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Roger Clinton Williamson
Iowa State University

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POLAR EFFECTS IN FREE RADICAL REACTIONS

by

Roger Clinton Williamson, Jr.

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In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

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GENERAL INTRODUCTION

Polar effects in free radical reactions were first noticed in the copolymerization of vinyl compounds where an alternation of monomer units is found in the polymer formed (1, p. 132). This alternating tendency is especially noticeable when one of the vinyl monomers has an electron supplying group (phenyl, vinyl, alkyl, alkoxy or acyloxy attached to the double bond, and the other monomer has an electron withdrawing group (carboalkoxy and nitrile) attached to the double bond (1, p. 132).

Price (2a, 2b, 2c) has ascribed this effect to permanent charge distributions in both the attacking radical and the monomer. A more quantitative concept of the effect these permanent charge distributions have on copolymerizations was developed by Alfrey and Price (2b). According to these authors, the rate constant for the reaction of monomer one radical ($M_1\cdot$) with monomer two (M_2) is a function of four independent terms

$$k_{12} = P_1 Q_2 e^{-e_1 e_2}$$

where P_1 is related to the reactivity of $M_1\cdot$, Q_2 to the reactivity of M_2 and e_1 and e_2 are quantities related to the charges on $M_1\cdot$ and M_2 respectively.

$$e_1 = c_1(rDkT)^{-\frac{1}{2}}$$

c_1 is the actual charge on $M_1\cdot$, r the separation of the charges in the transition state, D the effective dielectric constant, k the Boltzmann constant and T the absolute temperature. If the charge on $M_1\cdot$ and M_1 are the same, the rate constant for the reaction of $M_1\cdot$ with M_1 is

$$k_{11} = P_1Q_1e^{-e_1^{\;2}}$$

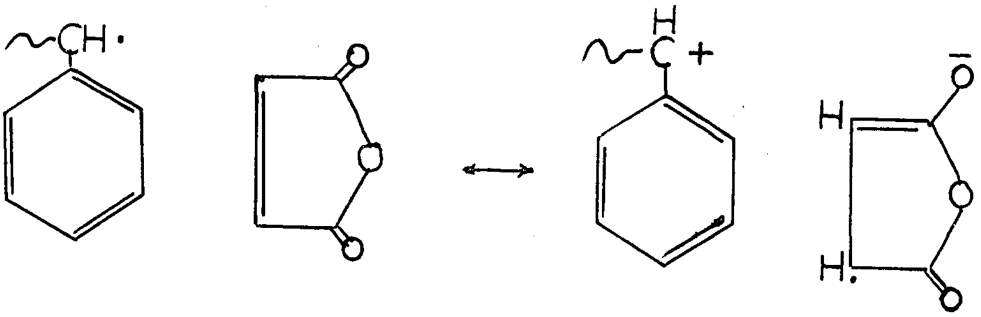
Walling and Mayo (3) have criticized this concept on the grounds that it would be susceptable to changes in the dielectric medium of the solvent. The Price suggestion was shown to be contrary to experimental results since no changes in polymer composition were observed as the dielectric constant of the solvent was varied. Walling (1, p. 134) suggests that the radical and the monomer mutually polarize one another as they approach the transition state. This happens only when they are close to one another and the lines of force do not radiate into the surrounding medium.

The best evidence for polar effects in copolymerization reactions comes from a study of the copolymerization of meta and para-substituted styrenes by Walling, Briggs, Wolfstirn and Mayo (4), and meta and para-substituted alpha-methylstyrenes with maleic anhydride by Walling, Seymour and Wolfstirn (5). A good straight line could be obtained for the copolymerization of substituted styrenes with a slope of 0.5 when the σ constant of the substitutent is plotted as a function of its relative reactivity. However, no correlation could be obtained from the substituted alpha-methylstyrenes - maleic anhydride system, or from substituted styrenes - methyl methacrylate copolymerization. In both of these systems both electron supplying and electron withdrawing groups caused increasing reactivities in the respective monomers.

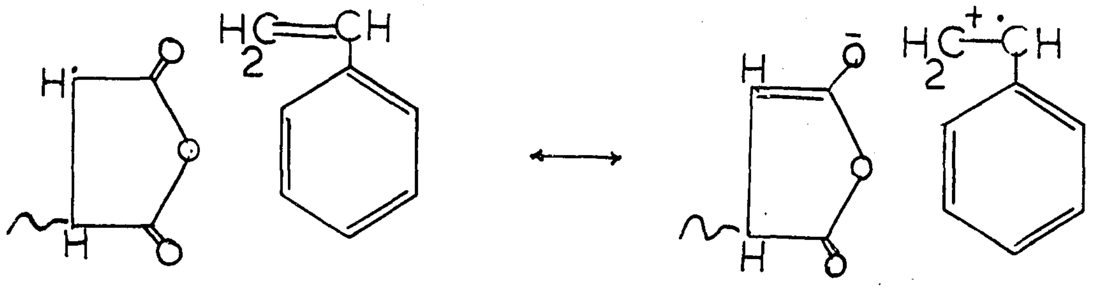
Another aspect of copolymerization kinetics that is susceptible to polar effects is the cross termination of the two radicals. Thus, an acceptor radical (one which has an electron withdrawing group on the alpha carbon atom) should terminate faster with a donor radical (one with an electron donating group on the alpha carbon atom) than a termination reaction involving two similar radicals. This has been demonstrated to be the case in several systems by numerous workers, whose results are tabulated by Walling (1, p. 146). For example, the cross termination rate constant between styrene and methyl methacrylate polymer radicals is two times as great as the bimolecular termination rate constant of either of the radicals.

Walling (7) has also shown that crossed thermal initiation rate constants are influenced by polar effects. The crossed initiation rate constant for styrene and methyl methacrylate is about three times as fast as that for styrene alone, which is much faster than that for methyl methacrylate.

Polar effects have been shown to be important in the addition of thiols to double bonds and in the ability of thiols to undergo chain transfer reactions with growing polymer radicals. Thus, Walling (8) has shown that thioglycolic acid adds much faster to alpha-methylstyrenes which have electron-donating groups in the para-position, while electron-withdrawing groups retard the rate of addition. Electron-withdrawing groups substituted in a thiol result in larger chain transfer constants with donor radicals and have little effect on the reactivity toward acceptor types of radicals. Due to this work the polar effect was formulated as one in which electron transfer had occurred between the donor radical and the acceptor monomer, or between an acceptor radical and a donor monomer. In both cases the donor assumes a carbonium ion-like structure in the transition state. For the attack of a styrene radical on maleic anhydride these structures could be



and, for the conjugate reaction in which the maleic anhydride radical attacks styrene,



Thus, in the systems p-methoxystyrene - methyl methacrylate and p-methoxy-alpha-methylstyrene - maleic anhydride, one would expect enhanced reactivity since the p-methoxy substituent can stabilize a plus charge and both methyl methacrylate and maleic anhydride are electron acceptors and can stabilize a negative charge.

Another radical reaction in which polar effects are often observed is the process of hydrogen abstraction. The most notable of these processes has been the photochlorination of aliphatic and aralkyl compounds with sulfuryl chloride and chlorine. Thus, Kharasch and Brown (9), Bruylants, Tits and Danby (10) and Bruylants, Tits, Dieu and Gauthier (11) chlorinated a series of carbonyl-containing alkanes and found that the reactivity at the alpha carbon atom was less than that of the same carbon atom in an unsubstituted alkane. When esters were chlorinated the reaction took place only on the O-alkyl portion of the molecule (10). These results demonstrate that the carbonyl group definitely retards the ability of the chlorine atom, an atom which prefers to attack at centers of high electron density, to attack the carbon-hydrogen bond of the carbon adjacent to the carbonyl group. This polar effect of the carbonyl function is also operative (but diminished) further along the chain. den Hertog and Smit (12) have shown that in the chlorination of hexanoyl chloride the following order of relative reactivities are found when no solvent is used: β position, 0.57; γ position, 2.1; δ position, 2.9; and ε position, 1.0. When benzene is used as a solvent, the relative reactivities change to: β position, 0.95; γ position, 4.3; δ position, 15; and ε position, 1.0. These results show that the β and γ positions are deactivated by the carbonyl group. The δ position shows a marked increase in relative reactivity in benzene consistent with a solvent effect increasing the selectivity of the chlorine atom.

The same deactivation observed in carbonyl compounds can also be detected in chlorinated hydrocarbons. In general, the chloro-substituent deactivates the reactivity of adjacent hydrogen atoms by an inductive effect which decreases the electron density in the immediate vicinity of the hydrogen atom. This has been demonstrated decisively by Brown and Ash (13a, b) in the chlorination of a series of chloro-substituted compounds with sulfuryl chloride and by Henne and Hinkamp (14) in the photochlorination of fluorosubstituted hydrocarbons.

The most quantitative estimation of polar effects in hydrogen atom abstraction by chlorine atoms is that involving chlorination of substituted toluenes. This allows the use of the Hammet equation, $\log \frac{k}{ko} = \sigma\rho$ (15) in correlating relative reactivities, where k/ko are the relative rates of the substituted and unsubstituted toluene, σ is a substituent constant and ρ is the slope of the correlation whose magnitude depends on the nature of the reaction and its sensitivity to polar effects. Kooyman (16) chlorinated a series of seven toluenes with sulfuryl chloride, and found a good fit with the Hammet equation. Walling and Miller (17), using the photochlorination method, obtained a good fit with seven of their nine compounds which gave a ρ value of -0.76. The two points that deviated were for the meta and para-phenyltoluenes, where the para-isomer is capable of stabilizing a plus charge in the transition state. Since the Hammet equation has been widely used to correlate ionic reactions, it can be inferred that a correlation with this equation indicates some polar character in the transition state of a radical reaction.

Bromination of substituted-toluenes with both bromine and N-bromosuccinimide (NBS) was performed by Kooyman, van Helden and Bickel (18). While these authors obtained straight lines of the following correlation for these reactions, $\log \frac{k}{ko}$ (Br_2) = $-1.05\ \sigma$ (80^{o}) and $\log \frac{k}{ko}$ (NBS) =

$-1.55\ \sigma$ (80°), Russell (19) has shown their data are better correlated with enhanced σ or σ^+ values by the following correlations: $\log \frac{k}{ko}$ (Br_2) = $1.10\ \sigma^+$ and $\log \frac{k}{ko}$ (NBS) = $-1.50\ \sigma^+$. Recent work by Russell, De Boer and Desmond (20), Pearson and Martin (21) and Walling, Rieger and Tanner (22) has shown the mechanism of bromination by the two methods to be the same. That is, both brominate via the bromine atom. Thus, the two different ρ-values mentioned above must be in error. In fact, Martin has repeated this work with both bromine and NBS and has found the ρ-values to be essentially the same (-1.46 for NBS (80°) and -1.38 for bromine (80°)) with both correlations fitting Brown and Okamoto's σ^+ values (23). Walling _et al_. find their data on the bromination of substituted -toluenes to fit the following equation: $\log \frac{k}{ko} = -1.38\ \sigma^+ + 0.097$ (80°). Russell, De Boer and Desmond's work in this area involved photobromination and NBS-bromination of a series of aralkyl hydrocarbons and found that the relative reactivities of this series to be the same for both processes.

Another radical process involving hydrogen abstraction is the reaction of the trichloromethyl radical with reactive carbon-hydrogen bonds. Huyser (24) has demonstrated the importance of polar effects in the reaction of substituted-toluenes with bromotrichloromethane in the presence of an initiator. The results of this investigation again show that the log of the relative reactivities is better correlated with σ^+ constants according to the following equation: $\log \frac{k}{ko} = -1.46\ \sigma^+\ (50^\circ)$.

One of the most heavily investigated areas in hydrogen atom abstraction has been the autoxidation of hydrocarbon followed by the reaction of the resulting hydrocarbon radical with oxygen.

While no extensive work has been done on the autoxidation of ketones, acids, esters, etc., it has been shown that the hydroperoxide formed is usually alpha to the carbonyl group (25, 26, 27). This shows that any polar effects operating must be overshadowed by the resonance stabilization of the incipient radical.

The most quantitative work on the polar effect in autoxidations has been carried out by Walling and Mc Elhill (28) and Russell (29). Walling and Mc Elhill have shown that electron-donating groups in the para-position of substituted-berzaldehydes increase their rate of reaction, while those with electron-withdrawing groups decrease their rate of autoxidation. Russell has autoxidized a series of meta and para-substituted cumenes and toluenes using an initiator and obtained good agreement with the Hammet equation according to the following equations: $\log \frac{k}{ko}$ (cumenes) $= -0.43\ \sigma\ (90^\circ)$, and $\log \frac{k}{ko} = -0.60\ \sigma\ (90^\circ)$ for toluenes.

Recent work of Howard and Ingold (30) has shown the inhibition of the autoxidation of styrene by phenols to involve the abstractions of the phenolic hydrogen by peroxy radicals. They have also extended their work to the ability of _meta_ and _para_-substituted phenols to inhibit the autoxidation of styrene (31). The results of this investigation show that the relative abilities of these to inhibit autoxidation are better correlated by σ^+ parameters. The correlation obtained has a slope of -1.49 (65°). Other work done in this area has shown that the magnitude of these polar effects depends on the structure of radical and the phenol. Thus, Godsoy _et al_. (32) have shown that by using the styrenylperoxy radical and substituted hindered phenols, a straight line with a value of $\rho = -2.5$ (60°) is obtained and that by using the 1,1-diphenylpiorylhydrazyl radical with the same phenols a value of $\rho = -5$ (30°) is obtained. Hammond _et al_. (33), using the cumylperoxy radical, found a ρ value of -3.7 (62.5°) in reactions with substituted phenols. The magnitude of the values of ρ is also dependent upon the solvent used as pointed out by Howard and Ingold (31).

Polar effects are also important in the cleavage of benzoyl peroxides, tetrararyldibenzoyltetrazanes, and _t_-butyl phenylperacetates. Swain, Stockmayer and Clark (34) thermally decomposed a series of _meta_, _meta_' and _para_, _para_' substituted benzoyl peroxides in dioxane, with 3,4-dichlorostyrene present to prevent induced decomposition, and found a good Hammett $\sigma\rho$ plot, with $\rho = -0.38$ (80°). Wilmarth and Schwartz (35) decomposed a series of substituted tetraarylbibenzoyltetrazanes in acetone. Since the radicals formed also reunite in an equilibrium type process, these authors measured the effect of the substituents on both the equilibrium constant (K) and the rate of the forward reaction (k). They obtained the following relationships: $\log \frac{K}{Ko} = -1.52\ \sigma$ and $\log \frac{k}{ko} = -0.55\ \sigma$ (-30°). Bartlett and Rückhart (36) thermally decomposed a series of t-butyl-meta and para-substituted pherylperacetates in chlorobenzene solution and obtained a good correlation with σ^+ constants with $\rho = -1.09$ (91°).

This study of polar effects in free radical reactions was undertaken to determine the nature of these polar effects in the transition state for hydrogen atom abstraction by a chlorine or peroxy radical. It was also a goal to determine the importance of solvent effects when polar effects are important in determining the reactivity of a carbon-hydrogen bond.

The second half of this study was undertaken to secure a more detailed knowledge of the relative propagation and termination rate constants in the autoxidation of aralkyl hydrocarbons, aralkenyl hydrocarbons and benzyl-type ethers.

PHOTOCHLORINATION OF SUBSTITUTED TOLUENES AND AUTOXIDATION OF SUBSTITUTED CUMENES, STYRENES AND BENZYL PHENYL ETHERS

Introduction

Competitive photochlorination of two or more substituted toluenes offers the easiest means of obtaining the relative reactivities of the respective carbon-hydrogen bonds toward the chlorination, since the absolute rate for the reaction of chlorine atoms with a carbon-hydrogen bond is too fast to measure by standard techniques. Absolute rate constants could be obtained if the rate were known for one of the substrates under investigation. This has been done for a number of hydrocarbons in the gas phase by competing them against methane, which in turn has been competed with hydrogen whose absolute rate of reaction with the chlorine atom is known. For the purpose of the work undertaken here, relative reactivities will provide all the information needed to determine the polar character of the transition state in the chlorine atom abstraction of the hydrogen atom from a carbon-hydrogen bond. The kinetics of the competitive photochlorination of two substrates is outlined in the scheme below:

$$Cl_2 \xrightarrow{h\nu} 2\ Cl\cdot$$

$$Cl\cdot + R_1H \xrightarrow{k_1} R_1\cdot + HCl$$

$$Cl\cdot + R_2H \xrightarrow{k_2} R_2\cdot + HCl$$

$$R_1\cdot + Cl_2 \xrightarrow{fast} R_1Cl + Cl\cdot$$

$$R_2\cdot + Cl_2 \xrightarrow{fast} R_2Cl + Cl\cdot$$

$$Cl\cdot \text{ (or } R\cdot) + R\cdot \text{ (or } Cl\cdot) \longrightarrow \text{nonradical products}$$

To obtain the relative reactivities of the two substrates all that has to be done is to either measure the amounts of the two chlorides formed, if all of the product comes from the reaction of the aralkyl radicals with molecular chlorine, or measure the disappearance of the two substrates. The latter method was the one employed in this work. The rate of disappearance of each of the substrates is as shown in the following scheme:

$$\frac{-d[R_1H]}{dt} = k_1[R_1H][Cl\cdot]$$

$$\frac{-d[R_2H]}{dt} = k_2[R_2H][Cl\cdot]$$

By dividing the first equation by the second and cancelling common terms, the following expressions are found:

$$\frac{d[R_1H]}{d[R_2H]} = \frac{k_1[R_1H]}{k_2[R_2H]}$$

$$\frac{d[R_1H][R_2H]}{d[R_2H][R_1H]} = \frac{k_1}{k_2}$$

Integration of this equation gives the following:

$$\frac{k_1}{k_2} = \frac{\log[R_1H]_f - \log[R_1H]_o}{\log[R_2H]_f - \log[R_1H]_o}$$

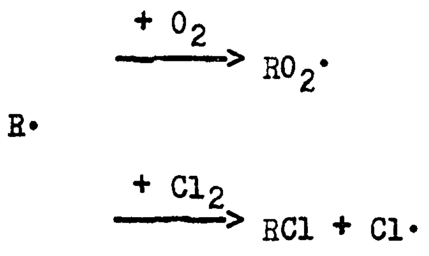
or,

$$\frac{k_1}{k_2} = \frac{\log[R_1H]_o - \log[R_1H]_f}{\log[R_2H]_o - \log[R_1H]_f}$$

All that is needed to obtain the relative reactivities is a knowledge of the concentration of both substrates at the start of the reaction $[RH]_o$ and when the reaction is stopped $[RH]_f$.

One of the chief advantages in running competitive kinetics outside of simplicity, is that if one of the substrates is contaminated with an impurity capable of inhibiting the reaction, the rates of reaction of both substrates will be inhibited to the same degree and valid relative rate constants can still be obtained after the reaction starts (37).

Since oxygen is a known inhibitor of chlorination reactions, it must be rigorously excluded from the reaction media. The mechanism for this inhibition is presumably by competition of oxygen with Cl_2 for the aralkyl radical according to the following reactions:



$$R\cdot \begin{cases} \xrightarrow{+\ O_2} RO_2\cdot \\ \xrightarrow{+\ Cl_2} RCl + Cl\cdot \end{cases}$$

The resulting peroxy radical and chlorine atom can then abstract a hydrogen atom or terminate. The chlorine atom abstracts a hydrogen atom much faster than the peroxy radical as can be seen by the rates of the two processes for the cumene molecule.

$$k_{Cl\cdot} = 2.1 \times 10^{10} \frac{\text{liter}}{\text{mole-second}}$$

and

$$k_{RO_2\cdot} = 1.3 \frac{\text{liter}}{\text{mole-second}}$$

The rate constant for the chlorine atom was obtained from the known absolute rate between Cl• + H_2 —> HCl + H• through successive relative rates, while the absolute rate constant for the peroxy radical is the one obtained by Melville and Richards (38). This relative nonreactivity of the peroxy radical in the hydrogen atom abstraction process combined with its known tendency to terminate quite rapidly (38) makes the peroxy radical a retarder or inhibitor of chlorination reactions.

Walling and Miller (17) have suggested another complication in photochlorination of aromatic substrates. They observed that p-chlorotoluene was more reactive in benzene solution than in carbon tetrachloride solution when compared to toluene. This was explained by employing Russell's postulate and saying that the chlorine atom complexed with the aromatic solvent and was made less sensitive to polar effects. This is generally not the case for radical chlorination reactions, where, if only polar effects are operative in the transition state, there is only a small effect of aromatic solvents on relative reactivities observed in photochlorinations. If, however, the relative reactivity is controlled by bond disassociation energies, the solvent used is quite important in determining relative reactivities. This problem will be dealt with in more detail later.

Side reactions which might complicate the reaction by interference with the chain process, such as reaction of the chlorine or aralkyl radical with the solvent (carbon tetrachloride in this investigation) are of the following type:

$$Cl\cdot + CCl_4 \longrightarrow Cl_2 + \cdot CCl_3$$

$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3$$

neither of which should be very important since the reverse reaction of the first should occur much faster than the forward one and molecular chlorine should react with the aralkyl radical in preference to its reaction with carbon tetrachloride.

The autoxidation of organic substrates is another well established free radical process of both theoretical and commercial nature. The following mechanism is well established for the autoxidation of cumene:

$$\text{Initiator} \xrightarrow{k_i} 2R\cdot$$

$$R\cdot O_2 \xrightarrow{\text{fast}} RO_2\cdot$$

$$RO_2\cdot \xrightarrow{kp} RO_2H + R\cdot$$

$$2RO_2\cdot \xrightarrow{k_t} O_2 + \text{non-radical products}$$

$$ek_i \frac{[\text{initiator}]}{2} = k_t$$

where k_i, k_p and k_t are the rate constants for initiation, propagation and termination, respectively.

The rate of oxidation, which is an experimentally determinable quantity, is then given by this expression:

$$\frac{-d\ O_2}{dt} = Ri + Rp - Rt$$

or

$$\frac{-d\ O_2}{dt} = 2e\ k_i[\text{initiator}] + k[O_2][R\cdot] - k_t[RO_2\cdot]^2$$

where e is the efficiency of the initiator.

If a steady state concentration of peroxy radicals is assumed, as it must be if we have a controlled chain process, then the rate of initiation must equal the rate of termination:

$$\frac{2e\ k_i\ [\text{initiator}]}{2} = k_t\ [RO_2\cdot]^2$$

$$[RO_2\cdot] = \left(\frac{e\ k_i\ [\text{initiator}]}{k_t}\right)^{\frac{1}{2}}$$

and

$$[R\cdot][O_2]k = k_p[RH](ROO\cdot)$$

Upon substituting the above expressions into the oxidation rate equation, the following rate expression is obtained:

$$\frac{-d\ O_2}{dt} = \frac{k_p[RH][R_i]^{\frac{1}{2}}}{[kt]^{\frac{1}{2}}} + \frac{Ri}{2}$$

If the above absolute rate expression is used to obtain values of k_p for different substrates, then several quantities must be known or determinable. Rates of initiation can be experimentally determined by plotting the rate of oxidation versus the concentration of the substrate. As [RH] approaches zero, the rate of oxidation approaches $\frac{Ri}{2}$. The value of k_t is much more difficult to determine experimentally, and can only be measured by elaborate techniques. Recent developments using electron spin resonance spectrometers capable of detecting small concentration of radicals have led to the determination of the concentration of peroxy radicals in oxidizing cumene at 74°C (39). By knowing the concentration of peroxy radicals by any means and the rate of initiation, k_t can be determined. However, it is still impossible to obtain values of k_t with any degree of accuracy. Therefore, only the ratio $\frac{k_p}{k_t^{\frac{1}{2}}}$ can at this time be accurately measured. Since only the propagation reaction involves the abstraction of a hydrogen atom, and this is the process under investigation, some way must be found to either separate k_t from k_p or neglect it in comparing the propagation rate constant of one substrate to another.

Bolland (40) has made the assumption that k_t is independent of the structure of the peroxy radical in comparing the rates of oxidation of a series of olefines. Russell has demonstrated this to be the situation in the peroxidation of a series of meta and para substituted toluenes and cumenes (29), but he has also shown that this assumption is incorrect when comparing oxidations involving attack upon 1^o, 2^o and 3^o carbon-hydrogen bonds (41). Walling and Mc Elhill (28) have shown the structure of the peroxy radical is important in the autoxidation of substituted benzaldehydes. For this investigation k_t will be assumed to be independent of the structure of the peroxy radical unless stated to the contrary.

In comparing the rate of oxidation between two substrates, the rate of initiation must not be a function of the substrate being oxidized. Fortunately, this is true in most cases, but where it is not, the differences are small. Since the rate of oxidation is proportional to the square root of R_i, these small changes are minimized even further. Therefore, the same value of R_i was used throughout this investigation.

