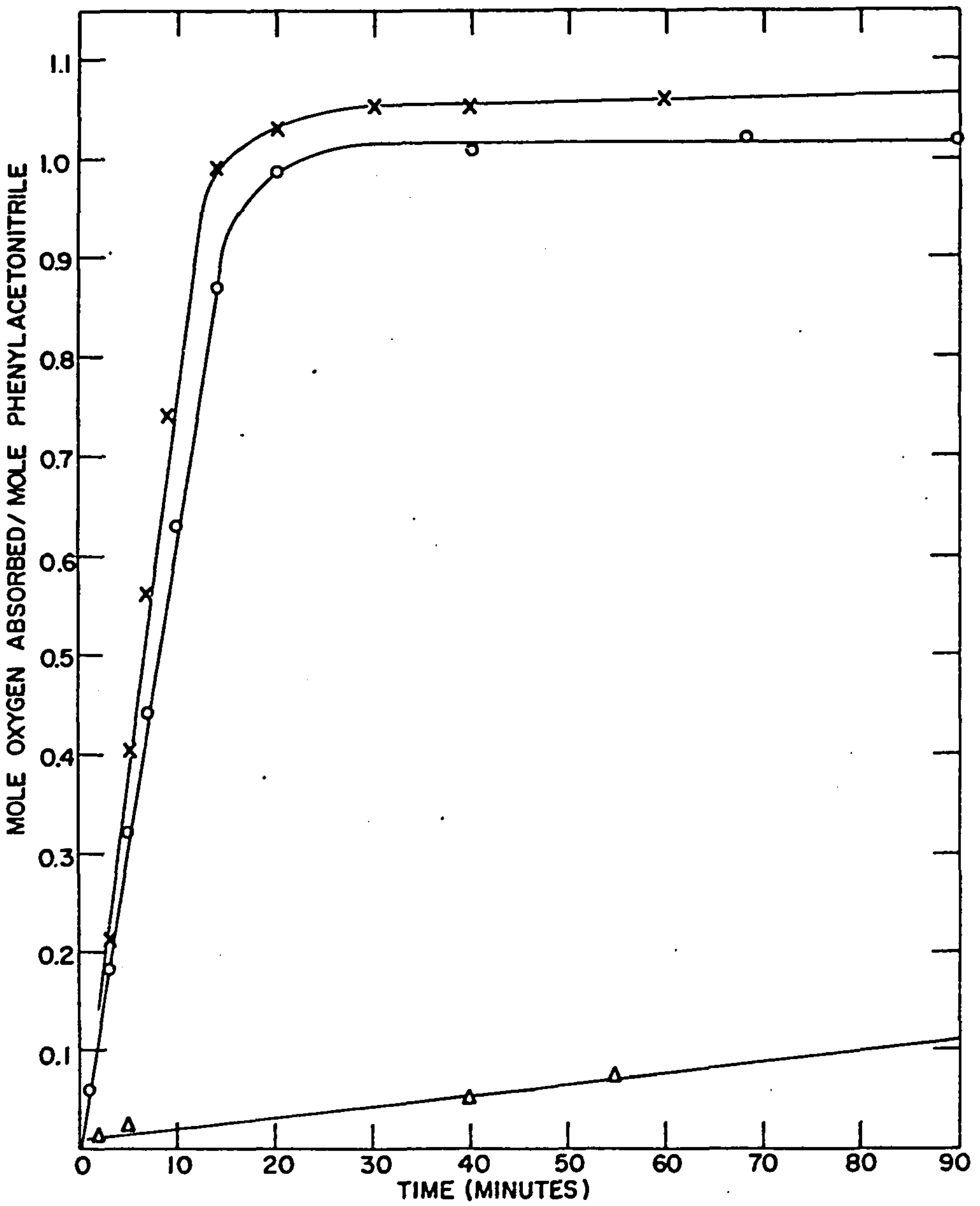

MOLE OXYGEN ABSORBED/ MOLE PHENYLACETONITRILE
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)

Figure 21. Effect of addition of ferric chloride (*ca.* one mole per cent) on the rate of oxidation of diphenylacetonitrile (3.05×10^{-3} mole in 25 ml. of 0.389 M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure)

○ no additive

x ferric chloride added

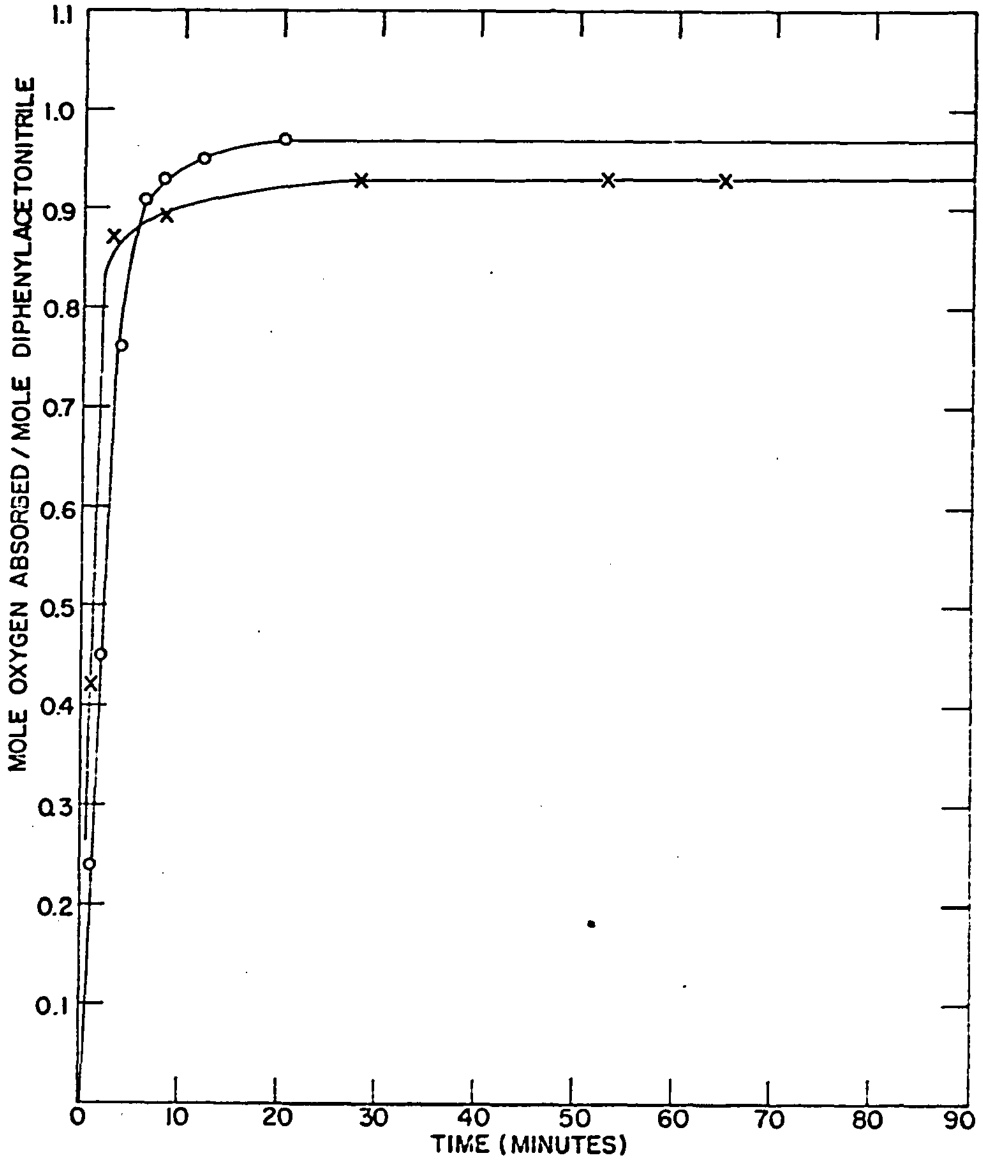
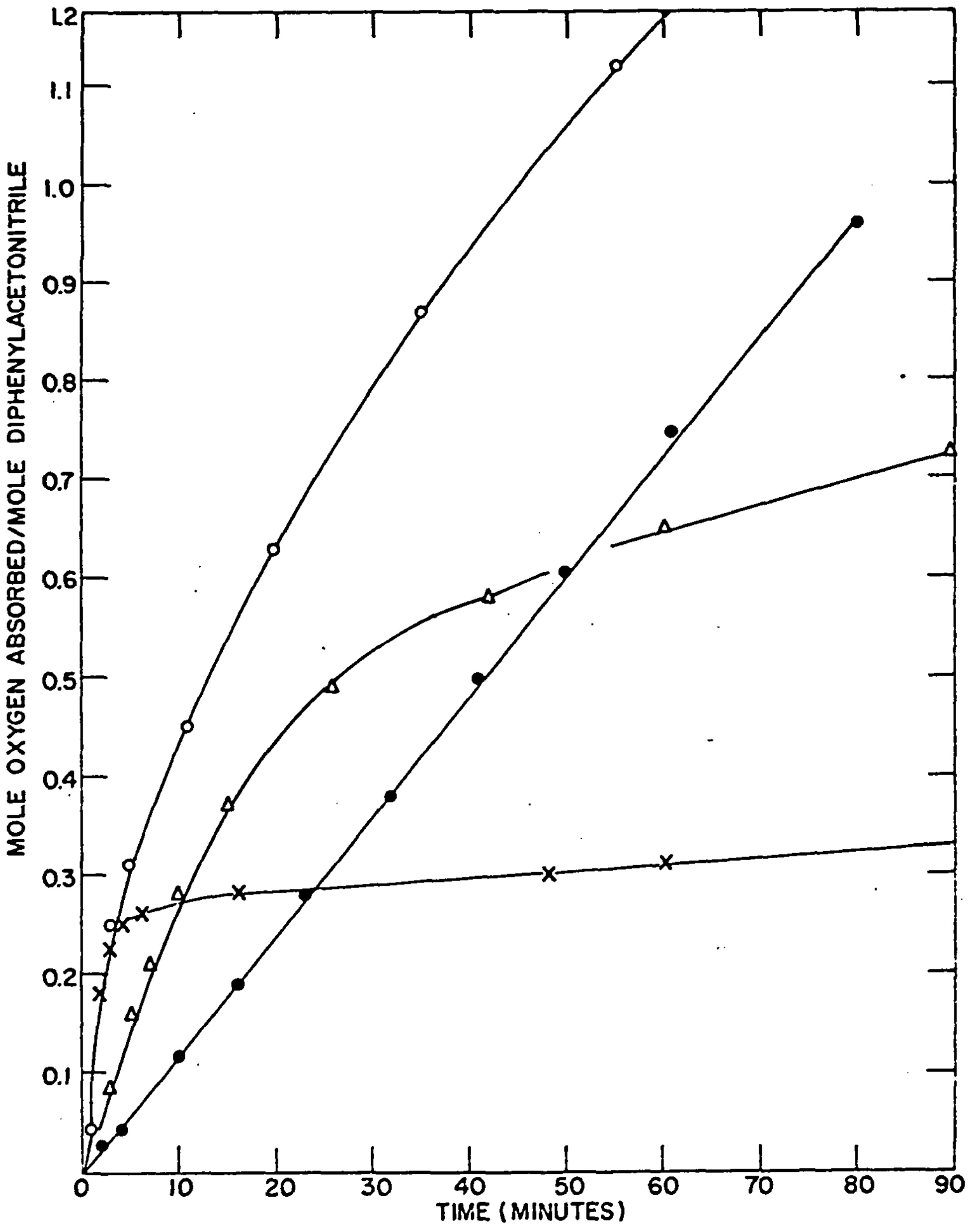

MOLE OXYGEN ABSORBED / MOLE DIPHENYLACETONITRILE
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)

Figure 22. Effect of additives on rate of oxidation of diphenylacetonitrile in 25 ml. of piperidine at 25°C and 700 mm. oxygen pressure

- ○ 3.07×10^{-3} mole substrate; 15 mg. cupric chloride added
- ● 3.04×10^{-3} mole substrate; one mole per cent ferric chloride added
- △ 3.04×10^{-3} mole substrate; 1.3 g. solid potassium hydroxide added
- × 3.40×10^{-3} mole substrate; 3 ml. of 0.389 M potassium *t*-butoxide/*t*-butanol added


MOLE OXYGEN ABSORBED/MOLE DIPHENYLACETONITRILE
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)

Oxidation of Fluorene Derivatives

The autoxidation of the hydrocarbons fluorene, 9-phenylfluorene, and 2-nitrofluorene proceeds with remarkable ease (Figure 23, Tables 53 to 55). Previously, these compounds have been reported to undergo autoxidation by an ionic mechanism[68]. However, on the basis of analogy to the behavior of other carbanions, a homolytic mechanism is to be preferred.

The products of the oxidation of fluorene was fluorenone, isolated in yields of approximately 93%. In the case of 2-nitrofluorene the products appeared to be a complex mixture and no separation was attempted. The tertiary hydrocarbon 9-phenylfluorene yielded 9-phenylfluorenol along with significant amounts of a white solid identified as <u>bis</u>-(9-phenylfluorenyl)-peroxide.

Both fluorene and 2-nitrofluorene absorb slightly more than one mole of oxygen per mole of hydrocarbon. This may be due to further slow oxidation of the ketone or to degradative attach of oxygen on the hydrocarbon. The stoichiometry of the reaction of 9-phenylfluorene with oxygen is approximately 0.75 moles oxygen per mole hydrocarbon. A probable mechanism for the oxidation of these hydrocarbons then would involve the following steps:

(151) $RH \xrightleftharpoons{B-} R:^- + BH$

(152) $R{:}^- + O_2 \longrightarrow R\cdot + \cdot O_2^-$

(153) $R\cdot + O_2 \longrightarrow RO_2\cdot$

(154) $RO_2\cdot + R{:}^- \longrightarrow RO_2{:}^- + R\cdot$

(155) $RO_2{:}^- + RO_2H \longrightarrow RO{:}^- + ROH + O_2$

(156) $RO_2H + R{:}^- \longrightarrow RO{:}^- + ROH$

(157) $RO_2\cdot + R\cdot \longrightarrow RO_2R$

The importance of the various steps is determined by the particular compound undergoing oxidation.

Analysis for the presence of hydrogen peroxide in the oxidation of fluorene has not been entirely satisfactory. The addition of lead sub-acetate in catalytic amounts to a solution undergoing autoxidation seems to have little effect (Figure 24, Tables 56 to 58). Perhaps a reaction of the type

(158) $R{:}^- + H_2O_2 \longrightarrow ROH + {}^-OH$

could account for this discrepancy.

