1952

The reactions of radicals produced in the decomposition of aliphatic azo compounds and di-alkyl peroxides

George Bond Lucas
Iowa State College

THE REACTIONS OF RADICALS PRODUCED IN THE DECOMPOSITION OF ALIPHATIC AZO COMPOUNDS AND DI-ALKYL PEROXIDES

by

George Bond Lucas

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:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1952

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

From a survey of the existing work in the literature, it becomes immediately apparent that there is a vast difference between the behavior of free radicals in the vapor phase and in solution. Even from solvent to solvent, the behavior of similar free radicals varies. Thus, to speak of the reactivity of radicals without specifying the solvent conditions is to neglect an important aspect of the picture. The effect of solvent is varied and complex. What a specific radical will do depends both upon its own nature and the nature of the medium in which it is contained. There are examples that may be culled from the literature which indicate that local environment may be of equal or of greater importance than the gross environment, as is usually assumed by most workers.

This work was initiated with the hope of elucidating the course of radical reactions in solution. The procedure followed was the analysis of products from similar sources under conditions of varying medium. The sources of free radicals used were chosen because of their unambiguous cleavage reactions to produce the radicals and because the radicals themselves were sufficiently complex to be

representative and sufficiently stable to be limited in the number of reactions possible.

The work reported was exploratory only and many of the conclusions reached are tentative. These conclusions are worthy of being drawn, however, because they point the way to future experiments which may be devised to test their validity. It is believed that this work is one more step in elucidating the exceedingly complex but extraordinarily fascinating course of free radical reactions.

HISTORICAL

Polymerization and Alkyl Free Radicals

The free radical polymerization of vinyl compounds is generally accepted to follow the schematic mechanism outlined below[1]:

1a	$2M \xrightarrow{k_1} 2R\cdot$	initiation	$k_1 M^2$
1b	$A \xrightarrow{k_1} 2R\cdot$	initiation	$k_1 A$
2	$M + R\cdot \xrightarrow{k_p} R\cdot$	propagation	$k_p M R\cdot$
3	$2R\cdot \xrightarrow{k_t} X \text{ or } RR$	termination	$k_t R\cdot^2$

Process 1a is thermal or photo initiation of monomer whereas process 1b is initiation by some known radical source such as benzoyl peroxide[1], or an azo-bis-nitrile[2]. R· is a radical species capable of propagating a chain and M is monomer. The termination step can destroy radicals by either dimerization (RR) or disproportionation (X). This latter is a well established phenomenon[3] and involves the abstraction

---

[1]Price, "Advancing Fronts of Chemistry", Vol. I, High Polymers, Reinhold Pub. Corp., New York, 1945, p. 37.

[2]Arnett, J. Am. Chem. Soc., 74, 2027 (1952).

[3]Shulz and Husemann, Z. physik. Chem., 39B, 246 (1938).

of a hydrogen atom from one radical species by another, forming two products, an olefin and a saturated hydrocarbon.

$$2\ C_6H_5\overset{\displaystyle CH_2R}{\underset{\displaystyle H}{C}}\cdot \longrightarrow C_6H_5CH{=}CHR + C_6H_5CH_2CH_2R$$

If a steady state concentration of radicals and an equivalence in their ability to propagate chains is assumed, then such a mechanism as proposed above fits the experimentally determined rates[2,3,4,5] for 1b

$$-\frac{dM}{dt} = k\,A^{\frac{1}{2}}\,M\ ,$$

and for 1a

$$-\frac{dM}{dt} = k'\,M^{2}\ .$$

It had been noted that if the monomer was diluted with an inert solvent then the molecular weight of the polymer formed was a smaller one than found if pure monomer was polymerized[6]. In many cases the molecular weight was

---

[4]Price and Kell, J. Am. Chem. Soc., 63, 2789 (1941).

[5]Overberger, J. Polymer Sci., 6, 539 (1951).

[6]Staudinger and Schwalbach, Ann., 488, 8 (1931).

proportional to the concentration of monomer[7]. The assumption of "chain transfer" as an explanation for this effect was first advanced by Flory[8]. He envisioned the growing polymer chain, in the presence of a hydrocarbon diluent, as being capable of abstracting a hydrogen atom from solvent, thus stopping the chain growth.

$$R\cdot + SH \xrightarrow{k_3} RH + S\cdot$$

$$\text{Rate} = k_3 R\cdot \; SH$$

If the species S· is just as capable of starting chains as R· then the initiation of chain transfer by R· will not affect the kinetic law for the overall reaction but will only result in decreasing the size of the polymer formed.

Much work has been done in recent years to establish chain transfer as a valid phenomenon. Mayo[9] has studied the subject extensively from the standpoint of the degree of polymerization, $\bar{P}$, which is defined as the rate of chain growth divided by the total rate of chain termination (by chain transfer with solvent, with monomer and by termination) or

---

[7]Staudinger and Trommsdroft, ibid., 502, 201 (1933).

[8]Flory, J. Am. Chem. Soc., 59, 251 (1937).

[9]Mayo, ibid., 65, 2324 (1943).

$$\overline{P} = \frac{k_p \, R\cdot \; M}{k_3 \, R\cdot \; SH + k_t \, R\cdot^{\,2} + k_4 \, R\cdot \; M} \quad .$$

Inverting both sides of this equation, dividing numerator and denominator by $R\cdot \; M$ and assuming a steady state concentration of free radicals $k_1/k_t^{\frac{1}{2}} M$ *, he obtains

$$k/\overline{P} = \frac{k_3 \; SH}{k_p \; M} + \frac{\left(k_1 k_t\right)^{\frac{1}{2}} + k_4}{k_p} \quad .$$

In the absence of solvent, the first term on the right vanishes and the second term is the reciprocal of the degree of polymerization in the absence of solvent, $\overline{P}_o$. Making this substitution and defining k_3/k_p as C, the transfer constant, the simple expression

$$1/\overline{P} = C \, \frac{SH}{M} + \frac{1}{\overline{P}_o}$$

is obtained. Thus the reciprocal of the degree of polymerization is a linear function of the solvent-monomer ratio where the slope, the transfer constant, is a measure of the ability of solvent to react with the growing chain. The larger the value of C, the smaller will be the polymer chains for a given monomer.

---

*In this derivation it is assumed that the initiation is bimolecular in monomer, process 1a.

By making a plot of the reciprocal of the degree of polymerization against solvent-monomer ratios, Mayo obtained linear relationships for styrene in a variety of solvents. By evaluating the transfer constants, he found that, as chain transfer agents, benzene and cyclohexane were the least reactive of the solvents studied, their transfer constants being identical within experimental error. Among the hydrocarbons in the following table the results correlate well with the known reactivity of these hydrocarbons with atomic bromine and chlorine.

Table 1

Chain Transfer Constants of Various Solvents in Styrene Polymerization

Solvent	Transfer constant x 10^5 60°	100°
Benzene	0.15	1.84
t-Butylbenzene	0.6	5.5
Toluene	1.25	6.45
Ethylbenzene	6.7	16.2
i-Propylbenzene	8.2	20.0
Diphenylmethane	23	42
Triphenylmethane	35	80
Fluorene	750	1240
Pentaphenylethane	200,000	---
Cyclohexane	0.24	1.6
n-Heptane	4.4	9.5
Decalin	4	---
Carbon tetrachloride	900	1810

Gregg and Mayo[10] showed that both the over-all second order rate constant and the transfer constant for the polymerization of styrene in carbon tetrachloride were independent (at low conversions and within experimental error) of average polymer chain lengths over a wide range of polymer chain lengths. From this they concluded that either all the individual rate constants in the polymerization (initiation, growth, transfer and termination) were independent of chain length or else there was a mutual compensation of trends. They also found that the ability of a solvent to react as a chain transfer agent followed the expected ability of the radical formed to partake of resonance stabilization.

Nozaki[11] proposed the following sequence in decreasing order of resonance stability of substituted methyl radicals:

$$R-\overset{|}{\underset{|}{C}}\cdot$$

where R is

phenyl>vinyl>cyano=carbomethoxy>chloro>aklyl>acyl>hydrogen. The same order was observed for the tendency of the radical to abstract hydrogen (chain transfer).

Reconsidering the fundamental reaction characteristic of chain transfer

---

[10]Gregg and Mayo, Disc. Faraday Soc., 2, 328 (1947).

[11]Nozaki, ibid., 2, 337 (1947).

$$R\cdot + SH \longrightarrow RH + S\cdot$$

if the species, S·, is incapable of reacting with monomer, then SH is called an inhibitor or retarder and will prevent or reduce the rate of polymerization[1]. It is not necessary that the growing chain abstract hydrogen from the inhibitor. An additional reaction

$$R\cdot + A \longrightarrow RA\cdot$$

where RA· is some radical incapable of promoting polymerization, is possible and, in fact, is believed to be the method of quinone inhibition[12].

It has long been known that quinones and hydroquinones inhibit the polymerization of olefins and have often been used as stabilizers for these[12]. However Suess[13], and later Breitenbach[14], showed that hydroquinone is not a radical inhibitor of the polymerization of styrene in the absence of oxygen. It was therefore presumed that the inhibitor activity of hydroquinone was due to its oxidation to benzoquinone by oxygen. This hypothesis can quite likely be

---

[12]Bovey and Kolthoff, Chem. Revs., 42, 491 (1948).

[13]Suess, Pilch and Rodorfer, Z. physik. Chem., 179A, 179, 36 (1942).

[14]Breitenbach, Springer and Hoeischy, Ber., 71, 1438 (1938).

extended to the case of methyl methacrylate since Walling[15] obtained the first reliable kinetic data on the thermal polymerization of this olefin in the presence of hydroquinone, and showed that hydroquinone had no influence on the rate of polymerization.

Breitenbach[14] found quinhydrone, in small amounts, to be a product of the benzoquinone inhibited polymerization of styrene and on the basis of this postulated a novel mechanism of quinone inhibition. He dismissed a free radical mechanism but assumed an "activated" hydrogen atom as the chain carrier in styrene.

$$C_6H_5CH{=}CH_2 \longrightarrow C_6H_5CH{=}CHH^*$$

$$C_6H_5CH{=}CHH^* + C_6H_5CH{=}CH_2 \longrightarrow C_6H_5CH{=}CHCH{=}CH_2H^*$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C_6H_5$$

Two of these "activated" molecules could collide with quinone with transfer of hydrogen, producing hydroquinone and dimer

$$2\ C_6H_5CH{=}CHH^* + C_6H_4O_2 \longrightarrow C_6H_6O_2 + \text{styrene dimer}\ .$$

---

[15] Walling and Briggs, J. Am. Chem. Soc., 68, 1141 (1946).

Price[16] polymerized styrene in the presence of a large amount of chloranil using benzoyl peroxide as initiator and noted the marked disappearance of the red-orange color of chloranil. The polymer formed contained about one chloranil unit, held by chemical union, per polymer molecule. Since polymerization did occur he concluded that chloranil was not an inhibitor in this reaction but only a chain transfer agent analogous to carbon tetrachloride. However, conclusions drawn from this experiment are of little worth since Price used such a high concentration of benzoyl peroxide and took no precaution to eliminate oxygen nor to prevent thermal polymerization. There undoubtedly were active centers still present even after the consumption of all the chloranil.

From his and Breitenbach's[14] data, Price proposed a mechanism for quinone inhibition[17,18,19].

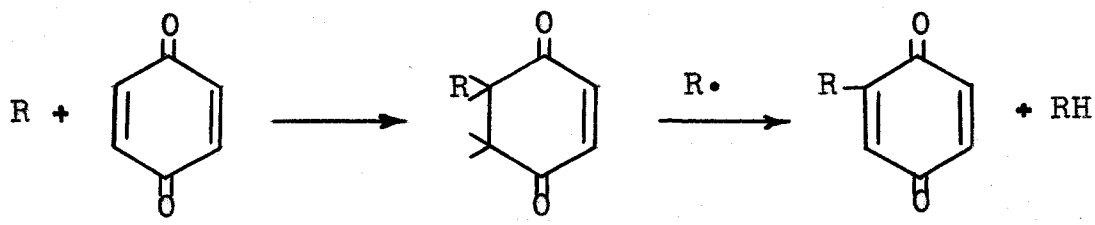
---

[16]Price, ibid., 65, 2381 (1943).

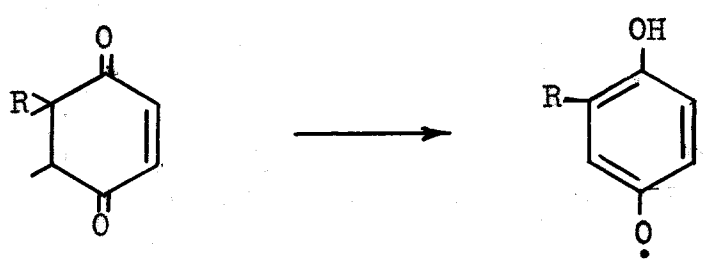
[17]Price, Ann. N.Y. Acad. Sci., 44, 368 (1943).

[18]Price, "Reactions at Carbon-Carbon Double Bonds", Interscience, N.Y., 1946, p. 86.

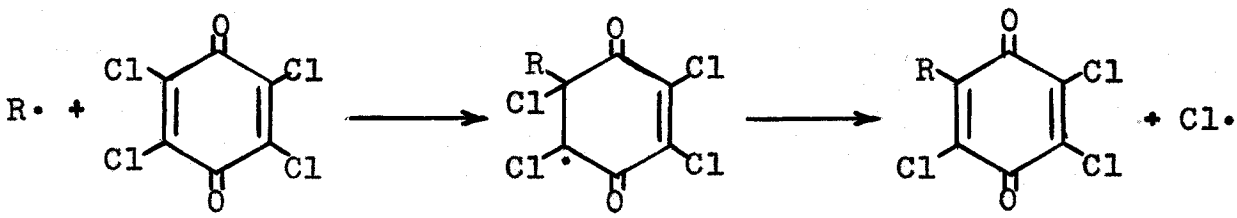
[19]Price and Read, J. Polymer Sci., 1, 44 (1946).



The intermediate alkyl quinone and semiquinone radicals were postulated as less reactive species than the growing polymer chain and would preferentially react only with other radicals. Price[19] later revised his mechanism to include the tautomerism,



This semiquinone radical should be less reactive than the tautomeric alkylated quinone radical. He further suggested a mechanism for chain transfer by chloranil



The reaction could be bimolecular involving monomer rather than a two step process, i.e., chain transfer whereby the radical donates an atom instead of abstracting one.

There is sufficient analogy for the mechanism proposed by Price. Benzenediazonium chloride reacts with p-benzoquinone to give 2-phenyl-benzoquinone[20], and diacyl peroxides, both aliphatic and aromatic, react with 2-methyl-1, 4-naphthoquinone to give substitution in the 3- position[21]. Melville and Watson[22] proposed a twofold mechanism for quinone inhibition. For diradicals such as those produced in thermal or photochemical polymerization, inhibition takes place analogous to a Diels-Alder reaction, stopping the two chains simultaneously. The quinone acts as the dienophile

---

[20]Kvalnes, J. Am. Chem. Soc., 56, 2478 (1934).

[21]Fieser and Oxford, ibid., 64, 2060 (1942).

[22]Melville and Watson, Trans. Faraday Soc., 44, 886 (1948).

and alkylation occurs on carbon. Reaction with the quinone has to occur before the polymer chain proceeds beyond a dimer for then the radical centers would no longer be suitably situated for such a concerted reaction*. However, monoradicals[23], such as those produced in the benzoyl peroxide initiated polymerization, react with quinone to produce radicals which are incapable of further promulgating chains and can only be removed from the system by reaction with other radicals.

However, nuclear alkylation does not explain the observation of Foord[24] that phenanthraquinone has inhibitory powers of the same order of magnitude as benzoquinone where the mechanism proposed by Price[18] could not obtain.

Schonberg[25,26,27] found that styrene adds to phenanthraquinone in the presence of sunlight to give an O-alkylated

---

[23]Kern and Feuerstein, J. prakt. Chem. (2), 158, 186 (1941).

[24]Foord, J. Chem. Soc., 48 (1940).

[25]Schonberg and Mustafa, Nature, 153, 195 (1944).

[26]Schonberg and Mustafa, Chem. Revs., 40, 181 (1947).

[27]Schonberg, J. Chem. Soc., 387 (1944).

*Kern had indeed found that in the inhibited polymerization of styrene by high concentrations of benzoquinone, there was formed an adduct containing two styrene and one quinone units per molecule.

adduct. This is similar to a Diels-Alder addition with the quinone acting as diene. Similarly, in both light and dark, stilbene adds to tetrachloroquinone-1,2[28] to form 2,3-diphenyl-5,6,7,8-tetrachlorobenzodioxene.

Bartlett, Hammond and Kwart[29] extensively studied the quinone inhibited, benzoyl peroxide initiated, polymerization of allyl acetate; and using chloranil, presented evidence for, at least, 27 per cent attack of chains at the oxygen function. This evidence was obtained by cleavage of the polymer with hydroiodic acid giving tetrachlorohydroquinone. Destructive distillation also gave tetrachlorohydroquinone. Before analyzing the polymers, these workers established the fact that no chloranil remained. This work indicated that chloranil does not function as a chain transfer as postulated by Price[19]. Analyses of the ultraviolet absorption spectra of allyl acetate polymers, polymerized in the presence of benzoquinone were made using as model substances p-xyloquinone, hydroquinone diphenyl and dimethyl ethers. The absorption spectra were complex and did not agree well with any of the models and the polymer did not show any quinone chromophore at 440 mu. These experiments

---

[28]Schonberg and Latif, J. Am. Chem. Soc., 72, 4828 (1947).

[29]Bartlett, Hammond and Kwart, Disc. Faraday Soc., 2, 342 (1947).

indicate that the mode of inhibition probably consists of alkylation at both oxygen and carbon.

By following simultaneously the disappearance of monomer, peroxide and quinone during kinetic determinations on allyl acetate, these workers reported the following results:

(1) With chloranil and trichloroquinone there is a strong initial retardation and little monomer is converted to polymer. As the polymerization proceeds the polymerization increases and approaches that observed in the absence of quinone.

(2) With duroquinone[30] there is a continual linear relationship between logarithms of initiator and monomer concentrations* with the slope of the line slightly lower than in the absence of the quinone.

(3) Benzoquinone, in low concentrations, is similar to the chlorinated quinones while at concentrations of 0.5 molar it behaves like a retarder whose concentration is not altered during the run.

In no case was total inhibition observed and the stronger the retarder the more rapidly it is consumed and the sharper

---

[30]Bartlett and Altschul, J. Am. Chem. Soc., 65, 812, 816 (1945).

*During the uninhibited polymerization of allyl acetate there is a linear relationship between initiator and monomer concentrations.

the change in rate between the early and late stages of the reaction.

The following relationship between monomer and inhibitor was derived by the authors assuming reaction with inhibitor (k_3) gave inactive products and chain termination (k_t) took place between radical chains and monomer:

$$\ln \frac{I_o}{I} = \frac{k_t + k_p}{k_3} \ln \frac{M_o}{M} \quad .$$

No such simple relationship between the disappearance of benzoquinone and monomer was found, as would be expected if benzoquinone gave inactive products. Duroquinone, however, gave experimental verification of this equation and although chloranil and trichloroquinone seemed to obey it, so little conversion of monomer occurred that it was difficult to draw conclusions.

Hence it seems that more benzoquinone molecules were required to stop a given number of polymer chains than in the case of other quinones. These authors offer this as supporting evidence that benzoquinone is capable of copolymerizating in certain systems. They also followed the duroquinone retarded polymerization of vinyl acetate, the data for which lent further support to the proposed mechanism for duroquinone retardation.

Cohen[31,32] analyzed the benzoquinone inhibited, benzoyl peroxide-initiated polymerization of styrene. There was first a period of total inhibition followed by polymerization at only slight retardation. From analyses of the amount of free and bound benzoic acid produced by the decomposition of benzoyl peroxide in the systems (1) pure benzene, (2) ethylbenzene, (3) benzene-styrene-benzoquinone, (both high and low concentrations), (4) benzene-benzoquinone, (5) benzene-styrene, and (6) benzene-hydroquinone monoethyl ether he concluded that benzoquinone does not influence the decomposition of benzoyl peroxide nor its reaction with monomer, but must destroy the chain at some later point. The hydroquinone derivatives, which contain free hydroxyl groups, seemed to react with benzoate radicals, thus destroying initiator before chains can be started. Since he believed the hydroquinone mono ethers to be possible products of the inhibited polymerization, he asserted that these would account for the slight retarding effect during the later periods of polymerization. In support of this contention the ultra-violet absorption spectra of the reaction mixtures showed a dimunition of the quinone absorption

---

[31]Cohen, ibid., 69, 1057 (1947).