In a competitive oxidation, the kinetics of the reaction become more complicated. Since R_i is not dependent on the substrates used, only the reactions involved in the propagation and termination steps will be discussed in the following sequence:

$$R_1O_2\cdot + R_1H \xrightarrow{k_{11}} R_1O_2H + R_1\cdot$$

$$R_1O_2\cdot + R_2H \xrightarrow{k_{12}} R_1O_2H + R_2\cdot$$

$$R_2O_2\cdot + R_2H \xrightarrow{k_{22}} R_2O_2H + R_2\cdot$$

$$R_2O_2\cdot + R_1H \xrightarrow{k_{21}} R_2O_2H + R_1\cdot$$

$$2R_2O_2\cdot \xrightarrow{k_{t\ 11}} O_2 + \text{non-radical products}$$

$$2R_2O_2\cdot \xrightarrow{k_{t\ 22}} O_2 + \text{non-radical products}$$

$$R_1O_2\cdot + R_2O_2\cdot \xrightarrow{k_{t\ 12}} O_2 + \text{non-radical products}$$

If the propagation or hydrogen abstraction reaction is not dependent on the structure of the peroxy radical, relative reactivities of the two substrates are easily obtained from the following expressions:

$$\frac{d[R_1H]}{dt} = k_{p1}[R_1H][RO_2\cdot]_{total}$$

$$\frac{d[R_2H]}{dt} = k_{p2}[R_2H][RO_2\cdot]_{total}$$

By dividing the top equation by the bottom one, and integrating, an equation relating the two propagation rate constants is obtained:

$$\frac{k_{p1}}{k_{p2}} = \frac{\log\ [R_1H]_o - \log\ [R_1H]_f}{\log\ [R_2H]_o - \log\ [R_2H]_f}$$

However, when the propagation reactions are dependent on the structure of the peroxy radical, the following equation relating the disappearance of the two substrates exists:

$$\frac{d[R_1H]}{d[R_2H]} = \frac{k_{11}[R_1O_2\cdot][R_1H] + k_{21}[R_2O_2\cdot][R_1H]}{k_{22}[R_2O_2\cdot][R_2H] + k_{12}[R_1O_2\cdot][R_2H]}$$

Here again the relative rate of disappearance of the two substrates is independent of the termination rate constants, provided that long kinetic chains are involved.

If a steady state concentration of peroxy radicals exists, the cross propagation rates must be equal to one another:

$$k_{12}[R_1O_2\cdot][R_2H] = k_{21}[R_2O_2\cdot][R_1H]$$

and

$$[R_1O_2\cdot] = \frac{k_{21}[R_2O_2\cdot][R_1H]}{k_{12}[R_2H]}$$

By substituting this value of $[R_1O_2\cdot]$ into the expression relating the disappearance of the two substrates and cancelling like terms, the following rate expressions result:

$$\frac{d[R_1H]}{d[R_2H]} = \frac{\dfrac{k_{11}[R_1H]}{k_{12}[R_2H]} + 1}{\dfrac{k_{22}[R_2H]}{k_{21}[R_1H]} + 1}$$

$$\frac{d[R_1H]}{d[R_2H]} = \frac{[R_1H]}{[R_2H]}\left(\frac{r_1[R_1H] + [R_2H]}{r_2[R_2H] + [R_1H]}\right) \text{ where } r_1 = \frac{k_{11}}{k_{12}}$$

and $r_2 = \frac{k_{22}}{k_{21}}$.

It is readily seen that the only information that can be obtained concerning the various rate constants are the relative values r_1 and r_2. For reactions in which the ratio $[R_1H]/[R_2H]$ remains constant, r_1 and r_2 can be obtained from the differential equation, but when this ratio is not constant, an integrated form must be employed.

$$\text{Differential form } r_2 = \frac{[R_1H]}{[R_2H]}\left(r_1 \frac{\Delta[R_2H][R_1H]}{\Delta[R_1H][R_2H]} + \frac{\Delta R_1H}{\Delta R_1H} - 1\right)$$

$$\text{Integrated form } r_2 = \frac{\log\frac{[R_2H]_o}{[R_2H]_f} - \frac{1}{\rho}\log\frac{1-\rho\,\frac{[R_1H]_f}{[R_2H]_f}}{1-\rho\,\frac{[R_1H]_o}{[R_2H]_o}}}{\log\frac{[R_1H]_o}{[R_1H]_f} + \log\frac{1-\rho\,\frac{[R_1H]}{[R_2H]}}{1-\rho\,\frac{[R_1H]_o}{[R_2H]_o}}}$$

$$\rho = \frac{1 - r_1}{1 - r_2}$$

The usual method for obtaining values for r_1 and r_2 is to perform a competitive reaction at three different ratios of $[R_1H]/[R_2H]$ and to determine the amounts of substrates that have reacted. For each experimental result a series of values for ρ are assumed and values of r_2 and r_1 are calculated for each assumed ρ. These values of r_2 and r_1 are then plotted against one another and a straight line of a different slope is obtained for each experiment. Theoretically, these three lines should intersect at a point, but the usual result is a triangle whose center is taken as the value of r_2 and r_1. The size of this triangle is taken as a measure of the experimental error. These types of solutions will be shown in the results section.

The application of the copolymerization equation to competitive autoxidations has been accomplished successfully by Walling (28), Russell (41) and Alagy *et al*. (42 and 43).

Chlorinations and oxidations were performed to determine the nature of the polar contribution to the transition state for hydrogen atom abstraction by the chlorine atom and peroxy radical. By invoking the Hammond postulate one can imagine a whole spectrum of different transition states in the radical abstraction of a hydrogen atom (44). These can be considered to involve the following three resonance structures:

$R - H + X\cdot$	$R + H\cdot\ X -$	$R\cdot + H\ X$
I	II	III

Structure I depicts the transition state for an extremely reactive radical involving little or no bond breaking and little energy of activation. The transition state resembles the reactants. The only polar effect that could arise in a reaction involving such a transition state would involve the electron density of the carbon-hydrogen bond.

Structure II represents a structure wherein the carbon-hydrogen bond is partly broken and the X-H bond is partly formed with charge separation.

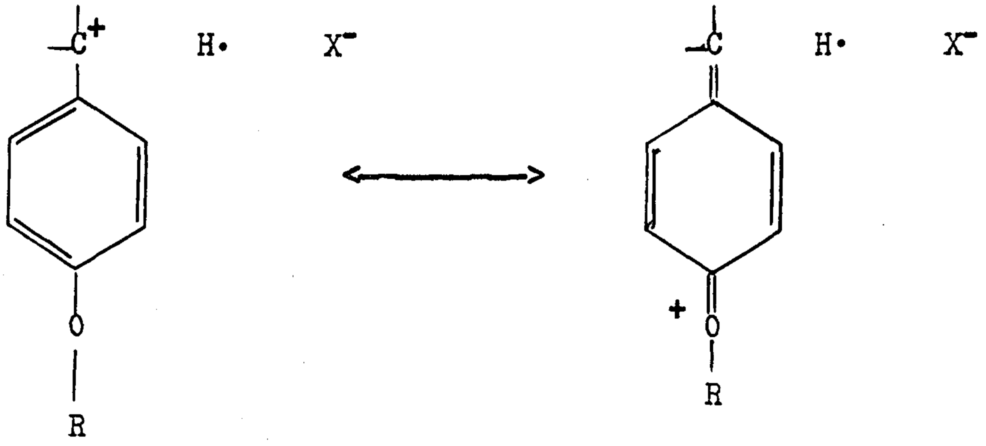
Structure III resembles a transition state in which the carbon-hydrogen bond is almost completely broken and the XH bond almost completely formed. Any stabilization of this transition state coming from the R group would have to be due to stabilization of the radical formed.

If the transition state is thought of as being a resonance hybrid of the three states (I, II and III), then the greater the electromegativity of X·, the more structure II contributes to this hybrid and the more the polar effect will be important. However, if X· is a very reactive radical it will resemble structure I no matter how electromegative it is.

To determine which of these resonance structures best describes the transition state for chlorine atom hydrogen abstraction, it was decided to photochlorinate a series of meta and para substituted toluenes. Substituents in these positions should not affect the entropy of activation, and any changes in reactivity would be due to changes in the energy of activation. A quantitative correlation in changes of rates of reaction of side chain aromatic compounds with changes in substituent is available in the Hammet equation. By observing whether σ or σ^+ values or radical stabilities are needed to correlate these reactivities in relation to the unsubstituted compound, one should be able to decide which of the three forms of the transition state is the most important.

The same concept was employed for the peroxy radical, but substituted cumenes were used instead of toluenes since they are more reactive and should have given more reproducible rate data.

These two pieces of research are essentially repeats of previous work with the exception of using substituents such as p-phenoxy, p-phenyl and p-methoxy substituents that are capable of stabilizing transition state II by the following type of resonance contributions:



This was precisely why the repetition of previous work was undertaken, since it is extremely difficult to determine the importance of structure II to the transition state if such substituents are not used. This is especially true for reactive radicals where II is of less importance.

Results and Discussion

The relative reactivities of eight substituted toluenes, compared to toluene toward the chlorine atom, are listed in Table 1. The photochlorinations used for comparative purposes were all run in carbon tetrachloride solution, but it is readily seen that in the one competitive reaction of p-chlorotoluene versus toluene where the solvent was changed to benzene there is essentially no difference in the two relative reactivities. This is in direct contradiction to the results of Walling and Miller as discussed in the introduction but in complete accord with the concept that when polar effects are important in radical reactions that solvents which have an important effect upon relative reactivities involving different bond strengths now have but little effect. Since the results given here are in accord with a considerable amount of other work and since no convincing argument is offered by Walling and Miller for the difference in reactivities, it appears that they are in error. Nevertheless, the concentration of aromatic substrate was kept at around one molar (a high solvent to substrate ratio) to minimize any complexing of the chlorine atom.

The relative reactivities listed in Table 1 were obtained from the previously derived equation:

$$\frac{k_a}{k_b} = \frac{\log [A]_o - \log [A]_f}{\log [B]_o - \log [B]_f}$$

where the subscripts o and f denote initial and final concentrations and A and B represent a substituted toluene and toluene respectively.

The data of Table 1 are plotted in Figure 1 as a function of the σ constants compiled by Brown and McDaniel (45-46) and in Figure 2 versus the σ^+ constants of Brown and Okamoto (23) with the exception of the σ^+ constant for the

Table 1. Comparative photochlorinations at 40° in carbon tetrachloride solution

Hydrocarbon A	$[A]_i$	$[A]_f$	$[B]_i$	$[B]_f$	k_a/k_b	Estimated uncertainty
p-phenoxytoluene	.204	.113	.806	.636	2.50	± .02
p-phenyloluene	.500	.290	.395	.278	1.55	± .01
p-xylene[a]	.807	.404	.660	.515	1.57	± .01
m-xylene[a]	.763	.430	.654	.525	1.30	± .02
m-phenoxytoluene	.399	.226	.596	.307	.86	± .01
p-chlorotoluene	.667	.490	.333	.230	.79	± .01
p-chlorotoluene	.266	.0196	.0133	.0092	.79	± .02
p-chlorotoluene[b]	.667	.520	.333	.240	.77	± .01
m-chlorotoluene	.582	.320	.330	.120	.595	.005
p-nitrotoluene	.734	.715	.294	.270	.50	± .02

[a] Divided by two for statistical correction.

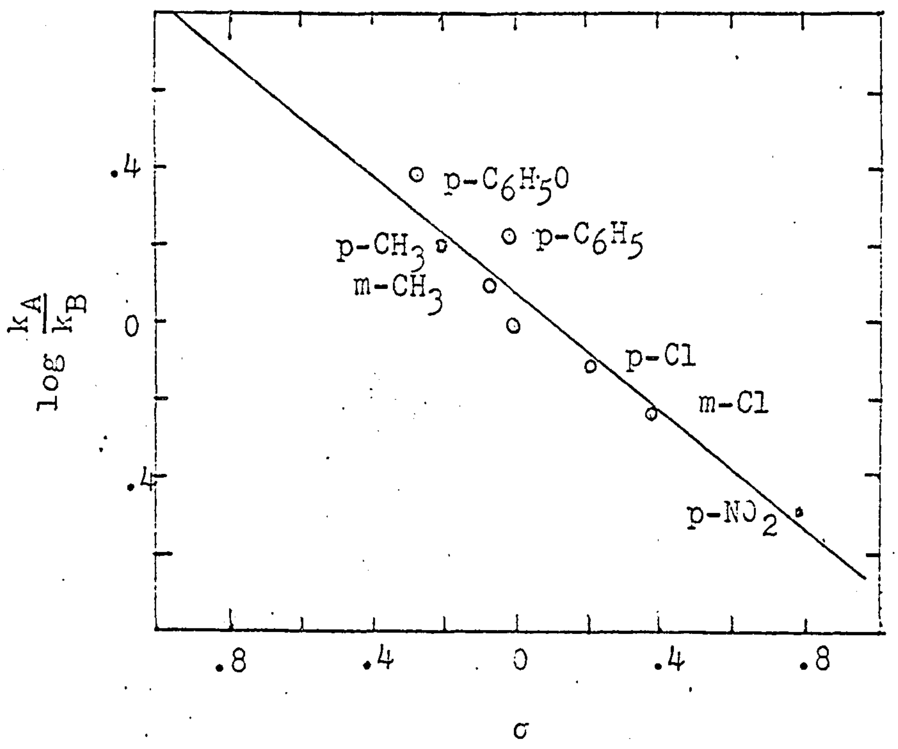
[b] Benzene as solvent.

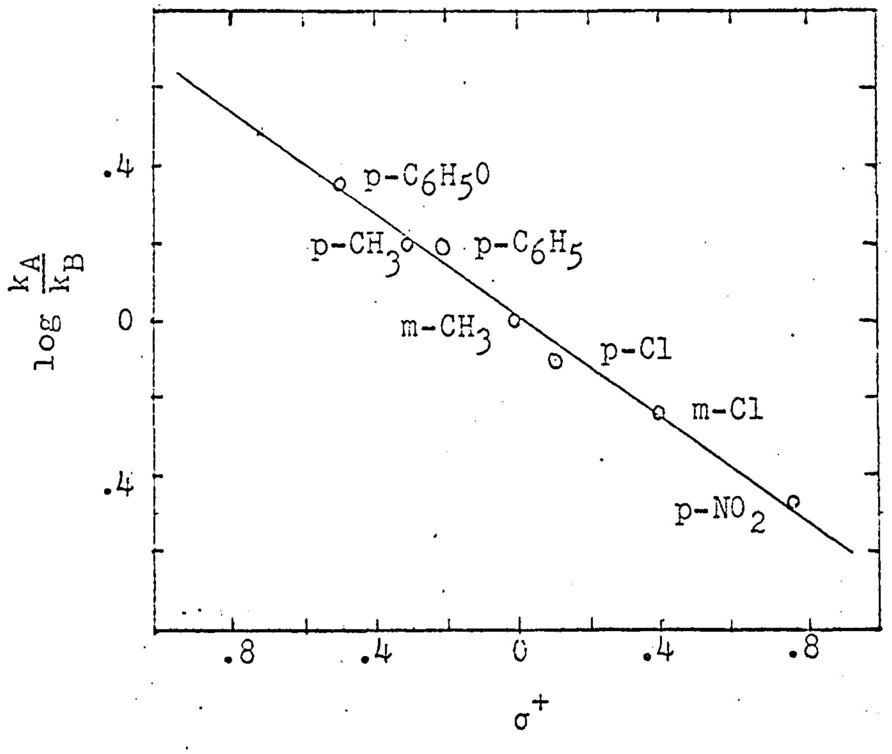
p-phenoxy substituent. Brown and Okamoto's value was not used since it did not come from solvolysis data but from electrophylic substitution data. Consequently, this constant was obtained by plotting the relative rates of solvolysis of a series of <u>meta</u> and <u>para</u> substituted benzhydryl chlorides obtained by Packer, Vaughan and Wilson (47) versus Brown and Okamoto's σ^+ values as shown in Figure

Figure 1. Log relative reactivities of the photochlorination of substituted toluenes at 40^o in carbon tetrachloride solution versus σ $\log k_A/k_B = -0.764\ \sigma + .079$ Std. Dev. = 0.06 log units

Figure 2. Log relative reactivities of the photochlorination of substituted toluenes at 40^o in carbon tetrachloride versus σ^+ $\log k_A/k_B = -0.663 + .014$

Std. Dev. = 0.02 log units


$\log \frac{k_A}{k_B}$
.4
0
.4
.8
.4
0
.4
.8
σ
p-C_6H_5O
p-C_6H_5
p-CH_3
m-CH_3
p-Cl
m-Cl
p-NO_2


$\log \frac{k_A}{k_B}$
.4
0
.4
.8
.4
0
.4
.8
σ^+
p-C_6H_5O
p-CH_3
p-C_6H_5
m-CH_3
p-Cl
m-Cl
p-NO_2

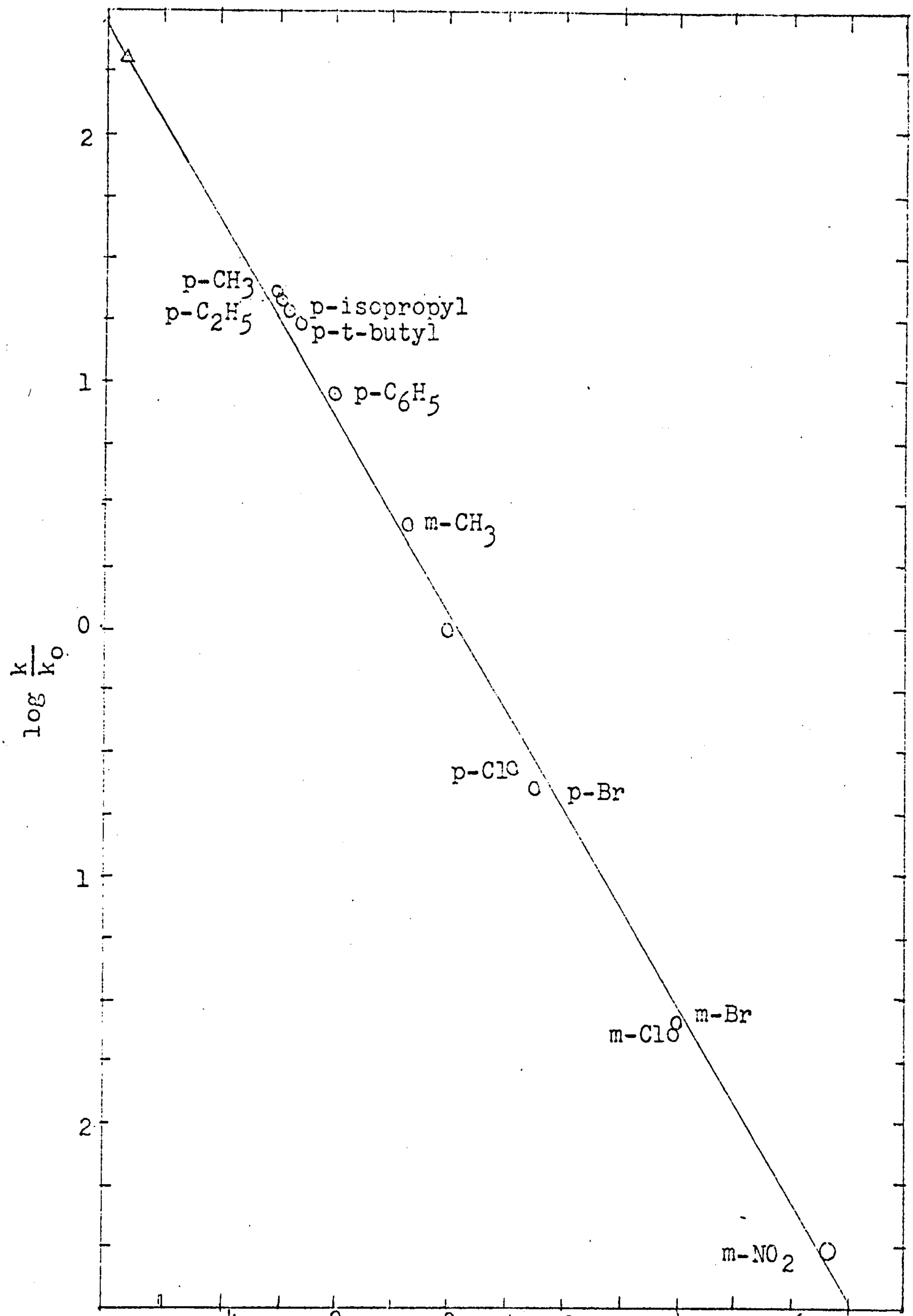
3. The σ^+ constant for the p-phenoxy substituent was then taken from the straight line in the above mentioned plot.

The best straight line for the σ plot had a correlation of $\log k_A/k_B = -0.764 + 0.06$ with a standard deviation of 0.06 log units, while the best straight line with the σ^+ plot gave a correlation of $\log k_A/k_B = -0.663 + .014$ with a standard deviation of 0.02 log units.

Comparison of the two straight lines of Figures 1 and 2, both visually and by their standard deviations, shows the σ^+ correlation to be a better fit to the data.

Previous workers had obtained values of $\rho = -1.5$ at 80° (16) and $\rho = -0.76$ at 70° (17) when correlated with σ-constants. The second of the sets of workers employed no solvent, and the ρ value of -1.5 was obtained using sulfuryl chloride as the chlorinating reagent in benzene solutions. Neither of these workers employed a substituent such as p-phenoxy. Walling and Miller (17) observed high relative reactivities for m- and p-phenyltoluene and remarked that this may be due to the enhanced reactivities this substituent shows in benzhydryl chloride solvolysis. Kooyman's data (16) can be questioned on the competitive technique employed, competing each of the toluenes versus t-butylbenzene, and in the method of analysis for appearance of product which consisted of determining the amount of benzyl chloride formed by hydrolysis (the neopentyl type from t-butylbenzene should

Figure 3. Log relative rates of solvolysis of substituted benzhydryl chlorides versus σ^+ constants


log $\frac{k}{k_o}$
2
1
0
1
2
σ^+
.4
.2
0
.2
.4
.6
p-CH_3
p-C_2H_5
p-isopropyl
p-t-butyl
p-C_6H_5
m-CH_3
p-Cl
p-Br
m-Cl
m-Br
m-NO_2

not hydrolyze) and a total chloride determination. While this type of analysis could yield non-quantitative conclusions, it is difficult to imagine this causing the ρ-value to be twice as great as Walling's and the one from Figure 1. The use of sulfuryl chloride should not cause this difference since in benzene the attacking species is the chlorine atom complexed with benzene (37).

The results of the autoxidation of ten cumenes in both chlorobenzene and acetic acid solution are given in Table 2. It is readily seen that in all cases where oxidation took place in acetic acid the rates of oxidation were slower than in chlorobenzene in acetic acid solution. p-Methoxy, p-t-butoxy and p-phenoxy cumene all failed to undergo significant oxidations. After an initial absorption of oxygen only enough oxygen reacted to counterbalance the amount of nitrogen formed from the decomposition of the azobisisobutyronitrite (AIBN hereafter) used as a catalyst. This phenomena can be explained by acetic acid being a strong enough acid to bring about the well known decomposition of cumylhydroperoxide to phenol and acetone for these three hydroperoxides since these three substituents should lower the energy of activation for this process. The phenol produced should then inhibit further oxidation.

Due to the fact that p-methoxy, p-t-butoxy and p-phenoxy cumene all oxidize slower than would be expected

Table 2. Rates of oxidations of cumenes (1.0 *M*) at 60°
0.1 *M* AIBN in chlorobenzene or acetic acid

Substituent	Solvent	$\frac{\text{Rate} - \frac{R_i}{2}}{[\text{RH}][\text{AIBN}]^{\frac{1}{2}}} \times 10^{5}$[a]	Relative values of $\frac{k_p}{(k_t)^{\frac{1}{2}}}$
p-Methoxy	C_6H_5Cl	1.52	1.33
p-t-Butoxy	C_6H_5Cl	1.35	1.18
p-Phenoxy	C_6H_5Cl	1.25	1.10
p-Isopropyl[b]	C_6H_5Cl	1.49	1.31
p-Isopropyl[b]	CH_3CO_2H	1.16	1.38
None	C_6H_5Cl	1.14	1.00
None	CH_3CO_2H	0.84	1.00
p-Bromo	C_6H_5Cl	0.90	0.79
p-Bromo	CH_3CO_2H	0.72	0.86
p-Carbomethoxy	C_6H_5Cl	0.67	0.59
p-Carbomethoxy	CH_3CO_2H	0.66	0.79
p-Nitro	C_6H_5Cl	0.52	0.46
p-Nitro	CH_3CO_2H	0.51	0.61

[a] Mole-liter^{-1}-second^{-1}.

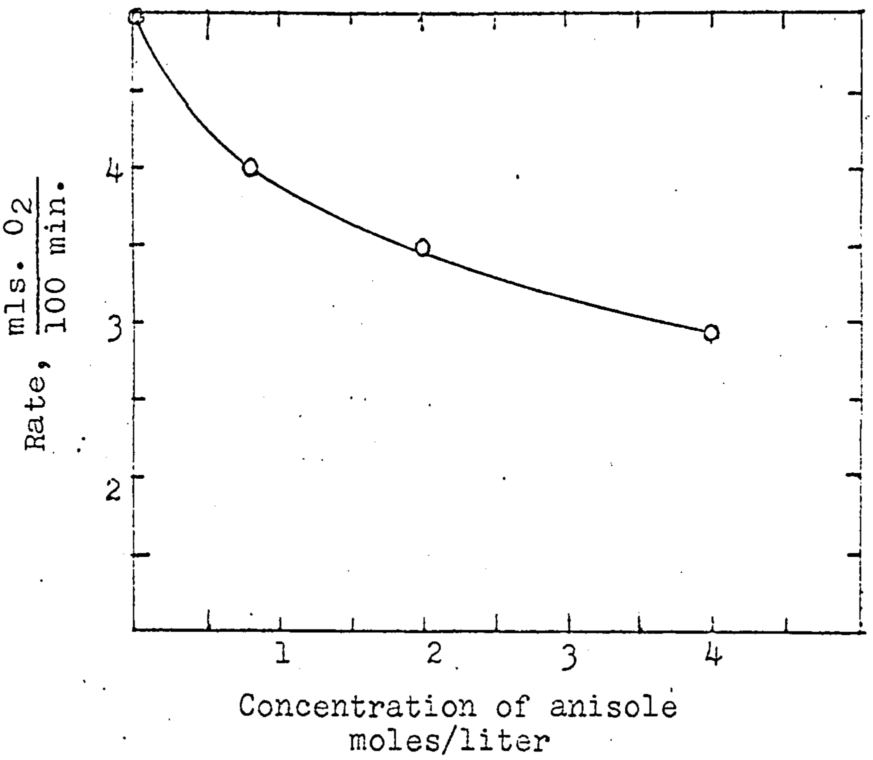
[b] Divided by two for a statistical correction.