Figure 23. Rates of oxidation of fluorene derivatives in 0.389 M potassium t-butoxide/t-butanol at 25°C and 700 mm. oxygen pressure

○ fluorene (2.68×10^{-3} mole)

△ 2-nitrofluorene (2.81×10^{-3} mole)

× 9-phenylfluorene (2.96×10^{-3} mole)

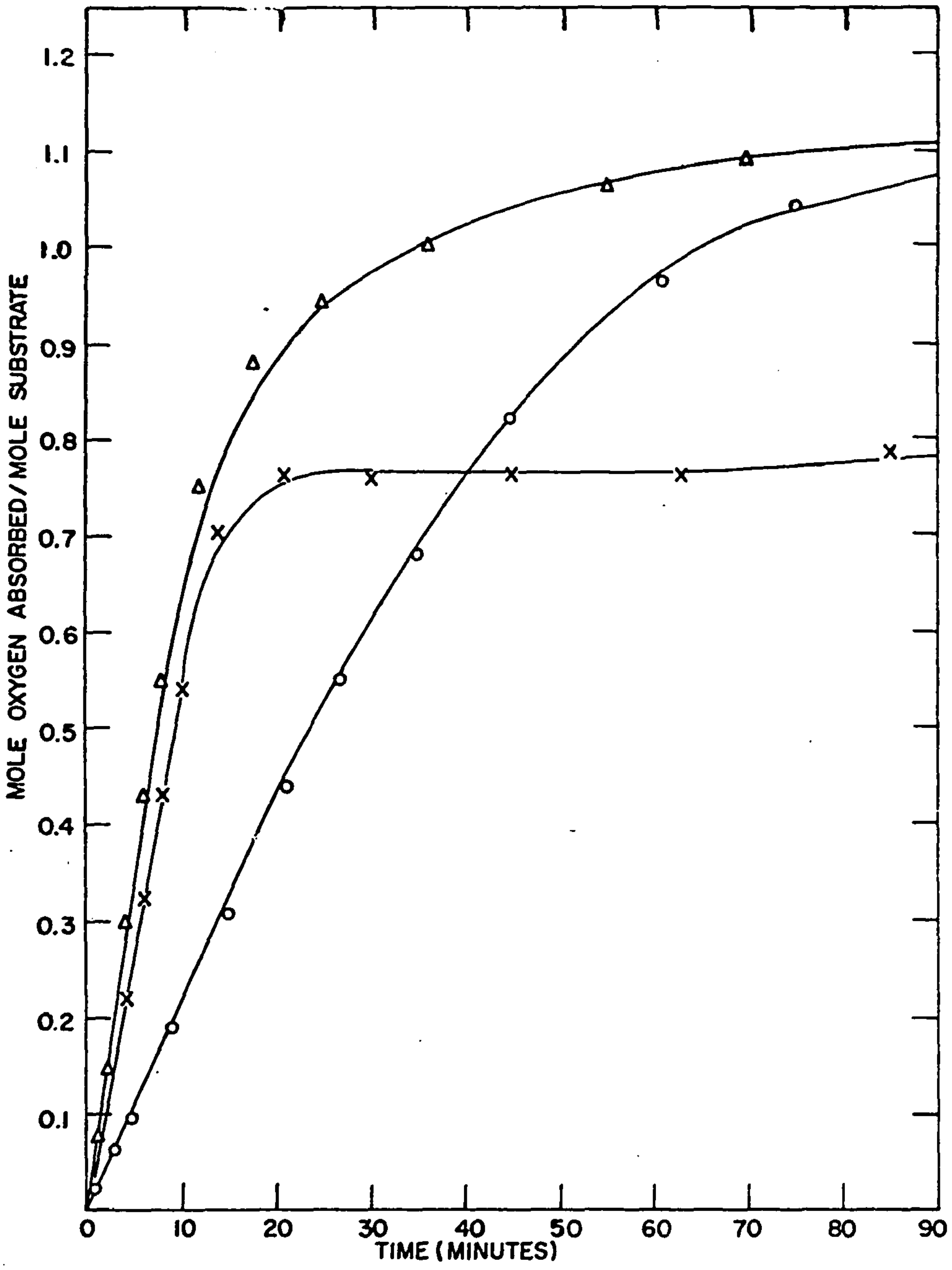
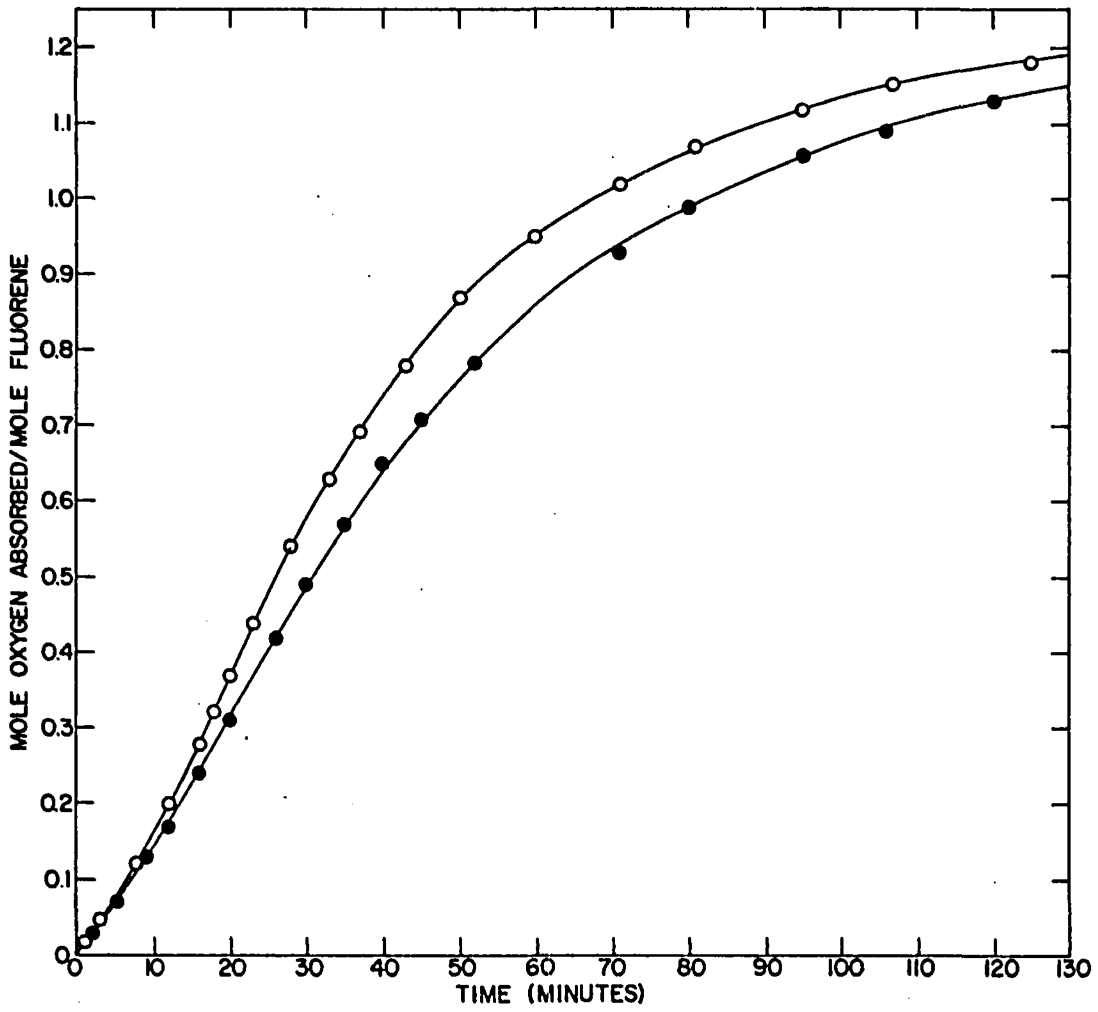

MOLE OXYGEN ABSORBED/MOLE SUBSTRATE
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)

Figure 24. Effect of addition of lead sub-acetate on rate of oxidation of fluorene in 25 ml. of 0.335 M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure

○ 4.62 x 10^{-3} mole substrate; no additive

● 4.71 x 10^{-3} mole substrate; lead sub-acetate (ca. one mole per cent) added


MOLE OXYGEN ABSORBED/MOLE FLUORENE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
0
10
20
30
40
50
60
70
80
90
100
110
120
130
TIME (MINUTES)

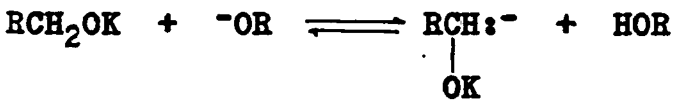
Oxidation of Alcohols

Primary and secondary aromatic alcohols are readily autoxidized in an excess of 0.39 N potassium t-butoxide/ t-butanol solution to form the corresponding acids and ketones in quantitative amounts (Figure 25, Tables 59, 61, 65 and 71). The initial rates are in order of the expected acidity of the compounds, i.e., 9-fluorenol, p-nitrobenzyl-alcohol, benzhydrol, and benzyl alcohol. The latter two compounds are autoxidized only after induction periods; with benzyl alcohol the induction period is quite prolonged. The problem of the final stoichiometry of the oxidations is not quite clear since several of the compounds continue to absorb oxygen for long periods of time.

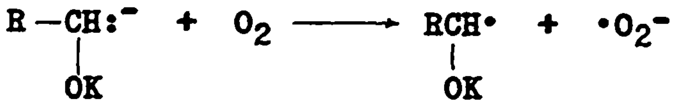
The addition of cupric ion in trace quantities has little effect on the length of induction period, stoichiometry, or rate of oxidation of benzyl alcohol. On the other hand, ferric ion slows down the reaction considerably so that oxygen absorption continues at a slow rate for extended periods of time (Figure 26, Tables 59 to 61). The effect of concentration of base on the rate of autoxidation of p-nitrobenzyl alcohol is portrayed in Figure 27 (Tables 62 to 64). In a deficiency of base, oxidation proceeds at a slow rate and ceases after the base present has been neutralized by the product, p-nitrobenzoic acid. In the presence of an excess of base the autoxidation proceeds rapidly, finally achieving a stoichiometry of 0.85 moles oxygen absorbed to mole of p-nitrobenzyl alcohol. The addition of lead sub-acetate has a retarding effect on the initial rate of oxidation. However, the ultimate stoichiometry is approximately the same as in the absence of additive.

To account for these results, the following reaction sequence is suggested:

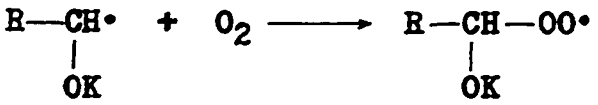
(159) $R{-}CH_2{-}OH + KOR \rightleftharpoons RCH_2OK + HOR$

(160)


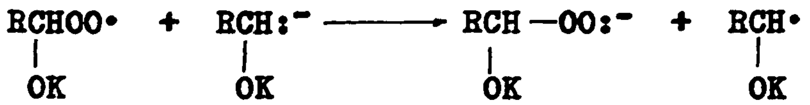
$$RCH_2OK + {}^-OR \rightleftharpoons \underset{\displaystyle OK}{\underset{|}{RCH:^-}} + HOR$$

(161)


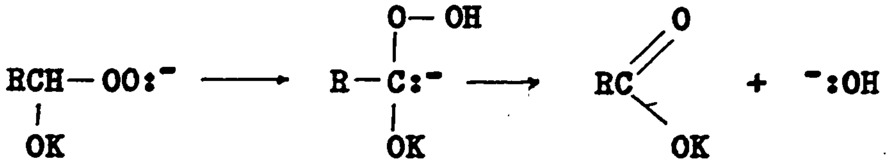
$$R{-}\underset{\displaystyle OK}{\underset{|}{CH:^-}} + O_2 \longrightarrow \underset{\displaystyle OK}{\underset{|}{RCH\cdot}} + \cdot O_2^-$$

(161)


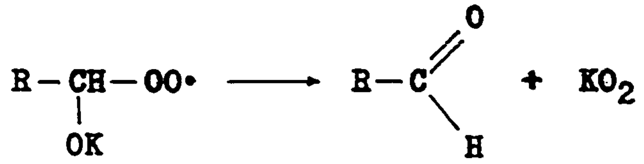
$$R{-}\underset{\displaystyle OK}{\underset{|}{CH\cdot}} + O_2 \longrightarrow R{-}\underset{\displaystyle OK}{\underset{|}{CH}}{-}OO\cdot$$

(162)


$$\underset{\displaystyle OK}{\underset{|}{RCHOO\cdot}} + \underset{\displaystyle OK}{\underset{|}{RCH:^-}} \longrightarrow \underset{\displaystyle OK}{\underset{|}{RCH}}{-}OO:^- + \underset{\displaystyle OK}{\underset{|}{RCH\cdot}}$$

(163)


$$\underset{\displaystyle OK}{\underset{|}{RCH}}{-}OO:^- \longrightarrow R{-}\overset{\displaystyle O{-}OH}{\overset{|}{\underset{\displaystyle OK}{\underset{|}{C}}}}:^- \longrightarrow RC\begin{smallmatrix} /\!\!/ O \\ \diagdown OK \end{smallmatrix} + {}^-{:}OH$$

(164) 

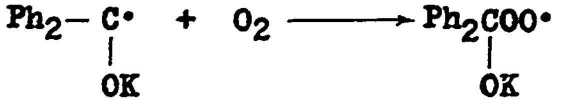
R = phenyl or p-nitrophenyl

The oxidation of secondary aromatic alcohols in excess potassium t-butoxide/t-butanol solutions leads to the formation of ketones. The oxidation of 9-fluorenol proceeds rapidly to form fluorenone. The addition of ferric ion appears to enhance the initial rate somewhat (Figure 28, Table 66). The surprising effect of ferric ion on the overall stoichiometry of the reaction is unexplained. The oxidation of benzhydrol is subject to catalysis and inhibition by metal ions (Figures 29 and 30, Tables 67 to 77). Ferric ion produces the most profound effect, inhibiting the reaction completely, while cupric ion causes rate enhancement. The occurrence of the inhibition and catalysis points to a free radical pathway for the reaction with the following chain steps:

(165) $Ph_2CHOK \overset{RO^-}{\rightleftharpoons} Ph_2{}^-\ddot{C}OK$

(166) 

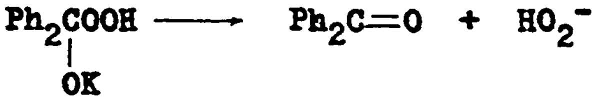
$$Ph_2\underset{OK}{C}{:}^- + O_2 \longrightarrow Ph_2\underset{OK}{C}\cdot + \cdot O_2^-$$

(167) 

$$Ph_2-\underset{OK}{C}\cdot + O_2 \longrightarrow Ph_2\underset{OK}{C}OO\cdot$$

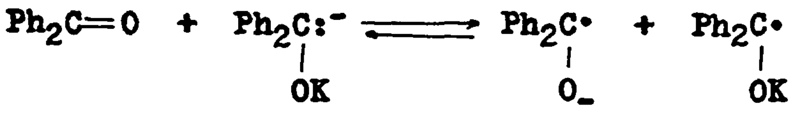
(167) 

$$\underset{\mathrm{OK}}{\mathrm{Ph_2COO\cdot}} + \underset{\mathrm{OK}}{\mathrm{Ph_2C{:}^-}} \longrightarrow \underset{\mathrm{OK}}{\mathrm{Ph_2COO^-}} + \underset{\mathrm{OK}}{\mathrm{Ph_2C\cdot}}$$

(168) 

$$\underset{\mathrm{OK}}{\mathrm{Ph_2COOH}} \longrightarrow \mathrm{Ph_2C{=}O} + \mathrm{HO_2^-}$$

The observed autocatalysis may be explained by the following equilibrium:

(169) 

$$\mathrm{Ph_2C{=}O} + \underset{\mathrm{OK}}{\mathrm{Ph_2C{:}^-}} \rightleftharpoons \underset{\mathrm{O_-}}{\mathrm{Ph_2C\cdot}} + \underset{\mathrm{OK}}{\mathrm{Ph_2C\cdot}}$$

Evidence for the intervention of ketyl radicals in these autoxidations has already been mentioned (see Review section).

The isolation of a crystalline pale yellow solid from the anhydrous oxidation medium appears to be especially significant. The solid liberates a gas on the addition of cold water. The color and hydrolysis behavior suggest that the solid may be potassium superoxide, KO_2, a paramagnetic solid. That this view is essentially correct was substantiated in experiments where the volume of evolved gas was measured. In the oxidation of 3×10^{-3} mole benzhydrol in 0.35 M potassium t-butoxide/t-butanol 2.22×10^{-3} mole of oxygen were absorbed. Addition of cold water brought about the evolution of 1.16×10^{-3} mole of gas, presumably oxygen. The hydrolysis of potassium superoxide proceeds according to the overall reaction

$$2\ KO_2 + 2\ H_2O \longrightarrow O_2 + H_2O_2 + 2\ KOH$$ [306]

It thus appears that the initiation reaction (166) is essentially valid as written.

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[306] P. George, Disc. Faraday Soc., 2, 196 (1947); see also E. Seyb, Jr., and J. Kleinberg, Anal. Chem., 23, 115 (1951).