[32]Cohen, J. Polymer Sci., 2, 511 (1947).

maximum during the induction period. Then, as polymerization proceeded, a considerable portion of quinone absorption returned. The overall mechanism proposed for the inhibition is that the radical reaction with quinone can take any of three courses (1) oxygen alkylation to form mono- and di-ethers, (2) dehydrogenation of the growing chain by quinone producing an olefin and a semiquinone radical, (3) nuclear alkylation of the quinone.

Schulz[33,34] believes that, in the thermal polymerization of styrene benzoquinone acts as a weak initiator as well as a strong inhibitor. He has obtained an equation relating inhibitor activity to its concentration

$$\frac{dM}{dt} = \frac{dM}{dt_o} \quad 1 + k_1 C_1$$

where $\frac{dM}{dt}$ is the rate of polymerization in the presence and $\frac{dM}{dt_o}$ in the absence of inhibitor, k_1 is the "inhibitor constant" and C_1 is the concentration of inhibitor. If k_1 is very large, $\frac{dM}{dt} = 0$, polymerization will not occur. Benzoquinone has $k_1 = 1.4 \times 10^4$.

---

[33]Schulz and Strassberger, Chem. Ber., 80, 232 (1947).

[34]Schulz, Hammerer and Lorentz, ibid., 327 (1947).

Mayo and Gregg[35] found a similar phenomenon with the triphenylmethyl inhibited polymerization of styrene. At low concentrations triphenylmethyl was an efficient inhibitor but at higher concentrations it seemed to act as an initiator.

From the preceding work, it can be seen that a detailed and accurate investigation of any or all types of chain termination steps (inhibition, chain transfer, dimerization and disproportionation) is extremely difficult in polymerization because of the great size of the molecule resulting from the chain propagation step and the smallness of the functional group resulting from the chain terminating step. The incorporation of one quinoidal function in a macromolecule with a molecular weight of several thousand is nearly undetectable by normal methods of analysis and its mode of attachment not readily fathomable. It became necessary then to find some system whose reactions were analogous to those of a growing polymer but considerably reduced in size.

Such a system was realized in the aliphatic azo-bis-nitriles and azo-bis-carboxylates first prepared by Thiele

---

[35]Mayo and Gregg, J. Am. Chem. Soc., 70, 491 (1948).

and Heuser[36] and later by Dox[37]. Thiele and Heuser found that 2-azo-bis-isobutyronitrile in boiling petroleum ether (ca. 110°) quantatively evolved nitrogen and formed tetramethyl succinonitrile in 50 per cent yield. Dox observed that when 2-azo-bis-methylethylacetonitrile or 2-azo-bis-diethyl-acetonitrile was added dropwise to hot, concentrated sulfuric acid, bis-methylethylacetic acid and bis-diethylacetic acid respectively were formed. He was also able to isolate di-methylethylacetic acid from the former reaction and bis-diethylacetonitrile from the latter.

A more complete product analysis was done by Bickel and Waters[38] in the thermal decomposition of dimethyl-2, 2-azo-bis-isobutyrate in boiling benzene. They obtained the products found in Table 2.

The following scheme gives a satisfactory explanation of the products:

---

[36]Thiele and Heuser, Ann., 290, 25 (1896).

[37]Dox, J. Am. Chem. Soc., 47, 1473 (1925).

[38]Bickel and Waters, Rec. trav. chim., 69, 312 (1950).

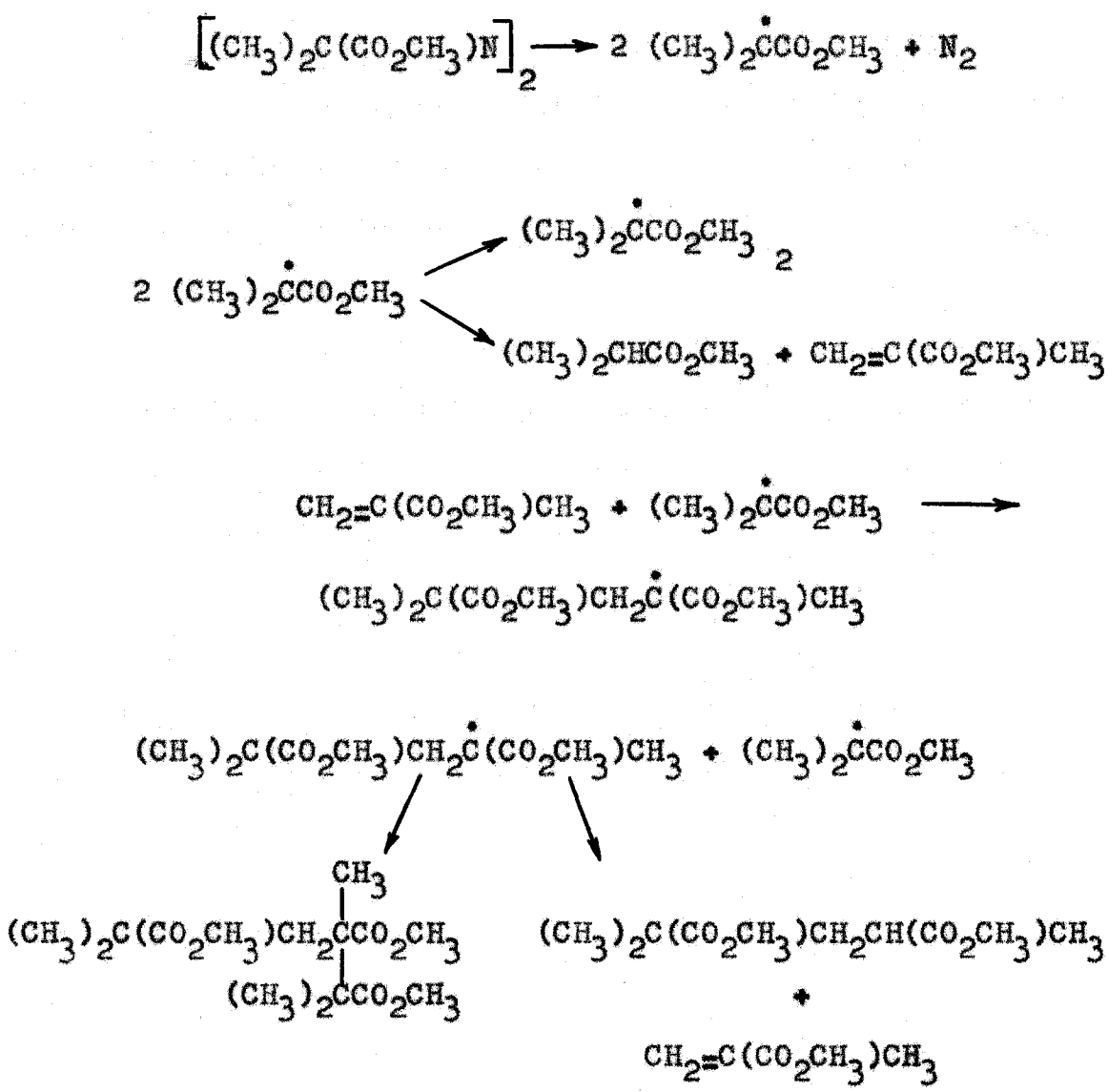
Table 2

Analysis of Decomposition Products

Products	Percentage
Dimethyl-bix-isobutyrate	41
Methyl methacrylate	4
Methyl isobutyrate	14
Dimethyl α, α, α'-trimethyl glutarate	15[b]
A twelve carbon methyl ester[a]	22[b]

[a]Probably $(CH_3)_2C(CO_2CH_3)C(CH_3)(CO_2CH_3)CH_2(CO_2CH_3)(CH_3)_2$.

[b]Water's reaction utilized high concentrations of starting material which fact would account for high yields of large molecular weight products.



These authors decomposed the same azo-ester in molten phenol at 100° and obtained essentially the same distribution of products. There was no evidence of attack on phenol either at oxygen (abstraction of hydrogen) or nuclear alkylation.

Overberger and Berenbaum[39] studied the products of decomposition of the two diasteromeric, dl and meso, 2,2'-azobix-2,4-dimethylvaleronitriles and obtained both the racemic and meso dinitrile as products. A mixture of 2,2'-azo-bis-isobutyronitrile and 1,1'-azo-bis-1-cyclopentanenitrile on decomposition in benzene gave the unsymmetrical as well as the two symmetrical dimers. Both of these observations support the contention that the radical pairs formed are free in solution and do not dimerize intramolecularly.

Ford and Waters[40] decomposed dimethyl 2,2'-azo-bis-isobutyrate and 2,2'-azo-bis-isobutyronitrile in the presence of iodine and bromine in inert solvents (benzene and toluene). With iodine the products were methyl α-iodoisobutyrate and α-iodoisobutyronitrile respectively. Yields of 75 per cent were obtained in both cases if the nitrile, or ester, was slowly added into the boiling iodine

---

[39]Overberger and Berenbaum, J. Am. Chem. Soc., 73, 4883 (1951).

[40]Ford and Waters, J. Chem. Soc., 1851 (1950).

solution. The yields were much lower (unreported) if the azo compounds were initially added to the reaction mixture.

The remainder of the reaction mixtures consisted of the previously mentioned dimers and disproportionation products. The reaction with bromine was not as straight forward and considerable quantities of hydrogen bromide were evolved, indicating that some substitution took place. However, the products obtained were methyl α-bromo-isobutyrate (29 per cent) and α-bromo-isobutyronitrile (26 per cent) from the azo-ester and azo-nitrile respectively. No attempts were made to isolate other reaction products. These results are completely consistent with a free radical mechanism for the decomposition.

These authors further found that azo-bis-nitriles and esters, in trace quantities, were capable of initiating chlorination of a number of hydrocarbons by sulfuryl chloride, probably by the following mechanism:

$$\left[R_2C(CN) - N\right]_2 \longrightarrow 2R_2\dot{C}(CN) + N_2$$

$$R_2\dot{C}CN + SO_2Cl_2 \longrightarrow R_2C(CN)Cl + SO_2Cl\cdot$$

$$SO_2Cl\cdot \longrightarrow SO_2 + Cl\cdot$$

$$Cl\cdot + RH \longrightarrow R\cdot + HCl$$

$$R\cdot + SO_2Cl_2 \longrightarrow RCl + SO_2Cl\cdot \quad .$$

These azo compounds seem to be better initiators in this chlorination than benzoyl peroxide. Iodine and chloranil inhibit the reaction; a further indication of the free radical nature of the reaction.

A patent has recently been issued for the use of "acyclic azo compounds bonded to discrete, tertiary, non-aromatic carbons with a cyano group on the tertiary carbon"[41] as catalyst for the preparation of sulfides and mercaptans from an olefin and hydrogen sulfide:

$$R_2C = CR'_2 + H_2S \xrightarrow{\text{cat.}} R_2CH-\underset{\displaystyle SH}{\overset{\displaystyle |}{C}}R'_2$$

The use of the azo compound is necessary for the reaction to proceed.

The nearest approach to understanding the manner in which quinones destroy active radicals, such as those formed in polymerization, has been made by Bickel and Waters[42] who found that dimethyl 2-azo-bis-isobutyrate, decomposed in boiling toluene containing p-benzoquinone, gave, besides an unreported amount of the dimethyl tetramethylsuccinate, hydroquinone di(2-cyano-2-propyl) ether and hydroquinone

---

[41] Pinkey, U.S. 2,551,813, May 8, 1951 to Du Pont. C.A., 45, P9559f (1950).

[42] Bickel and Waters, J. Chem. Soc., 1764 (1950).

mono(2-cyano-2-propyl) ether. When 2-azo-bis-isobutyronitrile was decomposed in chlorobenzene with chloranil, the products were tetrachlorohydroquinone di(2-cyano-2-propyl) ether. However, with hydroquinone in place of benzoquinone or chloranil, no reaction products were obtained from dimethyl-2-azo-bis-isobutyrate other than those obtained in its absence.

These experiments indicate that, if the reactivity of the dimethyl-cyano radical can be considered equivalent to that of the growing methyacrylonitrile chain, the destruction of polymer radicals by quinone comes at the oxygen atom rather than at a nuclear carbon as suggested by Price[1]. These experiments further substantiate the inability of hydroquinone to destroy active radicals.

Ziegler[43] obtained the diadduct, tetrachloroquinol di(2-cyano-2-propyl) ether exclusively by added 2-azo-bis-isobutyronitrile slowing to a boiling chlorobenzene solution of chloranil. It required 1.5 moles of the azo compound to completely destroy 0.5 moles of chloranil. All the chloranil was considered consumed when a test portion of the reaction mixture no longer gave a blue coloration with dimethylaniline.

---

[43]Ziegler, Deparade and Meye, Ann., 157, 141 (1950).

The azo-bis-nitriles and esters are highly efficient photosensitizers for free radical reactions[44].

The ultraviolet absorption spectra of a number of azo-bis-nitriles have been determined[45] and they all seem to have a weak band at about 3500 A with a molar extinction coefficient of about 10-12. Using the 3660 A mercury band, Lewis and Matheson[44] found that those azo-bis-nitriles studied photochemically initiate polymerization of both vinyl acetate and styrene. The quantum yield in the photopolymerization of vinyl acetate was approximately 300 and for styrene, approximately 50. This is far better than the frequently used photoinitiator, biacetyl, which has an quantum yield towards vinyl acetate of 10.3 and, for styrene, of 1.4[46].

Lewis and Matheson[44] first studied the kinetics of the thermal decomposition of a number of azo-bis-nitriles in a variety of solvents at 80° and even in the presence of an inhibitor. Their method consisted of following the nitrogen

---

[44]Lewis and Matheson, J. Am. Chem. Soc., 71, 747 (1949).

[45]Overberger, O'Shaughnessy and Shalit, ibid., 71, 2661 (1949).

[46]Agre, U.S. 2,367,660, Jan. 23, 1945 to Du Pont. C.A., 39, P3703 (1945).

evolution as a function of time. In all cases, after a short induction period which they were unable to prevent, the reaction was smoothly first order and showed little dependence upon solvent, even when chloranil was present. For example, 2-azo-bis-isobutyronitrile at 80°, in xylene, has a unimolecular rate constant, $k_1 = 9.2 \times 10^{-3}$ min.$^{-1}$; in xylene containing 0.012 moles per liter chloranil, $k_1 = 8.98 \times 10^{-3}$; and in glacial acetic acid $k_1 = 9.14 \times 10^{-3}$ min.$^{-1}$.

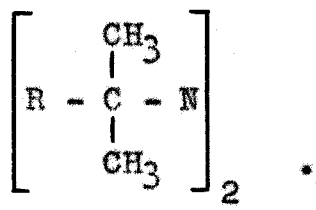
Ziegler and co-workers[47] studied the kinetics of the first order decomposition of both 2-azo-bis-isobutyronitrile and dimethyl-2-azo-bis-isobutyrate in nitrobenzene (a known inhibitor) and in a variety of other solvents. They obtained practically the same values for the rate constants as did Lewis and Matheson[44].

Overberger and co-workers[45] prepared a series of azo-bis-nitriles in order to study the polar and steric effects on the rate of decomposition and to investigate the use of the compounds as radical sources for polymerization. In their kinetic determinations (followed by the rate of nitrogen evolution) they were able to reduce, but never eliminate, an induction period. Nevertheless, they were able to show

---

[47]Ziegler, Deparade and Meye, Ann., 567, 141 (1950).

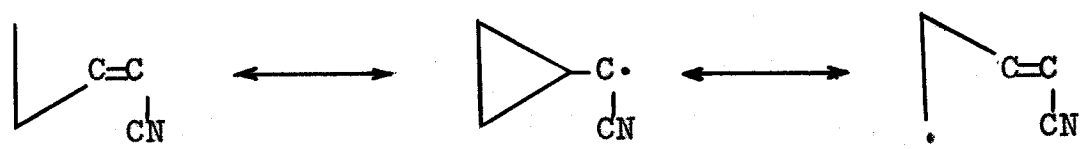
that the decompositions were strictly first order with a rate constant independent of the solvent used. The temperature at which the decompositions were run was nearly identical to that used by Lewis and Matheson (80.2 as opposed to 80) and in some cases, kinetic studies were made on identical compounds. When such was the case both workers were in good agreement as to the value of the unimolecular rate constant. Overberger found a large variation in the value of the unimolecular rate constant with the variation of R in the molecule:



If R is cyclohexyl, then $k_1 = 0.083 \times 10^{-4}$ sec.$^{-1}$ and if R is isobutyl, $k_1 = 7.1 \times 10^{-4}$ sec.$^{-1}$.

By consideration of Fischer-Herschfelder molecular models of the <u>trans</u> isomers of the above compounds a steric explanation was advanced. (The <u>cis</u> isomer was impossible to construct with models and in the preparation of these compounds only one isomeric modification was isolated in all cases. This indicates that these compounds exist in the stable <u>trans</u> modification.) Considerable crowding of groups across the nitrogen-nitrogen double bond was evidence in the cases where R is methyl, ethyl, <u>n</u>-butyl or <u>n</u>-propyl,

those compounds with intermediate rate constants, and extreme crowding in the case of R = i-butyl and very little in the case of R = cyclohexyl. The repulsive forces caused by this crowding magnified the carbon strain and weakened the carbon-nitrogen bond sufficiently to markedly increase the rate of decomposition. Overberger and Berenbaum[48] were able to separate two stereoisomeric forms (probably the dl and meso forms of the trans modification) of 2-azo-bis-2-cyclopropylacetonitrile, 2-azo-bis-2-isopropylacetonitrile and 2-azo-bis-2-tert-butylacetonitrile. In all three compounds the rates of decomposition of both stereoisomers were identical within experimental error. The unimolecular rate constant for 2-azo-bis-2-cyclopropylacetonitrile was quite large ($k = 33 \times 10^{-4}$ sec.$^{-1}$). This value, the authors explained, is probably less due to the steric interference in the azo compound but more to the resonance stabilization of the liberated radical which can partake of hyperconjugation with the cyclopropyl group,



---

[48] Overberger and Berenbaum, J. Am. Chem. Soc., 73, 2618 (1951).

Overberger and Biletch, however, showed that hyperconjugation was of no essential importance in phenyl-substituted 2,2'-azo-bis-benzylpropionitriles. There was no substantial difference between the three unimolecular rate constants of the unsubstituted, p-nitro, and p-chloro derivatives nor between these rate constants and the one for 2,2'-azo-bis-isobutyronitrile[49], thus indicating that the only effect of a phenyl and substituted phenyl group is steric. The rate data of Mayo and Overberger are summarized below.

Walling[50] copolymerized a number of systems (styrene-methyl methacrylate, styrene-methyl acrylate and styrene-vinyl acetate at 60° using 2-azo-bis-isobutyronitrile as initiator. By assuming a constant rate of initiation of polymerization by azo compound and assuming further that all fragments initiate chains, he calculated the ratio of chain termination to chain growth for each of the monomers using the calculations of Mayo[51].

---

[49]Overberger and Biletch, ibid., 73, 4880 (1951).

[50]Walling, ibid., 71, 1930 (1949).

[51]Mayo, Lewis and Walling, ibid., 70, 1529 (1948).