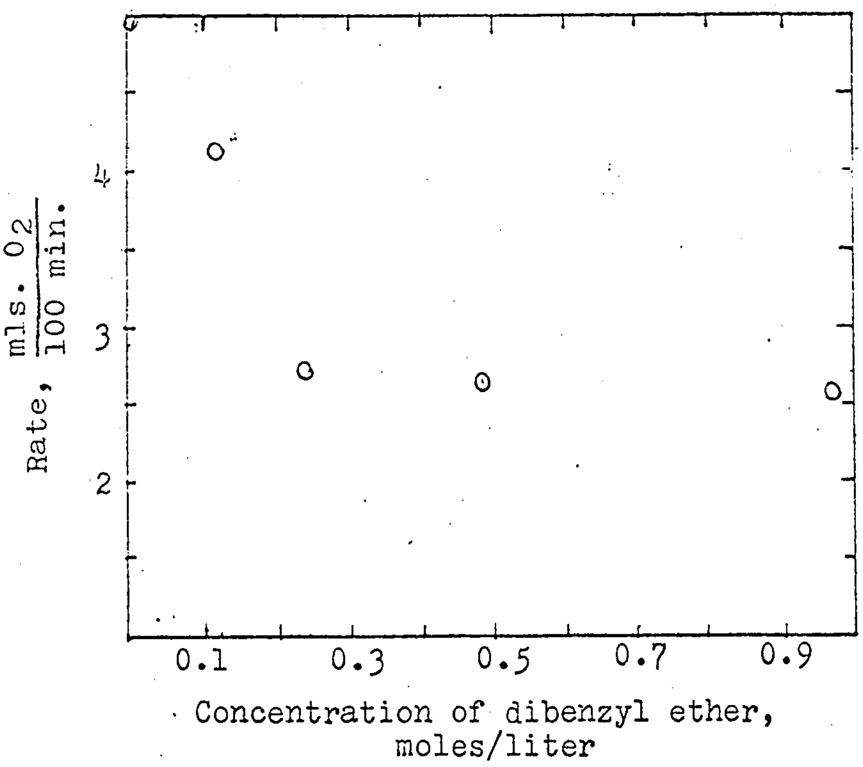
from either a σ or σ^+ correlation, in both acetic acid and chlorobenzene solution, it was decided to investigate the autoxidation of p-methoxy cumene in more detail. An investigation into the variation of $\frac{k_p}{(k_t)^{\frac{1}{2}}}$ for p-methoxycumene with concentration of p-methoxycumene showed an increase in this value as the concentration decreased and suggested that the substrate itself was in some way adversely affecting the rate of reaction, and that an an extrapolated infinite dilution the correct value of $\frac{k_p}{(k_t)^{\frac{1}{2}}}$ could be found. A similar investigation showed cumene to behave the same way. Since all these ethers had a phenyl ether linkage in common, it was thought that perhaps this general linkage could in some way retard the rate of oxidation.

Consequently, one-molar solutions of cumene containing various amounts of anisole, a known retarder of cumene oxidation (28), as a cosolvent with chlorobenzene were oxidized. The results can be seen in Figure 4. One-molar solutions of cumene containing diphenyl ether as cosolvent were also oxidized and results are shown in Figure 5. It is readily seen that while both others retard the rate of cumene oxidation, diphenyl ether is the most effective. It is known that diphenyl ether decreases the rate of initiation

Figure 4. The effect of anisole on the rate of oxidation of 1.0 M cumene in chlorobenzene at 60°, 0.1 M AIBN, total volume of solution always was 10 ml.

Figure 5. The effect of diphenyl ether on the rate of oxidation of 1.0 M cumene in chlorobenzene at 60°, 0.1 M AIBN, total volume of solution always was 10 ml.


Rate, $\frac{\text{mls. } O_2}{\text{100 min.}}$
4
3
2
1
2
3
4
Concentration of anisole
moles/liter


Rate, $\frac{\text{mls. } O_2}{\text{100 min.}}$
4
3
2
0.1
0.3
0.5
0.7
0.9
Concentration of dibenzyl ether,
moles/liter

of autoxidation of cumene by AIBN by decreasing the rate of decomposition and efficiency when used as the solvent (48, p. 64). Possibly, then, the rate of retardation observed for added diphenyl ether can be explained on this basis alone.

Walling (28) has observed that p-methoxybenzaldehyde undergoes peroxidation slowly and inhibits the peroxidation of other benzaldehydes. However, in competitive oxidation it reacts faster than any other substituted benzaldehyde. While no attempt was made to correlate his rates of oxidations with a σ or σ^+ relationship, it is evident that polar effects were important since the following order of reactivities was observed: p-methoxy > p-methyl > H > p-chloro > p-nitrobenzaldehyde for attack by the p-chlorobenzoyloxy radical. He also observed that the structure of the peroxy radical was important in determining relative reactivities. When these same compounds were allowed to compete for the p-methoxybenzoyloxy radical, the same order of reactivity as for the p-chlorobenzoyloxy radical was observed but all rates, both relative and absolute, were lower.

In view of this it was decided to competitively oxidize cumene and p-methoxycumene and determine their relative reactivities by the disappearance of each reactant. The competitive oxidation also afforded a means of determining whether the structure of the peroxy radical was important and if k_t varies with the structure of the peroxy radical. The second point was investigated by measuring the rates of oxidation of three mixtures of the two substrates and seeing if the rate was the additive of the fractional rate. Since it was observed that the rates were indeed additive, it appears that the termination rate constants are the same for cumyl and p-methylcumylperoxy radicals. That the structure of the peroxy radical was not important was also shown by the relative propagation rate constants determined from the rates of disappearance of the reactants. Toward the cumylperoxy radical, p-methoxycumene was 2.14 times as reactive as cumene while toward the p-methoxycumylperoxy radical p-methoxycumene was 2.06 times as reactive.

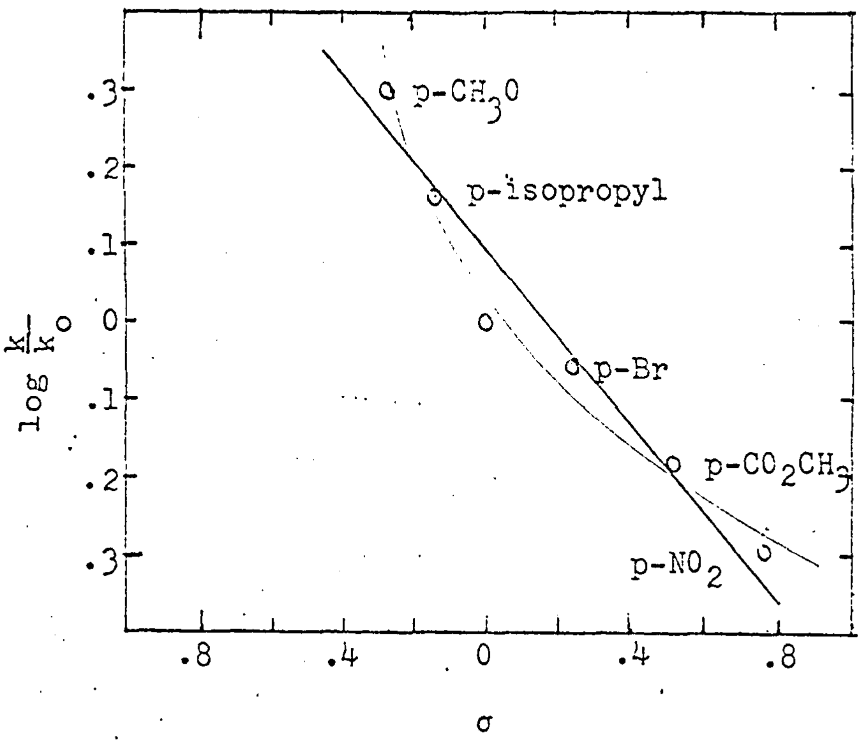
A value of 2.10 was used for the relative propagation rate constant for p-methoxycumene in the σ and σ^+ correlations of Figures 6 and 7.

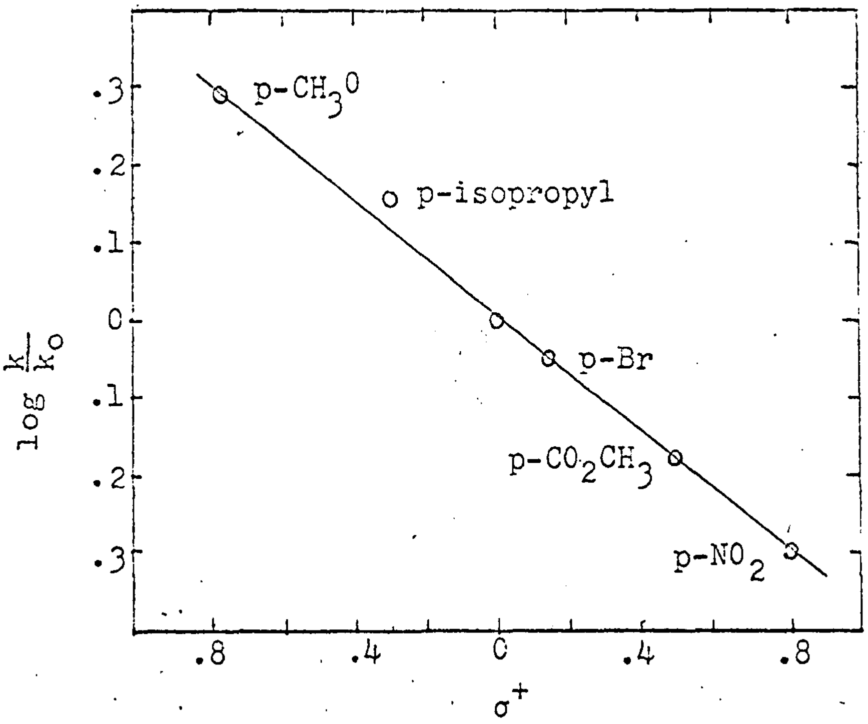
p-Nitrocumene was also competitively oxidized with cumene. The relative propagation rate obtained this way (0.51) agreed quite well with the one obtained from the rate of oxygen absorption (0.46). This was taken as sufficient evidence that the other substrates would behave similarly and further competitive oxidations were not performed.

The other ethers of this series, p-t-butoxy and p-phenoxycumene, were not competitively oxidized due to lack of

Figure 6. Log relative reactivities of autoxidation of substituted cumenes versus σ in chlorobenzene at 60o. $\log \frac{k}{k_o} = 0.546 + 0.092$
Std. Dev. 0.09 log units

Figure 7. Log relative reactivities of autoxidation of substituted cumenes versus σ^+ in chlorobenzene at 60°. $\log \frac{k}{k_o} = 0.375\ \sigma^+ + 0.003$
Std. Dev. 0.02 log units


log $\frac{k}{k_o}$
.3
.2
.1
0
.1
.2
.3
.8
.4
0
.4
.8
σ
p-CH$_3$O
p-isopropyl
p-Br
p-CO$_2$CH$_3$
p-NO$_2$


log $\frac{k}{k_o}$
.3
.2
.1
0
.1
.2
.3
.8
.4
0
.4
.8
σ$^+$
p-CH$_3$O
p-isopropyl
p-Br
p-CO$_2$CH$_3$
p-NO$_2$

substrate, but it is believed that the relative reactivities of these compounds are also greater than the rates of oxidation suggest.

By comparing Figures 6 and 7 it is quite evident that the relative rates of autoxidation are better correlated by σ^+ than by σ. Figures 8 and 9 also show this same trend in acetic acid, but since the faster reacting substrates could not be used, little will be made of these correlations. Since there does appear to be definite polar contributions to the transition state for autoxidations it might have been expected that acetic acid, a good polar solvent, would lower the energy of activation and thus increase the rates of reaction. However, in view of the fact that frequently the dielectric constant of a solvent (a macroscopic property) is not applicable to transition states (a microscopic principle), it is not too surprising that the rates of autoxidations in acetic acid solution were lower than in chlorobenzene solution.

Since both photochlorination and autoxidation are better correlated by σ^+ than by σ-constants, it would appear that the transition state of these reactions involves contributions from structure II. It seemed advisable to compare this data with a compilation of radical hydrogen abstraction reactions contained in the recent investigation of Ingold (31) as shown in Table 4. From this compilation it

Table 3. Rates of co-oxidation of various compounds at 60° in 10 ml. of benzene solution and 0.1 M AIBN

Reactants[a]	Initial concentration (moles/liter)	Final concentration (moles/liter)	Rate[b]		Figure
			Obs.	Calc.	
Cumene	1.000		5.00		17
p-Methoxycumene	0.000				
Cumene	0.800	0.630			
p-Methoxycumene	0.200	0.120			
Cumene	0.500	0.390	6.28	6.25	17
p-Methoxycumene	0.500	0.294			
Cumene	0.200	0.160			
p-Methoxycumene	0.800	0.500			
Cumene	0.000				
p-Methoxycumene	1.000		7.51		17
Cumene	0.800	0.618			
p-Nitrocumene	0.200	0.171			
Cumene	0.500	0.385	3.70	3.66	17
p-Nitrocumene	0.500	0.430			

[a] The first compound in each group is R_1H and the second, R_2H.

[b] Ml. oxygen/100 minutes.

Table 3. (Continued)

Reactants[a]	Initial concentration (moles/liter)	Final concentration (moles/liter)	Rate[b]		Figure
			Obs.	Calc.	
Cumene	0.200	0.136			
p-Nitrocumene	0.800	0.730			
Cumene	0.000				
p-Nitrocumene	1.000		2.30		17
Cumene	1.000		4.05	5.00	4
Anisole	0.800				
Cumene	1.000		3.50	5.00	4
Anisole	2.000				
Cumene	1.000		2.91	5.00	4
Anisole	4.000				
Cumene	1.000		4.15	5.00	4
Diphenyl ether	0.120				
Cumene	1.000		2.68	5.00	5
Diphenyl ether	0.240				
Cumene	1.000		2.65	5.00	5
Diphenyl ether	0.480				

Table 3. (Continued)

Reactants[a]	Initial concentration (moles/liter)	Final concentration (moles/liter)	Rate[b]		Figure
			Obs.	Calc.	
Cumene	1.000		2.60	5.00	5
Diphenyl ether	0.960				
Cumene	0.800		3.55	4.50	10
Benzyl phenyl ether	0.200				
Cumene	0.500	0.486	2.90	3.72	10
Benzyl phenyl ether	0.500				
Cumene	0.200		2.28	2.95	10
Benzyl phenyl ether	0.800				
Cumene	0.000		2.45		10
Benzyl phenyl ether	1.000				
Dibenzyl ether	0.500		6.75		10
Benzyl phenyl ether	0.000				
Dibenzyl ether	0.450		5.38	6.28	10
Benzyl phenyl ether	0.100				
Dibenzyl ether	0.250		3.22	4.59	10
Benzyl phenyl ether	0.500				

Table 3. (Continued)

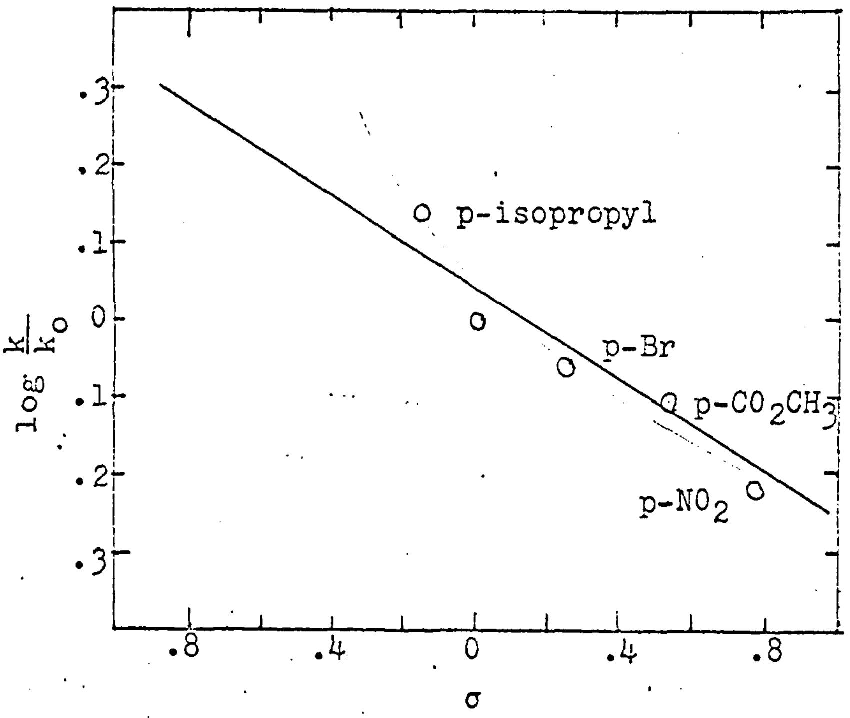
Reactants[a]	Initial concentration (moles/ liter)	Final concentration (moles/ liter)	Rate[b]		Figure
			Obs.	Calc.	
Dibenzyl ether	0.050		2.47	2.87	10
Benzyl phenyl ether	0.900				

appears that the majority of hydrogen abstraction reactions are better correlated with σ^+ constants. It would seem that in the light of this investigation, and other recent investigations, that if the radical abstracting the hydrogen atom is electronegative or capable of stabilizing a negative charge and thus generating a positive charge on the substrate being attacked, a σ^+ correlation should be obtained. Thus, the only reaction in Table 4 that should not give a σ^+ correlation is the phenyl radical reaction with toluenes. This radical is fairly active, is not electronegative and has no way to stabilize a negative charge that is generated on the ring since this gives eight π electrons. In the opinion of this author, this is the only reaction that should show little polar effects.

Reactions 4 and 7 in Table 4 appear to contradict this statement. This is especially so of reaction 4 where

Figure 8. Log relative rates of autoxidation of cumenes in acetic acid at 60° versus σ

Figure 9. Log relative rates of autoxidation of cumenes in acetic acid at 60° versus σ^+


.3
.2
.1
0
.1
.2
.3
$\log \frac{k}{k_o}$
p-isopropyl
p-Br
$p\text{-}CO_2CH_3$
$p\text{-}NO_2$
.8
.4
0
.4
.8
σ

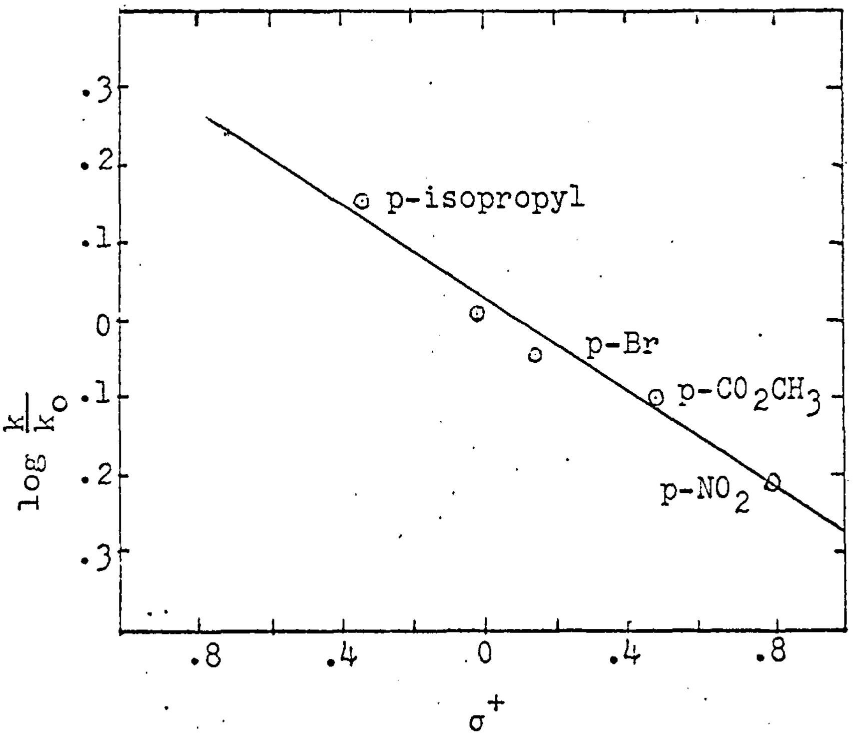

.3
.2
.1
0
.1
.2
.3
$\log \frac{k}{k_o}$
p-isopropyl
p-Br
$p\text{-}CO_2CH_3$
$p\text{-}NO_2$
.8
.4
0
.4
.8
σ^+

Table 4. Some typical hydrogen atom abstraction reactions

Reaction number	Reaction	Solvent	σ		σ^+	
			ρ	Std. dev.	ρ	Std. dev.
1[a]	$RO_2\cdot$ + Phenols, 65°	Styrene			-1.49	0.024
2[a]	$RO_2\cdot$ + Phenols, 62.5°	Chlorobenzene	-3.7			
3[a]	DPPH· + Phenols, 30°	CCl_4	-6.4	0.301	-4.54	0.064
4[a]	R· + Thiophenols, 110°	Toluene	-0.433	0.008	-0.287	0.025
5[a]	$Cl_3C\cdot$ + Toluenes, 80°	Chlorobenzene			-1.46	0.014
6[b]	Br· + Toluenes, 80°	Reactants			-1.36	0.05
7[c]	RO· + Toluenes, 40°	Reactants	-0.83			
8[d]	$RO_2\cdot$ + Cumenes, 60°	Chlorobenzene	-0.54	0.09	-0.375	0.015
9[d]	Cl· + Toluenes, 40°	CCl_4	-0.764	0.06	-0.663	0.02
10[e]	Phenyl· + Toluenes, 60°	CCl_4 + Reactants	Little effect of substituents			

[a] Reference 31.

[b] Reference 21.

[c] Reference 49a.

[d] This work.

[e] Reference 49b, p. 70.

R• represents the 1-cyanocyclohexyl radical. There is an extremely good correlation with σ constants and very poor correlation with σ^+. However, it is still felt that since this radical should be an extremely good acceptor radical by stabilizing an incipient negative charge generated in the transition state, that repetition of this work is in order. Reaction 7 shows a better fit with σ-constants than with σ^+ constants according to the authors, but they do not use any substituents such as p-phenoxy or p-t-butoxy and their data correlate almost as well with σ^+ as with σ. The p-methoxy substituent could not be used in this reaction as in photochlorinations since reaction readily takes place on the methyl ether group.

During the autoxidation of cumenes it was decided that while meaningful differences in rates were being obtained, a more reactive substrate might give larger absolute differences in rate for different substituents. Consequently, a series of meta and para substituted benzyl phenyl ethers were prepared. These substrates were chosen since it was known that dibenzyl ether oxidizes much faster than cumene and it was assumed that benzyl phenyl ether would oxidize about half the rate of bibenzyl ether. Bis-substituted dibenzyl ethers were not prepared due to the difficulty in their preparation. Instead, several benzyl-substituted and phenyl-substituted benzyl phenyl ethers were prepared.

The results of the rates of peroxidation as shown in Table 5 were surprising and, in a way, disappointing. Not only were the rates much slower than those of cumene, but there is little if any meaningful difference in their rates. Several possible explanations for the slow rates of oxidation are possible. One possible explanation is that in this reaction, a phenyl ether bond is again present, which inhibits the overall rate of oxidation just as diphenyl ether inhibits cumene oxidations. Credence is given to this concept by the fact that p-methoxybenzyl phenyl ether has the slowest oxidation rate of all the compounds examined. This compound has two such bonds. When an alkyl or benzyl group replaces the phenyl group the rate of oxidation becomes quite fast as shown in Table 6. Another explanation is that the phenoxy group decreases the electron density at the reactive methylene group by an inductive effect. This mechanism would seem in doubt due to the rates of oxidation of p-methyl and p-nitrophenyl benzyl ether since the p-nitro group should increase this inductive effect and the p-methyl group should decrease it. Both substituents have a slight accelerating effect on the rate of oxidation as shown in Table 5. A third possible explanation is that the rate of oxidation might be slow due to the fact that the benzylic radical formed may be a stable radical that reacts slowly with oxygen similar to the triphenyl methyl radical. This does not seem very plausable in view of the many other benzylic ethers that oxidize quite readily. A fourth explanation is that the rate of termination is much greater for these substrates than for cumene or for dibenzyl ether itself. Support is gained for this concept from the fact that benzyl phenyl ether retards the rate of oxidation of cumene and dibenzyl ether as shown in Figure 10. Further support was obtained from a competitive oxidation of benzylphenyl ether and cumene wherein the ether was found to disappear five times faster than cumene.