Figure 25. Comparison of oxidation rates of primary and secondary alcohols in 25 ml. of 0.389 M potassium t-butoxide/t-butanol at 27 ± 2°C and 700 mm. oxygen pressure

△ 9-fluorenol (3.78×10^{-3} mole)

○ p-nitrobenzyl alcohol (4.19×10^{-3} mole)

● benzhydrol (3.54×10^{-3} mole)

× benzyl alcohol (3.79×10^{-3} mole)

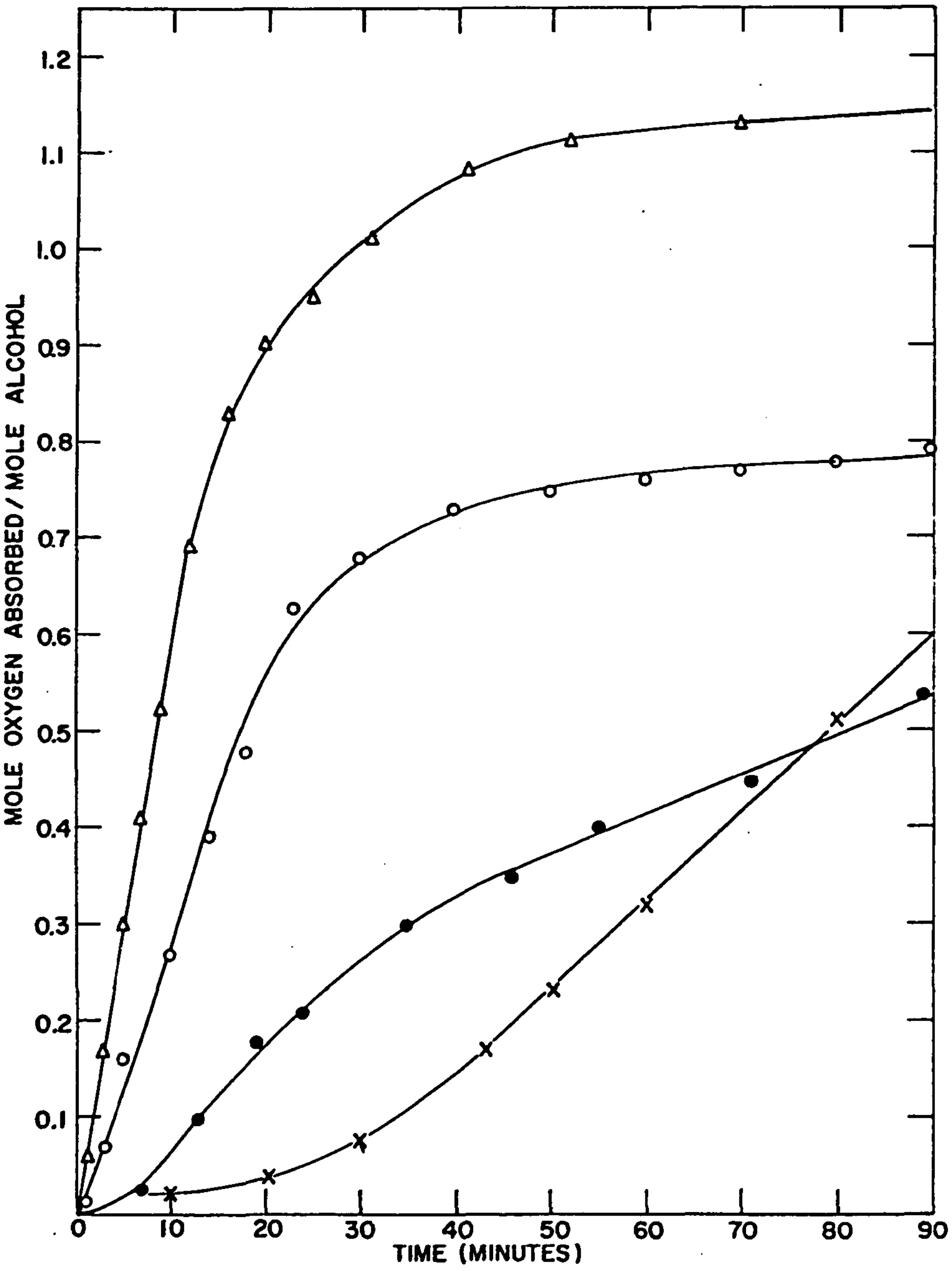

MOLE OXYGEN ABSORBED / MOLE ALCOHOL
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)

Figure 26. Effect of additives on rate of oxidation of benzyl alcohol in 25 ml. of 0.389 M potassium *t*-butoxide/*t*-butanol at 22°C and 700 mm. oxygen pressure

Curve 1	3.79×10^{-3} mole substrate; no additive
Curve 2	4.05×10^{-3} mole substrate; cupric sulfate added
Curve 3	3.88×10^{-3} mole substrate; ferric chloride added

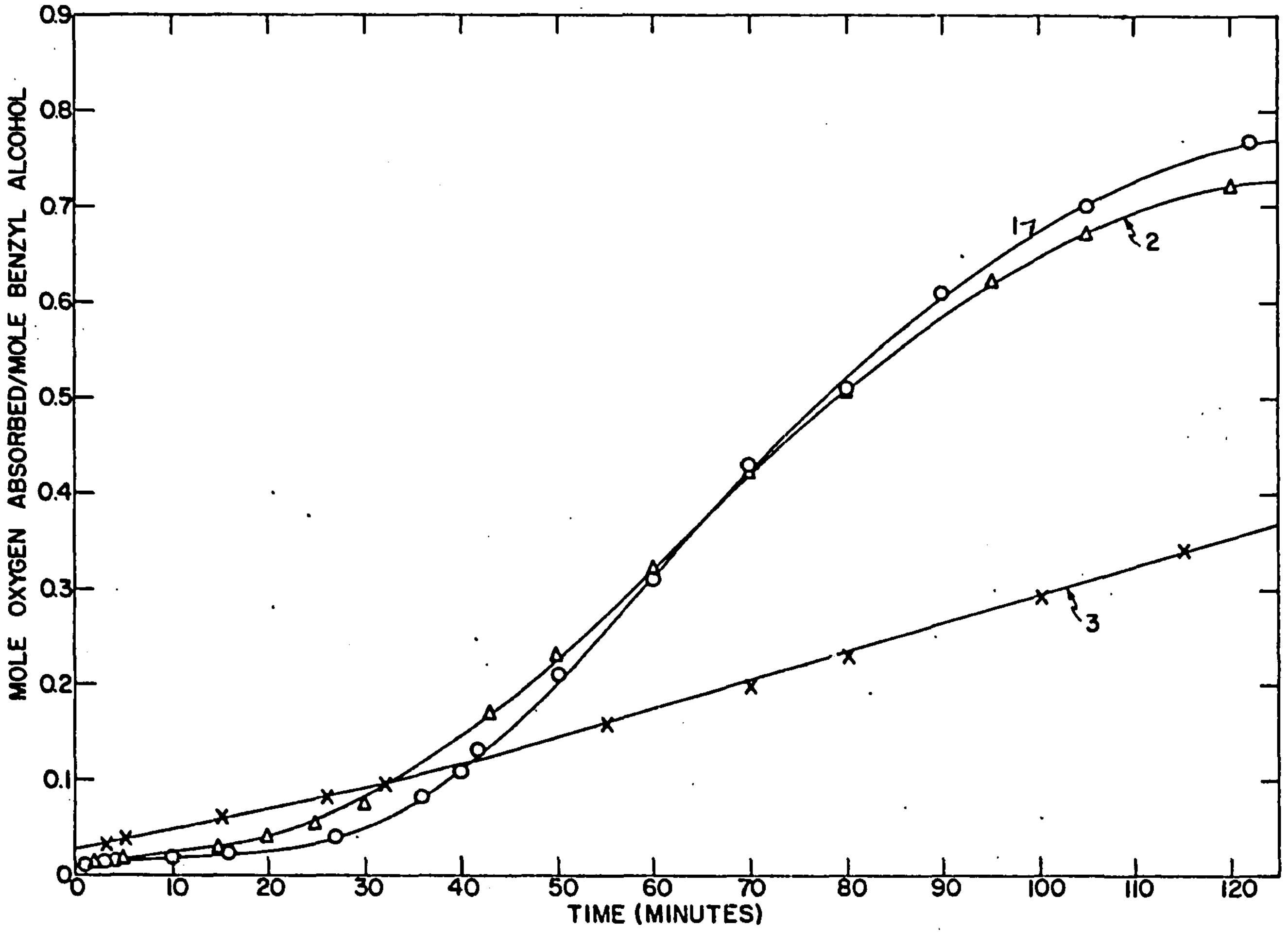

MOLE OXYGEN ABSORBED/MOLE BENZYL ALCOHOL
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
TIME (MINUTES)
0
10
20
30
40
50
60
70
80
90
100
110
120
1
2
3

Figure 27. Effect of lead sub-acetate on rate of oxidation of *p*-nitrobenzyl alcohol in 25 ml. potassium *t*-butoxide/*t*-butanol at 27°C and 700 mm. oxygen pressure

Curve 1	4.19×10^{-3} mole substrate in 0.335 M base (Molar ratio = 2.0)
Curve 2	4.28×10^{-3} mole substrate in 0.335 M base; lead sub-acetate added
Curve 3	4.53×10^{-3} mole substrate in 0.123 M base (Molar ratio = 0.68)

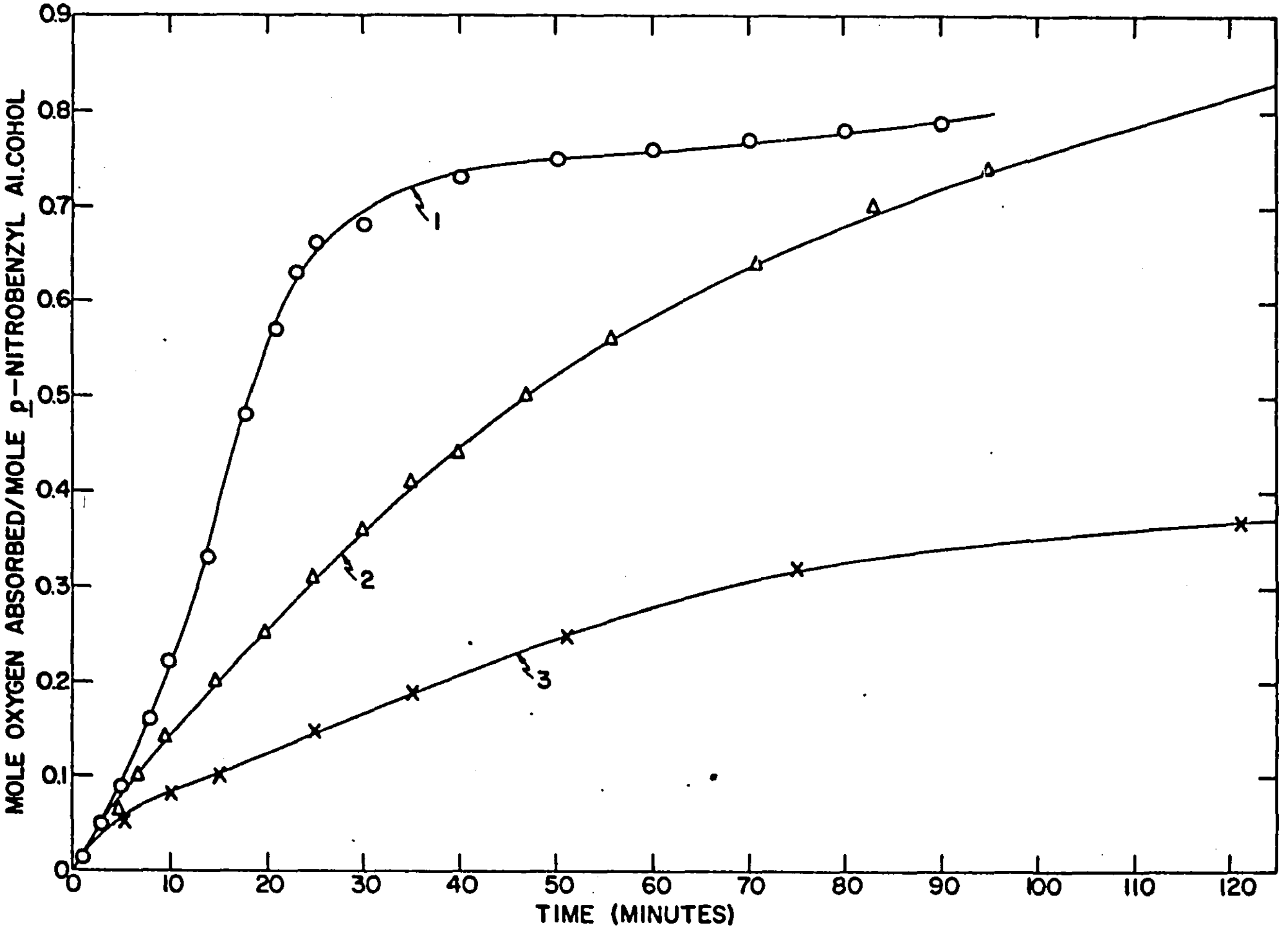

MOLE OXYGEN ABSORBED/MOLE p-NITROBENZYL ALCOHOL
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME (MINUTES)
1
2
3

Figure 28. Effect of addition of ferric chloride on rate of oxidation of 9-fluorenol in 25 ml. of 0.389 M potassium t-butoxide/ t-butanol at 30°C and 700 mm. oxygen pressure

○ 3.78×10^{-3} mole substrate; no additive

△ 3.96×10^{-3} mole substrate; ferric chloride (ca. one mole per cent) added

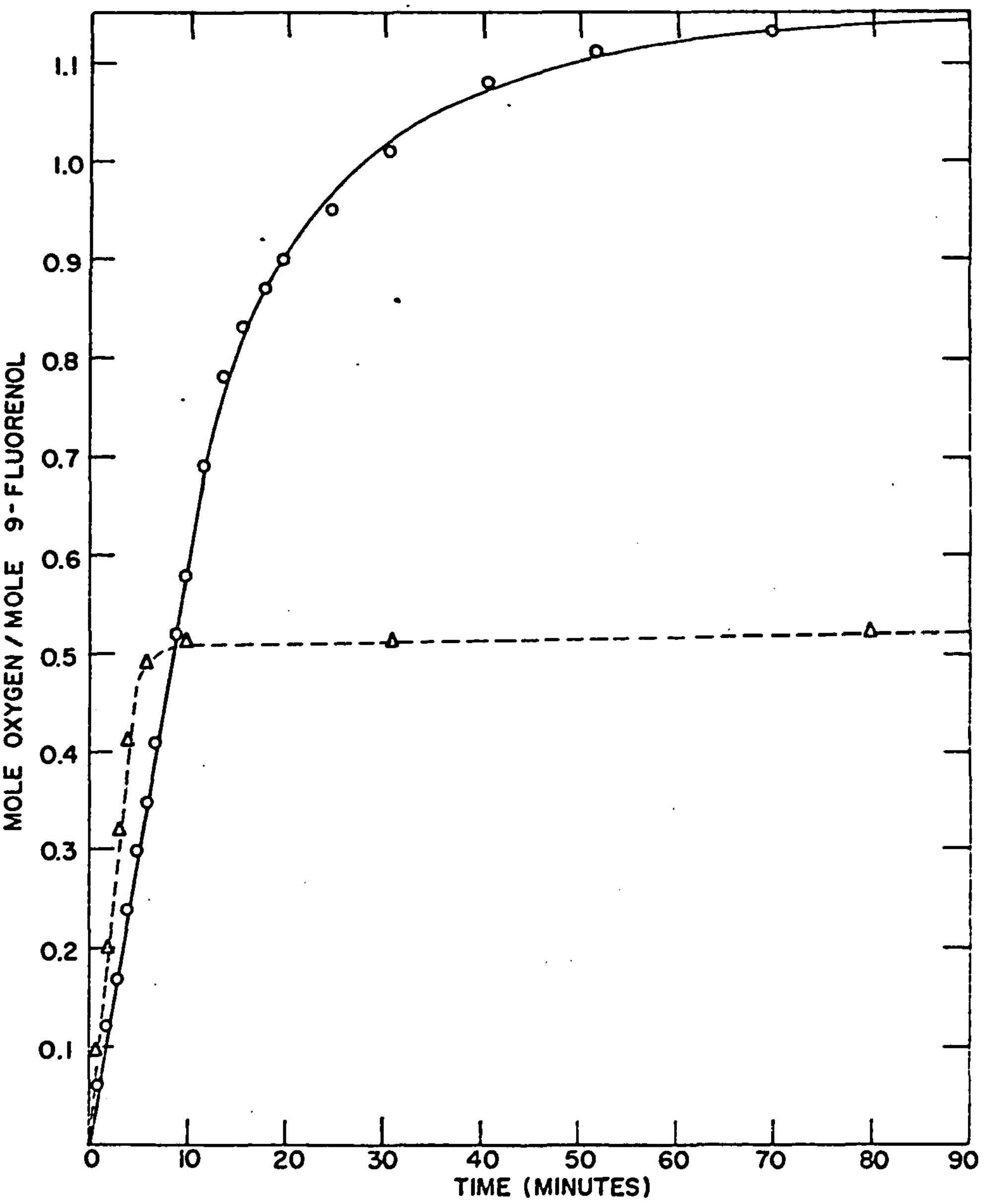

MOLE OXYGEN / MOLE 9-FLUORENOL
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)

Figure 29. Effect of additives on rate of oxidation of benzhydrol in 25 ml. of 0.335 M potassium t-butoxide/t-butanol at 27°C and 700 mm. oxygen pressure

○ 3.54×10^{-3} mole substrate; no additive

● 4.46×10^{-3} mole substrate; lead sub-acetate added

△ 3.87×10^{-3} mole substrate; copper sulfate added

▲ 3.61×10^{-3} mole substrate; potassium ferricyanide added

× 3.62×10^{-3} mole substrate; ferric chloride hexahydrate added

\+ 4.25×10^{-3} mole substrate; oxidation performed in 25 ml. of 0.72 M potassium hydroxide/absolute ethanol