Table 3

Unimolecular Rate Constants for Aliphatic Azo Compounds

Compound	M.P. (°C.)	Temp. (°C.)	Solvent	Rate (10^4 x $sec.^{-1}$)	Ref.
2-Azo-bis-isobutyronitrile	-	80.2	toluene	1.72 -1.60	45
" " "	-	80.0	xylene	1.5	44
2-Azo-bis-2-methyl-butyronitrile	-	80.2	toluene	0.94 -0.80	45
" "	-	80.0	xylene	0.99	44
2-Azo-bis-2-methyl-valeronitrile	-	80.2	toluene	1.74 -1.65	45
2-Azo-bis-2,3-dimethyl-butyronitrile	-	80.2	toluene	1.03 -1.02	45
2-Azo-bis-2-methyl-capronitrile	-	80.2	toluene	1.58	45
2-Azo-bis-2,4-dimethyl-valeronitrile	74-76	80.2	toluene	7.1	45
" " "	56-57	80.2	toluene	10^a	45
2-Azo-bis-2-cyclohexyl-acetonitrile	-	80.2	toluene	0.083	45
" "	-	80.0	xylene	0.047	44
2-Azo-bis-2-methyl-heptylonitrile	-	80.0	xylene	1.6	44
Dimethyl-2-azo-bis-isobutyrate	-	80.0	xylene	1.09	44

Table 3 (Cont'd)

Compound	M.P. (°C.)	Temp. (°C.)	Solvent	Rate (10^4 x $sec.^{-1}$)	Ref.
2-Azo-bis-2-cyclopropyl-acetonitrile	64-65	80.2	toluene	35[a]	48
" " "	76-77	80.2	toluene	25[a]	48
4-Azo-bis-4-cyano-pentanoic acid	-	80.0	water	0.99	44
2-Azo-bis-2,3,3-trimethyl-butyronitrile	114-116	80.2	toluene	0.77[a]	48
" " "	116-118	80.2	toluene	1.09[a]	48

[a]For comparison of rates of decomposition, values of the rate constant at 80.2° have been calculated from those at the nearest experimental temperature using the experimental activation energy.

However, Walling's values may be in error because of the assumption that all azo fragments initiate chains. Arnett[1,52] found that 2-azo-bis-isobutyronitrile as initiator for methyl methacrylate was only 50 per cent efficient instead of 100 per cent as postulated by Walling[50]. The same azo compound was, at best, 82 per cent efficient in the polymerization of styrene. Arnett attributed the 50 per cent efficiency towards methyl methacrylate to the unsymmetrical cleavage of the initiator

$$RN = NR \longrightarrow RN = N\cdot + R\cdot \quad .$$

To only one of these, he ascribed the necessary requirements to initiate polymerization. This reactive radical he chose to be the fragment RN = N·, reasoning that if the fragment R· would initiate polymerization, then the efficiency of initiation should be 100 per cent since the subsequent reaction,

$$R\text{-}N = N\cdot \longrightarrow R\cdot + N_2$$

should give an active radical. Nitrogen probably would be evolved by the reaction,

$$R\text{-}N = N\cdot + M \longrightarrow R\cdot + N_2 \quad .$$

---

[52]Arnett and Peterson, ibid., 74, 2031 (1952).

Arnett, however, gave no reason for efficiency of 80 per cent against styrene other than to state that both Tobolsky and Cohen[53,54] obtained similar results.

Arnett's methods of determining radical efficiency are worthy of note. In method I, using only with methyl methacrylate, he applied the rate equation of Goldfinger, et al.[55],

$$R = \frac{k_p}{k_t^{\frac{1}{2}}} F k_1 C^{\frac{1}{2}} M$$

where R is the rate of polymerization, k_p, k_t and k_1 are the rate constants for chain propagation, termination, and initiation, respectively. C and M are concentrations of initiator and monomer, respectively; F is a constant, either 1 or 2, equal to the number of radicals, produced from an initiator molecule, which start chains. The average degree of polymerization (DP) is given by the relationship,

$$\frac{1}{DP} = \frac{1}{DP_k} + k^{*}[56] \quad ,$$

---

[53]Tobolsky, 118th National Meeting of the American Chemical Society, Chicago, Illinois, Sept., 1950.

[54]Cohen, ibid.

[55]Ahere, Goldfinger, Mark and Naidus, Ann. N.Y. Acad. Sci., 94, Art. 4, 267 (1943).

[56]Schulz and Blaschke, Z. physik. Chem., B51, 75 (1942).

where k^* is the transfer constant for growing chains with monomer and $\frac{1}{DP_k}$ is the degree of polymerization if there is no transfer or

$$DP_k = \frac{TR}{Fk_1C}$$

where R is the rate of polymerization and T is 1 or 2 depending on whether the termination reaction is disproportionation or combination of two growing chains. Combining (3) and (2) gives

$$\frac{1}{DP} = \frac{F}{T}\frac{k_1C}{R} + k' \quad .$$

Since $\frac{C^{\frac{1}{2}}}{R}$ is a constant, 1/DP is a linear function of $C^{\frac{1}{2}}$ with a slope of $(F)(k_1C^{\frac{1}{2}})/TR$ and an intercept, k'. Determination of the slope in the polymerization gave a value F/T = 0.49, which can only result if F = 1 and T = 2. Thus only one radical per initiator molecule is a chain starter.

Their second method consisted of using azo-nitrile labeled with C^{14} on the nitrile group as initiator and counting the number of fragments appearing in the resulting purified polymer[52]. A sample of their data is given in Table 4.

The tertiary nature of the carbon atom alpha to the azo linkage seems to be necessary to insure the clean first

Table 4

Polymerization of Vinyl Monomers at 50° with Azo-bis-isobutyronitrile Containing C^{14}

Monomer	Conc.	Orig. azo-nitrile	Decomp. azo-nitrile	Combined azo-nitrile	Eff.
Methyl methacrylate	52% benzene	0.1997	19.2	11.3	0.59
	bulk	0.2096	13.6	7.07	0.52
Styrene	bulk	0.0475	20.0	13.2	0.66
	bulk	0.0395	5.59	4.14	0.74
Acrylonitrile	75% ethanol	0.00606	0.947	0.966	1.02
	" "	0.00607	0.577	0.606	1.05
Vinyl acetate	bulk	0.0455	1.41	1.17	0.83
	54% ethanol	0.0592	11.1	7.52	0.68
	" "	0.0592	7.09	4.89	0.69
	" "	0.0575	3.88	2.64	0.68
Vinyl chloride	67% in acetone	0.0103	2.92	2.25	0.77
	52% in acetone	0.0102	1.71	1.20	0.70

order reaction. Both azomethane, with a primary carbon, and ω,ω'-azotoluene, with a secondary carbon, do not give as clean cut a reaction. Azomethane decomposes at high temperatures unimolecularly[57] to give a mixture of products, mainly nitrogen and ethane, but some hydrogen, ethylene and methane and a high molecular weight compound containing nitrogen[58]. The yields of the various gases varied with percentage decomposition of the azo compound. The reaction involves radicals, because of the removal of lead mirrors by the fragments produced, which are probably methyl radicals[59]. The decomposition of ω,ω'-azotoluene in boiling decalin[38] and in the vapor phase[60] produced only about 84 per cent of the theoretical amount of nitrogen. The main products were toluene (12.5 per cent), bibenzyl (39 per cent) and stilbene (10.5 per cent) in addition to ammonia, hydrocyanic acid and some nitrogen-containing by-products. The probable reason for both the primary and secondary azo compounds giving a

---

[57]Ramsperger, J. Am. Chem. Soc., 49, 912 (1927).

[58]Riblett and Rubin, ibid., 59, 1537 (1937).

[59]Leermakers, ibid., 55, 3499 (1933).

[60]Williams and Lawrence, Proc. Roy. Soc., London, 156A, 455 (1936).

complex reaction sequence is the possibility of rearrangements of these compounds into the corresponding hydrazones.

$$R\text{-}CH_2\text{-}N = N\text{-}CH_2R \longrightarrow RCH = N - \overset{H}{N}\text{-}CH_2R$$

This rearrangement was already noted by Thiele[36].

Tertiary Alkyl Peroxides and Alkoxy Free Radicals

Primary and secondary dialkyl peroxides, like the primary and secondary dialkyl azo compounds, are not as stable as the tertiary members of the species. Dimethyl peroxide[61] and methylethyl peroxide[62] are exceedingly unstable towards shock, the former exploding even in the gaseous state. Increasing the branching on the α-carbon atom and increasing the molecular weight reduces the instability. Di-t-butyl peroxide is quite stable and may be distilled at atmospheric pressure[63]. However most di-tertiary alkyl peroxides are unstable towards heat and acid[64] although the

---

[61]Rieche and Brumshagen, Ber., 61, 951 (1928).

[62]Rieche and Hitz, ibid., 62, 218 (1929).

[63]Milas and Surgenor, J. Am. Chem. Soc., 68, 207 (1946).

[64]Hawkins, Quart. Revs. Chem. Soc., 4, 251 (1950).

range in stability is extreme. Di-t-butyl peroxide is one of the most stable, for it can be prepared in concentrated sulfuric acid[63] and decomposes only slowly in that medium.

Closely related to the di-tertiary-alkyl peroxides are the tertiary alkyl hydroperoxides from which many of the diperoxides have been prepared[65,66]. In general, their stability towards acids is comparable to the corresponding diperoxides. Tertiary-butyl hydroperoxide is comparatively stable in acid solutions and is prepared, along with the di-t-butyl peroxide, in a sulfuric acid medium[63]. Conversely, α-cumyl hydroperoxide is quite unstable in strong Lewis acids and readily decomposes in their presence[67]. The hydroperoxides are somewhat less stable towards heat than the corresponding diperoxides. Tertiary-butyl hydroperoxide explodes if distilled at atmospheric pressures although it distills easily at reduced pressures (4.5-5°/2mm)[63]. In the presence of hot, concentrated alkali, alkyl hydro-

---

[65] de Bataafsche Petroleum Maatschappij, Dutch Patent 65,254. C.A. 44, 4489 (1950).

[66] Kharasch, Fono, and Nudenberg, J. Org. Chem., 15, 753 (1950).

[67] Kharasch, Fono, and Nudenberg, ibid., 15, 748 (1950).

peroxides decompose to a mixture of aldehydes, ketones and acids[68]. However, in the cold, hydroperoxides are sufficiently acid to form stable salts of the alkali metals. Milas and Surgenor[63] prepared the strontium, barium, sodium and potassium salts of t-butyl hydroperoxide. Hock and Lang[69] utilized the sodium salt to purify α-cumyl hydroperoxide.

There are two general methods for the preparation of alkyl hydroperoxides and diperoxides. 1.) The reaction of hydrogen peroxide with alkyl hydrogen sulfates in the presence of acids or alkali usually from a mixture of the hydroperoxide and diperoxide. 2.) The controlled oxidation of hydrocarbons yield either the hydroperoxide, diperoxide or a mixture of both. Milas and Surgenor[63] obtained 66 per cent t-butyl hydroperoxide and 34 per cent di-t-butyl peroxide by adding 27 per cent hydrogen peroxide to t-butyl alcohol dissolved in 70 per cent sulfuric acid maintained between 0-5°. They also obtained[70] t-amyl hydroperoxide and di-t-amyl peroxide by the same method using t-amyl alcohol. Their yields in the latter experiment were unreported.

---

[68]Medvedev and Alekseeva, Ber., 65, 133 (1922); J. Gen. Chem. (U.R.S.S.), 1, 1193, 1200 (1931).

[69]Hock and Lang, Ber., 77, 257 (1944).

[70]Milas and Surgenor, J. Am. Chem. Soc., 68, 643 (1948).

Criegee and Dietrich[71] prepared triethylmethyl-1,1,2,2-tetramethylethyl; and pentamethylethyl hydroperoxides as well as 2,5-dihydroperoxy-2,5-dimethylhexane and 2,7-dihydroperoxy-2,7-dimethyloctane by essentially the same method. Hoffman[72a] obtained 2,4,4-trimethylpentane-2-hydroperoxide from diisobutylene, sulfuric acid and hydrogen peroxide and in the same manner obtained triptyl and 2-methylheptyl hydroperoxides using tripten(2,3,3-trimethyl-1-butene) and 2-methyl-1-heptene as starting olefins.

Since many hydroperoxides and diperoxides are unstable towards acid, particularly if the peroxy group is alpha to an aromatic system, the above method is not generally applicable. Acid-sensitive peroxides are most frequently prepared by controlled oxidation of hydrocarbons. Hock and Lang[69] obtained α-cumyl hydroperoxide from the air oxidation of cumene in the presence of sunlight. Vaughn and Rust[72b,73] prepared t-butyl hydroperoxide and di-t-butyl

---

[71]Criegee and Dietrich, Ann., 560, 135 (1948).

[72a]Hoffman, 121st National Meeting, American Chemical Soc., April, 1952, Milwaukee, Wisc.

[72b]Vaughn and Rust U.S. 2,395,523 Feb. 1946, C.A. 40, 3641 (1946).

[73]Vaughn and Rust U.S. 2,403,771 July 1946, C.A. 40, 5757 (1946).

peroxide by the air oxidation of isobutane using hydrogen bromide as a catalyst.

A third method of preparation of dialkylperoxides involves alkylation of a hydroperoxide or its salt. A variety of conditions have been utilized. Dickey and Bell[74] treated the alkali metal salts of many hydroperoxides with the desired alkyl halide to obtain the diperoxide. Although the alkyl halide may be primary, secondary or tertiary the hydroperoxide must be tertiary. Milas and Surgenor[63] prepared di-t-butyl peroxide by treating t-butyl hydroperoxide with t-butyl alcohol in strong acid. In a third variant Kharasch and co-workers[66] prepared di- α-cumyl peroxide by thermally decomposing α-cumyl hydroperoxide in α-cumyl alcohol, presumably by a free radical mechanism. Kharasch and co-workers[75] obtained t-butyl- α-cumylperoxide and t-butyltriphenylmethyl peroxide by oxidizing the desired alcohol with t-butylhydroperoxide in glacial acetic acid containing a trace of perchloric acid.

---

[74]Dickey and Bell, U.S. 2,403,709 July, 1946 C.A., 40, 6496 (1946) .

[75]Kharqsch, Fono, Nudenberg and Poshkus, J. Org. Chem. 15, 775 (1950).

The acid decomposition of hydroperoxides has been studied[66,67,75,76,77] and although many anamolies still exist, the initial step is believed to be as follows

$$ROOH + A \longrightarrow RO^{+} + AOH^{-} \quad \text{and} \quad ROOR + A \longrightarrow ROA^{-} + RO^{+}$$

Here A is an acid in the Lewis sense. If the group R contains an aromatic ring attached to the alpha carbon atom then rearrangement is possible[67]

$$C_6H_5(CH_3)_2CO^{+} \longrightarrow C_6H_5OC(CH_3)_2$$

$$C_6H_5OC^{+}(CH_3)_2 + C_6H_5(CH_3)_2COOH \longrightarrow C_6H_5(CH_3)_2CO + C_6H_5OH + (CH_3)_2CO$$

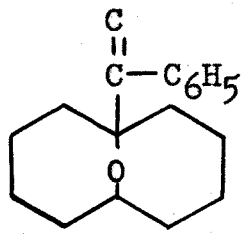
Kharasch[67] obtained only phenol and acetone as products of the acid decomposition of α-cumyl hydroperoxide. When triphenylcarbinol was treated with an acid solution of hydrogen peroxide, presumably forming the hydroperoxide, benzophenone and phenol were formed[76]. Criegee[78] found that 9-decalylperbenzoate in acid gave the isomeric

---

[76]Kharasch, Fono and Nudenberg, ibid., 16, 928 (1951).

[77]Kharasch, Fono and Nudenberg, ibid., 16, 150 (1951).

[78]Criegee, Ann., 560, 127 (1948).



while Bartlett[79] found that under acid conditions p-nitrophenyl-diphenylmethylhydroperoxide gave over 90 per cent phenol and p-nitrobenzophenone. This order of rearrangement is consistent with that observed in the pinacol-pinacolone rearrangement.

Di α-cumyl peroxide dissolved in glacial acetic acid with a trace of perchloric acid rapidly decomposed to the dimer of α-methylstyrene, phenol and acetone[66], the styrene dimer probably arose from the dehydration of the cumyl alcohol formed. Triphenylmethyl-t-butyl peroxide under the same conditions gave triphenylmethyl alcohol, phenol and benzophenone[76]. All of these products are completely consistent with the mechanism cited.

Milas and Surgenor[70] and George and Walsh[80] found that, in the vapor phase, tertiary alkyl peroxides undergo decomposition to form ketones and hydrocarbons, e.g., t-butyl

---

[79]Bartlett, Record Chem. Progress, 11, 48 (1950).

[80]George and Walsh, Trans. Faraday Soc., 42, 94 (1946).

peroxide gave methane and acetone[70]. In a recent review Leffler[81] compiled a list of the thermal decomposition products of some peroxides and hydroperoxides. Of the various peroxides compiled only the tertiary alkyl peroxides are presented in Table 5. Table 6 lists the products of autoxidation of some hydrocarbons taken from the same source.

The first detailed study of the decomposition of peroxides was made by Raley, Rust and Vaughn[82] who studied the kinetics and products of the vapor phase decomposition of di-t-butyl and di-t-amyl peroxides between the temperatures 140-160°. The decomposition of di-t-butyl peroxide was homogeneous, first order and a non-chain reaction, the rate constant for which was given as

$$k = 3.2 \times 10^{16}(e^{-39100/RT}) \quad .$$

The reaction was postulated as initially involving a scission of the oxygen-oxygen bond (rate determining step) after which the radicals fragmented to acetone and free methyl. With low initial peroxide concentration and a large amount of glass surface these methyl radicals combined on the walls

---

[81]Leffler, Chem. Revs., 45, 385 (1949).

[82]Raley, Rust and Vaughn, J. Am. Chem. Soc., 70, 88, 95 (1948).

Table 5

Decomposition Products of Alkyl Peroxides

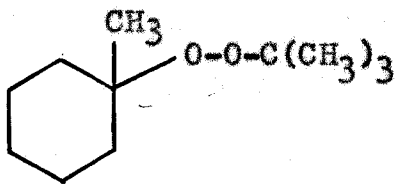
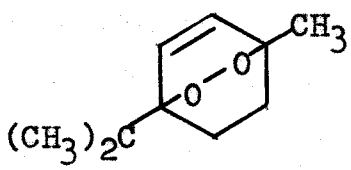
Peroxides	Conditions	Products
$(CH_3CH_2)_3\ COOC(CH_2CH_3)_3$	250° glass wool	$(CH_3CH_2)_2CO$ + $\underline{n}$-C_4H_{10}
$(CH_3)_3COOC(CH_3)_2C(CH_3)_3$	"	$(CH_3)_2CO$ + $(CH_3)_4C$
	"	C_2H_6 + $(CH_3)_2CO$ + $CH_3CH_2)\ CHCOCH_3$ $CH_3(CH_2)_3CHCOCH_3$
	distill in N_2	C_2H_6 + $\underline{n}$-C_3H_8 + $CH_3CH\ CH_2$
$(C_6H_5)_3COOH$	melt	$(C_6H_5)_2CO$ + C_6H_5OH

Table 6

Decomposition Products of Alkyl Peroxides

Hydrocarbon	Product
$C_6H_5CH(CH_3)_2$	$C_6H_5COCH_3$
p-$CH_3C_6H_4CH(CH_3)_2$	p-$CH_3C_6H_4COCH_3$
cyclohexene	cyclopentene-1-al
1-ethylcyclohexene	1-cyclopentenyl ethyl ketone

forming ethane. At higher initial peroxide concentrations and with little glass surface the methyl radicals preferentially attack acetone or peroxide forming methane and higher ketonic products.

$$(CH_3)_3CO_2 \longrightarrow 2(CH_3)_3CO\cdot$$
$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + (CH_3)_2CO$$
$$2CH_3\cdot \longrightarrow C_2H_6$$
$$CH_3\cdot + (CH_3)_2CO \longrightarrow CH_4 + \cdot CH_2COCH_3$$
$$CH_3\cdot + \cdot CH_2COCH_3 \longrightarrow CH_3CH_2COCH_3$$

In the presence of nitric oxide or propylene the rate of decomposition was uneffected, indicative of a non-chain decomposition. From the reaction with nitric oxide,

formaldoxime was isolated, formed probably by the mechanism

$$CH_3\cdot + NO \longrightarrow CH_3NO \longrightarrow CH_2 = NO \quad .$$

In the presence of propylene, hydrocarbons arising from attack upon olefin by methyl radical resulted. The products were complex but could be rationalized by the usual reactions of alkyl radicals, i.e., radical combination and disproportionation, although at these relative high temperatures disproportionation seemed to predominate. In the presence of large amounts of glass surface virtually no attack of methyl radicals upon olefin occurred. The radicals preferred to dimerize on the walls.