It would appear that the first and fourth possibilities, separately or in combination, explain the low rate of oxidation of benzylphenyl ethers. It is possible, however, that the two explanations are one and the same. If a contributing factor is a decrease in R_i as has been suggested for the retardation effect of diphenyl ether on cumene, then this decrease in R_i can actually be due to the termination of the initiator peroxy radical by the substrate. Since the decrease in R_i for AIBN in diphenyl ether was determined by the length of the induction period of a known amount of an inhibitor, 2,6,di-t-butyl-4-methyl phenol, it is not known whether the decrease in R_i was due to a decrease in the rate of decomposition of AIBN combined with a decrease in efficiency or whether the decrease is due

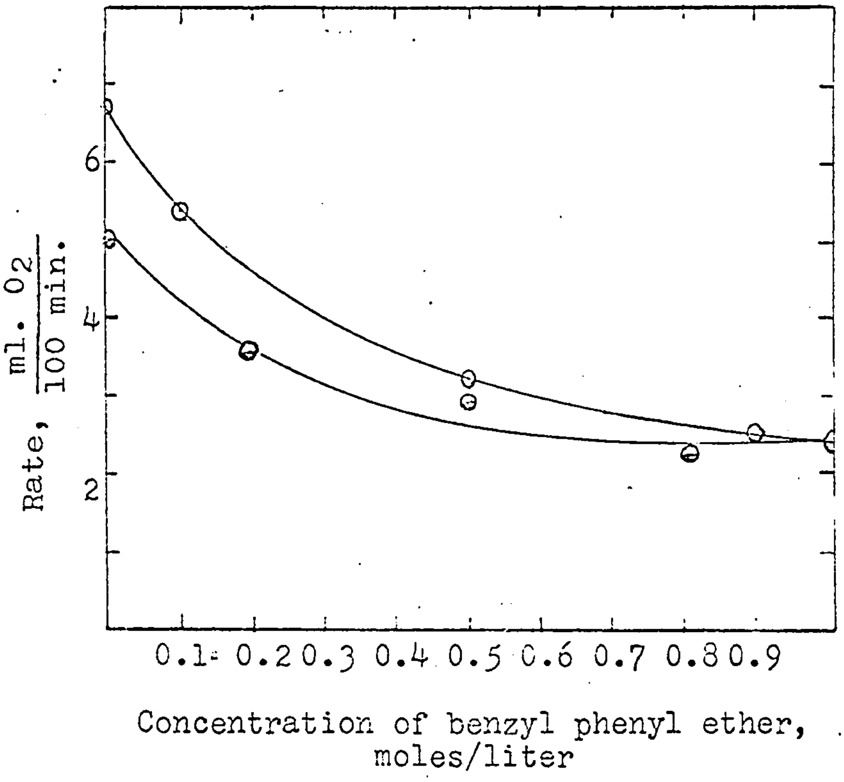


Figure 10. Plot of the rate of oxidation of mixtures of dibenzyl ether - benzyl phenyl ether, O; and cumene - benzyl phenyl ether, ⊖. Both oxidations in chlorobenzene solution at 60° and 0.1 M AIBN. Concentration of the reactive methylene group always 1.0 M, total volume of solution was always 10 ml.

to the termination of initiator peroxy radicals.

Even though the rates of oxidation of substituted benzyl phenyl ethers are low, a polar effect of some kind should have been observed since the rates of autoxidation of substituted toluenes are also low but show definite polar effects (29). That this was indeed not due to the slowness of reaction was demonstrated by both m-methyl and p-chlorobenzyl methyl ether having the same rate of oxidation as benzyl methyl ether. The only explanation that this author can give is that all of the polar effect is being stabilized by the etheral oxygen atom by resonance participation and that this participation completely overshadows any contribution from the aromatic ring.

$$C_6H_5CH = \overset{+}{O}\text{-}R$$

To determine whether the phenyl group was slowing the rate of reaction by a steric factor, a series of benzyl alkyl ethers was synthesized and autoxidized. The results show that this is definitely not the case since t-butyl benzyl ether oxidizes extremely fast. The rates of oxidation of this series and of benzyl alcohol are tabulated in Table 6. A more quantitative interpretation of the results of Table 6 is obtained in Figure 11 by plotting the log of the relative reactivities versus the σ^* values of Taft (50).

Table 5. Rates of oxidation of benzyl phenyl ethers at 60° in chlorobenzene solution (0.10 *M* AIBN)

Reactant	$\frac{\text{Rate} - \frac{R_i}{2}}{[\text{RH}][\text{AIBN}]^{\frac{1}{2}}} \times 10^{5}$[a]	Relative values of $\frac{k_p}{(k_t)^{\frac{1}{2}}}$
p-Methoxybenzyl phenyl ether	0.33	0.58
p-Methylbenzyl phenyl ether	0.68	1.20
m-Methylbenzyl phenyl ether	0.63	1.10
Benzyl phenyl ether	0.57	1.00
p-Chlorobenzyl phenyl ether	0.56	0.98
m-Chlorobenzyl phenyl ether	0.54	0.95
m-Nitrobenzyl phenyl ether	0.42	0.74
p-Nitrobenzyl phenyl ether	0.58	1.02
p-Methylphenyl benzyl ether	0.68	1.20
p-Nitrophenyl benzyl ether	0.68	1.20

[a] Mole $\text{liter}^{-1}\text{second}^{-1}$.

A good correlation is obtained with the benzyl alkyl ethers and benzyl alcohol, but dibenzyl ether is much more reactive and benzyl phenyl ether less reactive than the values of σ^* would predict. The choice of using σ^* constants seemed warranted since they cancel out any steric or resonance contributions to the transition state and only the inductive

Table 6. Rates of oxidation of alkyl benzyl ethers at 60° in chlorobenzene solution (0.1 M AIBN)

Reactant	Rate - $\frac{R_i}{2}$ / $[RH][AIBN]^{\frac{1}{2}}$ x 10^5	Relative values of $\frac{k_p}{(k_t)^{\frac{1}{2}}}$
Dibenzyl ether	2.58[a]	1.58
t-Butyl benzyl ether	2.44	1.49
Benzyl ethyl ether	1.77	1.08
Benzyl methyl ether	1.64	1.00
Benzyl alcohol	0.81	0.50
m-Methylbenzyl methyl ether	1.64	1.00
p-Chlorobenzyl methyl ether	1.64	1.00

[a] Corrected for a statistical factor of two.

effect of the substituents is involved. The lack of correlation of dibenzyl ether and benzyl phenyl ether is another example of these two ethers possessing abnormal reactivities. No standard means of explaining their reactivities is available.

Due to the well known formation of p-p'-dinitrobibenzyl in the base-catalyzed oxidation of p-nitrotoluene, it was decided to autoxidize p-nitrostyrene and see whether this compound could polymerize with itself in the presence

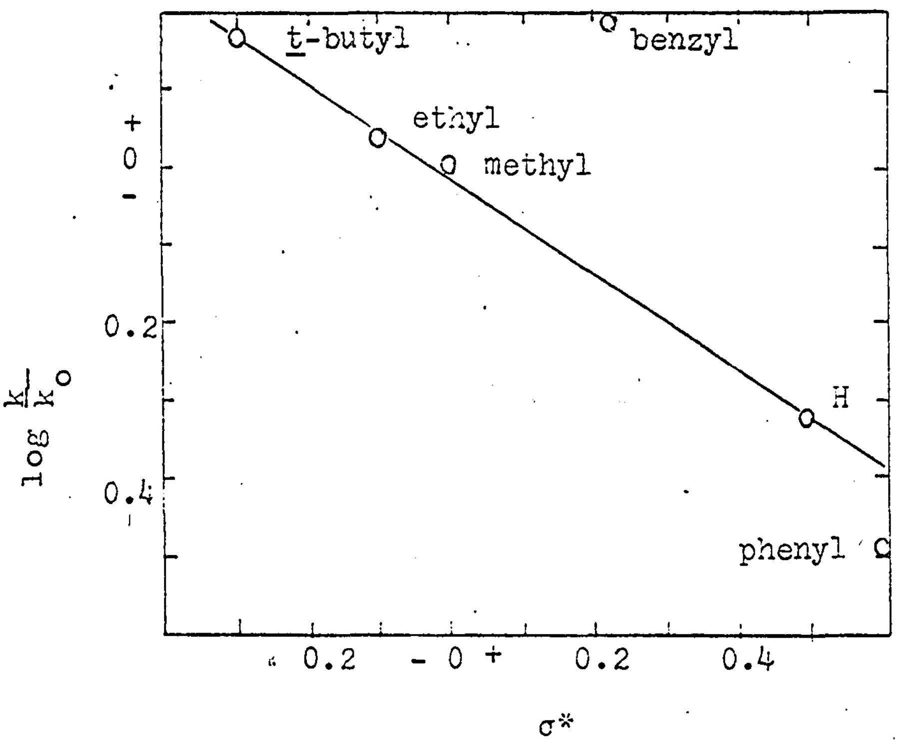
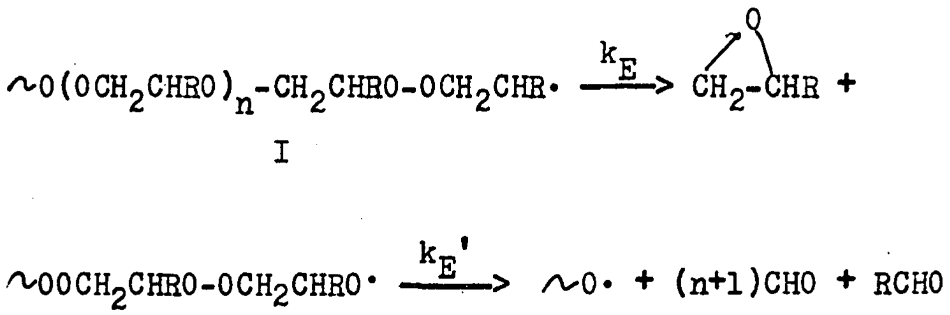


Figure 11. Correlation of log relative reactivities of the data from Table 6 with σ^* constants

of oxygen or whether a one to one copolymer with oxygen would be formed. The results of this work showed a one to one copolymer was formed at 60° in a solution saturated with oxygen at one atmosphere and consequently that the p-nitrostyrenyl radical did not possess any unusual stability towards oxygen. This would seem to rule out the formation of the di-nitrobibenzyl from the radical coupling of two p-nitrobenzyl radicals in the presence of oxygen since this radical should be as reactive to oxygen as the p-nitrostyrenyl radical.

A more sensitive qualitative test for comparison of the reactivities of benzyl and p-nitrobenzyl type radicals toward molecular oxygen was the study of the yield of benzaldehydes formed in autoxidation. The aromatic aldehydes are formed in the following manner (50b).



$$\underset{\text{I}}{\sim O(OCH_2CHRO)_n\text{-}CH_2CHRO\text{-}OCH_2CHR\cdot} \xrightarrow{k_E} \overset{O}{CH_2\text{-}CHR} +$$

$$\sim OOCH_2CHRO\text{-}OCH_2CHRO\cdot \xrightarrow{k_E'} \sim O\cdot + (n+1)CHO + RCHO$$

The decomposition of I to epoxide and β-peroxy alkoxy radical should depend on the reactivity of I to molecular oxygen. Reaction with oxygen should increase the molecular weight of the polymer chain and not give rise to aldehydes. Thus, if I(R=C_6H_5-) is more reactive to oxygen that I'(R=*p*-$NO_2C_6H_4$-), a higher yield of *p*-nitrobenzaldehyde than benzaldehyde would be expected in the oxidation of *p*-nitrostyrene and styrene. Table 7 summarizes the pertinent results.

From this data it follows that if k_E and k_E' have the same value for R=phenyl and *p*-nitrophenyl,

k_o

$$I + O_2 \xrightarrow{k_o} I\text{-}OO\cdot$$

must actually be somewhat (but not dramatically) less than R=*p*-nitrophenyl than when R=phenyl. Shapes of curves of aldehyde versus oxygen pressure actually suggest that in addition to k_o(*p*-nitrophenyl) < k_o(phenyl) that k_E'(*p*-nitrophenyl) < k_E'(phenyl).

During the course of the above investigation, the rate of oxidation of *p*-nitrostyrene was compared to that of styrene and found to be the same. This resulted in the preparation and autoxidation of *p*-methoxystyrene. This substrate oxidized 1.6 times faster than styrene under similar conditions. There thus appeared to be a definite polar effect present in the autoxidation of styrenes and an investigation into the question as to why *p*-nitrostyrene behaved abnormally was initiated.

The oxidation of various mixtures of styrene and

Table 7. Aldehydic products formed in oxidation of 1.0 M styrene and p-Nitrostyrene at 60°, 0.1 M AIBN, M-dichlorobenzene solvent

Substrate	Oxygen absorbed (m moles)[a]	Oxygen pressure (mm)	Aromatic aldehyde (m moles)	Moles aldehyde / Moles O_2 absorbed
Styrene	1.250	710	0.200	0.160
p-Nitrostyrene	1.500	710	0.330	0.220
Styrene	1.150	500	0.230	0.200
p-Nitrostyrene	1.231	500	0.330	0.268
Styrene	1.115	250	0.434	0.390
p-Nitrostyrene	1.010	250	0.320	0.319
Styrene	0.776	100	0.460	0.592
p-Nitrostyrene	0.986	100	0.345	0.350
Styrene	0.680	50	0.475	0.700
p-Nitrostyrene	0.720	50	0.330	0.458
Styrene	2.440	2280	0.252	0.103
p-Nitrostyrene	1.710	2280	0.263	0.154

p-nitrostyrene showed that the total rate of oxidation was additive of the fractional rates of each of the two substrates. Thus, the termination rate constants for these two substrates cannot be very different. This is shown in Figure 16 and Table 16 in the second part of this thesis.

It would not appear that *p*-nitrostyrene could somehow increase the rate of initiation of AIBN since the rate of initiation of the autoxidation of cyclohexene and cumene is essentially the same in nitrobenzene as in chlorobenzene (48, p. 56), the solvent used in the oxidations of the styrenes.

It thus appeared that if there were to be an explanation as to why no polar effect is apparent when the rates of oxidation of styrene and *p*-nitrostyrene are compared, it would have to come from the structure of the peroxy radical which partially determines the rate of propagation. This was subsequently shown to indeed be the situation as indicated in Tables 9 and 10 and in Figures 12 and 13. The data for Figures 12 and 13 come from Table 10 and the relative rates quoted in Table 10 come from Table 9. All of these values were obtained by competitive oxidations of mixtures of these substrates followed by kinetic analysis using the copolymerization equation. A sample calculation of converting from Table 9 to Table 10 will be illustrated for the *p*-methoxystyrenal peroxy radical. This radical prefers to attack *p*-methoxystyrene 1.26 times as fast as styrene and 2.50 times as fast as *p*-nitrostyrene, but in relation to styrene, it prefers to attack *p*-nitrostyrene $\frac{1.26}{2.50}$ or 0.50 times as fast.

The results of the above tables and figures indicate

Table 8. Rates of reaction of substituted styrenes toward the peroxy radical at 60° in chlorobenzene solution (0.1 M AIBN)

Substrate	$\frac{\text{Rate} - \frac{R_i}{2}}{[\text{RH}][\text{AIBN}]^{\frac{1}{2}}} \times 10^{5}$[a]	Relative values of $\frac{k_p}{(k_t)^{\frac{1}{2}}}$
p-Methoxystyrene	8.65	1.59
Styrene	5.45	1.00
p-Nitrostyrene	5.45	1.00

[a] Rate units in mole-liter^{-1}-second^{-1}.

Table 9. Relative propagation rate constants for styrenes toward peroxy radical at 60° in benzene solution (0.1 M AIBN)

M_1	M_2	$\frac{k_{11}}{k_{12}}$	$\frac{k_{22}}{k_{21}}$	$\frac{R_{21}}{R_{22}}$
p-Methoxystyrene	p-Nitrostyrene	2.50	0.15	6.65
Styrene	p-Methoxystyrene	0.59	1.25	0.80
Styrene	p-Nitrostyrene	1.61	0.25	4.00

Table 10. Relative propagation rate constants of substituted styrenes toward the indicated radical at 60° in benzene solution (0.1 *M* AIBN)

Radical	Substrate	Relative reactivity
p-Methoxystyrenyl peroxy	*p*-Methoxystyrene	1.26
	Styrene	1.00
	p-Nitrostyrene	0.50
Styrenyl peroxy	*p*-Methoxystyrene	1.66
	Styrene	1.00
	p-Nitrostyrene	0.62
p-Nitrostyrenyl peroxy	*p*-Methoxystyrene	1.64
	Styrene	1.00
	p-Nitrostyrene	0.25

that polar effects are important in both the radical and the substrate. This can be illustrated by the following structures:

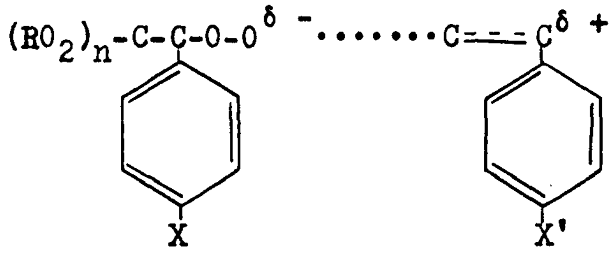
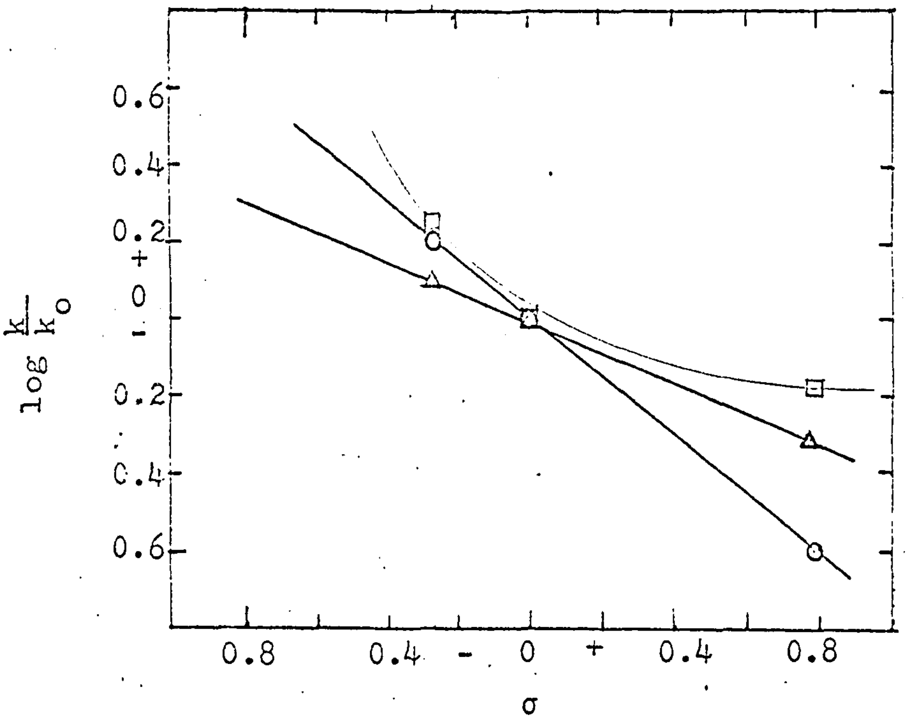
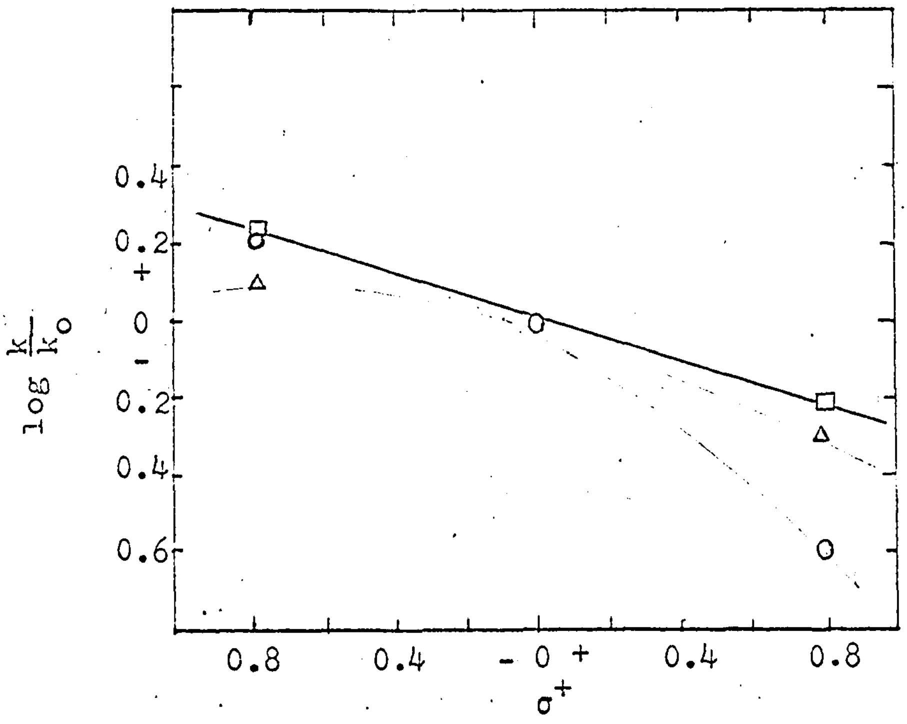


Figure 12. Correlation of log relative reactivities of substituted styrenes with σ constants. ○ -*p*-nitrostyrenyl peroxy radical; △ -*p*-methoxystyrenyl peroxy radical; □ -styrenyl peroxy radical

Figure 13. Correlation of log relative reactivities of substituted styrenes with σ^+ constants. ○ , △ and □ stand for the radicals above


0.6
0.4
0.2
+
0
-
0.2
0.4
0.6
log $\frac{k}{k_o}$
0.8
0.4
-
0
+
0.4
0.8
σ


0.4
0.2
+
0
-
0.2
0.4
0.6
log $\frac{k}{k_o}$
0.8
0.4
-
0
+
0.4
0.8
σ^+

This structure would imply that the most favorable transition state would occur when X is p-nitro and X' is p-methoxy, and the worst one would be when those substituents are reversed.

This structure also helped explain why the relative reactivities of these substituted styrenes toward the p-nitrostyrenyl and p-methoxystyrenyl peroxy radicals are better correlated by σ constants in Figure 12 and better correlated by σ^+ constants toward the styrenyl peroxy radical in Figure 13. The explanation proposed is that the polar effect in the substituted peroxy radical overshadows the polar effects of the substrate when substituted peroxy radicals are used, but toward the unsubstituted peroxy radical, only the polar effects of the substituents in the substrate are involved.

While these polar effects explain why styrene disappears faster than p-nitrostyrene in competitive autoxidation, they did not explain why these two substrates oxidize at the same rate. An explanation for this phenomenon has still not been obtained but presumably involves the absolute values of the propagation rate constants, k_p

$$ROO\cdot + CH_2 = CHR' \xrightarrow{k_p} ROOCH_2CHR\cdot'$$

Experimental

Photochlorination

Apparatus and procedure The photochlorination apparatus was designed so that the carrier gas after entering the system could be directed by the manipulation of one three-way stop cock either directly to a 500-ml mixing bulb or through a liquid chlorine reservoir and then to the mixing bulb. From the mixing bulb the gas continued to a reaction flask, which was approximately 30-ml in volume, and entered the reaction flask through a finely drawn inlet tube which reached nearly to the bottom of the flask. The gas that left the reaction flask passed through an ice-water condenser and a gas trap containing a 10% sodium hydroxide solution before exiting into the atmosphere. The reaction flask was mounted in a 40° constant temperature bath approximately 3 cm. from a 200-watt unfrosted tungsten lightbulb which was used for catalyzing the chlorination. The system was constructed completely of glass except for a short length of 1/4 inch "Tygon" tubing which directed the carrier gas to the chlorination reservoir when the reservoir was not being by-passed. The three-way stop cock which was used to direct the gas either through or around the chlorine reservoir was equipped with a "Teflon" stop cock plug. A ground ball joint was used to join the mixing bulb to the inlet tube which was constructed into the condenser so that the inlet tube entered the reaction flask through the ground glass joint that connected the condenser to the reaction flask.

The procedure used for the photochlorination involved first sweeping carrier gas through the sample which was to be chlorinated to remove traces of oxygen. The carrier gas which was Matheson prepurified nitrogen was dried over glass beads coated with phosphorus pentoxide. When it was desired to start the chlorination, the stop cock was adjusted in order to allow the nitrogen to pass over the top of the liquid chlorine. The liquid chlorine was allowed to warm to its boiling point and to vaporize. After the proper amount of chlorine had evaporated as determined by the calibration on the reservoir, the liquid chlorine was gradually cooled. After the liquid chlorine was sufficiently cool, the stop cock was adjusted so the nitrogen again bypassed the reservoir. Generally the flow of nitrogen was regulated so all the chlorine was added to the reaction mixture in about two hours. After the addition was complete, nitrogen was allowed to pass through the reaction mixture to remove traces of hydrogen chloride.

Method of analysis A known amount of an internal standard was added to the reaction mixture in the reaction flask after completion of the photochlorination. This insured against errors caused by losses on transfer. The unreacted toluene and substituted toluene were then analyzed by a g.l.c. unit equipped with a Burrell hot wire defector. In all determinations, a correction factor was determined to account for the difference in thermal conducting between the substrate and the standard.

Materials Commercial carbon tetrachloride was passed through silica gel and used without further purification.