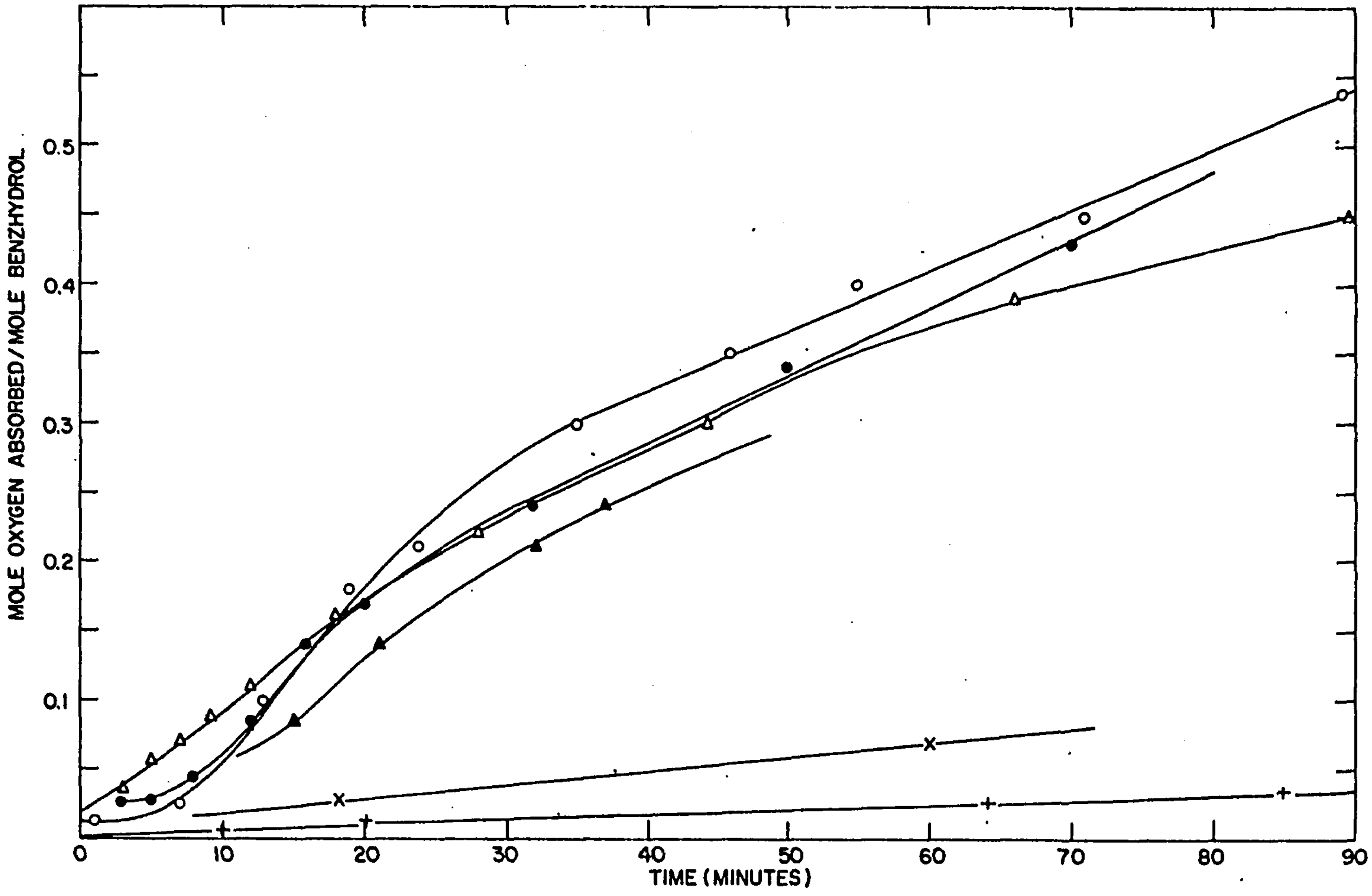

MOLE OXYGEN ABSORBED/MOLE BENZHYDROL
0.1
0.2
0.3
0.4
0.5
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)

Figure 30. Effect of additives on rate of oxidation of benzhydrol in 25 ml. of 0.389 M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure

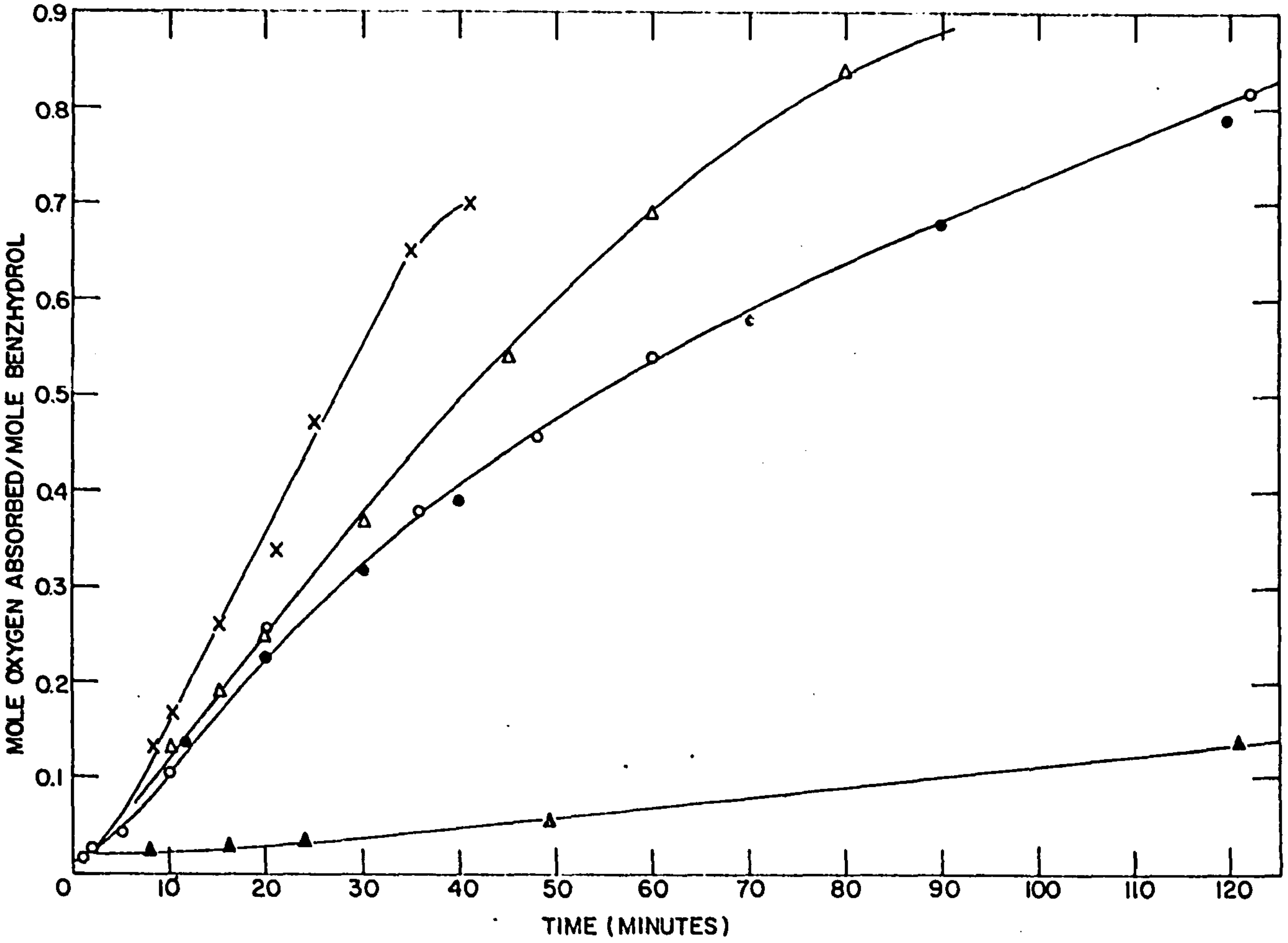
○ 3.40×10^{-3} mole substrate; no additive

● 3.67×10^{-3} mole substrate; chromic chloride hexahydrate added

△ 4.01×10^{-3} mole substrate; cupric chloride added

× 3.67×10^{-3} mole substrate; cupric acetate monohydrate added

▲ 3.78×10^{-3} mole substrate; ferric chloride added


MOLE OXYGEN ABSORBED/MOLE BENZHYDROL
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME (MINUTES)

DISCUSSION

One of the major objectives of the present work was to establish whether p-nitrobenzyl radicals could couple to form p,p'-dinitrobibenzyl in the presence of oxygen. All experimental results tend to indicate that this possibility exists, at least in the presence of sufficiently high concentrations of p-nitrobenzyl radicals. A somewhat similar conclusion had been reached earlier by Tsuruta, Fueno, and Furakawa[7] on the basis of kinetic investigations of the rate of oxygen absorption by basic solutions of p-nitrotoluene (see also p. 12 this thesis). However, the present results have demonstrated that under the reaction conditions employed by these workers, i.e., kinetic controlled experiments in methanolic potassium hydroxide, the major reaction product is not bibenzyl but rather, p-nitrobenzoic acid at least in t-butyl alcohol or ethanol solution (see Table 2). Therefore, the validity of their kinetic treatment is in serious doubt.

Although the oxidation of p-nitrotoluene cannot be inhibited by reagents that are potent inhibitors in the oxidation of 2-nitropropane[49], considerable evidence has been accumulated in support of a free radical mechanism. The oxidation as ordinarily conducted yields mainly p,p'-dinitrobibenzyl[32], but this is the product of a diffusion controlled reaction. When highly efficient stirring is used, the major product is *p*-nitrobenzoic acid, the latter yield increasing with increase in oxygen pressure. The oxidation produces the dimer and acid in quantitative amounts. The *p*-nitrobenzoic acid is not formed from the bibenzyl but from some other intermediate that readily reacts with oxygen. The *p*-nitrobenzyl radical appears to be the most likely intermediate that can be easily scavenged by oxygen. Other factors remaining constant, the yield of bibenzyl increases and the yield of acid decreases as the concentration of *p*-nitrobenzyl radicals increase. The *p*,*p*'-dinitrobibenzyl, then, can be formed by direct radical-radical coupling, or, conceivably by some alternative mechanism. A number of *a priori* alternative pathways to form dimer are listed in equations (170) to (175).

$$\text{(170)}\quad RCH_2\cdot + RCH_2{:}^- \longrightarrow [RCH_2CH_2R]^{\dot{-}}$$

$$\text{(171)}\quad [RCH_2CH_2R]^{\dot{-}} + O_2 \longrightarrow RCH_2CH_2R + \cdot O_2^-$$

$$\text{(172)}\quad RCH_2\cdot + CH_2{=}RH\ (\textit{aci}\ \text{form}) \longrightarrow [RCH_2CH_2RH]\cdot$$

$$\text{(173)}\quad [RCH_2CH_2RH]\cdot + O_2 \longrightarrow RCH_2CH_2R + \cdot O_2^-$$

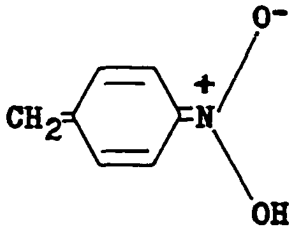
$$\text{(174)}\quad RCH_2{:}^- + O_2 \longrightarrow RCH{:}(\uparrow\uparrow) + HO_2^-$$

$$\text{(175)}\quad RCH_2{:}^- + RCH{:}(\uparrow\uparrow) \xrightarrow{RH} RCH_2CH_2R + B^-$$

R = *p*-nitrophenyl

The direct combination of a radical species (generally considered to possess largely electrophilic properties) with a carbanion (reaction 170) presents an intriguing possibility as an alternative source of p,p'-dinitrobibenzyl. Such a reaction does not appear to have been previously suggested in the chemical literature. However, the present system (p-nitrobenzyl radicals and anions) generates an excellent model for the incursion of such a reaction. Many of the preceding data are in apparent agreement with such a suggestion. Even so, the fact that no dimeric products of any sort were encountered in the basic oxidation of p-nitrodiphenylmethane seems to mitigate against this suggested radical-anion interaction. Also, no "crossed" dimerization appears to occur when small amounts of p-nitrotoluene are added to bis-(2,4-dinitrophenyl)-methane in an effort to induce oxidation in the latter compound in potassium t-butoxide solution. There is absolutely no doubt that this tetranitro derivative is predominantly ionized in this medium as evidenced by the intense blue color. Thus, it is concluded that the alternative scheme based on reactions (170) and (171) has no basis in fact.

An additional alternative to radical-radical coupling as the source of bibenzyl in the basic oxidation of p-nitrotoluene is presented in reactions (172) and (173). The aci form of p-nitrotoluene



should definitely be amenable to attack by free radicals. However, since the concentration of *aci*-form is undoubtedly a function of base concentration, being highest at low concentrations of base, this alternative would predict increasing yields of dimer as the basicity of the medium is lowered. This is in direct contradiction to the observed experimental data.

Finally, a third *a priori* mechanistic alternative leading to dimeric products from *p*-nitrotoluene in basic medium is presented in equations (174) and (175). Here, a carbene intermediate could seemingly be formed by interaction of a carbanion with oxygen. No radical intermediates would then become necessary. The product distributions would be determined entirely by competition between reactions (174) and (175).

(175) $RCH\colon (11) + O_2 \longrightarrow \quad \longrightarrow$ acid

Reaction (175) would only be important for a carbene in the triplet state (electrons unpaired) but not for the singlet state (electron spins coupled). Again, such a mechanism makes the lack of "crossed" dimers difficult to understand. Moreover, no products from the expected reaction (176) have been observed.

(176) $RCH{:}\ (11) + HOR \longrightarrow RCH_2OR$

Therefore, it appears that a mechanism involving radical-radical coupling best accounts for the available experimental data.

The distribution of p-nitrobenzyl groups between the two products (p,p'-dinitrobibenzyl and p-nitrobenzoic acid) will therefore be determined by competition between reactions (177) and (178), with reaction (177), bimolecular in p-nitrobenzyl radicals, being favored by high radical concentrations.

(177) $RCH_2\cdot + RCH_2\cdot \xrightarrow{k_c} RCH_2CH_2R$

(178) $RCH_2\cdot + O_2 \xrightarrow{k_o} RCH_2OO\cdot \longrightarrow$ p-nitrobenzoic acid

On this basis, the ratio of bibenzyl (BB) to acid (A) should be

$$(179)\quad \left(\frac{BB}{A}\right) = \frac{k_c\,[RCH_2\cdot]}{k_o\,[O_2]}$$

A single steady state assumption

$$(180)\quad R_i = 2\,k_i\,[RCH_2{:}^-]\,[O_2]$$

(181) $R_t = 2\ k_c\ [RCH_2\cdot]^2$

leads to the conclusion that

(182) $[RCH_2\cdot] = (k_i/k_c)^{\frac{1}{2}}\ [O_2]^{\frac{1}{2}}\ [RCH_2:]^{\frac{1}{2}}$

and

(183) $(BB/A) = \frac{(k_i k_c)^{\frac{1}{2}}}{k_o}\ [RCH_2:^-]^{\frac{1}{2}}\ /\ [O_2]^{\frac{1}{2}}$

That the ratio BB/A increases with a decrease in oxygen pressure or an increase in the concentration of $[RCH_2:^-]$ is evident from Tables 2 to 6 and Figure 6. However, the experimental results are not in quantitative agreement with a square root dependence on $[RCH_2:^-]$ concentration, nor with a reciprocal square root dependence on oxygen concentration. Undoubtedly, the termination reaction

(184) $RCH_2OO\cdot + RCH_2\cdot \xrightarrow{k_t} RCH_2OORH_2R$

(185) $RCH_2OOCH_2R \xrightarrow{^-OR} RCHO + RCH_2OH$

must be important.

The modified steady-state condition

(186) $2\ k_i\ [RCH_2:^-]\ [O_2] = 2\ k_c\ [RCH_2\cdot]^2 + 2\ k_t\ [RCH_2OO\cdot]\ [RCH_2\cdot]$

cannot readily be solved for $[RCH_2\cdot]$ unless an additional assumption is made. If it is assumed, therefore, that,

$$(187)\quad RCH_2{:}^- + RCH_2OO\cdot \xrightarrow{k_p} RCH_2\cdot + RCH_2OO{:}^-$$

$$(188)\quad k_p\,[RCH_2OO\cdot]\,[RCH_2{:}^-] = k_o\,[RCH_2\cdot]\,[O_2]$$

then,

$$(189)\quad [RCH_2OO\cdot] = \frac{k_o\,[RCH_2\cdot]\,[O_2]}{k_p\,[RCH_2{:}^-]}$$

and

$$(190)\quad 2\,k_i\,[O_2]\,[RCH_2{:}^-] = 2\,k_c\,[RCH_2\cdot]^2 + \frac{2\,k_t k_o\,[O_2]\,[RCH_2\cdot]^2}{k_p\,[RCH_2{:}^-]}$$

Final solution leads to a complex expression for $[RCH_2\cdot]$. However, when

$$(191)\quad 2\,k_c \ll (2k_t k_o/k_p\,[RCH_2{:}^-])$$

the solution becomes

$$(191)\quad [RCH_2\cdot] = \left(\frac{k_i k_p}{k_t k_o}\right)^{\frac{1}{2}} [RCH_2{:}^-],$$

and

$$(192)\quad \frac{BB}{A} = \frac{k_c}{k_o}\left(\frac{k_i k_p}{k_t k_o}\right)^{\frac{1}{2}} \frac{[RCH_2{:}^-]}{[O_2]}$$

an expression that is in favorable agreement with the observed kinetic relationship under conditions wherein the reaction is not complicated by the rate of diffusion of oxygen.