The pyrolysis of di-t-amyl peroxide was homogeneous and approximately first order with an overall activation energy of 37 kcal. per mole. The predominate products were n-butane and acetone but methane, ethane, ethylene, propane, methylethyl ketone and higher ketones were formed in small amounts. In this case the alkoxy radical fragments with preferential discharge of the larger group.

$$CH_3CH_2(CH_3)_2CO\cdot \longrightarrow CH_3CH_2\cdot + (CH_3)_2CO$$

Concurrent with this reaction, but of minor importance, is the elimination to form methyl radicals. Combination, disproportionation, and attack on other materials by these

radicals account completely for all products observed.

Vaughn and co-workers[83,84] further studied the thermal decomposition of di-t-butyl peroxide in the condensed state and in solution. High yields of isobutylene oxide were obtained when the pure peroxide was decomposed at 110° probably by the mechanism

$$CH_3\cdot + (CH_3)_3COOC(CH_3)_3 \longrightarrow CH_4 + \cdot CH_2(CH_3)_2COOC(CH_3)_3$$

$$\cdot CH_2(CH_3)_2COOC(CH_3)_3 \longrightarrow (CH_3)_2C\underset{O}{\diagdown\!\diagup}CH_2 + (CH_3)_3CO\cdot$$

The kinetics of the decomposition were studied in a range of solvents, i.e., cumene, t-butylbenzene, tri-n-butylamine and in all cases both the frequency factor (10^{16}) and the activation energy (39 kcal.) were identical within experimental error to that obtained in the vapor phase. This supported the contention that the initial and rate determining step in both solution and vapor phase was the unimolecular scission of the oxygen-oxygen bond.

Kharasch[85] followed the kinetics of the decomposition of di- α-cumyl peroxide and α-cumyl-t-butylperoxide by

---

[83] Raley, Rust and Vaughn, ibid., 70, 1336 (1948).

[84] Bell, Rust and Vaughn, ibid., 72, 337 (1950).

[85] Kharasch, Fono and Nudenberg, J. Org. Chem., 16, 105 (1950).

measuring the rate of methane evolution between the temperatures 128-158° in various solvents. He did not report the rate constants nor give any kinetic data other than the half-lives at various temperatures and in various solvents and the activation energies. He claimed a first order rate of methane evolution independent of solvent and surface. Actually Kharasch did not measure the primary process since methane is produced by a secondary reaction. However, if as is probable, all subsequent reactions after the initial cleavage of the peroxide were rapid then the rate of methane evolution was an adequate measure of the rate of cleavage provided correction was made for the ratio of the amount of methane evolved to the amount of peroxide decomposed.

The products of the decomposition of tertiary alkyl peroxides in solution are somewhat different from those formed in the vapor phase. The primary process is identical in both cases but the fate of the alkoxy radical formed is highly sensitive to the solvent. Fragmentation may still occur with the formation of ketone and an alkyl radical but there is the added reaction whereby the alkoxy radical may abstract hydrogen from solvent forming the tertiary alcohol.

$$RR'R''CO\cdot + SH \longrightarrow RR'R''COH + S\cdot$$

Raley, Rust and Vaughn[83] obtained both t-butyl alcohol and acetone as products of the thermal decomposition of di-t-butyl peroxide in solution. Kharasch[85] obtained acetophenone and α-cumyl alcohol from the decomposition of di- α-cumyl peroxide and acetone, acetophenone, t-butyl alcohol and α-cumyl alcohol from α-cumyl-t-butyl peroxide.

Temperature, solvent and source all had a profound influence upon the relative yields of alcohol and ketone[83,84,85]. Thus the subsequent reactions of the alkoxy radicals formed after the initial step were highly dependent upon these three conditions. The extreme range in products is illustrated in Tables 7, 8 and 9.

The temperature dependence of the product ratios followed the expected trend, e.g., fragmentation was favored with increasing temperature. This was noted in all three cases studied.

The effect of solvent upon the product ratios was also "normal". Higher alcohol yields were obtained in solvents where hydrogen abstraction gives a resonance stabilized radical, i.e., cumene was better than t-butyl benzene which in turn was better than dodecane. Of interest is the solvent tri-n-butylamine. Amines are known as excellent chain destroyers (inhibitors) in polymerization. In the work of

Table 7

Decomposition of t-Butyl Peroxide in Various Solvents

Temperature		Ketone	Alcohol	Ketone/ alcohol
		(moles/moles peroxide)		
125	Cumene	0.39	1.61	0.24
125	t-Butylbenzene	1.25	0.75	1.7
125	Tri-n-butylamine	0.1	9.9	0.053
135	Cumene	0.49	1.51	0.32
135	t-Butylbenzene	1.44	0.56	2.6
135	Tri-n-butylamine	0.1	1.9	0.053
145	Cumene	0.77	1.23	0.63
145	t-Butylbenzene	1.54	0.46	3.3
145	Tri-n-butylamine	0.1	1.9	0.053

Table 8

Products Derived from $(CH_3)COOR$ in Cyclohexane at 195°
(Yield in moles/100 moles peroxide reacted)*

	Products derived from $(CH_3)_3CO\cdot$		
RO·	alcohol	ketone	Ketone/alcohol
$CH_3O\cdot$	10	82	8.2
$CH_3CH_2O\cdot$	12	80	6.7
$CH_3(CH_2)_2CHO\cdot$	20	69	3.5
$(CH_3)_2CHO\cdot$	6	82	14
$(CH_3)_2CHCH_2O\cdot$	22	67	3.0
$(CH_3)_3CO\cdot$	8	94	12

*The relative proportions of alcohol and ketone from the t-butoxy radical are the only ones considered.

Table 9

Ketone-Alcohol Mole Ratios in Products Arising from the Attack of Free Alkoxy Radicals from Different Sources in Various Solvents at 138-140°

Peroxide-solvent	Ketone-alcohol ratios	
	Acetone	Acetophenone
	t-butyl alcohol	α-Cumyl alcohol
Di-t-butyl peroxide		
t-butylbenzene	2.90[a]	--
cumene	0.50[a]	--
dodecane	0.12	--
α-cumyl t-butyl peroxide		
t-butylbenzene	0.32	9.70
cumene	0.15	3.00
dodecane	0.04	1.70
Di- α -cumyl peroxide		
t-butylbenzene	--	--
cumene	--	1.40
dodecane	--	0.68

[a]Calculated by Kharasch and co-workers from the data in Table 5. The arithmatic mean between 135-145° was determined.

Raley, Rust and Vaughn[83], tri-n-butylamine gave almost exclusively t-butyl alcohol from t-butyl peroxide. This illustrates the excellent qualities of amines as radical traps. These authors did not report any products arising from solvent.

Quite surprising on a cursory glance was the effect of the source of the alkoxy radical on the product ratio. This is strikingly illustrated in Tables 8 and 9. If the rate determining step in the decomposition was the initial cleavage, as the kinetics show, then the radical formed should be "free" in every sense of the word and unaffected by its previous bondage. Such seems not to be the case. Vaughn and co-workers did not discuss this problem. However Kharasch[85] on the basis of the three peroxides he studied, di- α-cumyl peroxide, di-t-butyl peroxide and α-cumyl-t-butyl peroxide, rationalizes this fact with the hypothesis that since increasing temperature increases the preference of the alkoxy radicals to disproportionate then at any given temperature the t-butoxy radicals derived from the di-t-butyl peroxide contain more energy than the t-butoxy radical derived from α-cumyl-t-butyl peroxide. A similar line of reasoning suggests that α-cumyloxy radicals derived from α-cumyl peroxide contain less energy than those derived from α-cumyl-t-butyl peroxide.

The suspicion that the local environment of the free radicals, whatever their source, may be far more influential than would be expected prompted the following work dealing with tertiary alkyl peroxides.

EXPERIMENTAL

Apparatus and Materials

Potentiometric titrations

All potentiometric titrations were made on a Beckman pH meter, Model G, using glass and standard calomel electrodes.

Elemental analyses

All elemental analyses were done by G. Weiler and F. B. Strauss, Microanalytical Laboratory, 164 Banbury Road, Oxford, England.

Infra-red absorption spectra

All infra-red absorption spectra were made with a Baird Associates Infra-red Recording Spectrophotometer (Model B). This is a double beam instrument which automatically recorded the per cent transmission of the solution. All spectra taken were done using the Nujol or Hexachlorobutadiene mull technique.

Toluene

Toluene (Baker and Adamson, Reagent Grade) was distilled through a six-foot, helices packed column. The fraction boiling at 109-110° (uncorr.) was used in subsequent work.

Cumene

Cumene (Eastman Kodak, White Label) was distilled using round bottomed flask equipped with a Vigreux still head and condenser. The liquid boiling at 151.5-152° (uncorr.) was used. It was stored over calcium metal.

Tetralin

Tetralin (Eastman Kodak, White Label) was distilled under reduced pressure (91°/18mm) through a six-foot, helices packed column before use.

Chlorobenzene

Chlorobenzene (Paragon Division, Matheson Chemical Co.) was used without further purification.

Chloranil (Tetrachloroquinone)

Chloranil (Eastman Kodak, Yellow Label) was recrystallized once from glacial acetic acid and dried in a vacuum desiccator before use.

Azo-bis-diethylacetonitrile

This compound was prepared by the method of Dox[37] from diethyl ketone, hydrazine sulfate, and sodium cyanide. The dialkyl hydrazine was oxidized to the azo compound with bromine water. The yield (white platelets) was 60 per cent of the theoretical. After two recrystallizations from

absolute ethanol the melting point was 74-75°*. It was stored in a dark bottle and kept away from light. It was recrystallized once from ethanol and dried in a vacuum desiccator before use.

Azo-bis-dimethylacetonitrile

This compound was prepared in a manner analogous to the homolog above. The yield was 70 per cent of the theoretical. After two recrystallizations the white needles melted at 101-102°.

ω,ω'-Azo-bis-toluene

This compound was prepared by the method of Bickels and Waters[38] by the reduction and subsequent oxidation of benzalazine**. It was never obtained in a high state of purity but seemed contaminated by a high melting by-product (127-130°) which was believed to be benzalbenzylhydrazone. However after a number of recrystallizations from 95 per cent ethanol chilled in a dry ice-acetone bath, a product melting at 31-33° was obtained (lit. 29°). Since the nature of the experiments involving this compound did not necessarily

---

*All melting points are uncorrected.

**This was prepared by Mr. Burton Christensen of these laboratories.

require a pure material, the above fraction, melting at 31°, was used.

Di-t-butyl peroxide

This compound, donated by Shell Development Corporation, Emeryville, California, was distilled through a 44 plate center-rod column (45°/20mm) before use.

Cumene hydroperoxide (α, α-dimethylbenzylhydroperoxide)

Cumene hydroperoxide (79 per cent), donated by Hercules Powder Company was purified by first precipitating it as the sodium salt with 50 per cent sodium hydroxide and just neutralizing with 2 N sulfuric acid[69]. After washing with potassium carbonate to insure the complete removal of acid the material was distilled under reduced pressure (41°/ 0.01mm). Thus purified the peroxide had an iodometric titer of 98 per cent.

Cumyl alcohol (α, α-dimethylbenzyl alcohol)

This compound was prepared by the method of Kharasch[86] from cumene hydroperoxide. The product after distillation through a 44 plate, center-rod column (63°/2mm) and three recrystallizations from Skelly-solve B melted at 36-36.5°. It was stored in a vacuum desiccator.

---

[86]Kharasch, Fono and Nudenberg, ibid., 10, 113 (1951).

Di- α -cumyl peroxide

This peroxide was prepared by the thermal decomposition of cumene hydroperoxide in α -cumyl alcohol at 95°[66]. Although Kharasch reported near quantitative yields under these conditions, it was only obtained in yields of 5-10 per cent. After recrystallization from ethanol in a dry ice acetone bath it melted at 39-39.5°. It could not be titrated iodometrically.

Triphenylmethyl-t-butyl peroxide

This peroxide was prepared by the method of Kharasch[75] from t-butyl hydroperoxide and triphenyl carbinol in yields of 85 per cent. After recrystallization twice from ethanol it melted at 69-70°.

t-Butyl hydroperoxide

This peroxide was prepared by the method of Milas and Surgenor[63] by the oxidation of t-butyl alcohol. It was separated from the di-t-butyl peroxide by precipitating it as the sodium salt and neutralizing with 2N sulfuric cold acid.

Reactions

Decomposition of azo-bis-diethylacetonitrile in toluene

Three and three tenths g. (0.015 moles) of azo-bis-diethylacetonitrile was dissolved in 50 ml. of toluene and

the solution refluxed for 15 hours. The toluene was then distilled off at such a reduced pressure that the distilling temperature did not become greater than 50°. On standing at room temperature for 3-4 hours the residue, tetraethylsuccinonitrile, crystallized as white needles which on recrystallization from ethanol-water melted at 47-48°. The toluene distillate was again distilled at reduced pressure keeping the distilling temperature below 50°. A further small crop of crystals was obtained. The total yield was 2.09 g. (0.0109 moles) representing 73 per cent of the theoretical yield. Neither the distillate nor recrystallization residues gave any evidence of the presence of dibenzyl which would be expected if attack upon toluene by the aliphatic radicals occurred.

Decomposition of azo-bis-diethylacetonitrile in the presence of chloranil in toluene

Two and two tenths g. (0.010 moles) of azo-bis-diethylacetonitrile and 2.48 g. (0.010 moles) of chloranil were dissolved in 100 ml. of toluene and heated at reflux for 15 hours. The solution was then cooled, and extracted with 5 per cent sodium hydroxide until the extract was colorless. This basic extract was deep red in color due to the formation of chloranilic acid. Upon acidification with 5 per cent hydrochloric acid and after standing for one hour a

dirty solid formed which after repeated recrystallizations from glacial acetic acid melted at 140-140.9°. This proved to be tetrachlorohydroquinone monobenzyl ether. A yield of 0.53 g. (0.0016 moles) was obtained.

Calculated for $C_{13}H_8O_2Cl_4$: C = 46.3, H = 2.47, Cl = 42.1

Found: C = 46.6, H = 2.48, Cl = 41.6

The structure proof of this compound is given on page 70. The infra-red absorption spectrum is given in Figure 1.

The organic layer from the extraction was steam distilled and the distillate which contained all the toluene was extracted with ether and dried over sodium sulfate. After drying, the toluene-ether mixture was distilled under reduced pressure as in the preceeding experiment. This distillate yielded, after recrystallization from ethanol-water, 0.6 g. (0.0031 moles) of tetraethylsuccinonitrile. This amount of product represented 31 per cent of the azo-bis-acetonitrile decomposed.

The residue from the steam distillation was recrystallized from a large volume of ethanol and gave 1.55 g. (0.0046 moles) of tetrachlorohydroquinone di-(3-cyano-3-pentyl) ether which melted at 166-167°. The yield, based on the amount of azo-bis-acetonitrile decomposed, was 45 per cent.

Calculated for $C_{18}H_{20}O_2N_2Cl_4$: C = 49.3, H = 4.56, Cl = 32.4, N = 6.39

Figure 2.

229 -- Tetrachlorohydroquinone di(3-cyano-3-pentyl) ether.

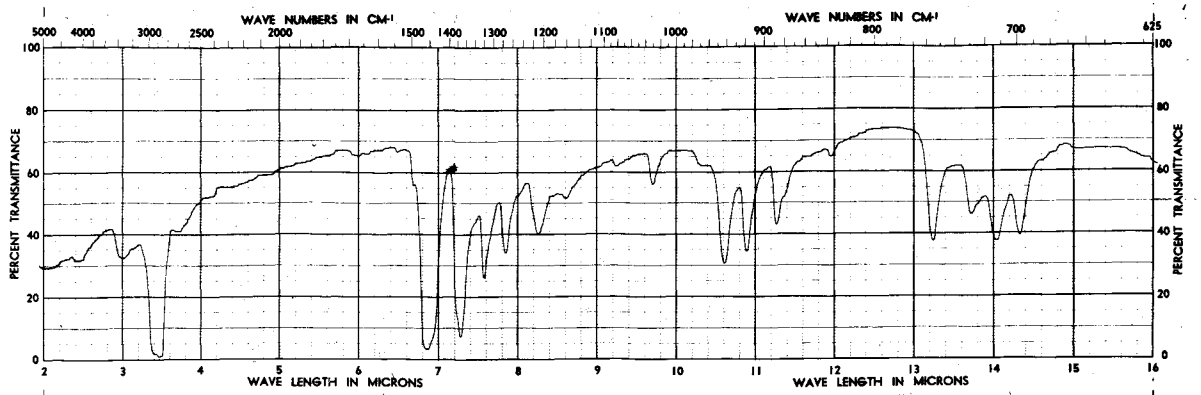
#3718 -- Tetrachlorohydroquinone mono(2-cyano-2-propyl) ether.

#3711 -- Tetrachlorohydroquinone di(2-cyano-2-propyl) ether.

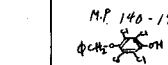
I. R. SPECTROPHOTOMETER
NaCl PRISM

NO. 3185					
DATE 5-19-52	INDEX Hedges				
SAMPLE 104-I Mono benzyl ether of tetrachlorohydroquinone					
FROM G. Lucas					
SAMP. CELL=	MM	CMS.			
REF. CELL	MM	CMS.			
CHEM.	MG.				mg.
SOLV. Nujol //					
VOL.	C.C.	%	C.C.	%	
F.S.	SO ID	C.	GAS	MM	

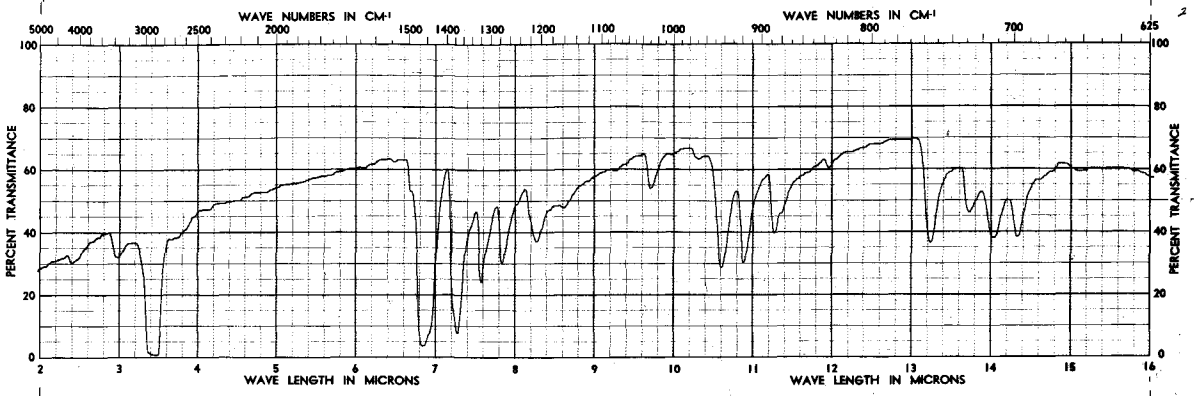
BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.

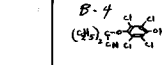


I. R. SPECTROPHOTOMETER
NaCl PRISM

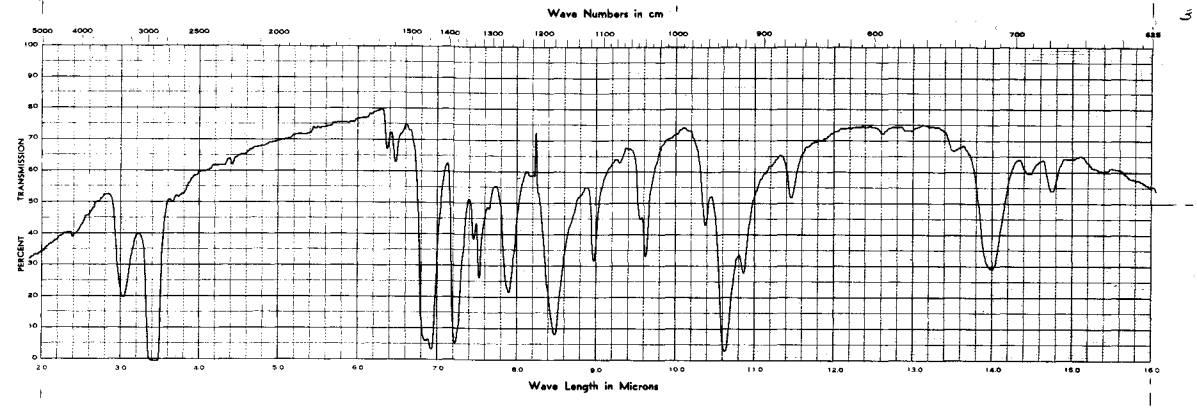
NO. 3187					
DATE 5-14-52	INDEX Hedges				
SAMPLE B-1 M.P. 140-140.9 					
FROM G. Lucas					
SAMP. CELL=	MM	CMS.			
REF. CELL	MM	CMS.			
CHEM.	MG.				MG.
SOLV. Nujol mull					
VOL.	C.C.	%	C.C.	%	
F.S.	SOLID	°C.	GAS	MM	

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.