Toluene (Fischer Reagent Grade) was rectified. The minimum purity was 99.9% by g.l.c. analysis.

p-Chlorotoluene (Matheson, Coleman and Bell) was rectified to remove traces of toluene. The fraction used was greater than 99% pure by g.l.c. analysis.

p-Phenoxytoluene was prepared by reacting the potassium salt of p-cresol with a slight excess of bromobenzene in the presence of catalytic amount of powdered copper at 270° for three hours (51). The potassium salt was prepared by reacting two moles of p-cresol with one mole of potassium hydroxide at 150°. This melt was then cooled and benzene added to azeotrope off the water formed in the reaction. The excess cresol then served as a solvent for the potassium salt in the reaction with bromobenzene. The reaction mixture containing the formed ether was washed with 15% aqueous sodium hydroxide (to remove the unreacted p-cresol), water, dried over sodium sulfate and distilled. The fraction used had a b.p. of 110-111° at 2 m.m.; reported b.p. of 292° at atmospheric pressure (51). The complete absence of other materials was determined by g.l.c. analysis.

p-Nitrotoluene (Eastman) was recrystalized from ethanol and dried under vacuum, m.p. 50.5-51°.

m-Chlorotoluene (Matheson, Coleman and Bell) was rectified to remove traces of toluene and p-chlorotoluene. G.l.c. showed greater than 98% purity.

Meta- and p-xylene (Phillips Research Grade) showed greater than 99.9% purity by g.l.c. analysis.

Autoxidation

Apparatus and procedure The oxidation reactions were carried out in a specially prepared reaction flask that was about 20 inches in length. The bottom of the flask was constructed from a 50-ml. erlenmeyer flask and joined to a standard tapered joint at the top of the reaction flask by approximately 16 inches of 8-10 mm. glass tubing and, for strength, by an outside jacket of 20 mm. tubing. The standard tapered joint fitted an adaptor which was connected to the system of a gas buret by a short length of rubber tubing. When AIBN was used as a catalyst it was generally added to the flask in a benzene solution; the benzene was removed at a pressure of 20-30 mm. Solutions that were to be oxidized were added by pipette to the reaction flask and the mixture cooled to dry-ice temperature. The entire system was alternately evacuated and filled with oxygen several times; the flask warmed to room temperature, and fastened to a reciprocating rack in a 60.00 ± 0.15°C oil bath. After allowing the temperature of the contents in the reaction flask to equilibrate to the temperature of the oil bath the gas buret was adjusted; the reciprocation started; and readings were taken periodically. The reciprocating rack was powered by a 1/3 horse power motor and operated between 145 to 150 cyclics per minute. The rate of oxidation did not change when the rate of shaking was increased by a factor of about two in control experiments. When competitive autoxidations were performed the length of time required for 15-20% reaction varied from four hours for the styrenes to 20 hours for the cumenes.

Method of analysis When the competitive oxidations were complete the reaction mixture was passed through a silica gel column followed by a 20-fold excess of benzene. When the highly polar substrate *p*-nitrostyrene was used the eluding solvent was a one percent solution of diethyl ether in benzene. A known quantity of an internal standard was then added to the eluded solution for g.l.c. analysis. This procedure was proven to be quantitative in eluting the substrates cumene, styrene, *p*-nitrostyrene and benzyl phenyl ether by adsorbing a known amount of each of these substrates on the column and eluting with a 20-fold excess of solvent. The amount of substrate in the eluent was shown to be the same as that added by g.l.c. analysis. Other substrates were shown to be eluted quantitatively after oxidation by following the 20-fold excess of solvent with an additional 100 ml. This 100 ml. of solution was then concentrated to about 5 ml. and this solution was tested for traces of the substrate by g.l.c. analysis. In all cases this last test was negative. The products of oxidation and unreacted AIBN, which could later interfere with the g.l.c. analysis, were retained on the silica gel column.

The g.l.c. unit used in the determination of unreacted hydrocarbons was a Perkin-Elmer model 154D chromatogram.

Materials All liquid hydrocarbons were passed over silica gel and stored over nitrogen at 5^o prior to use. Solids were kept in brown bottles stoppered under nitrogen. The solvents benzene and chlorobenzene were passed over silica gel while glacial acetic acid was used from freshly opened bottles. Benzene was used as the solvent in all competitive oxidations since chlorobenzene interfered with many g.l.c. determinations.

Azobisisabutyronitride (AIBN) obtained from Chemical Intermediates and the Borden Monomer-Polymer division was recrystallized from methanol and dried under vacuum, m.p.

with decomposition 101.5°-102°.

Cumene (Phillips 99 mole %) was rectified to remove a low boiling constituent and ethylbenzene. The fraction used was one showing no other peaks on g.l.c. analysis, $\underline{n}_D^{20}$ 1.4915; reported n_D^{20} 1.4915 (52, p. 1).

p-Methoxycumene was prepared by reacting 55 g. p-isopropylphenol dissolved in 150 ml 1:1 water-ethanol mixture containing 25 g. potassium hydroxide with 51 g. dimethylsulfate. The dimethylsulfate was added dropwise with stirring. Thirty minutes after the final addition 200 ml. of a 1:1 methanol-concentrated ammonia solution was added to destroy any unreacted dimethylsulfate. The reaction mixture was then washed with ether and the ether layer washed with 10% KOH solution, water, dried over sodium sulfate and the ether distilled off. Rectification of the remaining material gave 37 g. of the desired product, b.p. 85° at 10 mm., n_D^{20} 1.5033; reported $\underline{n}_D^{20}$ 1.5045 (53, p. 505).

p-t-Butoxycumene was prepared by the addition of isobutylene to p-isopropylphenol in the presence of a catalytic amount of sulfuric acid (54). A partial pressure of isobutylene was maintained over the reaction mixture by the use of a bubbler. The reaction mixture was stirred for 12 hours at room temperature. During this time the reaction mixture changed from a solid to a liquid. This liquid was then rectified and the fraction boiling at 111.7° at 12 m.m.

was used, n_D^{20} 1.4860.

p-Phenoxycumene and m-phenoxycumene were prepared from the p- and m-isopropylphenols by the procedure described for the phenoxytoluenes. The m-isopropylphenol was a gift from the Hercules Company. The para-isomer had a b.p. of 150° at 7 m.m.; reported b.p. 288.9° at 760 m.m. (55). The meta-isomer had a b.p. of 144° at 7 m.m., n_D^{20} 1.5570. G.l.c. analysis showed both compounds to be greater than 99.8% pure.

p-Bromocumene was prepared by the bromination of cumene in the dark using iodine as a catalyst. To 100 g. of cumene dissolved in 100 ml. of a 1:1 mixture of carbon tetrachloride and acetic acid was added one large crystal of iodine and 150 g. of bromine in 150 ml. carbon tetrachloride. The reaction was carried out overnight with gentle refluxing. The mixture was then washed with 10% sodium hydroxide solution, water and then dried over sodium sulfate. A crude distillation through a Vigreux column was followed by a careful rectification through a Todd column packed with glass helices to give a material with a b.p. of 110° at 22 m.m., n_D^{20} 1.5360; reported b.p. 123.5° at 53 m.m., n_D^{20} 1.5363 (29).

p-Nitrocumene was prepared by the procedure of Brown and Bonner (56). Rectification of the nitrated mixture through a 30 inch monel helices packed column gave the desired product, b.p. 110° at 5 m.m., n_D^{20} 1.5369; reported

$\underline{n}_D^{20}$ 1.5369 (56).

Methyl-p-isopropyl benzoate was synthesized by converting p-isopropylbenzoic acid to the acid chloride with thionyl chloride followed by treatment with excess methanol in pyridine (57). The resulting solution was then washed with water, dried over sodium sulfate and distilled, b.p. 118°-119° at 12 m.m., $\underline{n}_D^{20}$ 1.5108; reported $\underline{n}_D^{20}$ 1.5108 (29).

p-Diisopropylbenzene (Aldrich Chemical Co.) was distilled through a glass helices packed Todd column and the center fraction was collected, b.p. 112.3° at 30 m.m., $\underline{n}_D^{20}$ 1.4896; reported $\underline{n}_D^{20}$ 1.4898 (58).

All of the substituted-benzyl phenyl ethers were prepared by reacting equal molar quantities of potassium phenoxide with the corresponding benzyl chloride or bromide (the bromide was used when it was commercially available) in a 1:1 mixture of ethanol and tetrahydrofuran. The potassium phenoxide was always freshly prepared by reacting equal molar quantities of phenol and potassium hydroxide in a melt at about 150°. Enough solvent was then added to the cooled salt to give a saturated solution. The benzyl halide was then added dropwise over a period of approximately two hours with stirring and the resulting solution stirred under reflux overnight. Solvent was then removed with a Rinco evaporator until crystals began to form in the solution or until most of the solvent had been removed in the cases where the product was a liquid. All solutions containing solid products were then cooled in an ice bath and the solids filtered and recrystallized from ethanol. Liquids were rectified and the fractions chosen were those having a constant boiling point and refractive index. Special care had to be taken, however, in the preparation of p-methoxybenzyl phenyl ether. As little ethanol as possible should be used to dissolve the potassium phenoxide into tetrahydrofuran and this solution is added dropwise into a concentrated solution of p-methoxybenzyl chloride in tetrahydrofuran. If the normal procedure is followed the major product formed is p-methoxy-p'-hydroxy-diphenylmethane, m.p. 83-83.5°; reported m.p. 83-84° (59). Table 11 lists the physical properties of these benzyl phenyl ethers. All new compounds had n.m.r. spectra consistent with their structures.

p-Nitrophenyl benzyl ether [m.p. 105-105.5°; reported 106° (53, p. 433)] and p-tolyl benzyl ether [m.p. 39-40°; reported 41° (53, p. 434)] were synthesized by adding benzyl chloride dropwise to a saturated solution of the potassium salt of the corresponding phenol in a 1:1 ethanol tetrahydrofuran solution with stirring under reflux overnight. Both of these potassium salts were prepared by reacting potassium t-butoxide with the phenols in 150 ml of tetra-

Table 11. Physical constants of some benzyl phenyl ethers (R-O-C_6H_5)

R	Found			Reported		Reference
	m.p.	b.p.	n_D^{20}	m.p.	b.p.	
Benzyl	39 -39.2°			39°		60
p-Nitrobenzyl	90.3-90.7°			91°		61
m-Nitrobenzyl		163° at 1.5 m.m.	1.5980		182° at 2 m.m.	62
p-Chlorobenzyl	85 -85.5°			85.5-86.5°		63
m-Chlorobenzyl	36 -36.5°			36 -36.4°		63
m-Methylbenzyl		106° at 0.5 m.m.	1.5731		168-170° at 17 m.m.	64
p-Methylbenzyl	81.5-82°			New compound		
p-Methoxybenzyl	85.9-90.5°			New compound		

hydrofuran. One hundred fifty ml of ethanol was then added to dissolve the salt. The same workup procedure employed for the preparation of the substituted-benzyl phenyl ethers was used. Both solids were recrystalized from ethanol.

Benzyl methyl ether was prepared in the following manner: 20 g. (0.5 moles) of potassium was added slowly in small pieces to 300 ml. of a 1:1 methanol-tetrahydrofuran solution. After the last of the potassium had reacted 63 g. (0.5 moles) of benzyl chloride was then added slowly and the resulting solution was stirred and heated under reflux overnight. This solution was then washed with 10% sodium hydroxide solution, water and dried over sodium sulfate. Solvent was then distilled off and the remaining liquid rectified through a 15 inch spinning band column. The fraction used showed no impurities by g.l.c. analysis, n_D^{20} 1.5028; reported $\underline{n}_D^{20}$ 1.5022 (65).

Benzyl ethyl ether (Eastman) was distilled through a 15 inch spinning band column. The fraction used was pure by g.l.c. analysis, $\underline{n}_D^{20}$ 1.4950; reported n_D^{20} 1.4955 (52, p. 61).

Benzyl t-butyl ether was prepared by the reaction of potassium t-butoxide with benzyl chloride in a t-butyl alcohol - tetrahydrofuran solution at room temperature with stirring for seven days. Normal workup procedures were followed. The product had a b.p. of 39-40° at 0.5 m.m.,

$\underline{n}_D^{20}$ 1.4858; reported b.p. 38-41° at 0.5 m.m., $\underline{n}_D^{23}$ 1.4848 (66, p. 242).

Benzyl alcohol was obtained from Mr. Edward Janzen of these laboratories, $\underline{n}_D^{20}$ 1.4502; reported $\underline{n}_D^{20}$ 1.5396 (52, p. 61).

m-Methylbenzyl methyl ether was synthesized from m-methylbenzyl bromide and potassium methoxide using the same method and workup procedure as in making benzyl methyl ether. G.l.c. analysis showed 99% purity with the impurity being the m-methyl benzyl bromide, b.p. 47° at 2 m.m., $\underline{n}_D^{20}$ 1.5003.

p-Chlorobenzyl methyl ether was prepared from p-chlorobenzyl bromide in the same manner as the m-methyl isomer. G.l.c. analysis showed 100% purity, b.p. 60° at 2 m.m., $\underline{n}_D^{20}$ 1.5213.

Commercial styrene containing inhibitor was distilled through a silver jacketed, glass helices packed, 10 inch column. The center portion was used, $\underline{n}_D^{20}$ 1.5467; reported $\underline{n}_D^{20}$ 1.5469 (67, p. 1385).

p-Nitrostyrene was prepared according to Walling *et al.* who report a m.p. of 21.4° (68), found 21.2-21.5°. The copolymer of p-nitrostyrene with oxygen was a solid that could be recrystalized from acetone with a m.p. with decomposition of 120-122°. Analysis by Schwarzkopf: % carbon 53.22, % hydrogen 4.11, % nitrogen 7.92, % oxygen (by difference); calculated for a 1:1 copolymer; % carbon 53.04, % hydrogen 3.86, % nitrogen, 7.73, % oxygen 35.57.

p-Methoxystyrene was prepared by a procedure of Walling and Wolfstirn (69). This compound contained an autoxidation inhibitor which could not be removed by distillation, by washing with acid or base, or by passing it through alumina or silica gel. It was finally removed by reacting 15 g. of p-methoxystyrene with 0.08 g. AIBN and oxygen at 60°. Upon observing oxygen uptake the reaction was stopped and passed through silica gel to remove any unreacted AIBN and oxidized products. The resulting liquid was then flash distilled at 0.1 m.m. This liquid was then carefully distilled, giving a pure compound, b.p. 54-55° at 2 m.m., n_D^{20} 1.5618; reported b.p. 53-54° at 2 m.m., n_D^{20} 1.5612, 1.5608 and 1.5620 (69).

Due to the compounds prepared in this series needing to be exceptionally pure, there was a lot of each compound lost in purification procedures and yields were not considered or reported in this work. In general, however, a yield of around 30 g. was tried for and a per cent yield of around 35-40% was assumed. The reactants were then scaled up to give the required yield of product.

Vapor phase chromatograph columns were as follows:

1. Perkin-Elmer B: a two meter column with di-2-ethylhexyl sebacate as the liquid phase.

2. Perkin-Elmer O: a one meter column with silicone grease as the liquid phase.
3. XF 1105: one meter, 20% GE XF 1105 silicone oil on 80/100 mesh firebrick. XF 1105 is a methyl silicone with 5% of the methyl groups replaced by cyanomethyl groups.
4. XF 1150: one meter, 20% GE XF 1150 silicone oil on 80/100 mesh firebrick. XF 1150 is a methyl silicone with 50% of the methyl groups replaced by cyanomethyl groups.
5. Perkin-Elmer R: a two meter column with Ucon oil LB-550-X as the liquid phase.

Table 12. Conditions for g.l.c. analysis of competitive photochlorination and autoxidation reaction mixtures

Compound[a]	Temperature	Column	Helium flow (c.c./min.)	Retention time (minutes)
Toluene	150	1	100	3.2
p-Chlorotoluene	"	"	"	10.2
- Chlorobenzene(IS)	"	"	"	5.6
Toluene	150	1	100	3.2
m-Chlorotoluene	"	"	"	10.0
- Chlorobenzene(IS)	"	"	"	5.6

[a] The first two compounds in each series are the competing substrates; IS is the internal standard for the series. When two internal standards are listed, the first one is for the first substrate.

Table 12. (Continued)

Compound^a	Temperature	Column	Helium flow (c.c./min.)	Retention time (minutes)
Toluene	170	1	105	2.7
p-Xylene	"	"	"	4.6
Bromobenzene(IS)	"	"		8.7
Toluene	170	1	105	2.7
m-Xylene	"	"	"	4.6
Bromobenzene(IS)	"	"	"	8.4
Toluene	150	1	100	3.1
p-Nitrotoluene	210	2	90	2.6
Chlorobenzene(IS)	150	1	100	5.6
p-Phenoxytoluene(IS)	210	2	90	6.4
Toluene	150	1	100	3.2
p-Phenoxytoluene	210	2	90	6.4
Chlorobenzene(IS)	150	1	100	5.5
p-Nitrotoluene(IS)	210	2	90	2.5
Toluene	150	1	100	3.2
m-Phenoxytoluene	210	2	90	6.4
Chlorobenzene(IS)	150	1	100	5.6
p-Nitrotoluene(IS)	210	2	90	2.5
Cumene	145	4	50	2.6
p-Methoxycumene	"	"	"	10.8
Anisole(IS)	"	"	"	4.8
Cumene	145	4	50	2.6
p-Nitrocumene	200	3	30	8.7
Anisole(IS)	145	4	50	4.8
p-Nitrotoluene(IS)	200	3	30	5.0
Cumene	145	4	50	2.6
Benzyl phenyl ether	200	2	70	4.3
Anisole(IS)	145	4	50	4.8
p-Chlorobenzyl phenyl ether(IS)	200	2	70	5.6

Table 12. (Continued)

Compound[a]	Temperature	Column	Helium flow (c.c./min.)	Retention time (minutes)
Styrene	145	4	50	3.4
p-Nitrostyrene	200	3	30	7.3
Anisole(IS)	145	4	50	4.8
p-Nitrotoluene(IS)	200	3	30	5.0
Styrene	145	4	50	3.4
p-Methoxystyrene	"	"	"	15.9
Anisole(IS)	"	"	"	4.8
p-Methoxystyrene	145	4	50	15.9
p-Nitrostyrene	200	3	30	3.6
Anisole(IS)	145	4	50	4.8
m-Dichlorobenzene(IS)	200	3	30	2.6

AUTOXIDATION OF HYDROCARBON MIXTURES

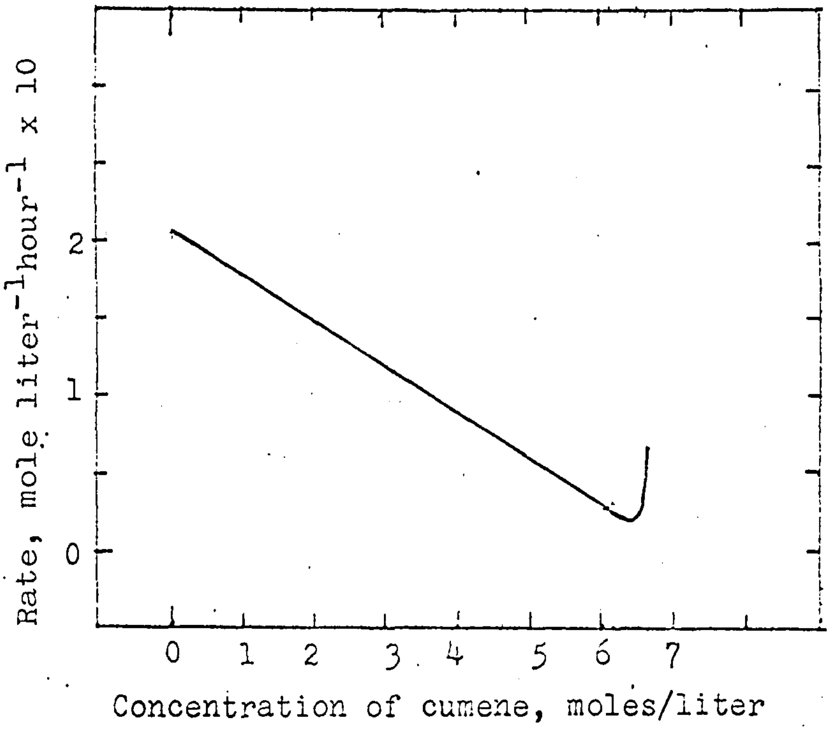
Introduction

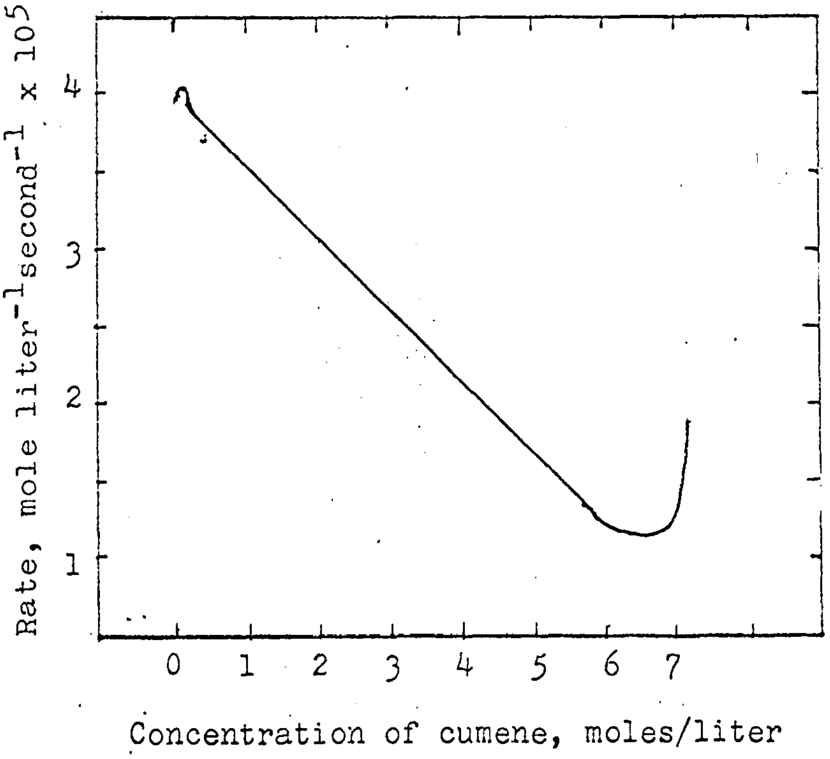
While there has been extensive research into the area of autoxidation of hydrocarbons in the liquid phase and several reviews have been written on the subject (70, 71, 72 and 73), there was little work done in the field of co-oxidation until that of Russell (29 and 41), Mayo _et al._ (74a) and Alagy _et al._ (42, 43 and 75).

Russell was the first to observe the fact that when the two peroxy radicals involved in the autoxidation of two hydrocarbons distinctly differ in their termination rate constants, a net retardation of the rate of oxidation may result. This phenomenon is especially noticeable when the more reactive substrate has the higher termination rate constant. An example of this is shown in Figure 14 where the rates of oxidation of various mixtures of tetralin (k_t = 2.4 x 10^7 mole^{-1} liter second^{-1})(74b) and cumene (k_t = 4.2 x 10^4 mole^{-1} liter second^{-1})(38) are plotted versus concentrations of these substrates. Based upon this observation numerous co-oxidations were performed and relative termination rate constants qualitatively estimated by noting whether a straight line, which would most likely indicate equality of k_t's or a curved line resulted. From

Figure 14. Plot of the data after Russell (41) for the co-oxidation of cumene and tetralin at 90° with *t*-butyl perbenzoate as catalyst

Figure 15. Plot of data after Alagy *et al*. (42) for the co-oxidation of cumene and tetralin at 60° using AIBN as catalyst


Rate, mole liter^{-1}hour^{-1} x 10
2
1
0
0
1
2
3
4
5
6
7
Concentration of cumene, moles/liter


Rate, mole liter^{-1}second^{-1} x 10^5
4
3
2
1
0
1
2
3
4
5
6
7
Concentration of cumene, moles/liter

the values of $\frac{k_p}{k_t^{\frac{1}{2}}}$ determined from the oxidations of the pure substrates relative values of k_p for a group of hydrocarbons toward the peroxy radical were obtained (41).

Alagy et al. (42) repeated the work of Russell on the co-oxidation of tetralin and cumene, and also did a thorough investigation of the rates of oxidation at high tetralin concentration. This investigation showed that a maximum rate occurred at these concentrations as is shown in Figure 15. These workers explained this maxima as something that should have been expected since a minimum was experienced at the lower end of the tetralin concentration range. Since then, these same workers have also determined the termination rate constants for a number of peroxy radicals from the shape of the co-oxidation rate curves (43).

Both sets of workers have employed the equation, or minor variations of it, for co-oxidation:

$$\frac{d([R_1H] + [R_2H])}{d_t}$$

$$= \frac{(k_{12}k_{11}[R_1H] + 2k_{12}k_{21}[R_1H][R_2H] + k_{22}k_{12}[R_2H])^2}{(2k_{t11}k_{21}{}^2[R_1H]^2 + 2k_{t12}k_{t21}[R_1H][R_2H] + 2k_{t22}k_{12}{}^2[R_2H]^2)^{\frac{1}{2}}}$$

A more workable form of this equation where the various rate constants are given in more usable ratios is the following:

$$\frac{d([R_1H] + R_2H])}{d_t}$$

$$= \frac{([R_1H]^2 r_1 + 2[R_1H][R_2H] + r_2[R_2H]^2)R_1^{\frac{1}{2}}/\delta_1}{([R_1H]^2 (r_1)^2 + 2\emptyset[R_1H][R_2H]r_1 r_2 \frac{\delta_2}{\delta_1} + (R_2H)^2 r_2^2 \frac{\delta_2}{\delta_1}^2)^{\frac{1}{2}}}$$

where r_1 and r_2 have the same significance as given previously, $\delta_1 = \frac{(k_{t11})^{\frac{1}{2}}}{k_1}$, $\delta_2 = \frac{(k_{t22})^{\frac{1}{2}}}{k_3}$ and $\emptyset = \frac{k_{t12}}{(k_{t11}k_{t22})^{\frac{1}{2}}}$.