Similarly, if the bibenzyl were formed by the reaction

$$(170)\quad RCH_2\cdot \; + \; RCH_2{:}^- \xrightarrow{k'_c} [RCH_2CH_2R]^{\dot{-}} \xrightarrow{O_2} RCH_2CH_2R$$

the kinetic relationship becomes

$$(193)\quad BB/A \; = \; \frac{k'_c}{k_o}\,\frac{[RCH_2\cdot]}{[R\cdot]}\,\frac{[RCH_2{:}^-]}{[O_2]} \; = \; \frac{k_i}{k_o}\,\frac{[RCH_2{:}^-]}{[O_2]}$$

Experimentally, it is extremely difficult to measure the ratio (BB/A) under conditions wherein the oxygen or $[RCH_2{:}^-]$ concentrations do not continuously vary. The ratio (BB/A) for a given oxidation represents the average value of (BB/A) as $[RCH_2{:}^-]$ varies from the initial starting concentration to zero. From Figure 6, the table which appears on the following page can be constructed. The ratio $(BB/A)_{avg.}/[RCH_2{:}^-]_{avg.}$ is reasonably constant and near unity for the lower carbanion concentrations, but rapidly approaches ∞ at high $[RCH_2{:}^-]$ concentrations wherein the diffusion controlled reaction becomes more of a problem. Under kinetically controlled reaction conditions the expected oxygen dependency is observed for pressures up to 860 mm. and then deviates badly at higher oxygen pressures.

Radical coupling reactions in the presence of oxygen are relatively rare although they do readily take place under

Table 7. Variation of product ratios in the oxidation of *p*-nitrotoluene[a, b]

$[RCH_2{:}^-]^{c}_{init.}$ $x10^3$	$[RCH_2CH_2R]$ $x10^3$	$[RCH_2{:}^-]_{avg.}$ $x10^3$	$[RCH_2CH_2R]_{avg.}$ $x10^3$	$(\frac{BB}{A})_{avg.}$	$\frac{(BB/A)_{avg.} x10^{-3}}{[RCH_2{:}^-]_{avg.}}$
5	1.86				
4	1.34	4.5	0.52		
3	0.88	3.5	0.46	11.5	3.28
2	0.50	2.5	0.38	3.2	1.28
1	0.20	1.5	0.30	1.67	1.11
0	0	0.5	0.20	0.67	1.34

[a] Data compiled from Figure 6

[b] Oxygen pressure = 700 mm. Hg

[c] Moles *p*-nitrotoluene taken per 25 ml. solvent

appropriate circumstances. For example, when autoxidations are carried out at higher temperatures, particularly at low oxygen concentrations dimeric products are obtained. Thus, the oxidation of diphenylmethane at 200° yields benzophenone along with considerable amounts of the coupling product, sym-tetraphenylethane[307]. When the oxidation is carried out at 100°, no dimer is formed. Similarly, passing oxygen through p-cymene at reflux temperatures (175°) gives 2,3-dimethyl-2,3-di-p-tolylbutane (32%)[308]. Still another example of radical coupling is the reported combination of p-methylbenzyl radicals as a termination process in the oil phase oxidation of p-xylene at 120-130°[309]. Here the high temperature and the thermal instability of the initially formed hydroperoxide must lead to high radical concentration under conditions wherein oxygen is not particularly soluble in the reaction medium.

More recently, the oxidative dimerization of the radicals formed from omega-phenylautophenone has been described[310].

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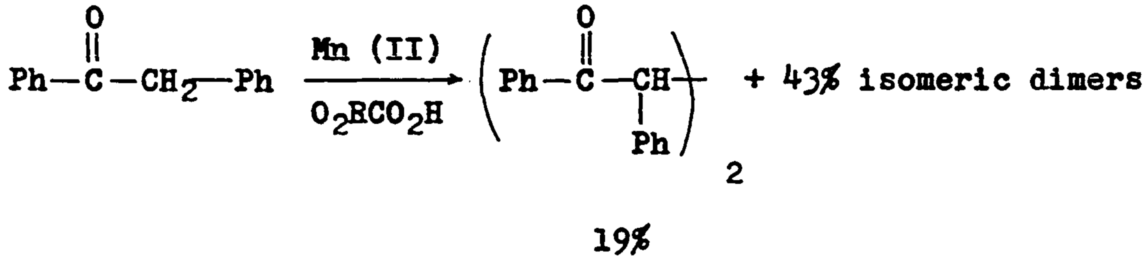
[307] F. Mashio and Y. Nakogawa, J. Chem. Soc. Japan, Ind. Chem. Sect., 55, 111 (1952).

[308] H. Pines, B. Kvetinskas, and V. N. Ipatieff, J. Am. Chem. Soc., 77, 343 (1955).

[309] E. J. Lorand and E. I. Edwards, ibid., 77, 4035 (1955).

[310] R. Van Helden and E. C. Kooyan, Rec. trav. chim., 80, 57 (1961).



$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}Ph} \xrightarrow[O_2RCO_2H]{Mn\ (II)} \underset{19\%}{\left(\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}\underset{Ph}{\underset{|}{CH}}{-}}\right)_2} + 43\% \text{ isomeric dimers}$$

Finally, dimeric products have been isolated in the photosensitized oxidation of 9-methylfluorene in acid solution; again, these conditions favor hydroperoxide decomposition[311].

Thus, the oxidation of p-nitrotoluene in basic solution differs markedly in regard to radical-radical interaction from the autoxidation of p-nitrotoluene or p-nitrocumene in the oil phase in the presence of small amounts of t-butylperbenzoate at 90°[312]. Under the latter conditions the radical concentration is extremely low (of the order of 10^{-8} M) and reaction (176) always occurs in preference to reaction (177). However, in the basic autoxidation of p-nitrotoluene, the radical concentration is certainly much greater, perhaps in the range 10^{-3} to 10^{-4} molar. Now, the amount of bibenzyl formed/unit time will depend chiefly upon (a) the rate of combination of oxygen with p-nitrobenzyl radicals (reaction 176), (b) the amount of free radical in solution, and (c) the rate of combination of p-nitrobenzyl radicals. The bimolecular rate constant for the coupling

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[311] W. Treibs and R. Schöllner, Chem. Ber., 94, 42 (1961).

[312] G. A. Russell, J. Am. Chem. Soc., 78, 1047 (1956).

of benzyl radicals in cyclohexane solution at 25° has been calculated as 4×10^7 liters/mole-sec[313]. The rate constant for the reaction of radicals with oxygen has been determined as 6.8×10^7 liters/mole-sec., in the case of the 1-tetralyl radical at 25°C[8]. The presence of any polar effect in the reaction of oxygen with p-nitrobenzyl radicals would tend to lower this latter value somewhat. Therefore, it is not too difficult to understand the high proportion of coupling product formed in the autoxidation of p-nitrotoluene in basic solution, particularly under diffusion controlled conditions.

Another significant difference between the oil-phase autoxidation of p-nitrocumene or p-nitrotoluene, and the autoxidation of p-nitrotoluene in basic solution involves the fraction of the total radical concentration that would exist as alkyl radicals. In the oil-phase oxidation nearly all radicals would be peroxy radicals due to

(194) $R\cdot + O_2 \xrightarrow{\text{very fast}} ROO\cdot$

(195) $ROO\cdot + RH \xrightarrow{\text{slow}} ROOH + R\cdot$

However, in oxidation in basic solution, particularly at lower oxygen pressures, a reverse situation may arise

(196) $R\cdot + O_2 \xrightarrow{\text{very fast}} ROO\cdot$

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[313] R. L. McCarthy and A. Mac Lachlan, Trans. Faraday Soc., 56, 1187 (1960).

$$(197)\quad ROO\cdot + R:^- \xrightarrow{\text{also very fast}} ROO:^- + R\cdot$$

The relative values of the rate constants for reactions (195) and (197) represent a real advantage in the use of basic media in autoxidation reactions.

Independent EPR experiments performed in a deficiency of oxygen have conclusively demonstrated that high concentrations of relatively stable free radicals can be formed by the action of oxygen on p-nitrotoluene in potassium t-butoxide solution[314]. Although the exact nature of these radicals is not completely clear their presence lends additional authenticity to the suggested one electron transfer initiation step.

$$RCH_2:^- + O_2 \longrightarrow RCH_2\cdot + \cdot O_2^-$$

Therefore, the conclusion that the formation of dimeric products in the oxidation of p-nitrotoluene in basic solution is well substantiated. Many of the cited examples of radical coupling processes in autoxidation reactions can be accounted for on the basis of similar reasoning, i.e., high concentrations of alkyl radicals under conditions wherein the concentration of oxygen in the medium is not particularly high, due either to solubility considerations or rapid

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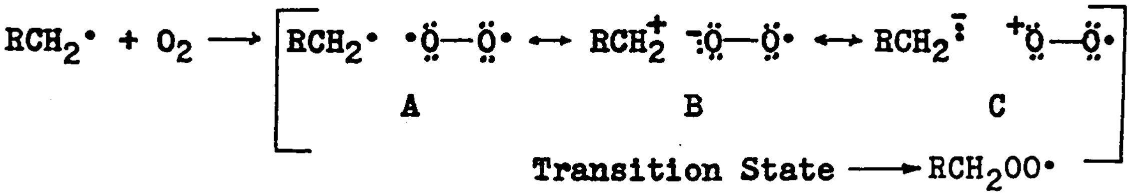
[314] G. A. Russell and E. Janzen, Dept. of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Personal communication regarding EPR measurements in the autoxidation of carbanions, September, 1961.

consumption. Also, the large proportion of dimer in the *p*-nitrotoluene systems is not unreasonable in view of the favorable kinetics of the process. The high rate constant (4×10^7 l/mole-sec.) for the coupling reaction along with the decreased rate constant for combination of *p*-nitrobenzyl radicals with oxygen (due to the intervention of unfavorable polar effects in the transition state)[315]



$$RCH_2\cdot + O_2 \longrightarrow \left[\underset{A}{RCH_2\cdot \;\; \cdot\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}\cdot} \longleftrightarrow \underset{B}{RCH_2^{+} \;\; ^{-}\!:\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}\cdot} \longleftrightarrow \underset{C}{RCH_2\overset{-}{:} \;\; ^{+}\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}\cdot} \right]$$

$$\text{Transition State} \longrightarrow RCH_2OO\cdot$$

and the increased concentration of radicals make the coupling reaction an inevitable occurrence.

A second object of this investigation was to determine the factors that control the mechanism by which oxygen reacts with a carbanion and to study the effects of structure on the rate of their reaction. Previous to this work only two examples of the direct reaction of a carbanion with oxygen via a one electron transfer process to yield the alkyl radical were known, i.e., perinaphthyl[63] and fluoradene[64] (see page 25). To this list of examples must be added the *p*-nitrobenzyl carbanion and its derivatives. In all probability such compounds as diphenylacetonitrile and *tris*-(*p*-nitrophenyl)-methyl anions react in a similar manner.

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[315] G. A. Russell, *J. Org. Chem.*, *23*, 1407 (1958).

Oxidations studied in t-butyl alcohol in the presence of t-butoxide ion at 25° can be conveniently grouped into four categories[136]:

Group I. Rapid oxidation, autocatalysis or inhibition could not be demonstrated.

p-nitrotoluene
p-nitrodiphenylmethane
bis-(p-nitrophenyl)-methane
phenylacetonitrile
diphenylacetonitrile
fluorene

Group II. Rapid oxidation autocatalysis, inhibition and catalysis.

nitroalkanes
tris-(p-nitrophenyl)-methane
benzyl alcohol
benzyhydrol

Group III. Not oxidized, substrate not ionized in t-butanol.

p-nitrocumene
p-tolunitrile[136]
methyl p-toluate[136]
triphenylmethane[136]
diphenylmethane[136]

Group IV. Oxidized very slowly or not at all; substrate ionized, cannot be initiated.

bis-(2,4-dinitrophenyl)-methane
2,4-dinitrotoluene
2,4,6-trinitrotoluene
phenylnitromethane
p-nitrophenylacetonitrile

Although it is certainly true that the rate of oxidation of a particular carbanion is affected by a large number of variables, e.g., solvent, state of aggregation in solution, metal ion, etc., one of the major factors is the stability of the carbanion. In general, the ease of oxidation of a carbanion *increases* with a *decrease* in the stability of the carbanion as measured by the stability of the parent hydrocarbon. An increase in the stability of the carbanion apparently brings about a decrease in the ease of electron transfer in the initiation and propagation reactions:

$$R{:}^- + O_2 \longrightarrow R\cdot + \cdot O_2^-$$

$$R{:}^- + ROO\cdot \longrightarrow ROO{:}^- + R\cdot$$

This implies, therefore, that the stability of the radical formed varies little with the nature of R, a conclusion in accord with previous data on the peroxide initiated oxidations of aralkylhydrocarbons[316]. Ample analogy for the second of these reactions is provided by the exceedingly facile electron transfer reaction from phenyl lithium to the 2,4,6-tri-*t*-butylphenoxy radical forming the phenoxide ion and the unstable, highly reactive phenyl radical[317]. Thus, the observed rates of oxidation,

p-nitrotoluene > 2,4-dinitrotoluene > 2,4,6-trinitrotoluene
9-fluorenal > *p*-nitrobenzyl alcohol > benzyhydrol >
    benzyl alcohol
p-nitrodiphenylmethane > *bis*-(*p*-nitrophenyl)-methane >
    bis-(2,4-dinitrophenyl)-methane

are in agreement with the predicted relative acidities of

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[316] G. A. Russell, *J. Am. Chem. Soc.*, *78*, 1047 (1956).

[317] E. Müller and K. Ley, *Chem. Ber.*, *87*, 922 (1954).

these compounds. In Table 7 are tabulated pK_a values for a number of weak acids that have been oxidized in t-butyl alcohol in the presence of t-butoxide. The correlation between anion stability and rate of oxidation therefore appears to be a useful guide to predicting relative orders of oxidation.

In some cases, even though the carbanion itself doesn't react directly with oxygen a free radical reaction involving long kinetic chains may be sustained when a suitable initiation step is provided. The reaction of 2,6-di-t-butyl-4-methyl phenol with oxygen in basic solution is most probably a long kinetic chain reaction. Similarly, the oxidation of durohydroquinone may be a long chain process. Those hydrocarbons that yield very stable anions react very slowly or not at all with molecular oxygen even in the presence of a catalyst capable of generating free radicals.

It appears on the basis of the foregoing that one of the most important reactions of oxygen with carbanions is a one electron transfer process. There appears to be little evidence that an ordinary carbanion can react directly with oxygen in an additive sense. This is eminently reasonable in view of the triplet structure of oxygen (2 unpaired electrons).

$$(199)\quad R:^{-} + \upharpoonleft\cdot\underset{\cdot\cdot}{\ddot{O}}-\underset{\cdot\cdot}{\ddot{O}}\cdot\upharpoonleft \rightleftharpoons R\cdot\upharpoonleft + \upharpoonleft\cdot\underset{\cdot\cdot}{\ddot{O}}-\underset{\cdot\cdot}{\ddot{O}}:^{-}$$

A direct reaction of the carbanion with oxygen to form $ROO:^{-}$ would involve the pairing of the spins of the electrons on

Table 8. pK_a values for various weak acids

Compound	Solvent	pK_a	Reference
p-nitrophenylacetonitrile	NH_2NH_2	13.43	318
	sulfolane	13.45	319
	EtOH	13.4	320
bis-(p-nitrophenyl)-methane	NH_2NH_2	15.90	318
	sulfolane	15.82	
tris-(p-nitrophenyl)-methane	NH_2NH_2	14.6	318
	EtOH	17.44	
diphenylmethane	Et_2O	35	321
triphenylmethane	Et_2O	33	321
fluorene	Et_2O	25	321
2-nitro-fluorene	sulfolane	17.59	319
9-phenyl-fluorene	sulfolane	18.49	319
	Et_2O	21	321
benzyl alcohol	Et_2O	18	321
benzhydrol	Et_2O	18	321

[318] N. C. Deno, J. Am. Chem. Soc., 74, 2039 (1952).