No. 1912					
DATE 2-29-52	INDEX Hedges				
SAMPLE B-4 					
From G. Lucas					
Samp. Cell :	mm.	cms.			
Comp. Cell :	mm.	cms.			
Chem.	mg.				mg.
Solv. Nujol mull					
Vol.	c.c.	%	c.c.	%	
F.S.	Solid	C.	Gas	mm.	

BAIRD ASSOCIATES
I. R. SPECTROPHOTOMETER
NA CL PRISM



Found: C = 50.1, H = 4.42, Cl = 31.7, N = 6.32

The infra-red absorption spectrum is given in Figure 2.

Decomposition of azo-bis-diethylacetonitrile in the presence of chloranil in chlorobenzene

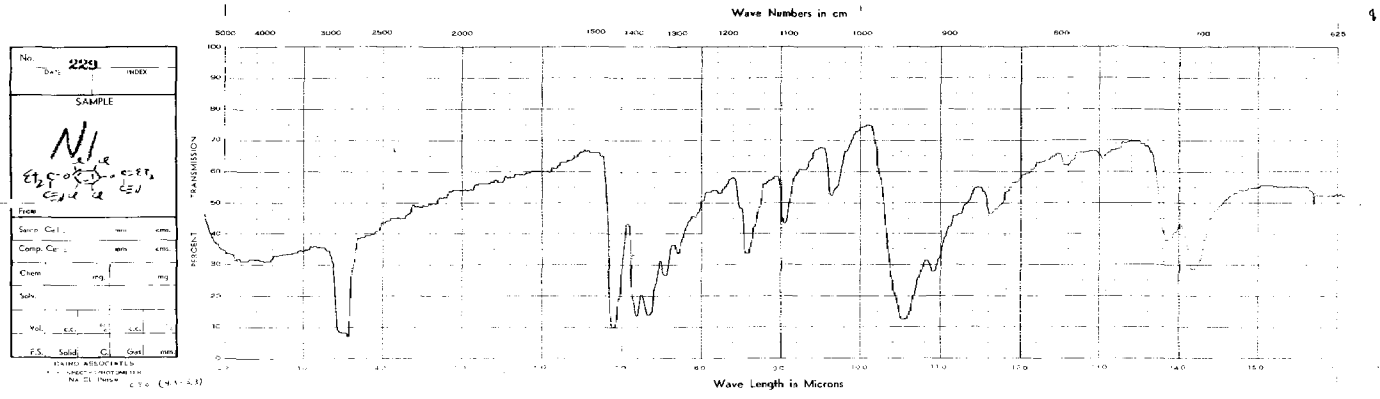
This decomposition was carried out and the products isolated in the same manner as in the above experiment.

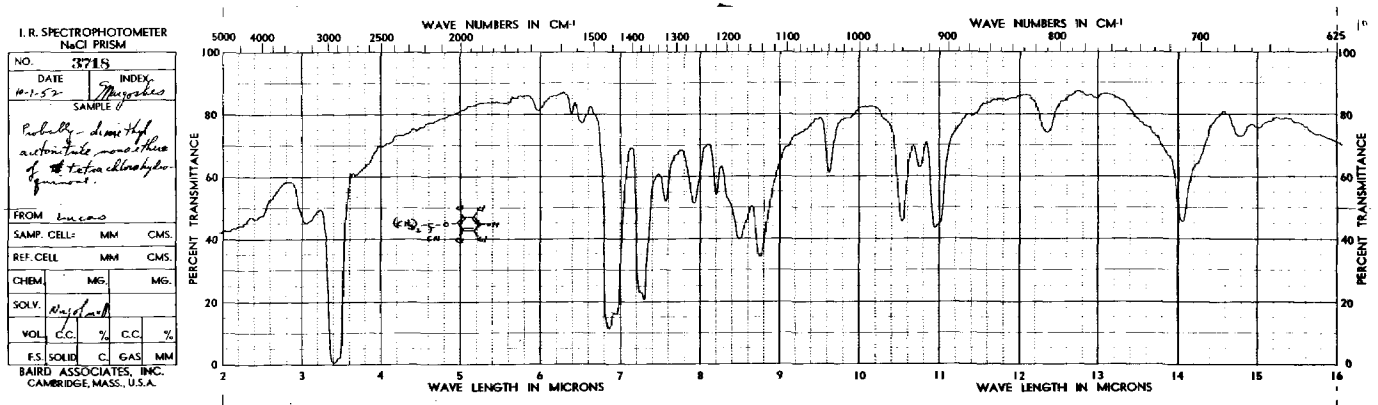
A phenolic product, tetrachlorohydroquinone mono(3-cyano-3-pentyl) ether, was obtained. Melting point 165° (with decomposition).

Calculated for $C_{12}H_{11}O_2NCl_4$: N = 4.08, Cl = 41.4
Found: N = 4.17, Cl = 40.7

This compound, both by mixed melting point determination and infra-red absorption analysis was shown to be different from the phenolic product, tetrachlorohydroquinone monobenzyl ether, obtained in the preceding experiment. The infra-red absorption spectrum is given in Figure 1.

Tetraethylsuccinonitrile and tetrachlorohydroquinone di-(3-cyano-3-pentyl) ether, identical in all respects to those compounds previously obtained, were isolated. The yields and material balances of this and the experiments below, are given in Tables 10 and 11.


No. 2229
SAMPLE
Free
Wave Numbers in cm
TRANSMISSION
PERCENT
Wave Length is Microns


I. R. SPECTROPHOTOMETER
NaCl PRISM
NO. 3718
DATE 10-1-52
INDEX Morgulies
SAMPLE
FROM Lucas
SAMP. CELL MM CMS.
REF. CELL MM CMS.
CHEM. MG. MG.
SOLV.
VOL. C.C. % C.C. %
F.S. SOLID C. GAS MM
BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
WAVE NUMBERS IN CM-1
PERCENT TRANSMITTANCE
WAVE LENGTH IN MICRONS

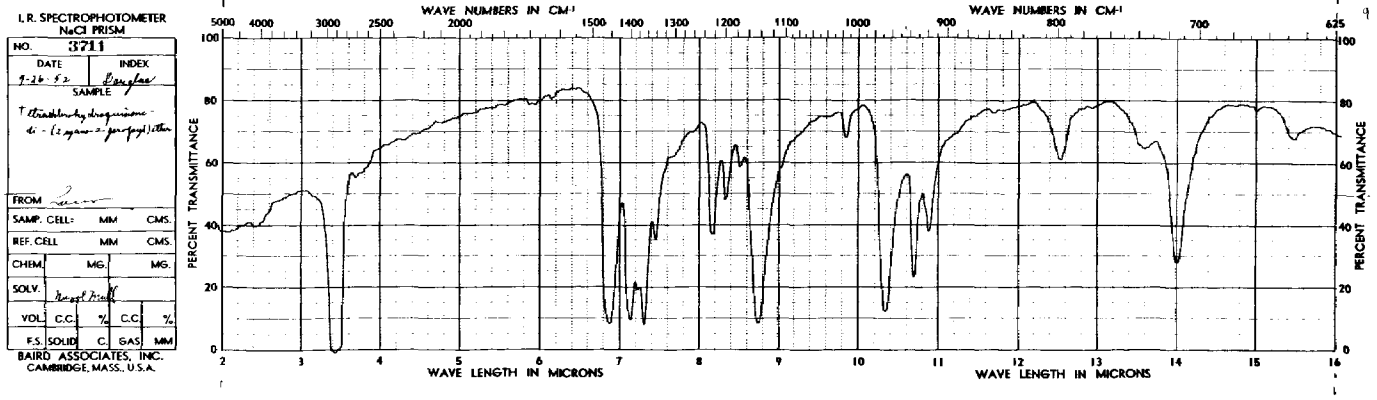

I. R. SPECTROPHOTOMETER
NaCl PRISM
NO. 3711
DATE 9-26-52
INDEX Douglas
SAMPLE
FROM Lucas
SAMP. CELL MM CMS.
REF. CELL MM CMS.
CHEM. MG. MG.
SOLV.
VOL. C.C. % C.C. %
F.S. SOLID C. GAS MM
BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
WAVE NUMBERS IN CM-1
PERCENT TRANSMITTANCE
WAVE LENGTH IN MICRONS

Table 10

Melting Points and Nomenclature of Products from Azo-bis-nitrile Decompositions

Compound	Melting point[a]	Nomenclature[b]
Tetrachlorohydroquinone monobenzyl ether	140 -140.9	B1
Tetrachlorohydroquinone dibenzyl ether[c]	173.5-173.8	N1
Tetrachlorohydroquinone mono(2-cyano-2-propyl) ether	134 -135	B2
Tetrachlorohydroquinone di(2-cyano-2-propyl) ether	166 -167	N2
Tetrachlorohydroquinone mono(3-cyano-3-pentyl) ether	165 (dec.)	B3
Tetrachlorohydroquinone di(3-cyano-3-pentyl) ether	166 -167	N3
Tetramethylsuccinonitrile	165 -166	S3
Tetraethylsuccinonitrile	47 -48	S2

[a]Uncorrected.

[b]Nomenclature used in Table 11.

[c]Not obtained as a reaction product.

Table 11

Products Derived from the Decomposition of Azo-bis-nitrile

Azo-bis-nitrile moles x 10^2	Additive moles x 10^2	Solvent 50 ml.	Products moles x 10^2	Alkyl radicals recovered moles x 10^2
DE-1.5	none	toluene	S2-1.09	2.2
DE-6.4	none	tetralin	S2-4.7	1.79
DE-0.5	chloranil 1.3	toluene	B1-0.08 N2-0.447 S2-0.31	0.765
DE-1.3	chloranil 1.3	chloro-benzene	B2-0.66 N2-0.67 S2-0.47	2.44
DM-1.0	none	toluene	S3-0.86	1.7
DM-0.94	chloranil 1.0	toluene	B3-0.036 B1-0.032 N3-0.27 S3-0.36	1.3
DM-1.1	chloranil 0.53	chlorine	B3-0.037 N3-0.29 S3-0.46	0.79

Decomposition of azo-bis-dimethylacetonitrile in the presence of chloranil in toluene

The experiment was pursued in a manner analogous to those above.

After extraction with 10 per cent sodium hydroxide the neutral fraction gave both tetramethylsuccinonitrile and tetrachlorohydroquinone di-(2-cyano-2-propyl) ether, isolated by the above techniques.

From the aqueous extract was isolated both tetrachlorohydroquinone monobenzyl ether and tetrachlorohydroquinone mono(2-cyano-2-propyl) ether. The monobenzyl ether was far less soluble in glacial acetic acid and fractional crystallization was employed for the separation. After fractional crystallization the infra-red spectrum of the mono(2-cyano-2-propyl) ether showed no absorption at 13.25 microns characteristic of the monobenzyl ether. This spectrum is shown in Figure 2.

The steam distillate from this reaction was searched for bibenzyl in the following manner. The last fraction from the recrystallizations of tetramethylsuccinonitrile was dried and an infra-red absorption spectrum determined. Bibenzyl has a strong absorption maximum at 13.25 microns, which peak is absent in tetramethylsuccinonitrile. The spectrum of the sample was essentially that of tetramethyl-

succinonitrile with no indication of any absorption at the above mentioned wavelength. This spectrum along with that of bibenzyl is given in Figure 3.

In the same fashion the residue after steam distillation was searched for tetrachlorohydroquinone dibenzyl ether. There was no evidence of absorption at the required 13.25 microns in the sample.

Decomposition of azo-bis-dimethylacetonitrile in the presence of chloranil in chlorobenzene

This reaction was carried out similarly to those preceding it. The products isolated were:

Tetramethylsuccinonitrile

Tetrachlorohydroquinone di(2-cyano-2-propyl) ether

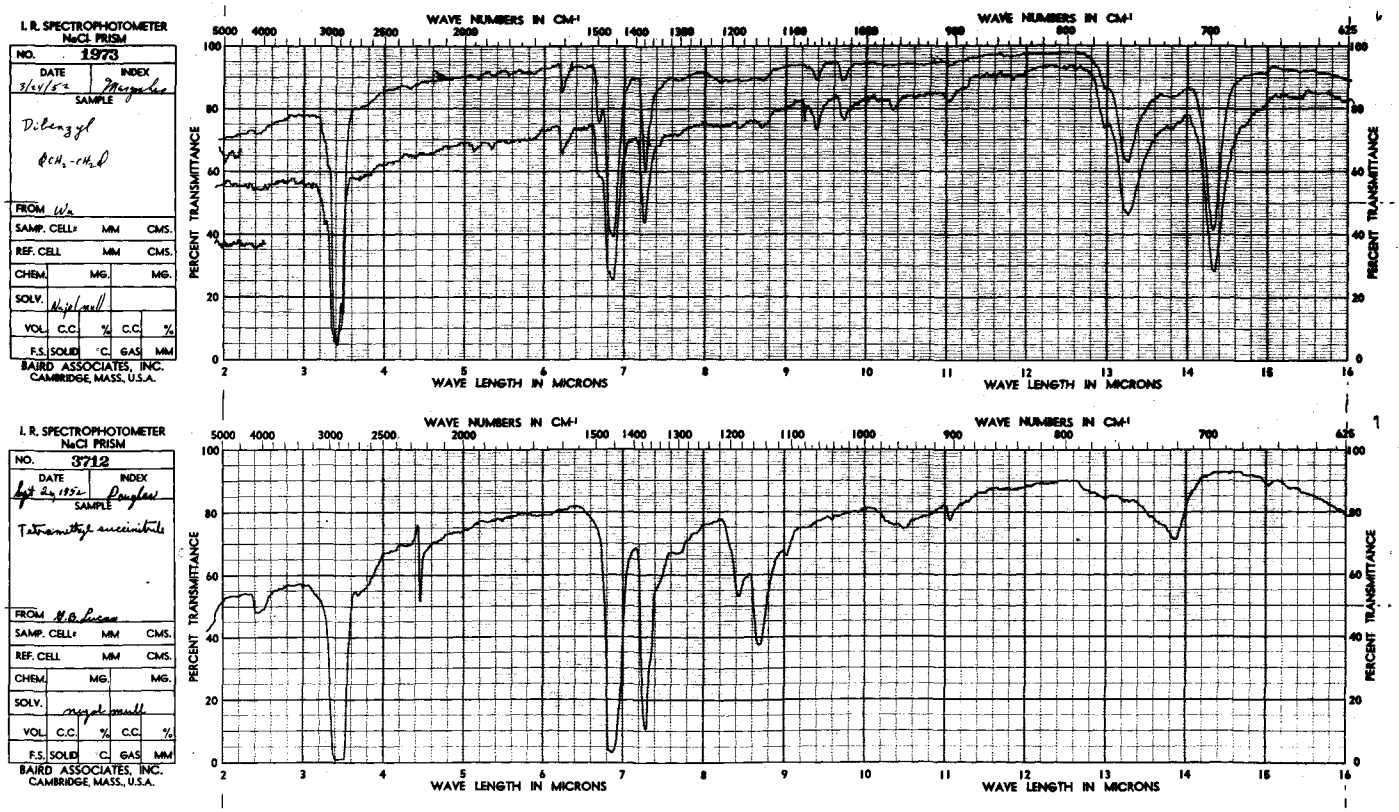
Tetrachlorohydroquinone mono(2-cyano-2-propyl) ether

Structure proof of tetrachlorohydroquinone monobenzyl ether. Neutral equivalent

A 0.1044 g. sample required 10.00 ml. of 0.03148 normal sodium hydroxide when titrated potentiometrically. The pH at the end point was 8.39. Neutral equivalent for $C_{13}H_8O_2Cl_4$, calc. 337, found 332.

Attempted independent syntheses of tetrachlorohydroquinone monobenzyl ether

Numerous methods for preparing tetrachlorohydroquinone


I. R. SPECTROPHOTOMETER
NaCl PRISM
NO. 1973
DATE
INDEX
SAMPLE
Dibenzyl
FROM
SAMP. CELL
REF. CELL
CHEM.
SOLV.
VOL.
F.S.
BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
WAVE NUMBERS IN CM-1
WAVE LENGTH IN MICRONS
PERCENT TRANSMITTANCE
I. R. SPECTROPHOTOMETER
NaCl PRISM
NO. 3712
DATE
INDEX
SAMPLE
Tetramethyl succinitrile
FROM
SAMP. CELL
REF. CELL
CHEM.
SOLV.
VOL.
F.S.
BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
WAVE NUMBERS IN CM-1
WAVE LENGTH IN MICRONS
PERCENT TRANSMITTANCE

monobenzyl ether, previously unknown, from tetrachlorohydroquinone and benzyl chloride were attempted. With aqueous or alcoholic sodium hydroxide or potassium carbonate in acetone[87] only tetrachlorohydroquinone dibenzyl ether could be isolated. With sodium hydride in dry diethyl ether, the starting materials were recovered unchanged.

Preparation of tetrachlorohydroquinone dibenzyl ether

Chloranil was reduced to the hydroquinone by refluxing with zinc metal in glacial acetic acid until the solution was clear. The hot solution was filtered and on cooling white needles of tetrachlorohydroquinone precipitated. These were filtered, air dried and used without further purification.

Eight g. (0.03 moles) of tetrachlorohydroquinone was added to 2.6 g. (0.065 moles) of sodium hydroxide in 100 ml. of water. The solution was heated to reflux and to the green refluxing solution was added dropwise 9.0 g. (0.07 moles) of benzyl chloride. After the addition was complete the solution was refluxed for two hours further. On cooling a precipitate formed which was filtered and recrystallized from 95 per cent ethanol. Melting point 173.5-173.8°. The compound was insoluble in base.

---

[87]Curd and Robertson, J. Chem. Soc., 714 (1933).

Calculated for $C_{20}H_{14}O_2Cl_4$: C = 56.0, H = 3.28, Cl = 33.2
Found: C = 57.8, H = 3.47, Cl = 31.8

The infra-red absorption spectrum of this compound is given in Figure 4.

Preparation of the benzyl ether of tetrachlorohydroquinone monobenzyl ether derived from the decomposition reactions

A 0.5 g. sample of suspected tetrachlorohydroquinone monobenzyl ether was dissolved in the minimum necessary 5 per cent sodium hydroxide and heated to reflux. Then 0.2 ml. of benzyl chloride was added dropwise and the solution was refluxed for four additional hours. A solid formed during reflux and after cooling it was extracted with diethyl ether, the ether evaporated and the solid recrystallized from 95 per cent ethanol. Melting point 173-175°. A mixed melting point with authentic tetrachlorohydroquinone dibenzyl ether, prepared above, showed no depression. The infra-red absorption spectra of the two samples, shown in Figure 4, were identical.

Reaction of tetrachlorohydroquinone mono(3-cyano-3-pentyl) ether with benzyl chloride

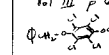
In the structure proof of tetrachlorohydroquinone monobenzyl ether this compound was converted to the known tetrachlorohydroquinone dibenzyl ether. Still to be

Figure 4.