Since r_1 and r_2 can be obtained from the copolymerization equation and δ_1 and δ_2 from the oxidations of the pure hydrocarbons, $\emptyset$ can be determined. While $\emptyset$, a measure of the ratio of the cross termination rate constant to the geometric mean of the two symetric rate constants, should be a constant, it is usually slightly dependent upon the concentration of hydrocarbons employed and a weighted average is usually quoted.

If these equations actually explain the kinetic behavior of these two substrates upon co-oxidation, then the derivative of this equation with respect to one of the substrate concentrations should determine the minimum point while the second derivative with respect to the same variable should determine if a maximum exists.

Unfortunately, the only time the first derivative was determined, the derivative contained rate constants not known and ratios that were also not obtainable (75). The authors did, however, attempt to use this derivative together with several assumptions to show that a maximum could be expected in a co-oxidation when the various termination rate constants were in the order $k_{t11} > k_{t12} > k_{t22}$ and the rates of oxidation of the pure substrates were in the order $R_1H > R_2H$.

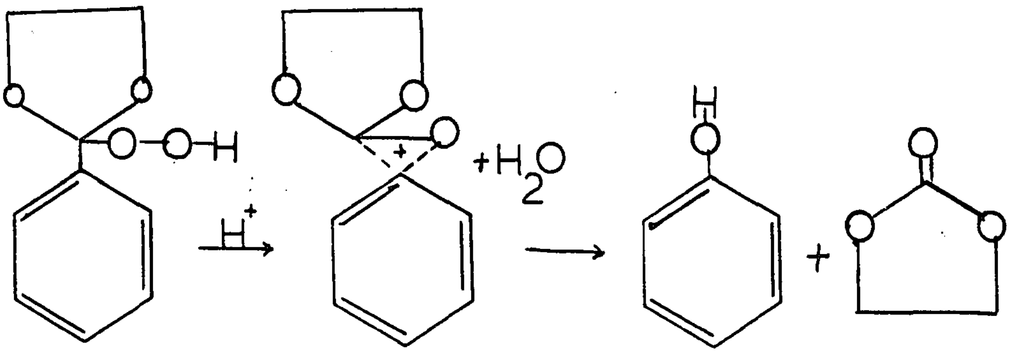
This same general phenomenon was also recognized much earlier in the field of copolymerization when Walling (76) observed a rate decrease upon the addition of a small amount of styrene to methyl methacrylate. This decrease was much greater than would have been expected due to a dilution effect and was attributed to a large cross termination rate constant. This was usually noticed when a strong alternating effect was found in the copolymer. The large cross termination rate constants were thus linked with a strong polar effect in the transition state for the termination reaction.

A curious example of rate retardation in co-oxidations having been observed in a single substrate was the autoxidation of p-cymene (p-methylcumene) as reported by Russell (29). From polar considerations this compound should have oxidized faster than cumene, but was actually only 0.44 times that of cumene. This was attributed to the methyl group also oxidizing and forming a primary preoxy radical since toluene retards the rate of oxidation of cumene more than would be expected of an inert diluent. In fact, a one to one mixture of toluene and cumene oxidized at the same rate as p-cymene when differences in concentrations were accounted for. The same rate was also observed when a three to one mixture of cumene and mesitylene was autoxidized. A further example of this effect may be the autoxidation of p-cyclohexylcumene in the presence of manganese stearate whose rate of oxidation is much slower than that of cumene under the same conditions (77).

The purpose of the work reported in the next section was to determine the effect of the structure of the peroxy radical on the hydrogen atom abstraction reaction, and to determine if the rate of oxidation of some of the slower reacting compounds was due to an abnormally high termination rate constant. To accomplish this, the rates of oxidation were obtained for the pure compounds and also for various mixtures with other substrates. The disappearance of the co-oxidants was also measured and correlated by the use of the integrated form of the copolymerization equations.

Results and Discussion

A number of hydrocarbons have been autoxidized and their rates tabulated in Table 13. One of the more interesting compounds in this series is 2-phenyl-1,3-dioxolane. The rates quoted for this compound were obtained from the initial slope of the plot of oxygen absorbed versus time. However, this rate begins to decrease as the reaction progresses and a curved line results. This decrease can not be explained by the concentration of substrate decreasing since in ten minutes the substrate concentration could not have decreased more than three percent while the rate had decreased by fourteen percent. Instead, it seems more logical to assume that the oxidation product was partially rearranging or decomposing to an inhibitor such as phenol. Total rearrangement or decomposition of either the peroxy radical or the hydroperoxide is ruled out by the fact that the peroxide can be isolated in fair yield (78). A small amount of benzaldehyde (less than one percent) was present in the dioxalane, and it possibly furnished the acid required for the rearrangement:



This explanation seemed quite probable since any positive charge in the transition state should be stabilized by the phenyl group and by the oxygen atoms on the alpha carbon atom. Support is also gained from the work of Rieche et al. who autoxidized 2-p-chlorophenyl-1,3-dioxolane and the unsubstituted substrate and found an almost quantitative yield (97.5 percent) of the 2-p-chlorophenyl-1,3-dioxolane hydroperoxide, and only a 61.5 percent yield of the 2 phenyl-1,3-dioxolane hydroperoxide (78). Since electron withdrawing groups should hinder and perhaps stop the rearrangement from occurring, the mechanism above seemed to be adequately explained.

This same polar effect can also be one of the reasons that this dioxolane is so reactive. Thus, the positive charge generated in the transition state for hydrogen atom abstraction can be stabilized by the phenyl group and the oxygen atoms on the alpha carbon atom. Another factor which could be important is that this peroxy radical may have an extremely low value for its termination rate constant.

If the rate of initiation is constant in these oxidations, then relative values of $\frac{k_p}{k_t^{\frac{1}{2}}}$ are given by the rates of oxidation. However, since the termination rate constants are known for only a few peroxy radicals, the relative k_p values can not be obtained. Even if these k_p values were determinable, a comparison of them would not mean very much since they would each involve a different peroxy radical. A more valid comparison can be obtained if a series of co-oxidations are performed and relative propagation rate constants obtained for a given peroxy radical. This has been done for most of the compounds in Table 13 and the results are compiled in Tables 14 and 15.

If Table 13 and Table 14 are compared, it becomes obvious that when competitive reactions are carried out, the measured relative reactivities are not in perfect agreement with the relative values of $k_p/k_t^{\frac{1}{2}}$. Thus, styrene appears much more reactive in Table 14 than in Table 13. This is accounted for by the styrenyl peroxy radical terminating quite rapidly in comparison to the other peroxy radicals and that in a competitive reaction where the disappearance of substrate is measured, termination rate constants are not a factor in the measurement of relative reactivities.

A relative value of these termination rate constants

Table 13. Autoxidation of vinyl and alkyl aromatic compounds at 60° (0.1 M AIBN)

Substrate	Rate - $\frac{\frac{R_i}{2}}{[RH][AIBN]} \times 10^{5}$ [a]	Relative $\frac{k_p}{k_t^{\frac{1}{2}}}$
3-Phenyl-1,3-dioxolane[b]	16.82	6.22
α-Methylstyrene[b]	11.31	4.16
Dibenzyl ether	6.00	2.21
Styrene	5.45	2.03
p-Methoxystyrene	8.65	3.20
p-Nitrostyrene	5.45	2.03
Tetralin[b]	2.72	1.00
Benzyl ethyl ether	1.71	0.63
p-Methoxycumene	1.48	0.54
Cumene	1.04	0.38
p-Nitrocumene	0.50	0.18
cis-Decalin[b]	0.56	0.21
2°-Butylbenzene	0.55	0.20
Bibenzyl[b]	0.46	0.17

[a] Mole liter^{-1} second^{-1}.

[b] Oxidations done in benzene as solvent. All others in chlorobenzene.

Table 14. Relative reactivities of various substrates toward the indicated peroxy radicals

Substrate	Peroxy radical					
	Styrenyl	α-Methylstyrenyl	Tetralyl	Cumyl	Benzyl ethyl ether	cis-Decalin
Styrene	2.44	1.05	1.11		11.00	
α-Methylstyrene	2.73	1.25	1.33			
Tetralin	1.00	1.00	1.00	1.00	1.00	1.00
Cumene	0.24		0.14	0.30	0.25	0.03
Benzyl ethyl ether	0.66		1.11	3.00	0.55	
cis-Decalin			0.50	0.47		0.05

Table 15. Relative reactivities of substrates not correlated with tetralin toward the indicated peroxy radicals

Substrate	Peroxy radical					
	Styrenyl	Dibenzyl ether	2-Phenyl-1,3-dioxolane	Cumyl	sec-Butylbenzene	Bibenzyl
Styrene	1.00	4.15	0.83	0.10		
Dibenzyl ether	0.62	1.00				
2-Phenyl-1,3-dioxolane	25.0		1.00			
Cumene				1.00		
sec-Butylbenzene				1.00		
Bibenzyl				0.38		

can be obtained from Figure 16 where the co-oxidation rate data for styrene versus all the substrates it was completed against are plotted. The greatest differences in k_t must exist between the tertiary peroxy radicals from cis-decalin, cumene, alpha-methylstyrene and 2-phenyl-1,3-dioxolane and the styrenyl peroxy radical. These differences are shown by the extremely large decreases in rate observed when a small amount of styrene, which has the largest k_t, is added to any of these substrates. This sharp decrease is due to a lowering of the total peroxy radical concentration. The shallow minimum observed when a small amount of alpha-methylstyrene or 2-phenyl-1,3-dioxolane is added to styrene may be due to the cross termination rate constant being larger than the geometric mean of the symmetrical termination rate constants. This results in a ϕ larger than unity and a retardation in rate results.

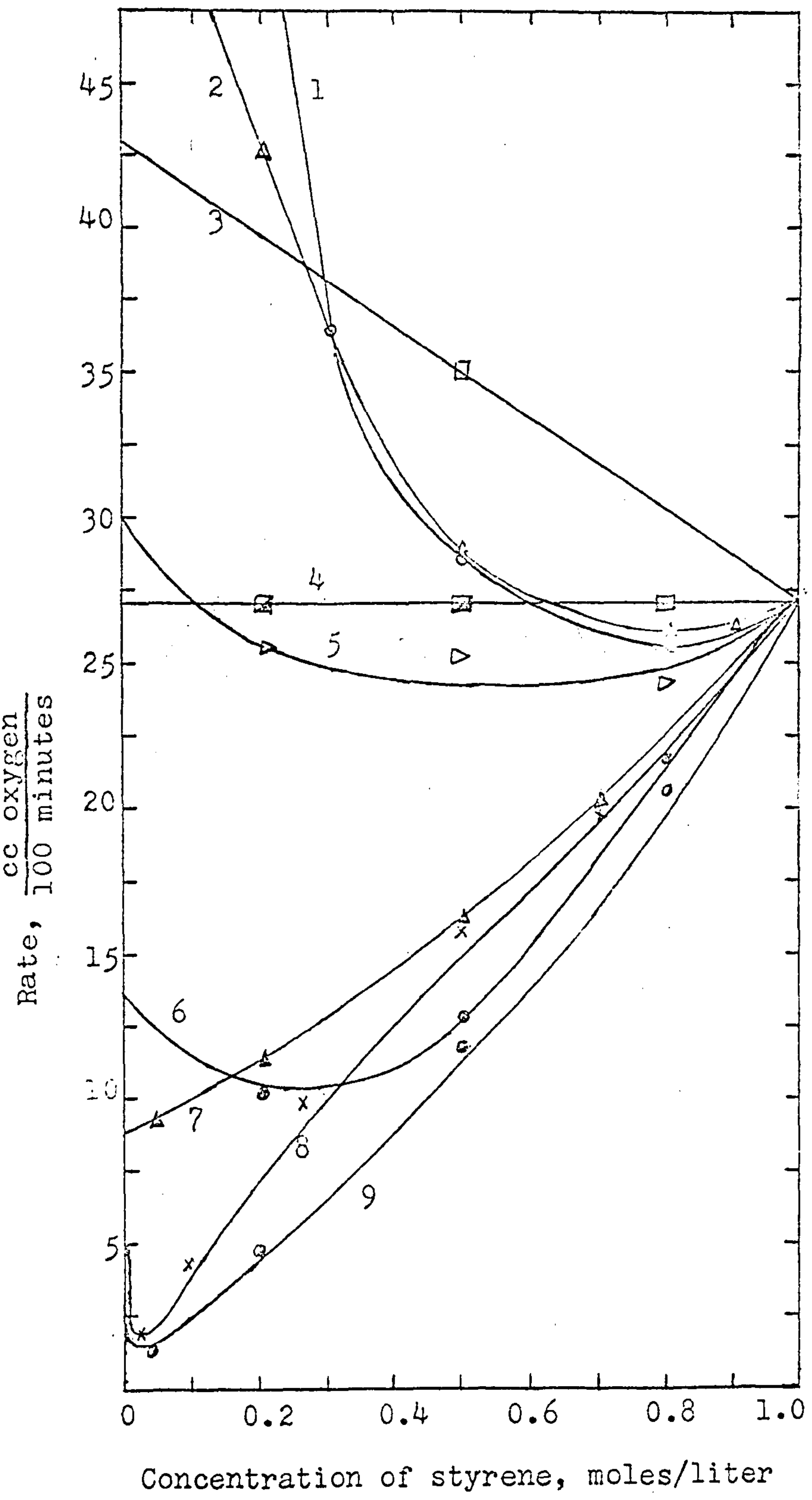
An interesting situation exists when ϕ is less than unity (the cross termination rate constant is less than the geometric mean). This would mean a slight maximum in the co-oxidation rate. Alagy et al. (42) have reported this to occur in the co-oxidation of tetralin and cyclohexene.

The competitive oxidations of styrene - tetralin and styrene - dibenzyl ether both involve secondary peroxy radicals in the termination reactions, but again the styrenyl peroxy radical probably terminates faster than

Figure 16. Rate of oxidation of mixtures of styrene and the following compounds in 10 ml. of benzene solution at 60° and 0.1 M AIBN. Concentration of total substrate concentration is 1 M.

1. 2-Phenyl-1,3-dioxolane
2. alpha-Methylstyrene
3. p-Methoxystyrene
4. p-Nitrostyrene

5. Dibenzyl ether
6. Tetralin
7. Benzyl ethyl ether
8. Cumene
9. cis-Decalin


45
40
35
30
25
20
15
10
5
0
0.2
0.4
0.6
0.8
1.0
1
2
3
4
5
6
7
8
9
Rate, $\frac{\text{cc oxygen}}{\text{100 minutes}}$
Concentration of styrene, moles/liter

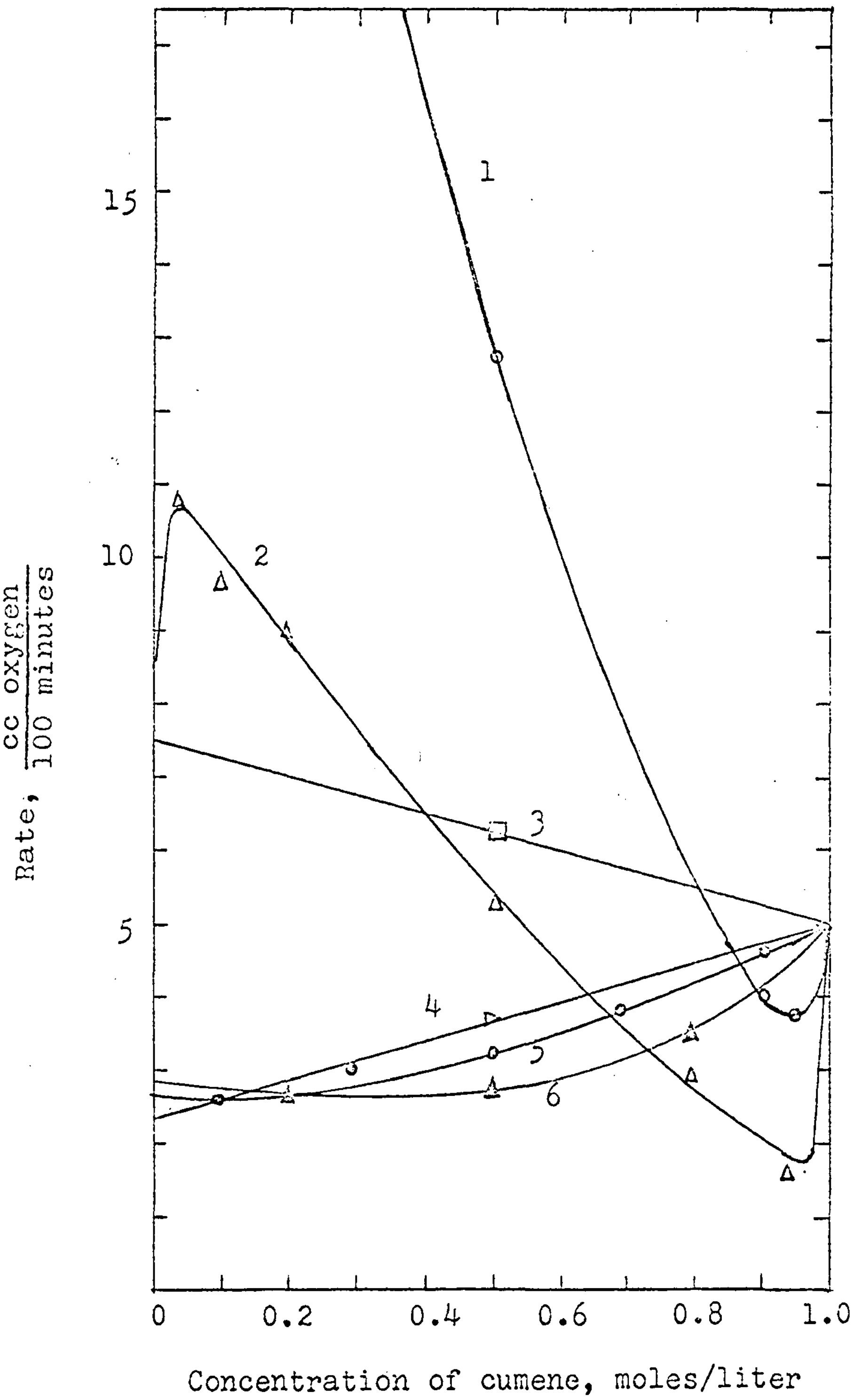
either the tetralyl peroxy radicals since a definite minimum is seen in Figure 16. Alternately ϕ may be much greater than one.

The benzyl ethyl ether peroxy radical, another secondary peroxy radical, apparently terminates slightly slower than the styrenyl peroxy radical since the co-oxidation rate curve contains only a slight minimum deviation from the straight line arising from the additive rates. Again this may also reflect a value of ϕ greater than one. The only substrates that have the same termination rate constants as the styrenyl peroxy radical are the substituted styrenes as indicated by the straight lines resulting from co-oxidations as shown in Figure 16.

Further proof of the high termination rate constant for the benzyl ethyl ether peroxy radical can be seen in its competitive oxidations with cumene in Figure 17 and with tetralin in Figure 18. Thus, the addition of a small amount of benzyl ethyl ether to either cumene or tetralin causes a sharp decrease in the rate of oxidation. This sharp decrease can be attributed to a decrease in the peroxy radical concentration brought about by the fast termination of the ether peroxy radicals. The rates of co-oxidation of both benzyl ethyl ether - cumene and benzyl ethyl ether - tetralin also show an increase when either a small amount of cumene or tetralin is added to the ether. This maximum

Figure 17. Rate of oxidation of mixtures of cumene and the following compounds in 10 ml. of benzene solution at 60°. Solutions always 1 M in substrate concentration and 0.1 M AIBN

1. Dibenzyl ether
2. Benzyl ethyl ether
3. p-Methoxycumene
4. p=Nitrocumene
5. *sec*-Butylbenzene
6. *cis*-Decalin


1
2
3
4
5
6
15
10
5
Rate, $\frac{\text{cc oxygen}}{\text{100 minutes}}$
0
0.2
0.4
0.6
0.8
1.0
Concentration of cumene, moles/liter

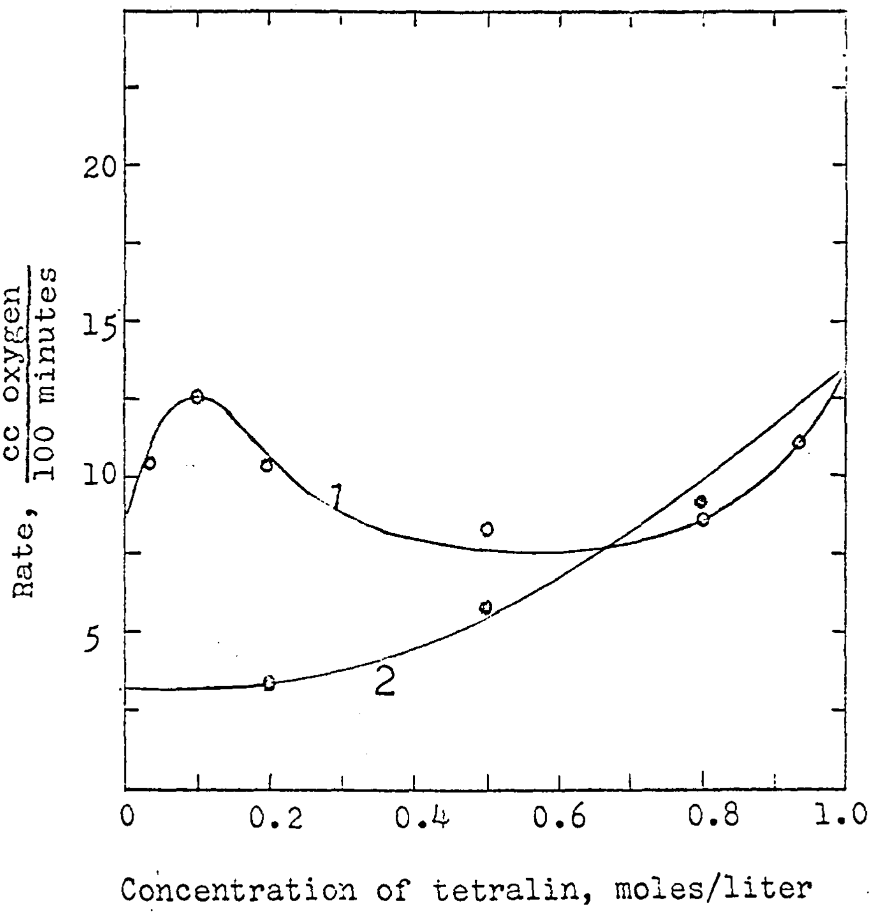


Figure 18. Rate of oxidation of tetralin - benzyl ethyl ether [1] and tetralin - cis-decalin [2] in 10 ml. of benzene solution at 60°. Solutions always 1 M in total substrate concentration and 0.1 M AIBN

in these two rate curves is similar to the maximum found by Alagy *et al*. (42) for the co-oxidation of tetralin and cumene, but the increase in rate occurs over a larger concentration range than for tetralin - cumene co-oxidation. This increase in rate is probably due to an increase in peroxy radical concentration brought about by the slower termination of the cumyl- and tetralyl-peroxy radicals.

If the aforementioned termination rate constants are considered, then the comparison of the relative reactivities of the substrates in Table 14 toward the styrenyl peroxy radical to those in Table 13 has some significance. Alpha-methylstyrene oxidizes about two times faster than styrene and yet its relative reactivity toward the styrenyl and tetralyl peroxy radicals is only 1.12 and 1.20 times as reactive respectively as styrene. This must reflect the difference in their termination rate constants.

This same comparison can be made for dibenzyl ether, tetralin, benzyl ethyl ether and cumene, all of whose relative rates of propagation compared to styrene become less when compared to the styrenyl peroxy radical. However, the value for cumene in Table 14 is questionable since the solution of the copolymerization equation gives a negative value for r_2, a result which has no physical meaning.

If the co-oxidation relative propagation rate constants of styrene versus dibenzyl ether, benzyl ethyl ether and tetralin are compared with the relative values of $\frac{k_p}{(k_t)^{\frac{1}{2}}}$ based on the oxidation of the pure substrate to those of the styrenyl peroxy radical, it becomes clear that the termination rate constants are in the following order: benzyl ethyl ether peroxy radical > tetralyl peroxy radical > bibenzyl ether peroxy radical.

When the relative propagation rate constants of dibenzyl ether, tetralin and benzyl ethyl ether are corrected by statistical factors it is found that dibenzyl ether and benzyl ethyl ether have a relative reactivity of about 1.5 times that of tetralin. This rate enhancement is probably due to the stabilization of the polar transition state by the oxygen atom on the *alpha* carbon atom.

Recently, Meyer *et al.* (79) have criticized the use of a statistical factor of four for hydrogen abstraction reactions on tetralin by claiming that only the two axial hydrogen atoms are in position to allow the incipient radical to be stabilized by the benzene ring. However, there is no experimental work to substantiate this claim and it is not believed by this author that the axial and equatorial hydrogen atoms in tetralin are that different in reactivity toward a peroxy radical.

While differences in termination rate constants can qualitatively account for the relative reactivity series for the styrenyl peroxy radical, it is quite apparent that these same relative reactivities toward the other peroxy radicals in Table 14 depend upon the structure of the peroxy radical. An illustrative example of this is the relative reactivities of styrene and benzyl ethyl ether. Thus, styrene is 20 times more reactive than benzyl ethyl ether toward the ether peroxy radical, 3.7 times more reactive toward the styrenyl peroxy radical and the two possess the same reactivity toward the tetralyl peroxy radical.