[319] C. H. Langford and R. L. Burwell, Jr., ibid., 82, 1503 (1960).

[320] R. S. Stearns and G. W. Wheland, ibid., 69, 2025 (1947).

[321] W. K. Mc Ewen, ibid., 58, 1124 (1936).

oxygen, an energetically extravagant process[61]. Even in the case of a very reactive carbanion where the excess energy is available, the direct reaction will probably involve the distinct steps (199) followed by (200)

$$(200)\quad R\cdot\uparrow \;+\; \uparrow\cdot\underset{\cdot\cdot}{\ddot{O}}-\underset{\cdot\cdot}{\ddot{O}}:^{-} \longrightarrow R\cdot\uparrow \;+\; \downarrow\cdot\underset{\cdot\cdot}{\ddot{O}}-\underset{\cdot\cdot}{\ddot{O}}: \longrightarrow ROO:^{-}$$

In any event, the process would most likely involve an initial electron transfer followed closely by reversal of spin and recombination.

SUMMARY

A detailed literature review of the autoxidation of carbanions, including alcohols, phenols, and organometallic compounds is presented.

The autoxidation of *p*-nitrotoluene in potassium *t*-butoxide/*t*-butanol solution yields *p,p*'-dinitrobibenzyl and *p*-nitrobenzoic acid in varying ratios, depending upon rate of agitation, oxygen pressure, and concentration of base. A detailed investigation of the stoichiometry of the reaction has furnished considerable evidence in support of a free radical mechanism involving *p*-nitrobenzyl radicals. The following reaction sequence has been proposed:

(1) $RCH_3 + {}^{-}{:}OR \longrightarrow RCH_2{:}^{-} + HOR$

(2) $RCH_2{:}^{-} + O_2 \longrightarrow RCH_2\cdot + \cdot\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}{:}^{-}$

(3) $RCH_2{:}^{-} + \cdot\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}{:}^{-} \longrightarrow RCH_2\cdot + {:}\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}{:}^{=}$

(4) $RCH_2\cdot + O_2 \longrightarrow RCH_2OO\cdot$

(5) $RCH_2\cdot + RCH_2OO\cdot \longrightarrow RCH_2OOCH_2R$

(6) $RCH_2OO\cdot + RCH_2{:}^{-} \longrightarrow RCH_2OO{:}^{-} + RCH_2\cdot$

(7) $2RCH_2\cdot \longrightarrow RCH_2CH_2R$

(8) $RCH_2OO{:}^{-} \longrightarrow \quad \longrightarrow \quad \longrightarrow RCO_2^{-}$

(9) $RCH_2OOCH_2R + {}^{-}OR' \longrightarrow RCHO + {}^{-}{:}OCH_2R + HOR'$

R = p-nitrophenyl

The oxidation rates of a number of other carbanions have also been determined. These compounds are o-nitrotoluene, 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, p-nitrocumene, 2,4-dinitrocumene, phenylnitromethane, p,p'-dinitrobibenzyl, p-nitroethylbenzene, meso-2,3-p-nitrophenyl butane, p-nitrodiphenylmethane, bis-(p-nitrophenyl)-methane, bis-(2,4-dinitrophenyl)-methane, mono-p-nitrotriphenylmethane, tris-(p-nitrophenyl)-methane, p-nitrophenylacetonitrile, phenylacetonitrile, diphenylacetonitrile, fluorene, 2-nitrofluorene, 9-phenylfluorene, benzylalcohol, p-nitrobenzyl alcohol, benzhydrol, 9-fluorenol, and p-nitroacetophenone. The effect of various metallic ion additives on the rates of oxidation of many of these compounds has been determined.

The factors affecting the rate of reaction of a carbanion with molecular oxygen are discussed. The ease of oxidation of a particular carbanion appears to parallel the stability of the carbanions as judged from the acidity (pK_a) of the parent hydrocarbon. This is interpreted in terms of the ionization potential of the carbanion and its effect on the ease of reactions (2) and (6).

APPENDIX

Table 9. Oxidation of p-nitrotoluene (4.78×10^{-3} mole) in 25 ml. of 0.123M potassium t-butoxide/t-butanol at 27°C and 700 mm. oxygen pressure[a,b]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[c]	Mole oxygen absorbed / Mole p-nitrotoluene
0			
1	2.96	0.11	0.023
2	5.2	0.19	0.040
3	6.9	0.26	0.054
5	10.5	0.39	0.082
7	12.4	0.46	0.097
9	14.4	0.53	0.11
12	17.4	0.65	0.14
18	23.5	0.88	0.18
24	28.9	1.08	0.23
30	33.5	1.25	0.26
40	39.4	1.47	0.31
60	47.7	1.78	0.37
80	54.5	2.04	0.43
130	65.6	2.45	0.51
180	73.9	2.76	0.58

[a] Molar ratio of base to p-nitrotoluene = 0.64

[b] Diffusion controlled conditions

[c] Corrected to STP

Table 10. Oxidation of p-nitrotoluene (4.78×10^{-3} mole) in 25 ml. of 0.345M potassium t-butoxide/t-butanol at 27°C and 700 mm. oxygen pressure[a,b]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[c]	Mole oxygen absorbed / Mole p-nitrotoluene
0			
1	2.5	0.095	0.020
2	5.5	0.21	0.044
4	12.2	0.46	0.096
8	24.6	0.92	0.19
12	36.6	1.37	0.29
20	53.0	1.98	0.42
35	69.6	2.60	0.55
55	79.0	2.95	0.62
70	82.0	3.07	0.64
110	85.1	3.18	0.67
165	88.5	3.31	0.69
240	93.5	3.50	0.73

[a] Molar ratio of base to p-nitrotoluene = 1.85

[b] Diffusion controlled conditions

[c] Corrected to STP

Table 11. Oxidation of *p*-nitrotoluene (4.45×10^{-3} mole) in 25 ml. of 0.514M potassium *t*-butoxide/*t*-butanol at 27°C and 700 mm. oxygen pressure[a,b]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($x10^3$)[c]	Mole oxygen absorbed / Mole *p*-nitrotoluene
0			
1	3.2	0.12	0.027
3	16.6	0.63	0.14
6	26.0	0.98	0.22
9	38.3	1.44	0.32
12	50.1	1.89	0.42
17	62.8	2.36	0.53
26	76.9	2.89	0.65
44	86.9	3.27	0.73
67	97.6	3.67	0.83

[a] Molar ratio of base to *p*-nitrotoluene = 2.89.

[b] Diffusion controlled conditions

[c] Corrected to STP

Table 12. Oxidation of p-nitrotoluene (5.43×10^{-3} mole) in 25 ml. of 0.933M potassium t-butoxide/t-butanol solution at 27°C and 700 mm. oxygen pressure

Time (minutes)	Ml. oxygen absorbed	Mole oxygen[b] absorbed ($\times 10^3$)	Mole oxygen absorbed / Mole p-nitrotoluene
0			
1	7.5	0.28	0.052
2	14.3	0.54	0.099
4	28.2	1.05	0.19
6	40.0	1.49	0.27
12	66.7	2.49	0.46
25	111.6	4.17	0.77
35	138.5	5.18	0.95
45	161.6	6.04	1.11
60	181.4	6.77	1.25
90	195.2	7.30	1.34
150	217.5	8.13	1.50
205	238.8	8.93	1.64
265	253.7	9.48	1.75
300	254.7	9.52	1.75

[a] Molar ratio of base to p-nitrotoluene = 4.29

[b] Diffusion controlled conditions

Table 13. Oxidation of p-nitrotoluene (8.15×10^{-3} mole) in 50 ml. of 0.352M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure under "rapid" shaking conditions[a,b]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[c]	Mole oxygen absorbed / Mole p-nitrotoluene
0			
1	17.7	0.67	0.08
3	44.0	1.66	0.20
5	66.1	2.49	0.31
10	103.1	3.88	0.48
14	126.1	4.75	0.58
20	157.1	5.92	0.73
30	176.5	6.65	0.82
40	189.0	7.12	0.87
50	200.4	7.55	0.93
65	211.7	7.97	0.98
85	219.5	8.26	1.01
111	224.0	8.43	1.03
146	228.0	8.58	1.05
170	229.3	8.63	1.06

[a] Rapid shaking = 220 shakes/min. in 250 ml. heavy-walled pressure bottle on Parr Hydrogenation Apparatus

[b] Molar ratio of base to p-nitrotoluene = 2.16

[c] Corrected to STP

Table 14. Oxidation of p-nitrotoluene (4.31×10^{-3} mole) in 25 ml. of 0.289M potassium t-butoxide/ t-butanol at 27°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole p-nitrotoluene
0			
2	6.3	0.23	0.054
4	14.2	0.53	0.12
8	30.6	1.14	0.27
10	37.7	1.41	0.33
20	62.2	2.33	0.54
31	76.4	2.86	0.66
40	83.8	3.13	0.73
60	86.3	3.22	0.75
160	96.7	3.61	0.84

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 15. Effect of lead sub-acetate (ca. 2 mole per cent) on the oxidation of p-nitrotoluene (4.28×10^{-3} mole) in 25 ml. of 0.289M potassium t-butoxide/t-butanol at 27°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole p-nitrotoluene
0			
3	6.5	0.24	0.057
7	22.9	0.86	0.20
13	42.9	1.60	0.38
20	58.0	2.17	0.51
42	65.5	2.45	0.57
60	67.0	2.50	0.59
91	70.0	2.62	0.61
120	72.3	2.70	0.63
150	74.1	2.77	0.65
180	75.6	2.83	0.66

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 16. Oxidation of *o*-nitrotoluene (3.33×10^{-3} mole) in 25 ml. of 0.352M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole *o*-nitrotoluene
0			
1	6.2	0.23	0.069
2	11.4	0.43	0.13
3	17.3	0.65	0.20
5	27.4	1.03	0.31
7	35.6	1.34	0.40
10	48.2	1.81	0.54
12	52.5	1.98	0.59
14	57.8	2.17	0.65
17	64.1	2.41	0.72
20	69.2	2.61	0.78
25	75.9	2.86	0.86
32	82.1	3.09	0.93
44	88.8	3.34	1.00
70	96.4	3.63	1.09
103	100.4	3.78	1.13
182	102.9	3.88	1.17

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 17. Oxidation of o-nitrotoluene (2.90 x 10^{-3} mole) in 25 ml. of 30% potassium hydroxide at 26°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed (x10^3)[b]	Mole oxygen absorbed / Mole o-nitrotoluene
0			
4	2.9	0.11	0.038
6	4.6	0.17	0.059
12	10.5	0.39	0.13
17	15.7	0.59	0.20
36	35.2	1.32	0.46
47	46.3	1.74	0.60
65	63.1	2.37	0.82
82	77.8	2.92	1.01
96	89.0	3.34	1.15
110	99.0	3.71	1.28
131	113.0	4.24	1.46
160	130.5	4.89	1.69
186	144.3	5.41	1.87
230	164.8	6.19	2.13
270	181.1	6.78	2.42

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 18. Oxidation of 4,4'-dinitrobibenzyl (2.12 x 10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 24°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed (x10^3)[b]	Mole oxygen absorbed / Mole 4,4'-dinitrobibenzyl
0			
2	2.0	0.076	0.036
11	2.7	0.10	0.047
35	4.2	0.16	0.075
50	5.7	0.22	0.10
70	8.0	0.30	0.14
135	15.6	0.59	0.28
218	24.1	0.91	0.43
380	38.0	1.43	0.67
468	44.2	1.66	0.78
620	54.7	2.06	0.97
1600	64.7	2.44	1.15

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 19. Oxidation of p-nitroethylbenzene (4.90×10^{-3} mole) in 25 ml. of 0.289M potassium *t*-butoxide/*t*-butanol at 27°C and 700 mm. oxygen pressure[a,b]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[c]	Mole oxygen absorbed / Mole *p*-nitroethylbenzene
0			
1	1.6	0.06	0.01
2	3.2	0.11	0.02
5	5.7	0.20	0.04
15	13.9	0.48	0.10
21	19.2	0.66	0.13
40	38.0	1.30	0.27
79	77.3	2.64	0.54
117	103.7	3.55	0.73
209	136.7	4.68	0.96
240	143.5	4.92	1.00

[a] Diffusion controlled conditions

[b] Molar ratio of base/*p*-nitroethylbenzene = 1.47

[c] Corrected to STP

Table 20. Oxidation of p-nitroethylbenzene (4.48×10^{-3} mole) in 25 ml. of 0.80M potassium t-butoxide/t-butanol at 25°C and 700 mm. oxygen pressure[a,b]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[c]	Mole oxygen absorbed / Mole p-nitroethylbenzene
0			
1	3.5	0.13	0.03
2	7.0	0.27	0.06
5	17.2	0.65	0.15
8	24.0	0.90	0.20
12	34.5	1.30	0.29
16	46.4	1.75	0.39
25	81.7	3.08	0.69
35	126.4	4.76	1.06
44	160.1	6.03	1.35
56	189.7	7.14	1.59
65	203.6	7.67	1.71
93	226.3	8.52	1.90
105	231.7	8.72	1.95
115	235.6	8.87	1.98

[a] Diffusion controlled conditions

[b] Molar ratio of base to p-nitroethylbenzene = 4.46

[c] Corrected to STP

Table 21. Oxidation of *p*-nitroacetophenone (4.02×10^{-3} mole) in 25 ml. of 0.289M potassium *t*-butoxide/*t*-butanol at 25°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed (x10^3)[b]	Mole oxygen absorbed / Mole nitroacetophenone
0			
1	3.8	0.14	0.35
2	9.2	0.35	0.087
4	19.8	0.74	0.18
8	41.7	1.57	0.39
12	59.2	2.22	0.55
16	72.6	2.73	0.68
20	80.7	3.03	0.76
25	86.4	3.25	0.81
32	90.8	3.41	0.85
53	96.0	3.61	0.90
117	106.4	4.00	0.99
342	112.4	4.23	1.05

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 22. Oxidation of p-nitrocumene (4.17×10^{-3} mole) in 25 ml. of 0.289M potassium t-butoxide/t-butanol at 27°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole p-nitrocumene
0			
60	4.5	0.17	0.041
90	5.7	0.21	0.050
168	10.3	0.38	0.091
460	16.3	0.60	0.14

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 23. Oxidation of 2,4-dinitrotoluene (4.27×10^{-3} mole) in 25 ml. of 0.335M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole 2,4-dinitrotoluene
0			
1	2.0	0.077	0.018
3	3.6	0.14	0.033
5	5.3	0.20	0.047
9	9.7	0.37	0.087
14	17.3	0.65	0.15
20	27.1	1.02	0.24
30	45.5	1.71	0.40
40	64.0	2.41	0.56
50	79.5	2.99	0.70
60	92.1	3.47	0.81
80	108.8	4.10	0.96
95	113.4	4.27	1.00
115	117.1	4.41	1.03
130	118.9	4.48	1.05

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 24. Oxidation of 2,4-dinitrotoluene (2.88×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 31°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole 2,4-dinitrotoluene
0			
1	1.8	0.066	0.023
3	3.8	0.14	0.049
5	4.9	0.18	0.063
7	7.4	0.28	0.097
10	8.8	0.32	0.11
21	21.5	0.80	0.28
33	38.8	1.44	0.50
51	57.9	2.14	0.74
80	81.5	3.02	1.05
101	93.9	3.47	1.20
178	118.6	4.39	1.52
200	123.3	4.56	1.58

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 25. Oxidation of 2,4,6-trinitrotoluene (2.27×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 30°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole 2,4,6-trinitrotoluene
0			
1	2.7	0.11	0.049
70	7.5	0.28	0.12
120	11.0	0.41	0.20
At this point ca. one mole per cent $FeCl_3$ added			
198	19.5	0.72	0.32
400	36.2	1.34	0.59

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 26. Oxidation of 2,4-dinitrocumene (2.80 x 10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 30°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed (x10^3)[b]	Mole oxygen absorbed / Mole 2,4-dinitrocumene
0			
1	1.7	0.064	0.023
3	3.3	0.12	0.043
5	4.9	0.18	0.064
7	7.0	0.26	0.093
9	9.0	0.33	0.12
15	15.9	0.59	0.21
20	21.9	0.81	0.29
30	32.1	1.19	0.43
40	41.8	1.55	0.55
65	59.7	2.17	0.78
81	67.7	2.47	0.88
113	79.2	2.89	1.03
120	81.9	2.99	1.07