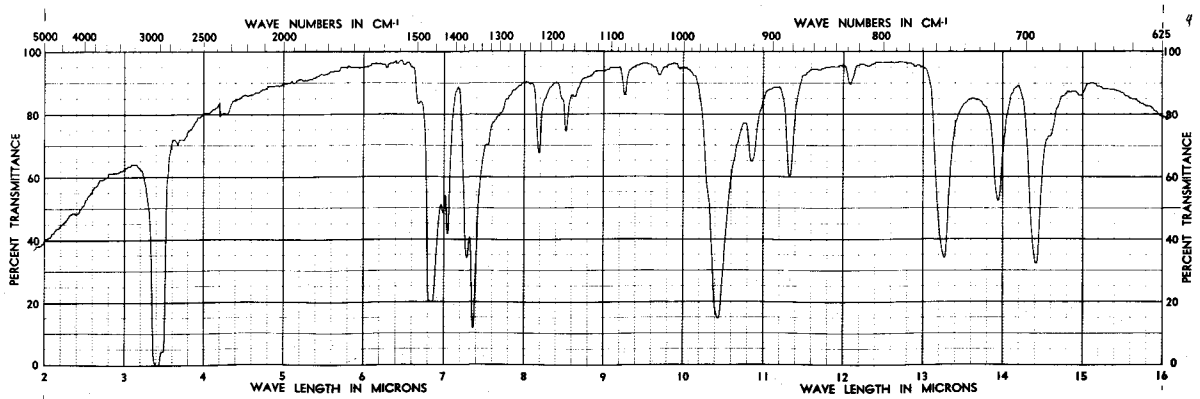
#1939 -- Benzyl ether of product phenolic.

#1603 -- Authentic tetrachlorohydroquinone dibenzyl ether.

I. R. SPECTROPHOTOMETER
NaCl PRISM

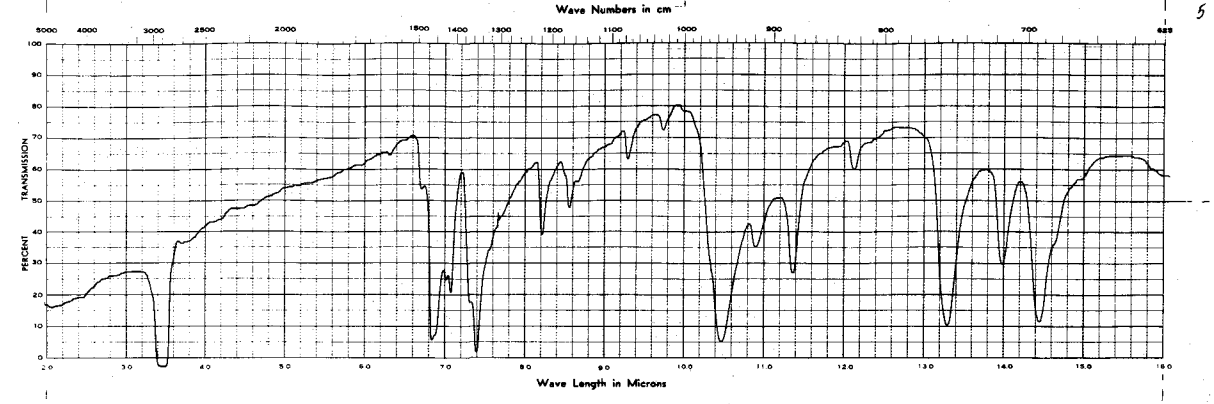
NO. 1939	
DATE 3-10-52	INDEX Hedges
SAMPLE Benzylether of B1 Vol III P 66 	
FROM G. Lucas	
SAMP. CELL= MM	CMS.
REF. CELL MM	CMS.
CHEM. MG.	MG.
SOLV. Nujol mull	
VOL. C.C. %	C.C. %
F.S. SOLID C. GAS	MM

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.



No. 1603	
DATE 11-14-51	INDEX Hedges
SAMPLE Tetra chloro Quinol Dibenzyl ether	
From G. Lucas	
Samp. Cell = mm.	cms.
Comp. Cell = mm.	cms.
Chem. mg.	mg.
Solv. Nujol mull	
Vol. c.c. %	c.c. %
F.S.; Solid	C. Gas mm

BAIRD ASSOCIATES
I. R. SPECTROPHOTOMETER
Na. CL. Prism



considered was the possibility that the ether function was cleaved and that an original cyano alkyl function was removed and replaced by a benzyl group.

Accordingly a small amount of tetrachlorohydroquinone mono(3-cyano-3-pentyl) ether was refluxed with dilute sodium hydroxide and benzyl chloride for three hours. The solution was cooled and extracted with diethyl ether. The ether solution was dried over sodium sulfate and the ether evaporated. The white solid was recrystallized from 95 per cent ethanol and melted at 230-250°. An admixture with tetrachlorohydroquinone dibenzyl ether showed a melting point depression. Therefore since the diethylacetonitrile group was not displaced by a benzyl group, it was concluded that no displacement occurred during the preparation of the dibenzyl ether from the monobenzyl ether.

Decomposition of azo-bis-toluene in the presence of chloranil in toluene

A 2.46 g. (0.014 moles) sample of chloranil and 0.21 g. (0.001 moles) of impure azo-bis-toluene were dissolved in 500 ml. of toluene and heated at reflux for 48 hours. After cooling, the solution was extracted with 10 per cent sodium hydroxide solution until the extracts were clear. Acidification of the aqueous extract with dilute sulfuric acid gave 0.29 g. (0.0009 moles) of solid which after

recrystallization from glacial acetic acid melted at 139-140°. A mixed melting point with the phenolic product derived from the reaction of azo-bis-diethylacetonitrile with chloranil in toluene gave no depression. The infra-red absorption spectra of both samples were identical. This established the identity of the compound as tetrachlorohydroquinone monobenzyl ether.

The organic residue from the extraction was steam distilled but no product was isolated from the distillate other than chloranil. The residue from the steam distillation consisted of reddish charred material from which no identifiable compound cound be isolated. Although the amount of tetrachlorohydroquinone monobenzyl ether obtained could probably account for all of the azo-bis-toluene introduced, the possibility of rearrangement of the azo-bis-toluene to benzal benzylhydrazone should be considered. Some or even a majority of the mono benzyl ether could be derived by chain transfer with solvent.

Decomposition of azo-bis-toluene in the presence of chloranil using as solvents both cumene and tetralin also gave tetrachlorohydroquinone monobenzyl ether, identical in all respects with that previously obtained.

Iodometric determinations of peroxides

Method 1

To a weighed amount of the peroxide (approx. 0.5 g.) in a stoppered erlenmeyer flask was added 25 ml. of glacial acetic acid and the flask flushed with carbon dioxide by adding a few small pieces of dry ice. The entire operation was carried out under an atmosphere of carbon dioxide. Two grams of potassium iodide, dissolved in 25 ml. of distilled water, and then 10 ml. of 32 per cent hydrochloric acid was added with swirling. The solution was then titrated to near the end point with 0.1 normal sodium thiosulfate. When the red color became faint the solution was diluted three to four times with distilled water as a high acid concentration obscured the end point. Starch indicator was added and the titration continued to the disappearance of the characteristic blue color.

This titration was applicable to cumene hydroperoxide.

Method 2[88]

The sample dissolved in glacial acetic acid was mixed in an inert atmosphere with an equal volume of constant boiling, aqueous hydrogen iodide (c.p. 56 per cent). The

---

[88]Dickey, Raley, Rust, Treser and Vaughn, Ind. Eng. Chem., 41, 1637 (1949).

container was closed, the mixture heated at 60° for 45 minutes and the liberated iodine titrated with standard thiosulfate after dilution with oxygen free water.

This determination was applicable to di-t-butyl peroxide and triphenylmethyl-t-butyl peroxide.

Determination of acetone

These determinations were made using a variation of the method of Siggia[89]. A volume of the test solution was pipetted into 50 ml. of a hydroxylamine hydrochloride solution (35 g. of hydroxylamine hydrochloride dissolved in 160 ml. of distilled water and diluted to one liter with 95 per cent ethanol). The liberated hydrochloric acid was then titrated potentiometrically with either 0.2 or 0.5 normal sodium hydroxide, depending upon the amount of acetone in the sample. The precision of the determinations, evaluated by synthetic mixtures, was ± 5 per cent.

For those samples which contained both acetone and acetophenone the total ketone and acetone contents were determined in separate samples. For the latter the sample was pipetted into a special distilling flask equipped with a long right angle side arm containing a condenser in the

---

[89]Siggia, "Quantitative Organic Analysis via Functional Groups", John Wiley and Sons, Inc., New York, 1949, p. 17.

vertical portion. Ten ml. of benzene (Baker and Adamson, thiophene free, reagent grade) was added as a carrier. The acetone and benzene were then distilled over a water bath into 50 ml. of hydroxylamine hydrochloride solution. This solution was titrated potentiometrically as above.

Determination of hydroxylic components

Methyl lithium[90], dissolved in di-n-butyl ether, was first equilibrated in a flask, equipped with a magnetic stirrer and connected to a gas buret, until the volume of gas no longer varied (2-3 hours). After equilibration, 1 or 2 ml. of sample was injected through a rubber nipple on the flask by means of a hypodermic syringe. The solution was stirred and the volume measured after variation caused by the heat of reaction had ceased. A blank of 0.87 ml. caused by introduction of one ml. of liquid was subtracted from each run. The precision was ± 10 per cent.

Decomposition of tertiary alkyl peroxides

Di-t-butyl peroxide was weighed on an analytical balance in a fifty ml. volumetric flask (approx. 20 millimoles per 50 ml.). The solution was diluted to the mark with cumene.

---

[90]Gilman, Zoellner and Selby, J. Am. Chem. Soc., 55, 1252 (1933).

Triphenylmethyl-t-butyl peroxide (20 millimoles per 50 ml.) was treated in the same manner.

Mixtures of triphenylmethyl-t-butyl and di-t-butyl peroxide (approx. 20 millimoles each per 50 ml.) were prepared in the same fashion.

Mixtures of di-t-butyl peroxide and di- α-cumyl peroxide were prepared by dissolving approximately 20 millimoles of di-t-butyl peroxide per 50 ml. and enough di- α-cumyl peroxide to insure that the concentration of t-butoxy and α-cumyloxy radicals during the major portion of the run would be approximately the same. The required concentrations were calculated from the observed first order rate constants[82,85].

$$\text{(di-}\alpha\text{-cumyl peroxide)} = \frac{k_B}{k_C}\ \text{(di-t-butyl peroxide)}$$

$$= \frac{20}{280}$$

$$= 0.072 \times 10^{-3} \text{ moles of di-}\alpha\text{-cumyl peroxide per 20 millimoles of di-t-butyl peroxide.}$$

Samples of di- α-cumyl peroxide were determined containing 0.072×10^{-3} moles of peroxide per 50 ml. solution.

The peroxide sample to be decomposed was pipetted from the volumetric flask into round bottomed, long-necked flask with a constriction in the neck. The flask was chilled in

an ice bath and evacuated with a Cenco Hivac vacuum pump. The flask was sealed at the constriction while still under vacuum and allowed to warm to room temperature. The flask was then immersed in a thermostated oil bath (172.5° ± 0.2) for a period of time calculated to give greater than 99 per cent decomposition*. The flasks were taken from the bath, allowed to cool to room temperature and opened and immediately determined for ketone and alcohol content by the previously mentioned methods. The data from the decompositions are tabulated in Tables 12, 13 and 14.

From the residues after the decompositions were isolated a white crystalline solid which readily sublimed melting point 117-118°. This was presumed to be bi- α -cumyl.

The decompositions of triphenylmethyl t-butyl peroxide always gave a yellow colored solution. From the residue was isolated, besides bi- α -cumyl, an impure white solid, melting at 164-166°. It did have an infra-red spectrum similar to that of triphenylmethyl alcohol and is believed to be benzpinacol diphenyl ether.

---

*It was assumed that triphenylmethyl-t-butyl peroxide had a first order rate constant of the same order of magnitude as di-t-butyl peroxide. No peroxide could be detected iodometrically after decomposition.

Table 12

Products of Decomposition of Peroxides

Run no.	Peroxide	Moles[a] x 10^3	Moles ketone x 10^3	Moles alcohol x 10^3	Moles product x 10^3
1	di-t-Butyl	20.47	7.25	31.25	38.5
2	di-t-Butyl	24.00	8.10	--	--
3	Triphenylmethyl-t-butyl	16.80	3.19	30.0	33.2
4	di- α -Cumyl	0.148	0.247	--	--

[a]All per 50 ml. solution in cumene.

Table 13

Products of Decomposition of Peroxide Mixtures

Run no.		Moles[a] x 10^3	Peroxide	Moles[a] x 10^3	Moles ketone x 10^3	Moles alcohol x 10^3	Total moles x 10^3
5	di-t-Butyl	22.42	Triphenyl-methyl-t-butyl	20.05	15.20	59.09	74.29
6	di-t-Butyl	25.59	Triphenyl-methyl-t-butyl	5.343	11.58	46.52	58.10
7	di-t-Butyl	24.91	di- α -Cumyl	0.0819	10.30[b]	43.75	54.05
8	di-t-Butyl	28.15	di- α -Cumyl	0.0912	9.96[c]	48.8	58.76
9	di-t-Butyl	24.3	di- α -Cumyl	0.0990	10.58[b]		

[a]All per 50 ml. solution in cumene.

[b]Total ketone titrated.

[c]Acetone only titrated.

Table 14

Product Comparison from Peroxide Decomposition

Run no.	Moles[a] t-butyl	Moles[a] other	Moles[a] ketone	Moles[a] alcohol	Per cent ketone	Per cent alcohol
1	40.94	--	7.25	31.25	17.7	74.5
2	48.00	--	8.10	--	16.9	--
3	16.80	16.80	3.19	30.0	19.0[d]	89.5
4	--	0.296	0.24	--	81.	--
5	64.89	20.05	15.20	59.09	23.4[d]	69.5
6	56.52	5.343	11.58	46.52	20.3[d]	75.0
7	49.82	0.0819	10.30[b]	43.75	20.7	87.5
8	56.30	0.0912	9.96[c]	48.8	17.8	87.0
9	48.60	0.0990	10.58[b]	--	21.8	--

[a]All x 10^3.

[b]Total ketone in sample.

[c]Only acetone.

[d]Computed only on the basis of t-butoxy radicals.

DISCUSSION

As shown in Tables 10 and 11 the radicals produced by the fragmentation of both aliphatic azo-nitriles studied (azo-bis-diethylacetonitrile and azo-bis-dimethylacetonitrile) gave no evidence for attack upon solvent, in the absence of chloranil, insofar as this attack could be recognized via product analysis. The information gained from the infra-red spectrum of the crude dinitrile formed in the reaction shows that any attack upon solvent certainly accounts for less than 5 per cent of the total reaction. However, in the presence of chloranil 7.6×10^{-2} moles of radicals (3.8×10^{-2} moles of starting material) produced a product equivalent to 4.8×10^{-3} moles of toluene attacked, or one out of every 16 radicals produced attacked solvent. If this reaction had proceeded in the absence of chloranil then the expected products, dibenzyl or 2-ethyl-2-cyano-1-phenylpropane or 2-methyl-2-cyano-1-phenylpropane, could have been quite easily characterized either by actual isolation or by the detection of a strong infra-red absorption ban at 13.2 μ. in the product formed. Since no evidence for the presence of a product, derivable from solvent could be obtained without the presence of chloranil,

it must be concluded that the presence of this is requisite for attack upon solvent to occur in these systems.

In Table 16 is given the fractional recovery of the products obtained in the various reactions. Table 15 gives the percentage of pertinent radicals needed to produce these products. In Run 1 and 4 of these tables the 73 per cent recovery of radicals represents that amount of azonitrile which dimerized. The other 22 per cent probably disappeared, for the most part, by disproportionation.

$$2\ (CH_3CH_2)_2\dot{C}CN \longrightarrow CH_3CH = C(CN)CH_2CH_3 + (CH_3CH_2)\ CHCN$$

If the attack upon toluene by dialkylmethyl radicals was just below the level of detectability then choosing as a solvent a compound such as tetralin, which would produce a radical seemingly more resonance stabilized one should then be able to recognize attack upon this solvent by a decreased yield of dinitrile or by the formation of products derived from that solvent. Tetralin should be far more effective than toluene since Gregg and Mayo found ethylbenzene to have a chain transfer constant six times that of toluene. But, as is shown in Table 10 the yield of dinitrile is in no wise diminished over the case of toluene nor was any evidence for the formation of naphthalene or

Table 15

Material Balance of Products Obtained from the Decomposition of Azo-bis-nitriles[a]

Run	Solvent	$R_2\dot{C}CN$	H·	$C_6H_5CH_2$·
1.	Pure toluene[b]	0.73	--	--
2.	Inh. toluene[b,d]	0.77	0.08	0.08
3.	Inh. chlorobenzene[b,d]	0.88	0.06	--
4.	Pure tetralin[b]	0.73	--	--
5.	Pure toluene[c]	0.86	--	--
6.	Inh. toluene[c,d]	0.69	0.04	0.02
7.	Inh. chlorobenzene[c,d]	0.775	0.03	--

[a]Based on one mole of dialkylcyanomethyl radicals consumed.

[b]Azo-bis-diethylacetonitrile.

[c]Azo-bis-dimethylacetonitrile.

[d]Inh. = Equimolar in chloranil.

Table 16

Material Balance in Azo-bis-nitriles Decomposition

Run	RR	ROC_6Cl_4OH	ROC_6Cl_4OR	$C_6H_5OC_6Cl_4OH$
2	0.31	--	0.453	0.08
3	0.37	0.063	0.447	--
6	0.385	0.019	0.287	0.017
7	0.46	0.025	0.27	--

bitetralyl obtained*. Thus, attack which may occur upon solvent is negligible in these cases.

The fact that no attack upon tetralin was detected also precludes the mechanism

$$R_2\dot{C}CN + C_6H_5CH_3 \longrightarrow R_2CHCN + C_6H_5\dot{C}H_2$$

$$C_6H_5\dot{C}H_2 + RCH_2C(R)CN \longrightarrow C_6H_5CH_3 + RCH = C(R)CN$$

*Dr. Cohen and Mr. Hamilton of these laboratories, have obtained evidence that azo-bis-dimethylacetonitrile catalyzes the oxidation of tetralin by oxygen. However, here the mechanism is probably;

$$R_2\dot{C}CN + O_2 \longrightarrow R_2C(CN)OO\cdot$$

$$R_2C(CN)OO\cdot + RH \longrightarrow R_2C(CN)OOH + R\cdot$$

occurring in toluene, where the latter step is the only manner in which benzyl radicals are destroyed. For, if tetralin were attacked in the same manner then the tetralyl radical should definitely prefer to disproportionate. Since no disproportionation products from tetralin were isolated, the mechanism can be dismissed as unimportant.

In Run 2, Table 15, all of the hydrogen atoms arising in the products must be considered as derived from toluene. In this case only 77 per cent of the original fragments are accounted for. Since this is not too different from the 73 per cent obtained in pure toluene, the rest of the starting material is probably accounted for as disproportionation products. In Run 6, however, 2 per cent of the hydrogen atoms should have arisen from disproportionation of the semiquinone radicals with dialkylcyanomethyl radicals.

$$ROC_6Cl_4O\cdot + (CH_3CH_2)_2\dot{C}CN \longrightarrow ROC_6Cl_4OH + CH_3CH = C(CN)CH_2CH_3$$

Here 71 per cent of the original fragments are accounted for, not too different from the case of pure toluene. In Run 3, 94 per cent and Run 7, 81 per cent of the fragments are obtained.