A possible explanation of this large change in the relative reactivities would be that the benzyl ethyl ether peroxy radical is the least sterically hindered of the three radicals and vastly prefers to attack the more reactive double bond. Models show that the styrenyl peroxy radical is slightly less hindered than the tetralyl peroxy radical, while they both are much more hindered than the ether peroxy radical. Since the energy of activation for a peroxy radical attacking styrene is about ten kcal. per mole (80) and about seven kcal. per mole for abstracting a hydrogen atom from cumene (38), the greater reactivity of styrene must be due to a higher probability of efficient collisions. Thus, as the peroxy radical becomes larger, there should be a lower probability of attack, and perhaps when the peroxy radical becomes large enough the lower energy of activation for hydrogen abstraction becomes dominant.

The relative reactivities of benzyl ethyl ether and tetralin toward the benzyl ethyl ether, styrenyl, tetralyl and cumyl peroxy radicals would also appear to be explained on the basis of their size, although the styrenyl and tetralyl radicals are in reverse order of that for styrene. However, this sort of reasoning does not seem to hold for the work done with alpha-methylstyrene, and perhaps it is not a valid explanation for the other series.

One of the more interesting series in Table 15 is that of _cis_-decalin and cumene. Cumene oxidizes two times faster than _cis_-decalin, but in competitive reactions _cis_-decalin is 1.56 times more reactive than cumene toward the _cis_-decalin peroxy radical. However, since _cis_-decalin is known to autoxidize at all positions (81), a mixture of _tertiary_ and _secondary_ peroxy radicals are formed which should give a low rate of oxidation. This view is supported by _cis_-decalin being more reactive in competitive reactions.

Bibenzyl and _secondary_-butylbenzene also autoxidize half as fast as cumene. Alagy _et al_. (43) have reported that _secondary_-butylbenzene has a termination rate constant that is a little faster than tetralin. This would explain why, in competitive oxidations with cumene, it is as reactive as cumene toward the cumyl peroxy radical, but it does not explain why the _sec_-butylbenzene peroxy radical appears to attack only cumene. This relationship is not shown in Table 15 since a negative value of r_2 is obtained when R_2H is sec-butylbenzene in the copolymerization equation. Bibenzyl also gives a negative r_2 in the co-oxidation with cumene and is somewhat less reactive in co-oxidations toward the cumyl peroxy radical than in the substrate autoxidation.

Table 16. Rate of autoxidation and competitive reactivity of some co-oxidations in 10 ml. of benzene solution at 60° and 0.1 M AIBN

R_1H	R_2H	$[R_1H]_o^a$	$[R_2H]_o^a$	$[R_1H]_f^a$	$[R_2H]_f^a$	Rate[b]	
						Calc.	Found
Styrene	p-Nitrostyrene	1.000	0.000				27.2
"	"	0.800	0.200	0.620	0.175	27.2	27.2
"	"	0.500	0.500	0.430	0.462	27.2	27.1
"	"	0.200	0.800	0.130	0.724	27.2	27.2
"	"	0.000	1.000				27.2
Styrene	p-Methoxystyrene	0.800	0.200	0.675	0.156		
"	"	0.500	0.500	0.415	0.376	35.0	34.8
"	"	0.200	0.800	0.162	0.617		
"	"	0.000	1.000				43.0
Styrene	2-Phenyl-1,3-dioxolane	0.800	0.200	0.730	0.162	37.5	25.5
"	"	0.500	0.500	0.377	0.230	56.2	28.3
"	"	0.300	0.700	0.186	0.388	67.5	36.7
"	"	0.000	1.000				85.2
Styrene	α-Methylstyrene	0.950	0.050			28.7	27.0
"	"	0.900	0.100			30.0	25.9
"	"	0.800	0.200	0.608	0.141	33.1	26.3
"	"	0.500	0.500	0.405	0.397	41.8	28.2
"	"	0.200	0.800	0.153	0.570	50.6	42.6
"	"	0.000	1.000				56.5

[a] Moles/liter.

[b] Ml. oxygen/100 min.

Table 16. (Continued)

R_1H	R_2H	$[R_1H]_o^a$	$[R_2H]_o^a$	$[R_1H]_f^a$	$[R_2H]_f^a$	Rate^b	
						Calc.	Found
Styrene	Dibenzyl ether	0.800	0.200	0.685	0.183	27.8	24.4
"	"	0.500	0.500	0.417	0.460	28.5	25.4
"	"	0.200	0.800	0.162	0.740	29.3	25.5
"	"	0.000	1.000				30.0
Styrene	Tetralin	0.800	0.200	0.656	0.186	24.6	22.8
"	"	0.500	0.500	0.413	0.439	20.4	12.5
"	"	0.200	0.800	0.167	0.728	16.3	10.3
"	"	0.000	1.000				13.4
Styrene	Benzyl ethyl ether	0.700	0.300	0.439	0.267	21.6	20.0
"	"	0.500	0.500	0.302	0.456	17.7	16.4
"	"	0.200	0.800	0.118	0.740	12.3	11.6
"	"	0.050	0.950			9.3	9.3
"	"	0.000	1.000				8.3
Styrene	Cumene	0.700	0.300	0.594	0.294	20.6	19.0
"	"	0.500	0.500	0.424	0.490	16.1	15.4
"	"	0.300	0.700	0.234	0.695	11.7	10.3
"	"	0.100	0.900			7.3	4.95
"	"	0.050	0.950			5.7	2.00
Styrene	*cis*-Decalin	0.800	0.200			22.8	19.3
"	"	0.500	0.500	oxidized product interferes		16.1	11.5
"	"	0.200	0.800			9.5	5.4
"	"	0.050	0.950			3.5	1.5
"	"	0.000	1.000				2.3

Table 16. (Continued)

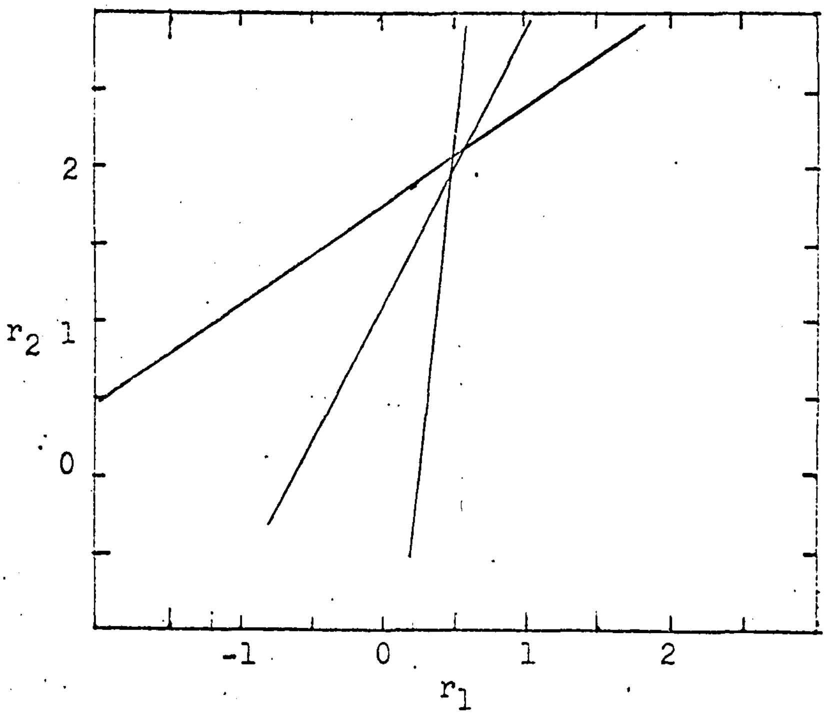
R_1H	R_2H	$[R_1H]^a_o$	$[R_2H]^a_o$	$[R_1H]^a_f$	$[R_2H]^a{}_f$	Rate^b	
						Calc.	Found
Cumene	Dibenzyl ether	0.950	0.050	g.l.c. analysis not performed		6.5	3.7
"	"	0.900	0.100			7.72	4.00
"	"	0.500	0.500			17.5	13.0
Benzyl ethyl ether	Cumene	0.800	0.200	0.680	0.186	7.8	8.7
"	"	0.970	0.030			8.4	10.5
"	"	0.900	0.100			8.1	9.8
"	"	0.500	0.500	0.360	0.455	6.4	5.25
"	"	0.200	0.800	0.134	0.749	5.7	2.91
"	"	0.070	0.930			5.3	1.82
Cumene	*sec*-Butyl benzene	0.900	0.100			4.8	4.60
"	"	0.800	0.200	0.625	0.164	4.6	4.00
"	"	0.500	0.500	0.432	0.468	3.9	3.28
"	"	0.200	0.800	0.163	0.764	3.1	2.89
"	"	0.100	0.900			2.9	2.60
"	"	0.000	1.000				2.65
Cumene	*cis*-Decalin	0.800	0.200	0.726	0.170	4.4	3.50
"	"	0.500	0.500	0.466	0.446	3.7	2.65
"	"	0.200	0.800	0.192	0.750	3.2	2.78
Tetralin	Cumene	0.800	0.200	0.662	0.177	rates not done	
"	"	0.500	0.500	0.408	0.482		
"	"	0.200	0.800	0.134	0.730		

Table 16. (Continued)

R_1H	R_2H	$[R_1H]^a_o$	$[R_2H]^a_o$	$[R_1H]^a_f$	$[R_2H]^a_f$	Rate^b Calc.	Rate^b Found
Tetralin	Benzyl ethyl ether	0.930	0.070			13.2	10.9
"	"	0.800	0.200	0.600	0.152	12.6	8.5
"	"	0.500	0.500	0.399	0.418	11.2	8.8
"	"	0.200	0.800	0.163	0.710	9.7	10.0
"	"	0.100	0.900			9.1	12.5
"	"	0.030	0.970			8.6	10.1
Tetralin	*cis*-Decalin	0.800	0.200	0.600	0.175	11.5	9.20
"	"	0.500	0.500	0.365	0.450	8.3	5.81
"	"	0.200	0.800	0.750	0.133	5.3	3.19

Figure 19. Solution of the co-oxidation equation for cumene (R_1H) and p-methoxycumene (R_2H); $r_1 = 0.50$, $r_2 = 2.06$

Figure 20. Solution of the co-oxidation equation for cumene (R_1H) and p-nitrocumene (R_2H); $r_1 = 1.40$, $r_2 = 0.25$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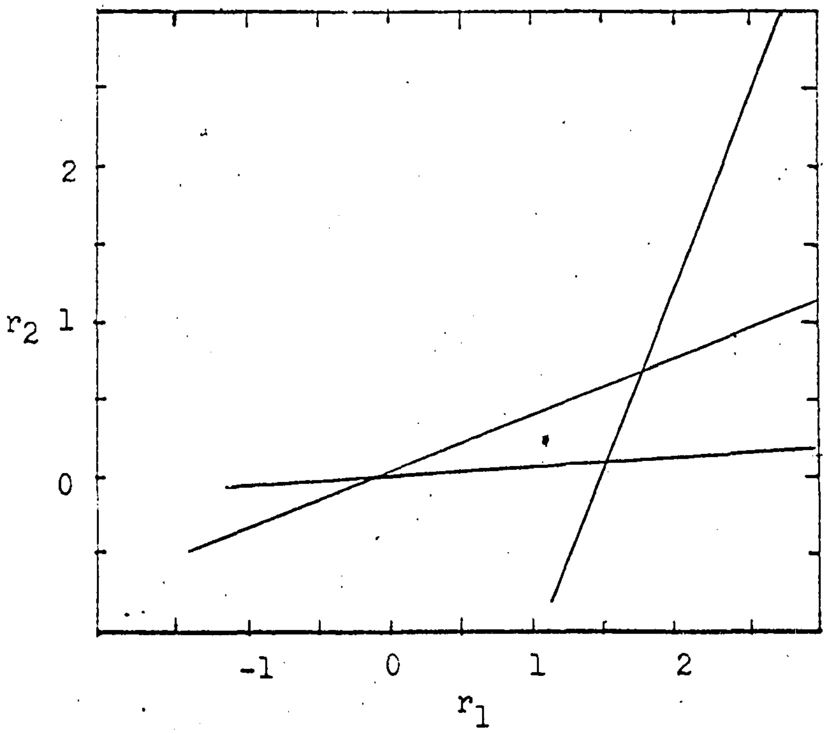
r_2 1
0
-1
0
1
2
r_1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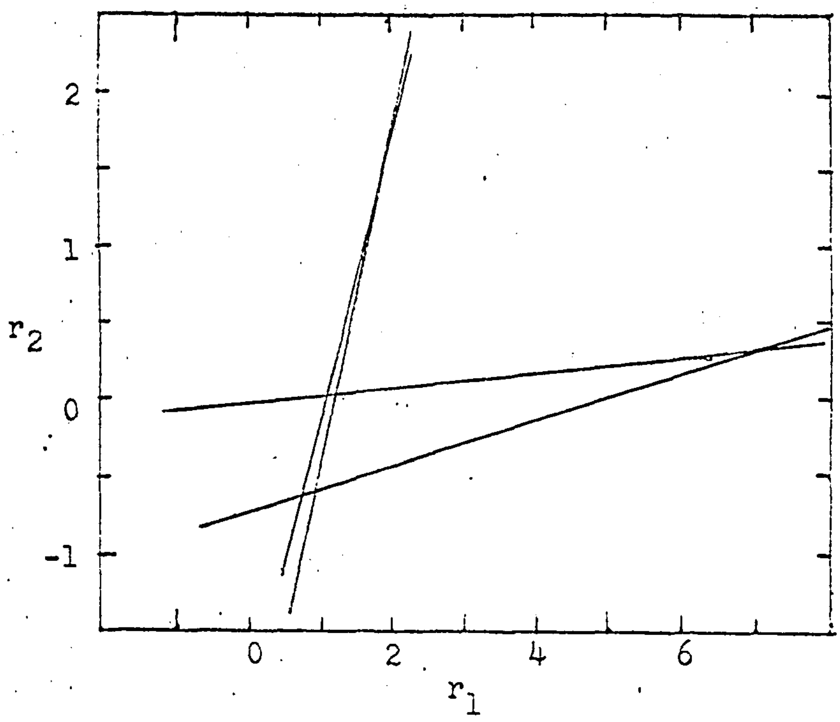
r_2 1
0
-1
0
1
2
r_1

Figure 21. Solution of the co-oxidation equation for tetralin (R_1H) and cumene (R_2H); $r_1 = 7$, $r_2 = 0.30$

Figure 22. Solution of the co-oxidation equation for cumene (R_1H) and *cis*-decalin (R_2H); $r_1 = 0.64$; $r_2 = 1.67$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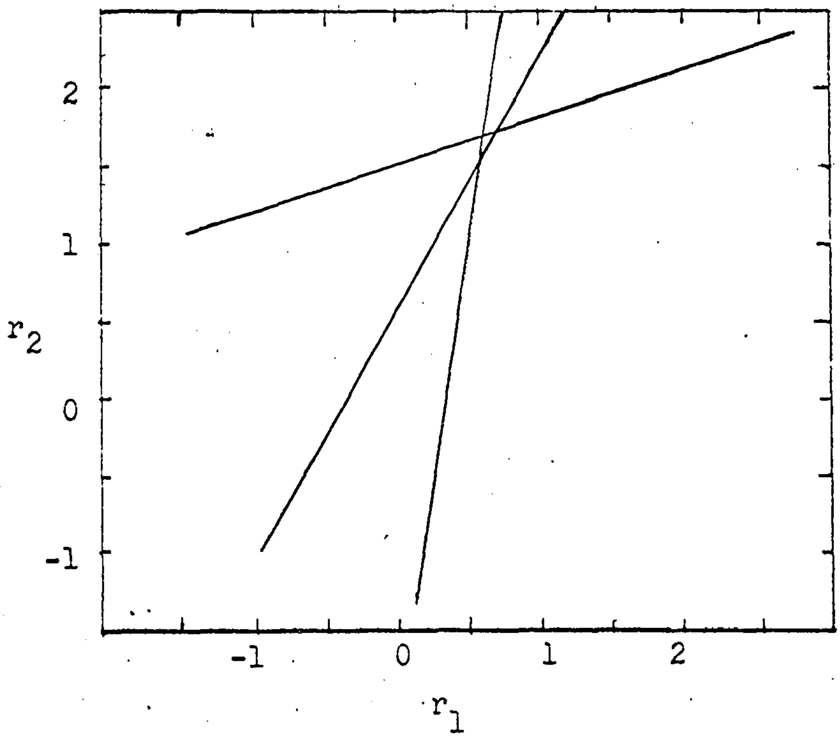
1
r_2
0
-1
0
2
4
6
r_1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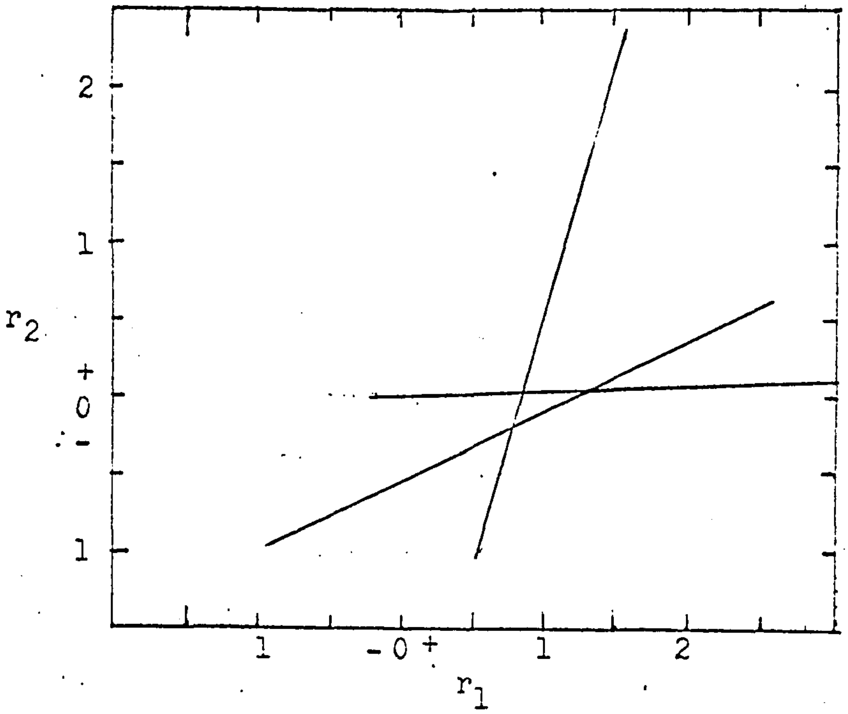
1
r_2
0
-1
-1
0
1
2
r_1

Figure 23. Solution of the co-oxidation equation for cumene (R_1H) and *sec*-butylbenzene (R_2H); $r_1 = 1.00$, $r_2 = 0.00$

Figure 24. Solution of the co-oxidation equation for benzyl ethyl ether (R_1H) and cumene (R_2H); $r_1 = 2.17$, $r_2 = 0.07$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1
r_2
+
0
-
1
1
-0+
1
2
r_1

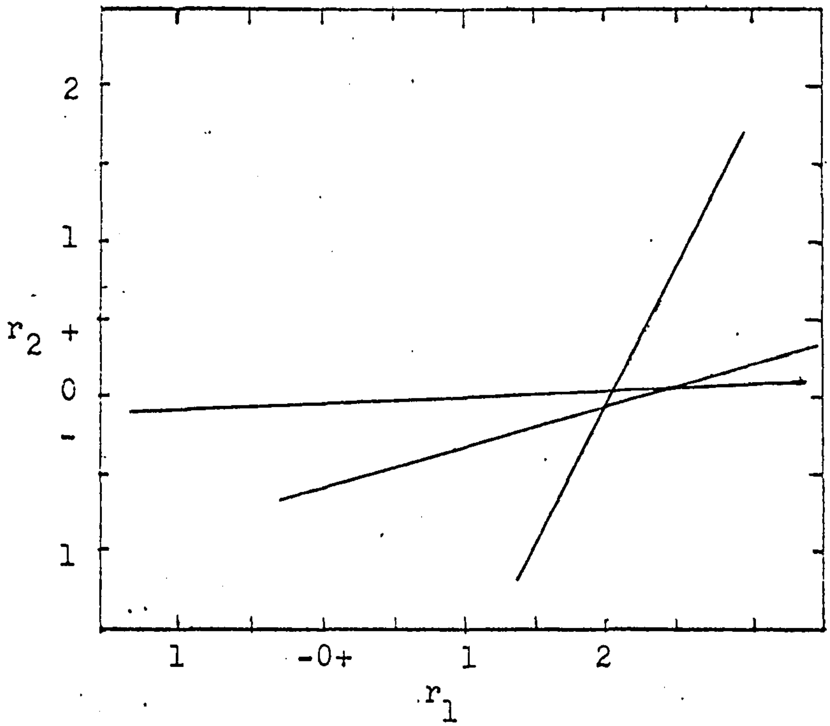
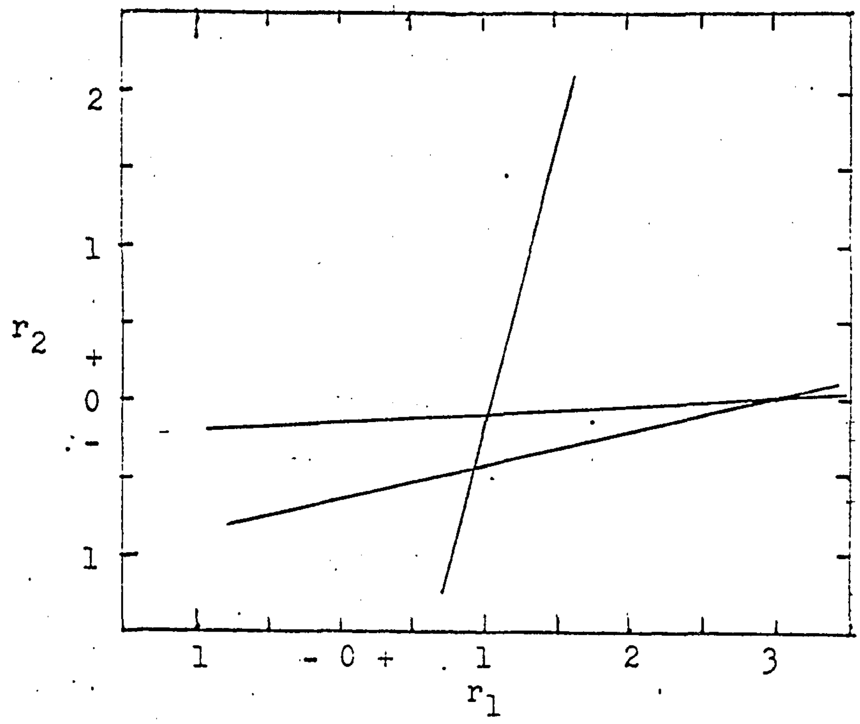

2
1
r_2
+
0
-
1
1
-0+
1
2
r_1

Figure 25. Solution of the co-oxidation equation for cumene (R_1H) and bibenzyl (R_2H); $r_1 = 3$ when only the point at where $r_1 = 3$, $r_2 = 0$ is considered

Figure 26. Solution of the co-oxidation equation for styrene (R_1H) and cumene (R_2H); all intercepts give a negative value for r_2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r_2
+
0
-
1
1
- 0 +
1
2
3
r_1

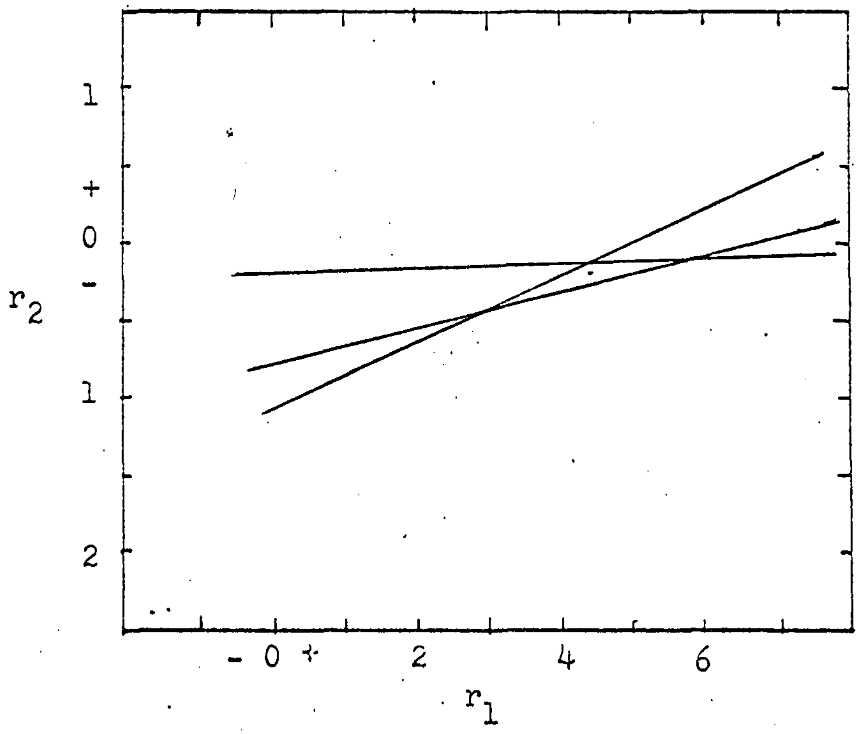
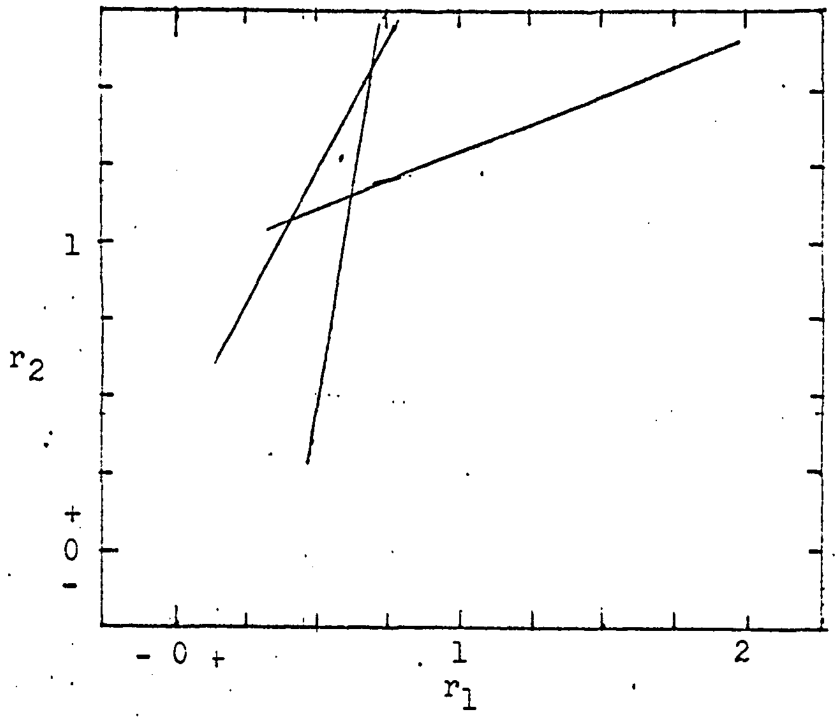