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 27. Oxidation of 2,4-dinitrocumene (3.05×10^{-3} mole) in 25 ml. of 30% ethanolic potassium hydroxide at 27°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole 2,4-dinitrocumene
0			
2	1.3	0.047	0.015
4	3.0	0.11	0.036
8	7.5	0.28	0.092
15	15.7	0.59	0.19
21	23.3	0.87	0.29
27	31.0	1.16	0.38
37	42.9	1.60	0.52
46	53.4	2.00	0.66
60	68.3	2.55	0.84
82	86.5	3.23	1.06
110	106.1	3.96	1.30
142	124.9	4.67	1.53
183	144.8	5.41	1.77
226	163.5	6.11	2.00
250	172.3	6.44	2.11
325	206.2	7.71	2.53
350	214.2	8.00	2.62

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 28. Oxidation of 4-nitrodiphenylmethane (3.75×10^{-3} mole) in 25 ml. of 0.352M potassium *t*-butoxide/*t*-butanol at 25°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole 4-nitrodiphenylmethane
0			
2	4.9	0.18	0.05
3	7.4	0.28	0.08
6	15.7	0.59	0.16
10	25.9	0.98	0.26
14	36.7	1.38	0.37
18	47.0	1.77	0.47
24	61.5	2.31	0.62
30	74.6	2.81	0.75
36	87.0	3.27	0.87
46	99.2	3.73	0.99

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 29. Oxidation of bis(4-nitrophenyl)-methane (2.84 x 10^{-3} mole) in 25 ml. of 0.289M potassium t-butoxide/t-butanol at 24°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed $(x10^3)^b$	Mole oxygen absorbed / Mole bis-(4-nitrophenyl)-methane
0			
2	2.6	0.097	0.034
4	3.5	0.13	0.046
6	4.4	0.17	0.060
10	6.2	0.23	0.081
20	10.6	0.40	0.14
42	18.6	0.70	0.25
90	27.9	1.05	0.37
165	32.5	1.22	0.43

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 30. Oxidation of <u>bis</u>-(2,4-dinitrophenyl)-methane (3.25×10^{-3} mole) in 25 ml. of 0.289M potassium <u>t</u>-butoxide/<u>t</u>-butanol at 25°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole <u>bis</u>-(2,4-dinitrophenyl)-methane
0			
2	1.5	0.055	0.017
6	2.5	0.094	0.029
22	3.3	0.13	0.040
120	11.9	0.45	0.14
180	16.6	0.62	0.19
283	23.3	0.88	0.27
660	43.8	1.65	0.51

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 31. Oxidation of mono-p-nitrotriphenylmethane (2.86 x 10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide /t-butanol at 25°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($x10^3$)[b]	Mole oxygen absorbed / Mole mono-p-nitrotriphenylmethane
0			
1	1.7	0.065	0.023
2	3.2	0.12	0.042
4	5.8	0.22	0.077
8	9.4	0.35	0.12
16	19.1	0.72	0.25
22	26.6	1.00	0.35
30	36.9	1.39	0.49
41	49.8	1.88	0.71
50	58.3	2.19	0.77
65	67.0	2.52	0.88
87	71.8	2.70	0.94
103	73.1	2.75	0.96
436	73.1	2.75	0.96

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 32. Oxidation of tris-(p-nitrophenyl)-methane (3.01×10^{-3} mole) in 25 ml. of 0.352M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	$\frac{\text{Mole oxygen absorbed}}{\text{Mole tris-(p-nitrophenyl)-methane}}$
0			
2	1.5	0.06	0.020
5	1.5	0.06	0.020
15	1.5	0.06	0.020
144	9.3	0.35	0.12
193	11.4	0.43	0.14
413	18.3	0.69	0.23
590	23.1	0.87	0.29
625	23.9	0.90	0.30

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 33. Oxidation of *tris*-(*p*-nitrophenyl)-methane (2.51 x 10^{-3} mole) in 25 ml. of 0.352M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of ferric chloride (*ca*. one mole per cent)[a]

0			
2	2.7	0.10	0.040
4	3.5	0.13	0.052
11	6.1	0.23	0.092
33	10.2	0.38	0.15
68	17.8	0.67	0.27
104	25.9	0.97	0.39
122	29.7	1.12	0.45
277	50.8	1.91	0.76
364	56.2	2.12	0.84
560	64.3	2.42	0.96

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 34. Oxidation of <u>tris</u>-(p-nitrophenyl)-methane (5.09×10^{-4} mole) in 25 ml. of 0.35M potassium hydroxide/absolute ethanol at 26°C and 700 mm. oxygen pressure[a,b]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[c]	Mole oxygen absorbed / Mole <u>tris</u>-(<u>p</u>-nitrophenyl)-methane
0			
1	1.7	0.065	0.13
3	2.9	0.11	0.22
5	4.8	0.18	0.35
7	6.8	0.25	0.49
10	8.8	0.33	0.65
15	10.5	0.40	0.79
23[d]	11.5[d]	0.43[d]	0.84[d]
33	11.5	0.43	0.84
50	11.5	0.43	0.84

[a] Diffusion controlled conditions

[b] Ratio base/substrate = 5.84

[c] Corrected to STP

[d] At this point color disappears

Table 35. Oxidation of tris-(p-nitrophenyl)-methane (2.49 x 10^{-3} mole) in 25 ml. of 0.70M potassium hydroxide/absolute ethanol at 26°C and 700 mm. oxygen pressure. Effect of addition of ferric chloride (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed (x10^3)[b]	Mole oxygen absorbed / Mole tris-(p-nitrophenyl)-methane
0			
2	2.2	0.083	0.033
4	5.1	0.19	0.076
6	9.4	0.35	0.14
10	18.6	0.70	0.28
16	29.6	1.12	0.45
22	38.2	1.44	0.58
30	47.2	1.78	0.71
35	51.6	1.94	0.78
45	57.8	2.17	0.87
60	63.0	2.37	0.95
82	65.9	2.48	1.00

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 36. Oxidation of tris-(p-nitrophenyl)-methane (2.07 x 10^{-3} mole) in 25 ml. of 0.70M potassium hydroxide/absolute ethanol at 26°C and 700 mm. oxygen pressure[a,b]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[c]	Mole oxygen absorbed / Mole tris-(p-nitrophenyl)-methane
0			
1	2.1	0.080	0.038
3	3.0	0.11	0.053
5	6.3	0.24	0.11
8	10.1	0.38	0.18
13	13.4	0.51	0.24
20	17.6	0.66	0.32
40	26.7	1.01	0.48
65	36.4	1.37	0.66
95	48.3	1.82	0.87
232	54.9	2.07	0.99

[a] Diffusion controlled conditions

[b] Ratio of base/substrate = 11.8

[c] Corrected to STP

Table 37. Oxidation of *sym*-trinitrobenzene (3.76×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 30°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole *sym*-trinitrobenzene
0			
2	3.2	0.12	0.032
5	3.4	0.13	0.035
10	3.4	0.13	0.035
17	3.4	0.13	0.035
30	3.9	0.15	0.040
57	5.3	0.19	0.051
90	10.4	0.38	0.10
110	19.3	0.71	0.19
141	31.0	1.15	0.31
170	40.8	1.51	0.40
210	51.6	1.91	0.51
245	59.0	2.18	0.58
688	85.5	3.16	0.84
720	85.5	3.16	0.84

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 38. Oxidation of sym-trinitrobenzene (3.88×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/ t-butanol at 30°C and 700 mm. oxygen pressure. Effect of addition of 0.1 ml. t-butylhydroperoxide[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole sym-trinitrobenzene
0			
1	2.1	0.078	0.020
3	3.2	0.12	0.031
15	3.2	0.12	0.031
145	12.5	0.46	0.12
161	19.8	0.73	0.19
200	32.8	1.21	0.31
226	40.7	1.51	0.39
302	59.6	2.21	0.57
345	66.7	2.47	0.64
385	72.5	2.69	0.69
422	76.6	2.83	0.73
460	79.5	2.97	0.77
680	83.6	3.10	0.80

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 39. Oxidation of sym-trinitrobenzene (3.77×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 30°C and 700 mm. oxygen pressure. Effect of addition of $HAuCl_4 \cdot 3H_2O$ (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole sym-trinitrobenzene
0			
2	2.9	0.11	0.029
4	3.5	0.13	0.034
52	6.4	0.24	0.064
86	16.7	0.62	0.16
107	21.2	0.79	0.21
140	35.0	1.31	0.35
165	47.3	1.77	0.47
185	52.9	1.98	0.53
235	63.7	2.38	0.63
260	67.9	2.54	0.67
327	74.1	2.77	0.73
430	77.9	2.91	0.77
500	77.9	2.91	0.77

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 40. Oxidation of sym-trinitrobenzene (3.62×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 30°C and 700 mm. oxygen pressure. Effect of addition of ferric chloride (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole sym-trinitrobenzene
0			
2	2.7	0.099	0.027
60	7.4	0.27	0.075
93	20.1	0.74	0.20
120	32.3	1.19	0.33
156	46.5	1.72	0.48
195	57.2	2.12	0.59
221	62.5	2.31	0.64
252	67.7	2.51	0.69
300	73.2	2.71	0.75
860	82.1	3.04	0.84

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 41. Oxidation of 2-nitropropane (3.23×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 23°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole 2-nitropropane
0			
1	0.5	0.020	0.006
5	1.6	0.060	0.019
11	5.8	0.10	0.031
15	12.6	0.47	0.15
20	23.6	0.89	0.28
30	44.4	1.68	0.52
40	62.0	2.34	0.72
55	80.4	3.03	0.94
75	95.4	3.60	1.11
91	103.1	3.89	1.20
110	109.4	4.13	1.28
265	128.4	4.85	1.50
330	131.3	4.95	1.53
370	133.3	5.03	1.56

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 42. Oxidation of phenylacetonitrile (3.46×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	$\frac{\text{Mole oxygen absorbed}}{\text{Mole phenylacetonitrile}}$
0			
1	5.2	0.20	0.058
3	16.4	0.62	0.18
5	28.8	1.09	0.32
7	40.3	1.52	0.44
10	57.8	2.17	0.63
14	80.0	3.01	0.87
20	90.5	3.41	0.99
40	93.3	3.51	1.01
68	93.8	3.53	1.02
90	93.8	3.52	1.02

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 43. Oxidation of phenylacetonitrile (3.68×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 25°C and 700 mm. oxygen pressure. Effect of addition of ferric chloride (*ca*. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole phenylacetonitrile
0			
1	5.9	0.22	0.060
3	14.9	0.79	0.21
5	38.7	1.46	0.40
7	54.6	2.07	0.56
9	71.6	2.71	0.74
14	96.3	3.64	0.99
20	100.2	3.79	1.03
30	101.8	3.85	1.05
40	102.5	3.88	1.05
60	103.2	3.90	1.06
90	103.3	3.90	1.06

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 44. Oxidation of p-nitrophenylacetonitrile (4.37×10^{-3} mole) in 25 ml. of 0.289M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole p-nitrophenylacetonitrile
0			
2	1.6	0.060	0.014
5	2.4	0.092	0.021
40	5.8	0.22	0.050
55	8.5	0.32	0.073
107	18.2	0.69	0.16
150	25.9	0.97	0.22
200	37.3	1.40	0.32
308	55.8	2.10	0.48
406	65.7	2.47	0.57
526	73.9	2.78	0.64
630	78.3	2.94	0.67
720	80.9	3.05	0.70

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 45. Oxidation of p-nitrophenylacetonitrile (3.92 x 10^{-3} mole) in 25 ml. of 0.289M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of potassium ferricyanide (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed $(\times 10^3)$[b]	Mole oxygen absorbed / Mole p-nitrophenylacetonitrile
0			
2	2.9	0.11	0.028
55	8.4	0.32	0.081
93	15.1	0.57	0.14
138	23.7	0.89	0.23
277	43.5	1.63	0.42
391	57.2	2.15	0.55
483	65.5	2.46	0.63
606	72.1	2.71	0.69

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 46. Oxidation of diphenylacetonitrile (3.05×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole diphenylacetonitrile
0			
1	19.3	0.73	0.24
2	36.3	1.37	0.45
4	61.7	2.32	0.76
6	73.7	2.77	0.91
8	75.8	2.85	0.93
12	77.0	2.90	0.95
20	78.3	2.95	0.97
180	78.3	2.95	0.97

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 47. Oxidation of diphenylacetonitrile (3.61×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 27°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed $(\mathrm{x}10^3)$[b]	$\frac{\text{Mole oxygen absorbed}}{\text{Mole diphenylacetonitrile}}$
0			
1	26.4	0.99	0.27
3	62.9	2.35	0.65
5	83.7	3.13	0.87
6	87.8	3.28	0.91
10	90.3	3.38	0.94
16	91.8	3.43	0.95

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 48. Oxidation of diphenylacetonitrile (3.08×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of ferric chloride (*ca*. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole diphenylacetonitrile
0			
1	36.2	1.36	0.44
3	71.0	2.67	0.87
4	72.1	2.71	0.88
8	73.1	2.75	0.89
28	75.1	2.83	0.93
53	75.1	2.83	0.93
65	75.1	2.83	0.93

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 49. Oxidation of diphenylacetonitrile (3.40×10^{-3} mole) in 25 ml. of piperidine + 3 ml. of 0.389M potassium t-butoxide/t-butanol at 24°C and 700 mm. oxygen pressure[a,b]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[c]	Mole oxygen absorbed / Mole diphenylacetonitrile
0			
2	16.0	0.60	0.18
3	20.1	0.76	0.22
4[d]	22.3	0.84	0.25
6	23.4	0.89	0.26
16	25.3	0.95	0.28
48	26.8	1.01	0.30
60	27.6	1.04	0.31

[a] Diffusion controlled conditions

[b] Addition of butoxide solutions brought about a color change from colorless to red

[c] Corrected to STP

[d] At this point there occurred an abrupt change to colorless

Table 50. Oxidation of diphenylacetonitrile (3.04×10^{-3} mole) in 25 ml. of piperidine at 25°C and 700 mm. oxygen pressure; 1.3 g. solid potassium hydroxide added[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	$\frac{\text{Mole oxygen absorbed}}{\text{Mole diphenylacetonitrile}}$
0			
1	1.0	0.038	0.013
3	6.8	0.26	0.086
5	12.8	0.48	0.16
7	17.2	0.65	0.21
10	22.7	0.86	0.28
15	29.5	1.11	0.37
26	39.2	1.48	0.49
42	47.2	1.78	0.58
60	52.5	1.98	0.65
90	59.0	2.23	0.73
210	66.6	2.51	0.83

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 51. Oxidation of diphenylacetonitrile (3.04×10^{-3} mole) in 25 ml. of piperidine at 25°C and 700 mm. oxygen pressure. Effect of addition of ferric chloride (*ca.* one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\text{x}10^3$)[b]	Mole oxygen absorbed / Mole diphenylacetonitrile
0			
2	2.3	0.087	0.029
4	3.8	0.14	0.046
10	9.2	0.35	0.12
16	15.5	0.58	0.19
23	22.4	0.85	0.28
32	30.5	1.15	0.38
41	40.1	1.51	0.50
50	49.2	1.85	0.61
61	60.3	2.27	0.75
80	77.3	2.92	0.96
105	90.4	3.41	0.12
141	95.2	3.59	1.18
162	97.2	3.67	1.21

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[a] Diffusion controlled conditions

[b] Corrected to STP

Table 52. Oxidation of diphenylacetonitrile (3.07×10^{-3} mole) in 25 ml. of piperidine at 25°C and 700 mm. oxygen pressure (15 mg. of cupric chloride added)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($x10^3$)[b]	Mole oxygen absorbed / Mole diphenylacetonitrile
0			
1	3.6	0.014	0.046
3	20.6	0.78	0.25
5	25.5	0.96	0.31
11	36.2	1.37	0.45
20	50.8	1.92	0.63
35	70.8	2.67	0.87
55	90.8	3.43	1.12
70	101.5	3.83	1.25
91	112.1	4.23	1.38
124	120.8	4.56	1.49
141	123.2	4.65	1.51

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 53. Oxidation of fluorene (2.68×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 25°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole fluorene
0			
1	1.6	0.061	0.023
3	4.5	0.17	0.063
5	7.0	0.26	0.097
9	13.2	0.50	0.19
15	22.3	0.84	0.31
21	31.2	1.18	0.44
27	39.3	1.48	0.55
35	48.6	1.83	0.68
45	58.0	2.19	0.82
61	68.5	2.58	0.96
75	74.2	2.79	1.04
130	82.3	3.10	1.16