Disproportionation is undoubtedly a higher energy path than is dimerization with attack by a radical, R, upon chloranil being of an intermediate energy. In any discussion

on the relative extent of dimerization and disproportionation, the following must be considered. Any reaction which involves a relative high activation energy, i.e., reaction with chloranil would preferentially destroy those radicals with higher thermal energies. With no other factors considered the result of this reaction would be to displace the energy distribution curve for the system to lower energies. The resulting radicals, being of lower energies would be more prone to dimerize than disproportionate giving an increase in the yield of dimerization products in the system. However it is more likely that the resulting radicals, by virtue of the enormous number of collisions they undergo, would soon redistribute their energy far faster then it is depleted. In other words, equipartition of energy probably occurs so rapidly that the distribution curve is essentially unaffected. There would, then, be the same fraction of high energy radicals in the later stages of the reactions as in the earlier and the relative yields of disproportionation and dimerization would be unaffected by the reaction with chloranil. However, the presence of chloranil might influence the disproportionation to dimerization ratio because of the disproportionation of the semiquinone radical itself once it is formed. The semiquinone radical will abstract hydrogen atoms from toluene, a reaction that is

unimportant with the dialkylcyano methyl radicals, and may prefer to disproportionate with a dialkylcyanomethyl radical rather than add to the latter. In the former case a C-H bond is broken and an O-H bond formed, and one C = C double bond is formed from a C-C single bond, a net gain of 64 kcal/per mole. In the latter case a C-O bond is formed with a net gain of 70 kcal/mole. Since the energetics are nearly similar and since the frequency of collisions with the proper stereochemistry for disproportionation will be relatively great, disproportionation should be favored. In this case the yield of dimer should be decreased by the preferred disproportionation reaction with chloranil.

Although, at present, there is some question as to whether dimerization requires an activation energy, there is no question about its being a much lower energy path than disproportionation. Why, then, do such large yields of disproportionation products obtain? It can be explained adequately by considering the stereochemistry of the approach of two radicals. In order to dimerize, two radicals must approach "head on". This means that only a small fraction of actual collisions will result in dimerization. However for species such as the dialkylcyanomethyl radicals, each with two alpha methylene or methyl carbons, there is eight-

fold statistical chance that the proper stereochemistry of approach will favor disproportionation over dimerization. However this latter path involves an appreciable activation energy such that only a small fraction of those collisions of the proper configuration will result in reaction. Since the number of collisions between two vicinal species in solution is very high (ca. 10^{12} -10^{14} per sec.) it is not surprising that dimerization is the predominate reaction.

As mentioned before, disproportionation with a semiquinone radical may require far less activation energy than symmetrical disproportionation. This would account for any increase in total disproportionation products in those systems containing chloranil. At this point it will simply be stated that most of the semiquinone radicals disproportionate rather than add*. Little can be said, without

---

*The reaction

$$ROC_6Cl_4O\cdot + (CH_3CH_2)_2C(CN)N = NC(CN)(CH_2CH_3)_2 \longrightarrow CH_3\dot{C}H\ C(CN)(CH_2CH_3)\text{-}N{=}N\text{-}C(CN)(CH_2CH_3)_2 + ROC_6Cl_4OH$$

$$CH_3\dot{C}HC(CN)(CH_2CH_3)N{=}N\text{-}C(CN)(CH_2CH_3)_2 \longrightarrow CH_3CH{=}C(CN)(CH_2CH_3) + R_2\dot{C}CN + N_2$$

cannot be distinguished from the reaction

further investigation, as to the effect of various systems upon the ratio. Certainly this ratio and its variation is of prime importance in understanding the reactions of free radicals in solution and is deserving of more study than it has received.

At present, however, of more importance is the apparent anomaly of the nature of the products formed by the simple addition of chloranil to the system. In all likelihood the undecomposed azo nitril should be a very poor hydrogen donor source.

The large yield of tetrachlorohydroquinone monobenzyl ether in those systems containing chloranil and toluene, although at first surprising is quite easy of rationalization. A disproportionation reaction between toluene and chloranil, independent of the azo-bis-nitrile, can be immediately ruled out. No reaction occurs between toluene and chloranil over any reasonable period of time*. Two

---

$RO\cdots H\cdots C(R')C(R'')(CN)N{=}N\text{-}R''' \rightarrow ROH + RC'{=}C(R'')(CN) + N_2 + R.'''$

and probably can be immediately ruled out since Lewis and Matheson[44] found chloranil had no effect on the rate of formation of nitrogen as this would require.

*Private communication from Dr. G. S. Hammond.

chain initiating steps, both of which are probably operative, can be proposed

2a.** $R\cdot + CH_3C_6H_5 \longrightarrow RH + \cdot CH_2C_6H_5$

2e. $ROC_6Cl_4O\cdot + CH_3C_6H_5 \longrightarrow ROC_6Cl_4OH + \cdot CH_2C_6H_5$

where R· is a dialkylcyanomethyl radical. The chain propagating step is exactly analogous to 2e. but where R· is now a benzyl radical. The kinetic chain length of the reaction need only be moderately long to produce recognizable amounts of monobenzyl ether.

It may seem puzzling, at first, that the radicals R· will attack certain molecules, forming intermediates sufficiently active to attack those molecules towards which R· itself is inert. But a consideration of the energy paths involved lends a ready explanation. The activation energy for the reaction 2a. probably represents a high barrier even though the products are somewhat more stable than the reactants (the resonance of the benzyl radical is approximately 24.5 kcal/mole[91]) since a carbon-hydrogen bond must be broken. The activation energy for this path is high enough so that only a microscopic fraction of the

---

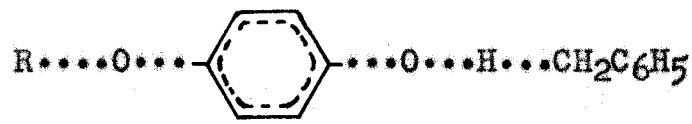
**Numbering refers to scheme used on page 103.

[91] Szwarc, Disc. Faraday Soc., 2, 39 (1947).

dialkylcyanomethyl radicals follow it. However the reaction

$$2b.\quad R\cdot + OC_6Cl_4O \longrightarrow ROC_6Cl_4O\cdot$$

probably involves a far smaller activation energy than 2a. even though the product may have approximately the same, or even less, stability than the reactants. The follow-up reaction, 2e, is quite rapid and although the activation energy is appreciable, it is not as great as that represented by 2a. In this latter case, 2b, a carbon-hydrogen bond (87.3 kcal/mole) is broken and oxygen-hydrogen bond (110.2 kcal/mole)[92] formed. Therefore the products are far more stable than the reactants. Since toluene is in extreme excess, as solvent, then the rate of reaction 2e should be independent of this reactant. Further stabilization of the transition state, and consequent decrease in the overall activation energy for the reaction, can be obtained by considering a simultaneous reaction of the type



In essence this is a termolecular radical reaction and although, in this case, it appears to be a feasible path energetically there is no kinetic evidence to support it.

---

[92] Pauling, The Nature of the Chemical Bond, p. 53, Cornell Univ. Press, Ithaca, New York 2nd Ed. 1948.

There would need be some method of following the yield of tetrachlorohydroquinone monobenzyl ether as a function of toluene concentration to establish its validity. However, as an assumption it seems logical particularly where the third body required is in such excess.

This type of secondary radical reaction appearing only in the presence of a third body, although unusual, is not unique. There have been discovered two similar reactions recently, both involving aliphatic azo-compounds. Bickel and Kooijman[93] have found that azo-bis-1-phenyl ethane heated in inert solvents, quantitatively evolves nitrogen and forms racemic and meso 2,3-diphenyl butane. No other products are formed. Apparently these radicals do not disproportionate. However, in the presence of 1-mercaptooctane, only 58 per cent of the total nitrogen is evolved, the rest being incorporated in a disproportionation product, bis-methylphenyl ketazine. Ethylbenzene is also formed in an equal amount. The rest of the radicals are accounted for in the above mentioned dl and meso 2,3-di-phenylbutane. Apparently the mercaptan has the power to disproportionate the radicals, a power they do not have themselves. These same authors found that this same azo compound will not

---

[93]Bickel and Kooijman, Nature, 170, 211 (1952).

dehydrogenate 9,10-dihydroanthracene but that with a 2 molar concentration of 1-mercaptooctane per mole of azo-bis-1-phenylethane and 9,10-dihydroanthracene, 10,10-dihydro-9,9'-bianthracyl was formed.

Harris and Waters[94] found that 2-azo-bis-methyl isobutyrate was a very poor radical source for decarbonylating aldehydes. The maximum yield of carbon monoxide was never greater than 5 per cent. The mechanism whereby this 5 per cent arose is

$$A\text{-}N{=}N\text{-}A \longrightarrow 2A\cdot + N_2$$
$$A\cdot + RCHO \longrightarrow AH + R\dot{C}O$$
$$R\dot{C}O \longrightarrow R\cdot + CO$$
$$R\cdot + RCHO \longrightarrow RH + R\dot{C}O$$

However with 0.5 mole per cent of mercaptan per mole of azo-ester and aldehyde, the reaction went quite readily with between 80-90 per cent of the theoretical amount of carbon monoxide evolved. The mechanism was given as follows:

$$A\cdot + RSH \longrightarrow AH + RS\cdot$$
$$RS\cdot + RCHO \longrightarrow RSH + R\dot{C}O$$

---

[94]Harris and Waters, ibid., 170, 211 (1952).

In all three cases the presence of a mercaptan was required to promote attack upon a carbon-hydrogen bond. It seems quite likely that the generalized scheme was

$$\text{a.} \quad A\cdot + RSH \longrightarrow AH + RS\cdot$$

$$\text{b.} \quad RS\cdot + R'H \longrightarrow RSH + R'\cdot$$

Reaction a. is well known to go readily but the seeming facility of reaction b. is surprising. Mathematical addition of reactions a. and b. gives a total reaction

$$\text{c.} \quad A\cdot + RH \longrightarrow R\cdot + AH$$

Thus RSH was acting as a true catalyst. Since c. was the net reaction, all thermodynamic functions of the reaction were dependent upon only A, RH, R and AH. In this respect these reactions differ from the reaction previously considered in this thesis where chloranil did not function as a catalyst but was consumed in the reaction*. However, since the thermodynamics were unaffected in the reaction in the presence of mercaptan, the explanation must be sought elsewhere. The most likely consideration, is again in the

---

*Although not detailed by either Waters or Kooijman, there is the strong indication that some mercaptan was consumed in the reactions. The probable reaction product of consumption would be the disulfide, RSSR, formed by the union of two mercaptyl radicals.

activation energy required for the reaction c. as compared with the two reactions a. and b. Simply stated, the species in the two latter reactions need to surmount a far lower energy barrier than the single former reaction. This in essence is the explanation that both Waters and Kooijman gave, but they gave no reason for the total lower activation energy other than to state that activation energies of reaction between carbon compounds seemingly cannot be extended to reaction of hetero atoms.

Although the strength of the sulfur-hydrogen bond is almost the same as the carbon-hydrogen bond (ca. 87 kcal/mole)[92], the facile polarization of the valence electrons of sulfur certainly should be the determining factor in the case of reaction a. and may well be of the highest importance in decreasing the activation energy of b. below that activation energy required for a carbon radical to abstract hydrogen from another carbon.

Although the large amounts of tetrachlorohydroquinone monobenzyl ether can be accounted for, the usual scheme for radical reactions as outlined below leaves some experimental facts of this reaction unexplained.

1. $\left[R_2C(CN)N\right]_2 \longrightarrow 2R_2\dot{C}CN + N_2$

2a. $R_2\dot{C}CN + C_6H_5CH_3 \longrightarrow R_2CHCN + C_6H_5CH_2\cdot$

2b. $R_2\dot{C}CN + C_6Cl_4O_2 \longrightarrow R_2C(CN)OC_6Cl_4O\cdot$

2c. $R_2\dot{C}CN + C_6Cl_4O_2 + C_6H_5CH_3 \longrightarrow R_2C(CN)OC_6Cl_4OH + C_6H_5CH_2\cdot$

2d. $C_6H_5\dot{C}H_2 + C_6Cl_4O_2 + C_6H_5CH_3 \longrightarrow C_6H_5CH_2OC_6Cl_4OH + C_6H_5CH_2\cdot$

2e. $R_2C(CN)OC_6Cl_4O\cdot + C_6H_5CH_3 \longrightarrow R_2C(CN)OC_6Cl_4OH + C_6H_5CH_2\cdot$

3a. $2R_2\dot{C}CN \longrightarrow R_2C(CN)_2$

3b. $R_2C(CN)OC_6Cl_4O\cdot + R_2\dot{C}(CN) \longrightarrow R_2C(CN)OC_6Cl_4OC(CN)R_2$

3c. $R_2\dot{C}CN + C_6H_5\dot{C}H_2 \longrightarrow R_2C(CN)CH_2C_6H_5$

3d. $2C_6H_5\dot{C}H_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5$

3e. $R_2C(CN)OC_6Cl_4O\cdot + \dot{C}H_2C_6H_5 \longrightarrow R_2C(CN)OC_6Cl_4O\ CH_2C_6H_5$

Reaction 1. is the initiation step, reactions 2a.-d. are chain propagation steps and reactions 3a.-e. are chain termination steps. Reactions 2c. and d. represent the termolecular formation of mono ethers discussed previously. However if reaction 2b. is dismissed as an actual course of the reaction, then there can be no formation of diether via step 3b. Nevertheless, the yield of diether is quite large in both systems studied. If 2b. is included then a consider-

able proportion of the radicals produced must be inert towards toluene, with which they undergo frequent collisions before finally colliding with a dialkylcyanomethyl radical. Thus a paradox is presented: from the exclusive formation of tetrachlorohydroquinone monobenxyl ether the radical $ROC_6Cl_4O\cdot$ seems to be an extremely reactive species while the evidence of high yields of $R_2C(CN)OC_6Cl_4OC(CN)R_2$ indicate that a very similar radical is rather inert. The first seeming explanation, that the radical $R_2C(CN)O\ C_6Cl_4O\cdot$ is inert whereas the radical $C_6H_5CH_2OC_6Cl_4O\cdot$ is a reactive species, is certainly unattractive since no resonance stabilization can be ascribed to the former that is not possible in the latter. There is certainly no steric difference at the site of the greatest density of the odd electron and the presence status of electronic theory gives no hint of a stabilization of a further sort. It seems quite easy then to dismiss any extreme difference in the reactivity of these two radicals. The explanation must be sought elsewhere.

It is equally difficult to explain both the high yields of tetra-alkylsuccinonitrile and the absence of formation of 2-cyano-2-dialkyl ethylbenzenes. The dialkylcyanomethyl radicals, although inert towards toluene, do attack chloranil in good yield, but in all cases, even in chlorobenzene,

the yield of mono ether is quite low or non-existent. It is hard to reconcile the apparent selectivity of these radicals. They either remain in solution and dimerize or, if they do attack chloranil, they seem to attack it in pairs. In fact, all evidence indicates that a substantial amount of the reaction proceeds via pairs of dialkylcyanomethyl radicals.

The reaction of pairs of radicals should not be dismissed lightly since these radicals are formed as pairs in the initial reaction

$$1.\quad RN{=}NR \longrightarrow 2R\cdot + N_2 \quad .$$

It seems that, since they may spend a fair proportion of their life-time in close proximity, they have a high probability of reacting before they separate. Rabinowitsch[95] calculated that vicinal particles in solution undergo at least 5×10^{12} collisions with each other before diffusing apart. Thus it is nighly likely that, with this large number of collisions, a significant percentage of these collisions should result in reaction. If this is interpreted in terms of the decomposition of azo-bis-nitriles, it means that a substantial quantity of tetraalkylsuccinonitrile and disproportionation products is formed from

---

[95]Rabinowitsch, Trans. Faraday Soc., 33, 1225 (1937).

radicals arising from the same molecule. In the same manner, the high yields of tertachlorohydroquinone di(2-cyano-2-propyl) and di(3-cyano-3-pentyl) ethers are rationalized by considering simultaneous attacks of two radical fragments derived from the same molecule, upon a chloranil molecule. These two reactions can be represented schematically by

$$1b.\quad RN{=}NR \longrightarrow \overline{R\cdot \quad R\cdot} + N_2$$

$$4a.\quad \overline{R\cdot \quad R\cdot} \longrightarrow RR$$

$$4b.\quad \overline{R\cdot \quad R\cdot} + C_6Cl_4O_2 \longrightarrow ROC_6Cl_4OR$$

where $\overline{R\cdot \quad R\cdot}$ represents two radicals, produced from the scission of the same molecule, "trapped" in the solvent cage, i.e., they react as a unit. There is the further possibility of escape from the cage,

$$5.\quad \overline{R\cdot \quad R\cdot} \longrightarrow 2R\cdot$$

which is a representative way of saying that the "caged" radicals diffuse apart and subsequently their eactions are those of "free" radicals. Once they have diffused apart they may then undergo any of the reactions 2-3.

There is the possibility that the recombination of radicals outside of the cage is a diffusion controlled reaction. If this were so it would require that the activation energy for recombination be very low (less than 4

kcal/mole) so that approximately every collision of radicals results in reaction. With any appreciable activation energy, then only a small fraction of collisions result in reaction.

Rabinowitsch[95] has derived the general expression for a bimolecular reaction in solution

$$\text{rate} = \frac{n\, e^{-E/RT}}{1 + \frac{a^2 \nu}{D_1 + D_2}\, e^{-E/RT}} \qquad (1)$$

where n is the coordination number (12 for closely packed spheres), ν the frequency of oscillation (app. 10^{12} sec.$^{-1}$), a the lattice constant (app. 10 Å), D_1 and D_2 the diffusion constants of the two reacting species, and E is the activation energy. In the case where E is quite large the rate of diffusion is negligible and the equation reduces to the Arrhenius equation

$$\text{rate} = Ae^{-E/RT} \quad . \qquad (2)$$

However if E is quite small then the equation reduces to

$$\text{rate} = \frac{n\,(D_1 + D_2)}{a^2} \qquad (3)$$

and the reaction is diffusion controlled.

Mayo[96] states that the rate of diffusion of small molecules in ordinary solvents is of the order of 10^{-5} cm.^{2}/sec. If equation (3) is applied to the dimethylcyanomethyl radicals, where $D_1 = D_2$, then the rate of combination, if diffusion controlled, is

$$k_t \sim 2 \times 10^{11} \text{ sec.}^{-1} \quad .$$

Although it is kinetically impossible to distinguish an operative cage effect, there is one excellent experimental means by which it can be studied. This is by the use of "scavengers". The term scavengers is herein applied to describe radical destroyers used in systems where no chain decomposition occurs. Chloranil is a scavenger when used in the decomposition of azo-bis-nitriles, but not when used in polymerization reactions. Iodine is an excellent scavenger in the decomposition of benzoyl peroxide for it destroys all benzoate radicals by the reactions[97].

$$(C_6H_5COO)_2 \longrightarrow 2\ \overline{C_6H_5COO}$$

---

[96] Walling, Briggs and Mayo, J. Am. Chem. Soc., 68, 1145 (1946).

[97] Hammond, J. Am. Chem. Soc., 72, 3737 (1950); Hammond and Soffer, ibid., 72, , (1950).

$$2\ \overline{C_6H_5COO} + I_2 \longrightarrow 2\ C_6H_5COOI$$

$$C_6H_5COOI \longrightarrow C_6H_5I + CO_2$$

By the proper choice of scavengers, it should be possible to study the cage effect. A scavenger needs be found which will not react readily with radicals which have a preferential low energy path, i.e., recombination in the cage, but will react with those radicals which do not have such a low energy path, i.e., radicals which have diffused outside of the cage. This would require a competition for radicals between scavenger and radical. If the activation energy for reaction with scavenger is sufficiently high then the predominate reaction will be combination of the radicals. The nature of the scavenger, chloranil, is somewhat different since the radicals may simultaneously react with chloranil. Better scavengers with which this reaction cannot occur are mercaptans. They compete unsuccessfully in the cage for radicals but elsewhere compete successfully*.

---

*Dr. Sen, of these laboratories, has found a limiting value in the yield of tetramethyl succinonitrile when azo-bis-dimethyl acetonitrile is decomposed in various concentrations of n-butyl mercaptan. This yield is highly solvent dependent.

One reaction of interest has been followed. Bawn and Mellish[98] followed the rate of reaction of 2-azo-bis-isobutyronitrile with the stable, colored free radical N,N'-diphenylpicyrylhydrazyl $\left[(C_6H_5)_2\dot{N}NC_6H_2(NO_2)_3\right]$ by colorometric means. The results were essentially negative, insofar as the cage effect was concerned. The rate was first order in azo-nitrile with a rate constant, within experimental error, of that obtained by nitrogen evolution.

This work must not be taken as general evidence that a cage effect is not operative with azo-nitriles. Due to the requirements of the experiments these workers used rather high concentrations of hydrazyl and it is probably that this radical was effective scavenger, but probably not selective in its action. An explanatory mechanism would be

$$A \longrightarrow \overline{R\cdot \quad R\cdot} + N_2$$

$$\overline{R\cdot \quad R\cdot} + BN\cdot \longrightarrow BNR + R\cdot$$

where BN represents an N,N-diphenylpicyrylhydrazyl radical. It would be of interest to find the variation in the yield of succinonitrile with concentration of hydrazyl.

---

[98] Bawn and Mellish, Trans. Faraday Soc., 47, 1216 (1951).

Matheson[99], to explain a complex rate expression derived by Schulz and Blaschke[100] for the benzoyl peroxide initiated polymerization of styrene, made use of the cage effect. Schulz, in order to interpret his polymerization data, required the expression

$$\frac{dM}{dt} = \text{constant} \times c^{\frac{1}{2}} M \left[\frac{K(M)}{1 + K(M)} \right]^{\frac{1}{2}}$$

where C is initiator, M monomer and K an "equilibrium constant" for an activated complex which he believed to be important. Matheson proposed instead the mechanism

$(C_6H_5COO_2) \xrightarrow{k_1} 2\overline{C_6H_5COO\cdot}$	$k_1 (C_6H_5COO)_2$
$2\overline{C_6H_5COO\cdot} \xrightarrow{k_2} (C_6H_5COO)_2$ or X	$k_2 (C_6H_5COO\cdot)$
$C_6H_5COO\cdot + M \xrightarrow{k_3} P_1\cdot$	$k_3 (M)(C_6H_5COO\cdot)$
$P_r\cdot + M \xrightarrow{k_4} P_r + 1\cdot$	$k_4 (P_r)(M)$
$P_r\cdot + P_n\cdot \xrightarrow{k_5}$ inactive polymer	$k_5 (P_r)(P_n)$

where step 2 is recombination of radicals in the cage. The

---

[99]Matheson, J. Chem. Phys., 13, 584 (1945).

[100]Schulz and Blaschke, Zeit. physik. Chemie, B51, 75 (1942).

product, x, is some product which is incapable of redissociating into benzoate radicals. Metheson has definitely shown that such products are formed, but he has not established that peroxide is not formed. Using the steady state assumption he obtained the expression

$$\frac{dM}{dt} = \frac{k_4}{k_5^{\frac{1}{2}}} \; C^{\frac{1}{2}} \; M \left[\frac{k_1 \; (k_3/k_2) \; M}{1 + k_3/k_2 \; M} \right]^{\frac{1}{2}}$$

which agrees with the experimentally determined equation.

It is possible to reinterpret the data of Arnett[2,52] on the basis of the modified cage effect. He found that azo-bis-isobutyronitrile was not 100 per cent efficient in promoting vinyl polymerization (Table 4) despite the fact that the rate of initiation was independent of the monomer concentration. Against the monomer, methyl methacrylate, this initiator was only 50 per cent efficient. This author drew the inference that only one half of each initiator was capable of initiating polymerization and concluded that the actual initiating step was

$$RN{=}NR \longrightarrow R\cdot \; + \; RN{=}N\cdot$$

with only the latter radical capable of initiating polymerization.

$$RN{=}N\cdot \; + \; M \longrightarrow R_1\text{-} \; + \; N_2$$

Not only is it difficult to imagine an initial fragmentation of this sort but when the efficiency of this initiator was compared with various other monomers it varied from 50 to 100 per cent. This observation is definitely not in keeping with the proposed mechanism.

It seems more likely that there was a competing cage effect, destroying radicals before they could react with monomer. This hypothesis would account for the variation in efficiency from monomer to monomer if the monomer was involved in both the initiation and wastage reactions.

The caged radical would have a different rate of reaction towards each monomer and the faster the rate the more efficient the radical would be because of the greater ease of reaction. It is interesting to note that the monomer towards which the dimethylcyanomethyl radical was most efficient (ca. 100 per cent) was acrylonitrile. Since the molecular structure of acrylonitrile is closely similar to the structure of the initiator radical, the implication to be drawn is that the radical, in adding to a double bond, required the least activation energy when the olefin was most similar to itself. This is not in accord with the hypothesis of Walling and Mayo[101], who, from a

---

[101] Walling and Mayo, Disc. Faraday Soc., 2, 295 (1947).

series of copolymerization studies, stated that stabilization of the transition state, in the addition of a radical to an olefinic bond, may be gained by electron transfer between the two species. If a radical which is more stable as a carbonium ion adds to an olefin which is more stable as a carbanion relative to a radical, then such stabilization is important. The converse obviously is also true. Styryl radicals are "electron donor" radicals since the carbonium ions have more resonance stabilization than the radicals and dialkylcyanomethyl radicals are "electron acceptors" since the anion is relatively more stable. Equally the radicals derived from acrylonitrile and methyl methacrylate are electron acceptors. Thus, from the hypothesis of Walling and Mayo, dialkylcyanomethyl radicals should require less activation energy in adding to styrene than to the latter two monomers. However, in the work or Arnett, this monomer, styrene, falls intermediate between methyl methacrylate and acrylonitrile for efficiency of dialkylcyanomethyl radicals.

The theory of Walling and Mayo is probably inapplicable in this case because the transition state for the operative mechanism

$$A \longrightarrow \overline{2R\cdot}$$

$$\overline{2R\cdot} + M \longrightarrow RMR$$

$$\overline{2R\cdot} + M \longrightarrow R\cdot + R'\cdot$$

would probably gain no stabilization by electron transfer. If, in a transition state involving two dialkylcyanomethyl radicals and a styrene molecule, the styrene transferred an electron to each radical it would place two like charges upon adjacent atoms. The columbic repulsion would certainly cancel any advantage due to resonance. The radicals should add in the same manner, that a diradical adds to a double bond. Monomer must be involved in the wastage step as well as in the chain initiation step since Arnett found that the efficiency of the initiator was independent of the monomer concentration.

Edwards and Mayo[102] obtained evidence for the caged recombination radicals in the thermolysis of acetyl peroxide in carbon tetrachloride solutions. In carbon tetrachloride, the reaction was complex with the formation of methane, ethane, methyl chloride and carbon dioxide. All of the products could be rationalized on the basis of the

---

[102] Edwards and Mayo, J. Am. Chem. Soc., 72, 1265 (1950).

formation of free alkyl radicals after the initial cleavage

$$(CH_3COO)_2 \longrightarrow 2CH_3COO\cdot$$

$$CH_3COO\cdot \longrightarrow CH_3\cdot + CO_2$$

These workers measured the total methane evolution as a function of the initial acetyl peroxide-carbon tetrachloride concentration and found that, at infinite dilution of acetyl peroxide about 0.025 millimoles of methane per millimole of peroxide were formed. This minimum of methane presumably came from interaction of radical pairs before they diffuse apart.

In summary, it should be noted that the reaction of radicals with chloranil in the cage is a three body collision and, although only second order in reactants, is actually a termolecular reaction. In this case, two radicals react with an even molecule forming an even product.

The variation in the yield of acetone and t-butyl peroxide with the nature of R when the peroxides $(CH_3)_3COOR$ were decomposed in solution as found by Kharasch[85], Bell[84] and their co-workers can be interpreted either on the basis of a variety of distinguishable t-butoxy radicals in solution, as proposed by Kharasch, or on the basis of mutual influence of radicals upon each other. Although Kharasch gave little discussion of the variation of products with

the source of the radicals, he did intimate that this variation probably reflects variation in the energy distribution in the primary decomposition products. A necessary conclusion of this assumption is that the reactions of alkoxy radicals are faster than "deactivating collisions" with other species, so that equipartition of energy between radicals does not occur. His explanation implies that those peroxides which require lower activation energies to cleave will have, on the average, more energy residing in the fragments. These higher energy fragments will undergo the more energetic reaction, such as fragmentation of the type

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2C{=}O + CH_3$$

more readily than the lower energy radicals. Since the number of collisions between vicinal particles in solution is high (ca. 10^{12}-10^{14}), it would seem unlikely that "deactivating collisions" would not occur, and not give a Boltzman distribution of energy, regardless of the source, of the radicals before they react. However, this equipartition has not been established and the hypothesis cannot be discarded immediately.

A hypothesis which considers mutual influence of radicals will account for Kharasch's observations equally

well. At least one molecule of solvent must be intimately concerned in this reaction since Kharasch obtained dicumyl, when cumene was solvent, in an amount sufficient to account for all of the hydrogen abstraction. No products were ever isolated that would correspond to abstraction of other groups than hydrogen, nor was there ever evidence of direct attack of radical upon radical. Considering all this in the light of a concerted attack of two radicals upon solvent, the following mechanisms can be written:

1. $R_3COOCR_3' \longrightarrow \overline{R_3CO\cdot \; R_3'CO\cdot}$

2a. $\overline{R_3CO\cdot \; R_3'CO\cdot} + SH \longrightarrow R_3COH + \overline{R_3'CO\cdot} + S\cdot$

2b. $\overline{R_3CO\cdot \; R_3'CO\cdot} + SH \longrightarrow R_2CO + RH + \overline{R_3'CO} + S\cdot$

2c. $\overline{R_3'CO\cdot} + S\cdot + SH \longrightarrow R_3'COH + SS$

$R_2'C{=}O + R'H + SS$

3. $\overline{R_3CO\cdot \; R_3'CO} \longrightarrow R_3CO\cdot + R_3'CO\cdot$

4. $2R_3CO + SH \longrightarrow R_2CO + RH + \overline{R_3CO + S\cdot}$

$R_3COH + \overline{S\cdot + R_3CO\cdot}$

5. $R_3CO\cdot + SH \longrightarrow R_2CO + RH + S\cdot$

$R_3COH + S\cdot$

6a. $R_3CO\cdot \longrightarrow R_2CO + R\cdot$

6b. $R\cdot + SH \longrightarrow RH + S\cdot$

Reaction 4. is an example of a termolecular reaction occurring outside of the cage, i.e., between radicals which have become kinetically free. If the reaction is between $R_3CO\cdot$ and $R'_3CO\cdot$ then it cannot be distinguished from the caged reaction. Reactions 5. and 6. are the two possible bimolecular mechanisms with which the termolecular mechanism must be in competition.

If termolecular processes, in these reactions, are important then changing the nature of one of the radicals would certainly influence the yield of products. Ketone and alcohol cannot be formed exclusively by reactions such as 2a. and 2b., for then changing the nature of one of the radicals would influence both decomposition reactions equally, maintaining a constancy in the yield of products in different systems. It is quite difficult, at this point, to identify a termolecular process with the formation of one definite product. Far more work is necessary to discover which reaction is termolecular.

From the mechanism outlined above, it can be seen that there are three possibilities which would influence the yield of products:

1. The radicals may compete in the cage for solvent by either of the two paths outlined.

2. The caged radicals may diffuse apart and these uncaged radicals may then compete for solvent.

3. The radicals may react with solvent by bimolecular processes.

These three possibilities could be distinguished experimentally if any one is of predominate importance. Such an experimental approach was followed in this research. Consider the three peroxides: R_1OOR_1, R_2OOR_2 and R_1OOR_2; where each of the alkoxyl radicals $R_1O\cdot$ and $R_2O\cdot$ is capable of producing ketonic and alcoholic products. By maintaining constancy of temperature and solvent, the following procedure was employed:

a. R_1OOR_1 and R_2OOR_2 were decomposed in separate systems under the same conditions and the yield of products were determined.

b. Under the same conditions R_1OOR_2 was decomposed and the yield of products was determined.

c. A mixture of R_1OOR_1 and R_2OOR_2 was decomposed and the yield of products was determined*.

If a reaction of caged radicals was of predominate importance then the yield of products would be significantly

---

*The concentration of R_1OOR_1 and R_2OOR_2 taken was such that the rates of decomposition of both peroxides were equal, i.e., $k_1 \ [R_1OOR_1]_o = k_2 \ [R_2OOR_2]_o$.

different in the systems a. and b. but probably very little different between the systems a. and c. If a termolecular reaction was still of prime importance, but the cage effect was not, then the difference in yield of products between a.-c. and a.-b. would be significant. Little prediction could be made on the difference between b. and c. It may or may not be significant. If only bimolecular reactions are involved then there should be no difference between the yields of products in a., b. and c. unless the effect proposed by Kharasch was important. In this case a. and b. should have significant differences in yield whereas c. should be in no way different from a.

In Tables 12, 13 and 14 are given all the pertinent data for the various peroxide decompositions. Deviation between individual runs, of which these tables represent the average, was 5 per cent. Determinations upon artificial mixtures of acetone, acetophenone, α-cumyl alcohol, and t-butyl alcohol indicated that the accuracy was about this same value. This would indicate a maximum variation in the ketone yields of about one part in twenty. Table 17 gives the percentage yields of acetone derived from di-t-butyl peroxide alone, and in the presence of the two other peroxides. In all cases the yield of acetone varied between 15-25 per cent, therefore the maximum error in the

Table 17

Percentage Yields of Acetone from t-Butoxy Radical in Cumene at 127°

In presence of	Per cent ketone t-butoxy radical	
	16 -17	
Triphenylmethyl-t-butyl peroxide[a]	23.4	25.3[d]
Triphenylmethyl-t-butyl peroxide[b]	20.3	20.6[d]
di- α -Cumyl peroxide	20.5-21[c]	

[a]Two peroxides in approximately equimolar concentrations.

[b]di-t-Butyl peroxide concentration five times triphenylmethyl-t-butyl peroxide concentration.

[c]Calculated assuming that the di- α -cumyl peroxide gave quantitative amounts of acetophenone.

[d]Percentage acetone produced from di-t-butyl peroxide assuming a constant amount, 19.3 per cent, produced by triphenylmethyl peroxide.

yields is of the order of one per cent. The first three entries in Table 17 represent directly determined acetone. The last entry, however, was obtained by subtracting an amount of ketone equivalent to twice the original di- α -cumyl peroxide concentration. This assumes that the

di- α-cumyl peroxide was completely converted to acetophenone. The per cent acetone recorded, in this case, represents the minimum amount obtained. Any error caused by this consideration would increase the yield of acetone. Although artificial mixtures of acetone and acetophenone could be separately determined by codistillation of the acetone with benzene, this practice failed on the unknown determinations. The yields of total hydroxylic components were determined and are recorded in Table 14 but their determination was not as accurate as were the ketone determinations, possibly because of the introduction of water into the systems. Since the individual hydroxylic components could not be separated analytically and because of the larger error in their determination, results obtained from their determination are not considered as reliable. These yields do indicate that the acetone determinations are probably reliable.

As can be seen in Tables 14 and 17 there is a definite change in the yield of acetone in the three systems. This change is greater than any experimental error in the determinations. In both cases where two peroxides were mixed there is an increase in the percentage of acetone formed. The per cent yields of acetone in the second and third row of Table 17 were computed on the basis of total t-butoxy

radicals consumed. Each mole of di-t-butyl peroxide produced two moles of t-butoxy radicals whereas each mole of t-butyl triphenylmethyl peroxide produced only one mole. It cannot be argued that the increased yield of acetone arose from the "normal" fragmentation of t-butyl triphenylmethyl peroxide. Decomposed alone, t-butyl triphenylmethyl peroxide gave 18-19 per cent of acetone, approximately the same as di-t-butyl peroxide. There should be no substantial change in the yield of acetone in the mixed peroxide system if each peroxide exerted no influence upon the other. Nevertheless the yield of acetone in this system was 23 per cent. Column three of Table 17 was computed assuming that even in the mixed system, t-butyltriphenylmethyl peroxide produced 19.3 per cent acetone. This would require an increase to 25 per cent in the yield of acetone derived from di-t-butyl peroxide. When the initial concentration of t-butyl triphenylmethyl peroxide is decreased to approximately one fourth of the concentration of di-t-butyl peroxide, then the yield of acetone is diminished presumably reaching the limiting value of 16-17 per cent. If the yield of acetone from t-butyl tripehnylmethyl peroxide is much greater than 19 per cent, it no way invalidates the reality of the phenomenon of acetone yield variation, for the increase in acetone yield must be due, in

any case, to mutual effect of the alkoxy radicals upon each other.

The data in Tables 14 and 17 definitely show that the decomposition of admixtures of the peroxides studied gave different percentage of products than does the decomposition of these same peroxides alone. Such an effect would not have been predicted by, nor can it be reconciled with, the hypothesis of Kharasch. For, whether or not equipartition of energy occurs, mixtures of peroxides should decompose with the same distribution of energy in the resultant fragments as the pure, unmixed peroxides and no effect upon the yield of products should be noted. A termolecular hypothesis not only would account for the product variation but would predict it.

It is interesting to note that the difference in acetone yield between di-t-butyl peroxide (33 per cent) and t-butyl- α-cumyl peroxide (13 per cent) obtained by Kharasch at 138° in cumene[85] is much larger than obtained with t-butyl triphenylmethyl peroxide. The unsymmetrical peroxide, t-butyl- α-cumyl peroxide, gave a decreased yield of acetone when compared with di-t-butyl peroxide whereas mixtures of di- α-cumyl peroxide and di-t-butyl peroxide gave an increased yield when compared to di-t-butyl peroxide. This is rather startling and it would

appear that the α-cumyloxy radical acts differently in the two systems. It is not easy to reconcile this fact with the above proposed termolecular hypothesis. There is the possibility that Kharasch's data on this peroxide are in error. In our attempts to prepare this peroxide by the method of Kharasch it was always found to be mixed with substantial amounts of α-cumyl alcohol. The peroxide of Kharasch could have been sufficiently impure to give significant lowering of the acetone yield. There is the further possibility that an increase in temperature in the system containing t-butoxy and α-cumyloxy radicals causes a decrease in the yield of acetone. This is hard to visualize since in every other system an increase in temperature causes an increase in the yield of acetone. If such a temperature dependence is observed in this system, it may be because of a different type of termolecular, or even bimolecular, reaction being involved. It may lead to a means of evaluating the nature of the transition state involved in the termolecular reaction.

The type of transition states involved in the formation of the products from the decomposition of tertiary alkyl peroxides is more difficult to visualize than the corresponding transition state in the decomposition of the aliphatic azo compounds. It is not yet known which product

was formed by a termolecular reaction. There are certain features that the termolecular transition state must have. It must adequately account for one product, either ketonic or alcoholic. Its nature must embody a competition of two radicals for hydrogen abstraction. It must be sufficiently stabilized by resonance, without requiring too rigid a transition state*, to make its formation feasible. It must be sufficiently sensitive to variation in alkoxy radical to account for change in product yield. (This sensitivity is probably embodied in its ease of formation, which must vary with alkoxy radical.) Any transition state which encompasses these features and is consistent with present knowledge will be an adequate transition state for the process.

In summary it seems quite possible that a definite termolecular reaction is operative but whether this reaction involves a modified cage effect or is homogeneous cannot be stated. The difference in acetone yields between mixed and unsymmetrical peroxides is not sufficiently large to make any unequivocal statement. If analogy can be drawn with

---

*Many highly resonance stabilized intermediates for various reactions can be written which cannot possibly be formed because of too rigid a configuration which makes the entropy of the process prohibitively high.

aliphatic azo compounds, then probably reaction in the cage is of importance. Much more work on these and analogous systems is needed before any decision can be reached.

SUMMARY

Evidence is given for the course of reaction outlined below when two radicals, similar or dissimilar, are produced in solution simultaneously and from the same molecule. The evidence is based on two systems: the decomposition of azo-bis-nitriles and tertiary alkyl peroxides.

1. The radicals, produced from the same molecule, may collide and react together or react simultaneously with a third species before either radical has left the site of formation. In this case the radicals are not kinetically free and the products formed are dependent upon the nature of both radicals concerned even though one of the radicals may not appear as an even product in the reaction.

2. If the radicals do not react while caged they may diffuse apart and then react with another molecule by either a kinetically third-order process or individually in bimolecular processes.

3. In the decomposition of the tertiary alkyl peroxides studied, the termolecular processes must be in competition with bimolecular processes.

ACKNOWLEDGMENTS

The author wishes to express his deepest appreciation to Professor George S. Hammond whose continual inspiration and unfailing enthusiasm sustained this work throughout all of its phases.

Sincerest thanks are accorded to Mr. Jay Curtice, without whose help this thesis could not have been written.

This work was supported, in part, by a grant from the Office of Naval Research.