[a] Diffusion controlled conditions

[b] Corrected to STP

[c] At end of this period, H_2SO_4 added, then $KMnO_4$-- no D_2 evolved

Table 54. Oxidation of 2-nitrofluorene (2.81×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 25°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole 2-nitrofluorene
0			
1	5.8	0.22	0.078
2	11.2	0.42	0.15
4	22.1	0.83	0.30
6	32.4	1.22	0.43
8	41.3	1.55	0.55
12	55.7	2.10	0.75
18	65.6	2.47	0.88
25	70.4	2.65	0.94
36	74.9	2.82	1.00
55	78.9	2.97	1.06
70	81.0	3.05	1.09
101	84.1	3.17	1.13
132	87.0	3.28	1.17
171	89.6	3.37	1.20
200	92.0	3.46	1.23
300	96.5	3.63	1.29

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 55. Oxidation of 9-phenylfluorene (2.96×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 25°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole 9-phenylfluorene
0			
1	3.9	0.15	0.051
2	7.9	0.30	0.10
4	17.0	0.64	0.22
6	25.5	0.96	0.32
8	34.0	1.28	0.43
10	42.6	1.61	0.54
14	54.8	2.06	0.70
21	59.7	2.25	0.76
30	59.7	2.25	0.76
45	59.7	2.25	0.76
63	59.9	2.26	0.76
85	61.1	2.30	0.78

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 56. Oxidation of fluorene (3.97 x 10^{-3} mole) in 25 ml. of 0.289M potassium t-butoxide/t-butanol at 25°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($x10^3$)[b]	Mole oxygen absorbed / Mole fluorene
0			
2	3.54	0.13	0.033
4	5.80	0.22	0.055
9	13.38	0.50	0.13
18	28.05	1.05	0.26
28	44.68	1.68	0.42
33	52.30	1.97	0.50
47	70.80	2.66	0.67
62	85.78	3.22	0.81
80	96.78	3.64	0.92
97	104.56	3.93	0.99
131	114.52	4.30	1.08
161	119.44	4.49	1.13
182	121.66	4.57	1.15
338	128.60	4.85	1.22
351	128.60	4.85	1.22

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 57. Oxidation of fluorene (4.62×10^{-3} mole) in 25 ml. of 0.335M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	$\frac{\text{Mole oxygen absorbed}}{\text{Mole fluorene}}$
0			
2	4.0	0.15	0.032
4	7.5	0.28	0.061
8	15.1	0.57	0.12
16	34.5	1.30	0.28
23	53.5	2.02	0.44
33	77.0	2.90	0.63
43	95.6	3.60	
50	106.8	4.02	0.78
60	116.6	4.39	0.95
71	124.6	4.69	1.02
81	131.2	4.94	1.07
95	137.3	5.17	1.12
125	145.2	5.47	1.18
162	149.3	5.62	1.22
181	151.4	5.70	1.23

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 58. Oxidation of fluorene (4.71×10^{-3} mole) in 25 ml. of 0.335M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of lead sub-acetate (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	$\frac{\text{Mole oxygen absorbed}}{\text{Mole fluorene}}$
0			
1	2.4	0.091	0.019
3	5.6	0.21	0.045
5	8.7	0.33	0.070
9	15.9	0.60	0.13
16	30.1	1.13	0.24
26	52.8	1.99	0.42
35	71.3	2.68	0.57
52	98.1	3.69	0.78
71	117.9	4.40	0.93
95	132.5	4.99	1.06
120	141.0	5.31	1.13
160	148.5	5.59	1.19
180	150.7	5.67	1.20

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 59. Oxidation of benzyl alcohol (3.79×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/ t-butanol at 22°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	$\frac{\text{Mole oxygen absorbed}}{\text{Mole benzyl alcohol}}$
0			
1	1.1	0.04	0.011
3	1.6	0.06	0.016
5	1.6	0.06	0.016
10	1.8	0.07	0.018
16	2.1	0.08	0.021
27	4.0	0.15	0.041
40	10.7	0.41	0.11
60	31.2	1.19	0.31
80	51.7	1.97	0.51
105	70.3	2.68	0.70
140	80.9	3.09	0.81
192	89.4	3.41	0.89
325	98.5	3.76	0.99
420	98.5	3.76	0.99

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 60. Oxidation of benzyl alcohol (4.05×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 23°C and 700 mm. oxygen pressure. Effect of addition of anhydrous cupric sulfate (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole benzyl alcohol
0			
1	0.9	0.034	0.008
2	1.5	0.055	0.014
5	1.7	0.065	0.016
10	2.2	0.083	0.020
20	4.1	0.16	0.040
30	8.0	0.30	0.074
43	17.7	0.67	0.17
50	24.3	0.92	0.23
60	35.0	1.30	0.32
80	54.7	2.07	0.51
95	66.2	2.51	0.62
120	77.2	2.92	0.72

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 61. Oxidation of benzyl alcohol (3.88×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 22°C and 700 mm. oxygen pressure. Effect of addition of anhydrous ferric chloride (*ca*. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole benzyl alcohol
0			
1	1.5	0.058	0.015
3	3.2	0.12	0.031
5	4.0	0.15	0.039
11	5.3	0.20	0.052
15	6.2	0.24	0.062
20	7.3	0.28	0.072
32	10.0	0.38	0.098
55	16.3	0.62	0.16
70	20.6	0.79	0.20
100	29.5	1.13	0.29
140	41.4	1.58	0.41
183	53.5	2.04	0.53
210	61.8	2.36	0.61
240	67.9	2.59	0.67

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 62. Oxidation of p-nitrobenzyl alcohol (4.19×10^{-3} mole) in 25 ml. of 0.335M potassium t-butoxide/t-butanol at 27°C and 700 mm. pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole p-nitrobenzyl alcohol
0			
1	1.6	0.06	0.014
2	3.4	0.13	0.031
3	5.4	0.20	0.048
4	7.6	0.29	0.069
5	10.0	0.37	0.088
8	18.1	0.68	0.16
10	24.3	0.91	0.22
12	30.0	1.13	0.27
14	36.8	1.39	0.33
16	43.5	1.64	0.39
18	53.5	2.01	0.48
21	63.1	2.38	0.57
23	70.6	2.66	0.63
25	73.2	2.76	0.66
30	75.9	2.86	0.68
50	83.4	3.14	0.75
70	86.0	3.24	0.77
90	87.8	3.31	0.79

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 63. Oxidation of p-nitrobenzyl alcohol (4.28×10^{-3} mole) in 25 ml. of 0.355M potassium t-butoxide/t-butanol at 27°C and 700 mm. oxygen pressure. Effect of addition of 75 mg. of lead subacetate[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($x10^3$)[b]	Mole oxygen absorbed / Mole p-nitrobenzyl alcohol
0			
1	1.4	0.053	0.012
3	5.0	0.19	0.044
5	7.1	0.27	0.063
7	11.5	0.43	0.10
10	16.0	0.60	0.14
15	23.0	0.87	0.20
25	34.9	1.32	0.31
40	50.1	1.89	0.44
56	63.9	2.41	0.56
71	73.2	2.75	0.64
95	84.3	3.17	0.74
126	93.7	3.53	0.82
142	97.0	3.65	0.85

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 64. Oxidation of p-nitrobenzyl alcohol (4.53×10^{-3} mole) in 25 ml. of 0.123M potassium t-butoxide solution at 27°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole p-nitrobenzyl alcohol
0			
1	2.74	0.10	0.022
3	4.97	0.19	0.042
5	6.43	0.24	0.053
10	9.83	0.37	0.082
15	12.59	0.47	0.10
25	18.05	0.68	0.15
51	29.69	1.11	0.25
75	38.13	1.43	0.32
120	44.70	1.67	0.37
167	51.22	1.91	0.42
190	53.49	2.00	0.44
240	57.03	2.13	0.47
302	60.29	2.25	0.50
356	63.91	2.39	0.52

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 65. Oxidation of fluorenol (3.78×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 30°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole fluorenol
0			
1	6.3	0.23	0.061
2	12.1	0.45	0.12
3	17.9	0.66	0.17
4	24.0	0.89	0.24
5	30.3	1.12	0.30
6	36.1	1.34	0.35
7	42.2	1.56	0.41
9	53.4	1.98	0.52
10	59.6	2.21	0.58
12	70.9	2.41	0.69
14	79.8	2.96	0.78
16	85.2	3.15	0.83
18	88.5	3.28	0.87
20	91.5	3.39	0.90
25	96.7	3.58	0.95
41	110.8	4.10	1.08
52	112.8	4.18	1.11
180	117.3	4.34	1.15

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 66. Oxidation of fluorenol (3.96×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 29°C and 700 mm. oxygen pressure. Effect of addition of anhydrous ferric chloride (*ca*. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole fluorenol
0			
1	10.3	0.38	0.096
2	21.2	0.78	0.20
3	33.8	1.25	0.32
4	43.8	1.62	0.41
6	52.2	1.93	0.49
10	54.0	2.00	0.51
31	54.5	2.02	0.51
80	55.1	2.04	0.52
150	55.1	2.04	0.52

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 67. Oxidation of benzhydrol (3.40×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole benzhydrol
0			
1	1.9	0.071	0.021
2	2.7	0.10	0.030
5	4.1	0.15	0.044
10	10.1	0.38	0.11
20	23.5	0.88	0.26
36	34.6	1.30	0.38
48	41.3	1.55	0.46
60	48.4	1.82	0.54
122	74.2	2.78	0.82
166	86.6	3.25	0.96
200	93.6	3.51	1.03
283	104.9	3.93	1.16
360	112.0	4.20	1.24
398	113.6	4.26	1.25
430	115.7	4.34	1.28

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 68. Oxidation of benzhydrol (3.67×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure. Effect of chromic chloride hexahydrate (*ca.* one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole benzhydrol
0			
1	1.7	0.063	0.017
3	3.2	0.12	0.033
5	4.9	0.18	0.049
7	7.4	0.28	0.076
12	13.4	0.50	0.14
20	22.5	0.84	0.23
30	31.4	1.17	0.32
40	38.4	1.44	0.39
70	56.9	2.13	0.58
90	66.6	2.49	0.68
120	77.7	2.90	0.79
155	87.7	3.28	0.89
200	96.4	3.60	0.98
295	106.6	3.98	1.08
376	108.2	4.04	1.10
482	109.2	4.08	1.11
510	109.2	4.08	1.11

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 69. Oxidation of benzhydrol (4.01×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of anhydrous cupric chloride (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole benzhydrol
0			
1	1.7	0.062	0.015
3	3.6	0.13	0.032
5	6.4	0.24	0.060
7	9.4	0.35	0.087
10	13.7	0.51	0.13
15	20.0	0.75	0.19
20	26.8	1.00	0.25
30	39.7	1.48	0.37
45	58.1	2.17	0.54
60	74.1	2.77	0.69
80	89.7	3.38	0.84
103	99.8	3.76	0.94
454[c]	73.4[c]	2.74[c]	0.68[c]

[a] Diffusion controlled conditions

[b] Corrected to STP

[c] At 103 minutes gas was evolved. From 103 min. to 454 min. a total of 26.4 ml. of gas was given off. Decomposition was very slow, e.g., from 103 to 143 min., a 40 minute period, 0.80 ml. gas was evolved.

Table 70. Oxidation of benzhydrol (3.67×10^{-3} mole) in 25 ml. of 0.389M potassium *t*-butoxide/*t*-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of cupric acetate monohydrate (*ca.* one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($x10^3$)[b]	Mole oxygen absorbed / Mole benzhydrol
0			
1	1.9	0.072	0.020
3	4.2	0.16	0.044
5	7.5	0.28	0.060
8	13.0	0.49	0.13
10	16.6	0.62	0.17
15	25.8	0.97	0.26
21	38.2	1.25	0.34
25	46.1	1.73	0.47
35	63.1	2.38	0.65
41	68.6	2.58	0.70
131[c]	50.8[c]	1.91[c]	0.52[c]

[a] Diffusion controlled conditions

[b] Corrected to STP

[c] After 41 minutes a gas was given off by the reaction mixture. The solid that had collected on the walls completely disappeared during the evolution of this gas (17.8 ml.).

Table 71. Oxidation of benzhydrol (3.78×10^{-3} mole) in 25 ml. of 0.389M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of anhydrous ferric chloride (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole benzhydrol
0			
2	2.5	0.093	0.025
4	2.6	0.099	0.026
8	2.7	0.10	0.026
16	3.2	0.12	0.032
24	3.6	0.13	0.034
50	6.0	0.22	0.058
121	14.3	0.54	0.14
186	21.3	0.80	0.21
226	24.6	0.92	0.24
326	32.1	1.20	0.32
891	45.5	1.71	0.45
1053	46.0	1.72	0.46

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 72. Oxidation of benzhydrol (3.54×10^{-3} mole) in 25 ml. of 0.335M potassium *t*-butoxide/*t*-butanol at 27°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($x10^3$)[b]	Mole oxygen absorbed / Mole benzhydrol
0			
1	1.3	0.05	0.013
7	2.5	0.09	0.026
13	9.5	0.36	0.10
19	16.9	0.64	0.18
24	20.1	0.75	0.21
35	26.8	1.05	0.30
46	32.9	1.24	0.35
55	37.7	1.42	0.40
71	42.1	1.58	0.45
89	51.0	1.92	0.54
103	55.7	2.09	0.59
121	60.7	2.28	0.65
264	86.3	3.24	0.92
402	93.0	3.50	0.99
536	95.0	3.57	1.01

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 73. Oxidation of benzhydrol (4.46×10^{-3} mole) in 25 ml. of 0.335M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of lead sub-acetate (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($x10^3$)[b]	Mole oxygen absorbed / Mole benzhydrol
0			
1	1.5	0.056	0.013
3	3.1	0.12	0.027
5	3.5	0.13	0.029
8	5.2	0.20	0.045
12	10.4	0.39	0.087
16	16.1	0.61	0.14
20	19.6	0.74	0.17
32	28.7	1.08	0.24
50	40.4	1.52	0.34
70	51.6	1.94	0.43
97	63.0	2.37	0.53
125	72.3	2.72	0.61
160	81.0	3.05	0.68
205	89.7	3.38	0.78
264	96.1	3.62	0.81

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 74. Oxidation of benzhydrol (3.87×10^{-3} mole) in 25 ml. of 0.335M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of anhydrous copper sulfate (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole benzhydrol
0			
1	1.3	0.051	0.013
3	3.8	0.14	0.036
5	5.7	0.22	0.057
7	7.2	0.27	0.070
9	9.0	0.34	0.088
12	11.8	0.44	0.11
18	16.6	0.63	0.16
28	22.7	0.85	0.22
44	31.2	1.18	0.30
66	39.7	1.50	0.39
90	46.2	1.74	0.45
116	50.0	1.88	0.49

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 75. Oxidation of benzhydrol (3.61×10^{-3} mole) in 25 ml. of 0.335M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of potassium ferricyanide (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole benzhydrol
0			
1	1.9	0.071	0.020
2	2.9	0.11	0.031
4	3.3	0.12	0.033
15	8.2	0.31	0.086
21	13.3	0.50	0.14
32	19.6	0.74	0.21
37	22.4	0.85	0.24
97	45.9	1.73	0.48
125	53.8	2.03	0.56
150	60.2	2.27	0.63
175	65.9	2.48	0.69
203	70.4	2.65	0.73
263	77.4	2.91	0.81
287	79.5	2.99	0.83

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 76. Oxidation of benzhydrol (3.62×10^{-3} mole) in 25 ml. of 0.335M potassium t-butoxide/t-butanol at 26°C and 700 mm. oxygen pressure. Effect of addition of ferric chloride hexahydrate (ca. one mole per cent)[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	$\frac{\text{Mole oxygen absorbed}}{\text{Mole benzhydrol}}$
0			
1	1.4	0.052	0.014
3	2.4	0.090	0.025
5	2.6	0.10	0.027
18	2.6	0.10	0.027
60	6.7	0.25	0.069
390	20.2	0.76	0.21
530	24.7	0.93	0.26

[a] Diffusion controlled conditions

[b] Corrected to STP

Table 77. Oxidation of benzhydrol (4.25×10^{-3} mole) in 25 ml. of 0.72M potassium hydroxide in ethyl alcohol at 26°C and 700 mm. oxygen pressure[a]

Time (minutes)	Ml. oxygen absorbed	Mole oxygen absorbed ($\times 10^3$)[b]	Mole oxygen absorbed / Mole benzhydrol
0			
1	0.70	0.026	0.006
6	0.70	0.026	0.006
10	0.70	0.026	0.006
20	1.7	0.064	0.015
64	3.2	0.12	0.028
85	3.9	0.15	0.035
Restart[c]			
2	2.5	0.094	0.022
11	3.7	0.14	0.033
26	6.7	0.25	0.059
46	12.5	0.47	0.11
63	18.1	0.68	0.16
84	26.1	0.98	0.23

[a] Diffusion controlled conditions

[b] Corrected to STP

[c] At this point *ca.* one mole per cent of anhydrous $CuSO_4$ was added, the flask flushed with oxygen and the reaction followed further.