1
+
0
-
r_2
1
2
- 0 +
2
4
6
r_1

Figure 27. Solution of the co-oxidation equation for styrene (R_1H) and p-methoxystyrene (R_2H); $r_1 = 0.590$, $r_2 = 1.255$

Figure 28. Solution of the co-oxidation equation for styrene (R_1H) and p-nitrostyrene (R_2H); $r_1 = 1.61$, $r_2 = 0.247$


r2
1
+
0
-
- 0 +
1
2
r1

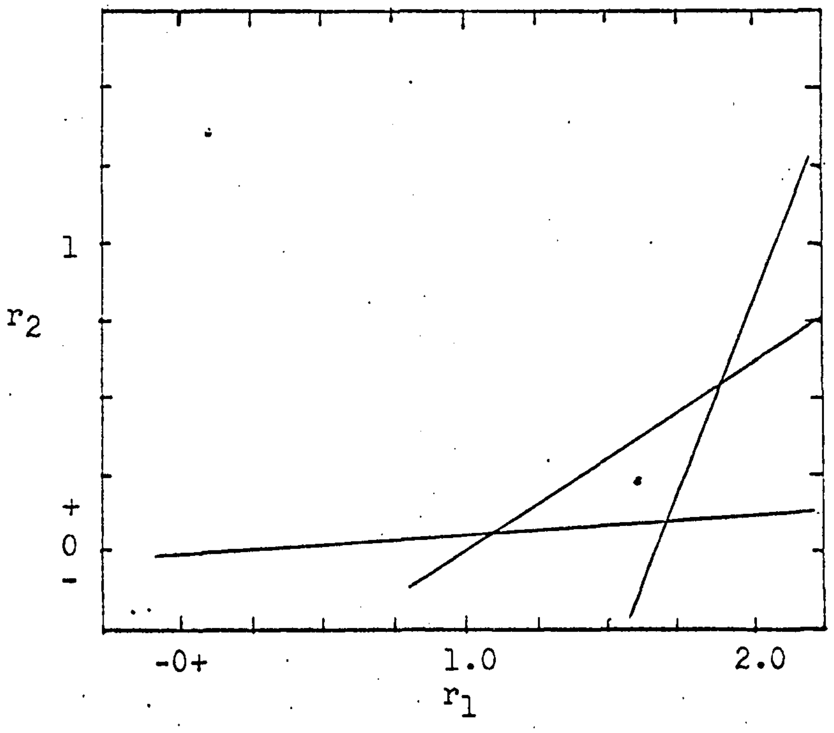
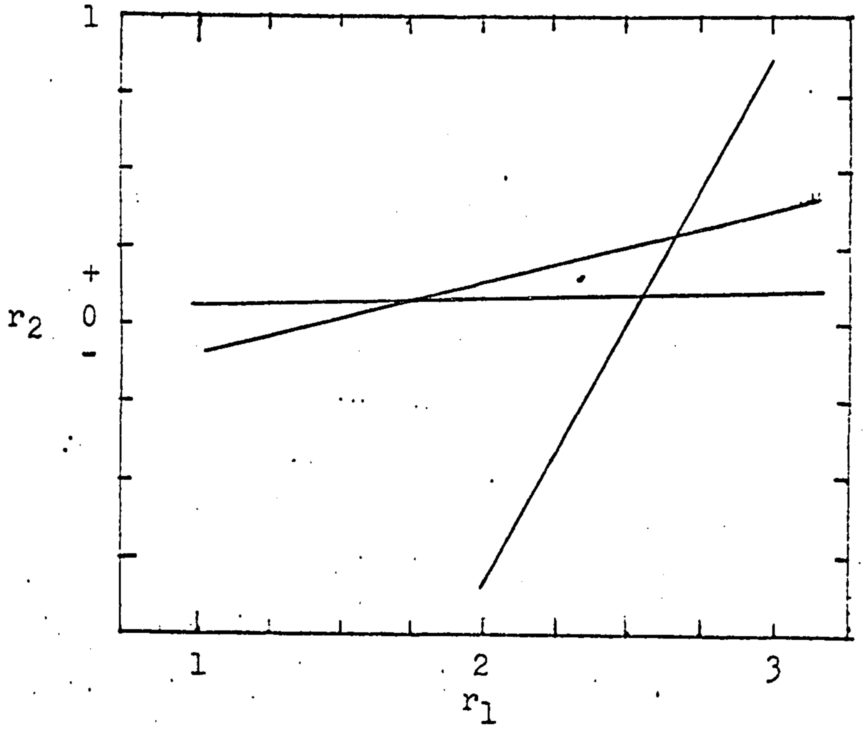

r2
1
+
0
-
-0+
1.0
2.0
r1

Figure 29. Solution of the co-oxidation equation for p-methoxystyrene (R_1H) and p-nitrostyrene (R_2H); $r_1 = 2.50$, $r_2 = 0.15$

Figure 30. Solution of the co-oxidation equation for styrene (R_1H) and dibenzyl ether (R_2H); $r_1 = 1.62$, $r_2 = 0.24$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+
0
-
r_2
1
2
3
r_1

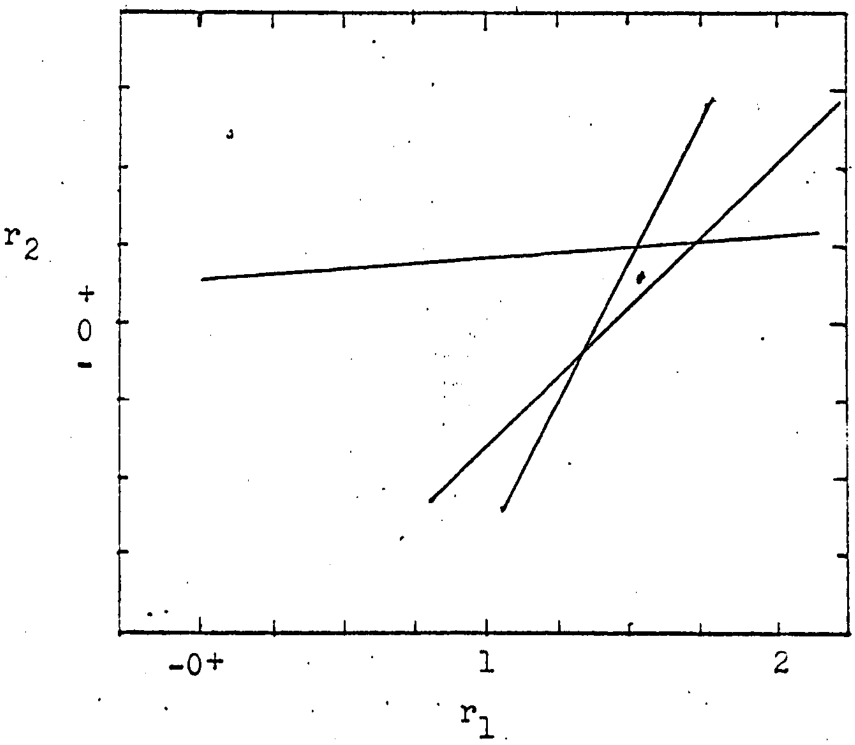
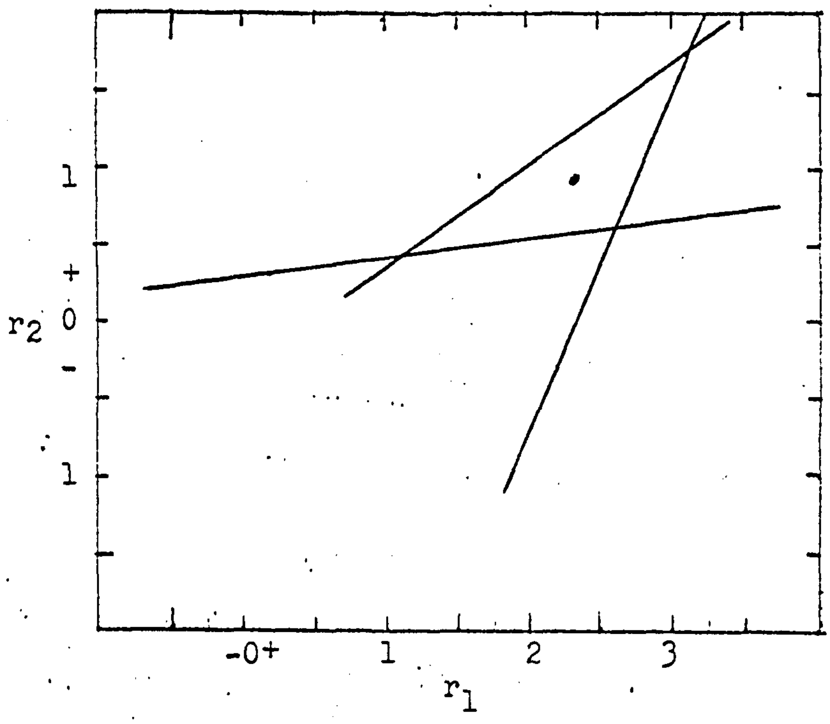

r_2
+
0
-
-0+
1
2
r_1

Figure 31. Solution of the co-oxidation equation for styrene (R_1H) and tetralin (R_2H); $r_1 = 2.40$, $r_2 = 0.90$

Figure 32. Solution of the co-oxidation equation for styrene (R_1H) and *alpha*-methylstyrene (R_2H); $r_1 = 0.89$, $r_2 = 1.21$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r2
-
1
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1
2
3
r1

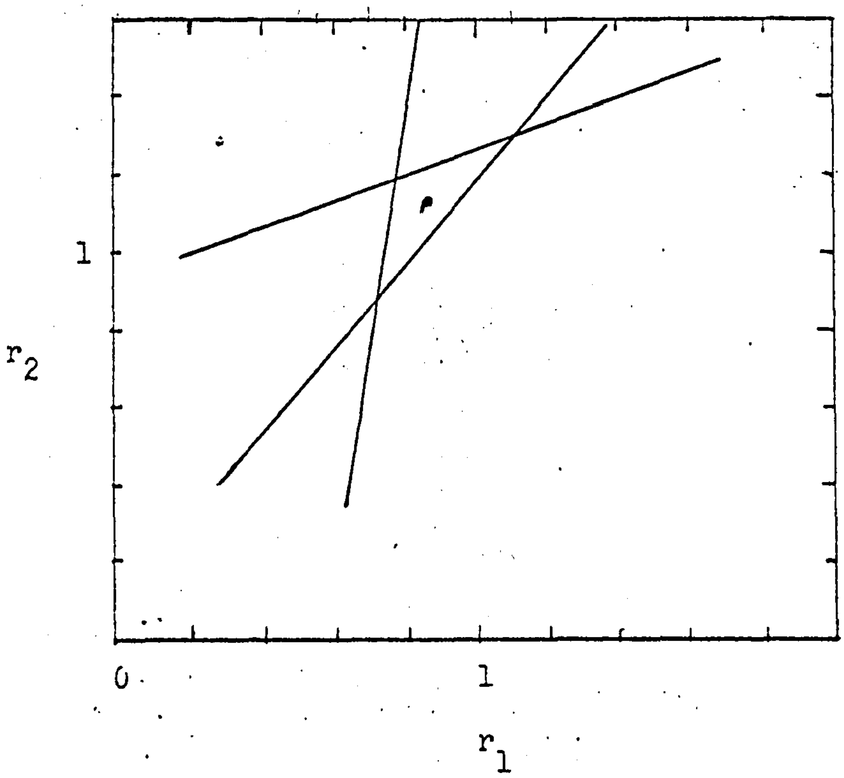
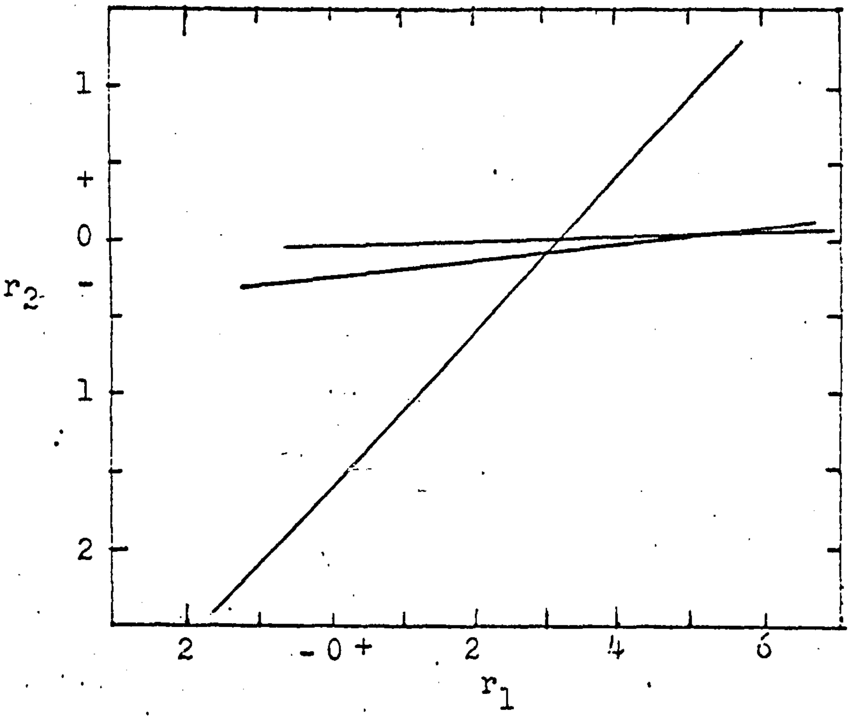

1
r2
0
1
r1

Figure 33. Solution of the co-oxidation equation for styrene (R_1H) and benzyl ethyl ether (R_2H); $r_1 = 3.70$, $r_2 = 0.05$

Figure 34. Solution of the co-oxidation equation for 2-phenyl-1,3 dioxolane (R_1H) and styrene (R_2H). The broken line is to show that this analysis was contaminated with some unknown oxidation product. $r_1 = 1.20$, $r_2 = 0.075$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0
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1
2
2
- 0 +
2
4
6
r1

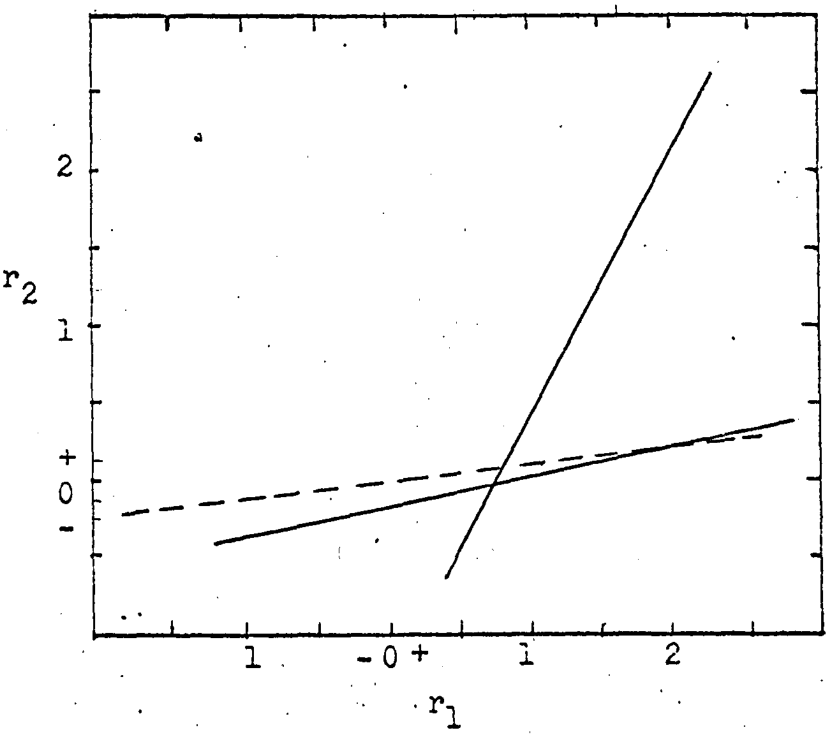
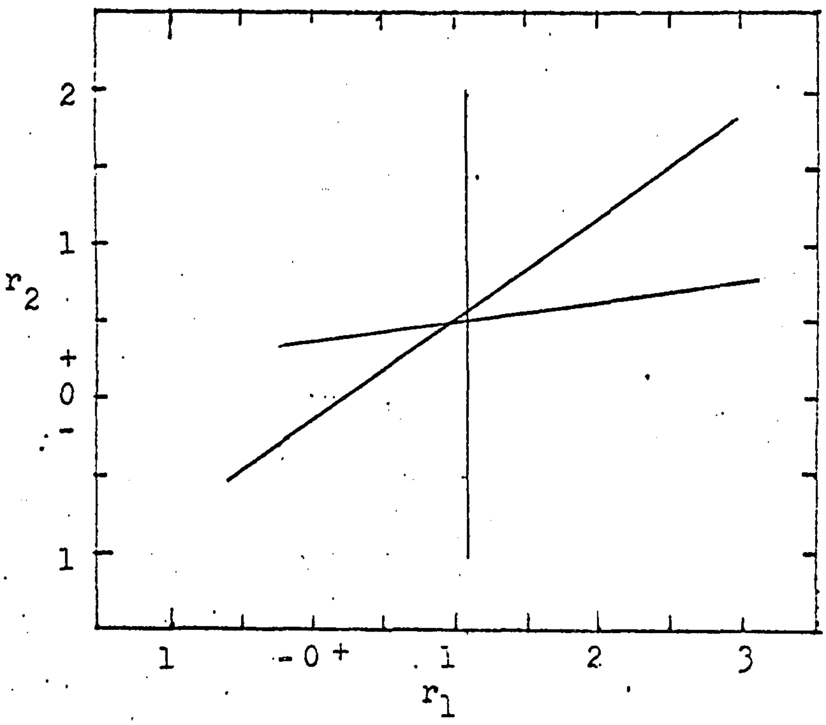

r2
2
1
+
0
-
1
- 0 +
1
2
r1

Figure 35. Solution of the co-oxidation equation for tetralin (R_1H) and benzyl ethyl ether (R_2H); $r_1 = 0.90$, $r_2 = 0.55$

Figure 36. Solution of the co-oxidation equation for <u>alpha</u>-methylstyrene (R_1H) and tetralin (R_2H); $r_1 = 1.25$, $r_2 = 0.75$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r_2
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-
1
1
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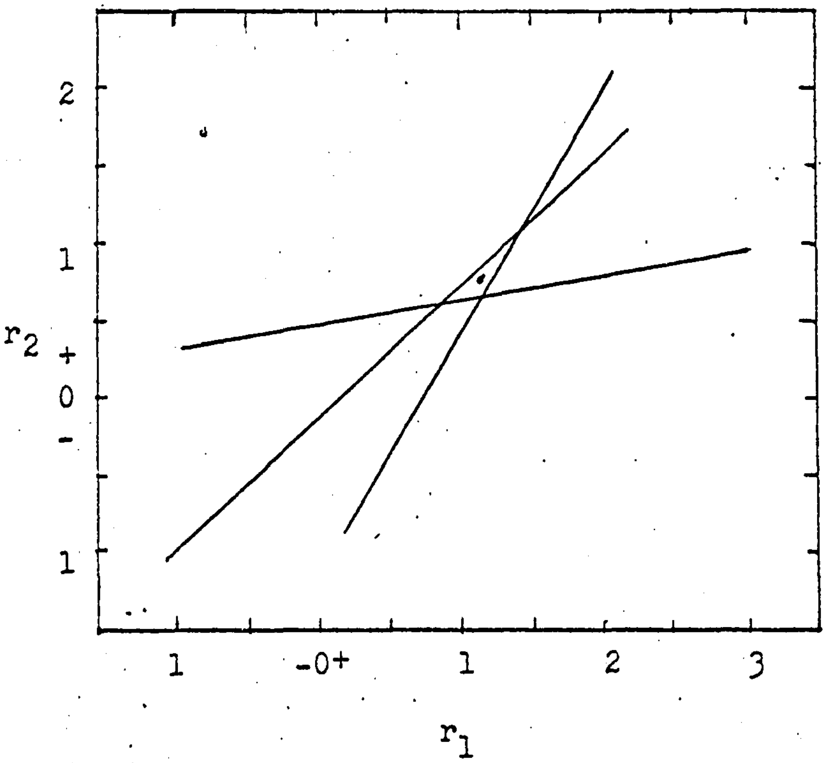
1
2
3
r_1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r_2
+
0
-
1
1
-0+
1
2
3
r_1

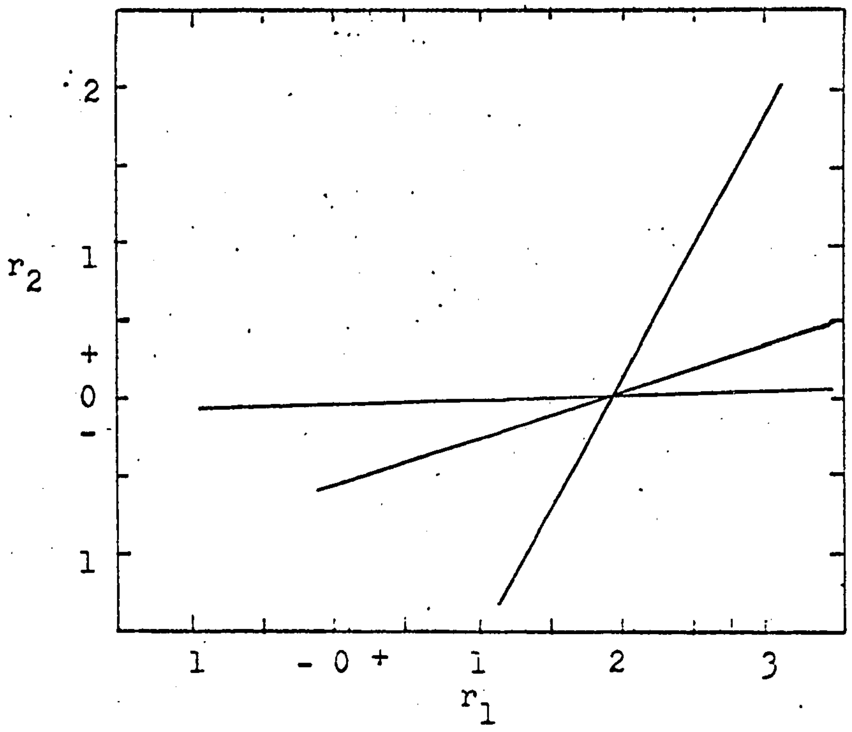

Figure 37. Solution of the co-oxidation equation for tetralin (R_1H) and *cis*-decalin (R_2H); r_1 = 1.95, r_2 = 0.05

Experimental

Apparatus and procedure

The same apparatus and procedure for both the oxidation and determination that were used for the previous competitive oxidations were used in this section.

Materials

Alpha-methylstyrene obtained from Mr. Robert Bridger was passed through silica gel and showed greater than 99.5% purity by g.l.c.

Tetralin (Eastman) was rectified with a fifteen inch spinning band column to remove a lower boiling point compound and decalin. Complete removal of the decalin was not possible but the fraction used showed 99.7% pure by g.l.c.

cis-Decalin, obtained from Mr. Dale Hendry, contained traces of the *trans* isomer and tetralin. Careful rectification through a Todd column gave a fraction that was greater than 99% pure with the major impurity being tetralin.

sec-Butylbenzene (Eastman) was distilled through a fifteen inch spinning band column to give material with n_D^{20} 1.4898; reported n_D^{20} 1.4901 (52, p. 1).

Bibenzyl (Eastman) was recrystalized from ethanol and dried under vacuum; m.p. 52.8-53.1°; reported m.p. 53° (52, p. 3).

2-Phenyl-1,3-dioxolane was prepared by the reaction of equal molar amounts benzaldehyde and ethylene glycol in the presence of a catalytic amount of p-toluenesulfonic acid. Benzene was used as a solvent and to azeotrope water from the reaction into a Dean-Stark trop. The reaction was stopped when about 80% of the theoretical amount of water had been collected. The resulting solution was washed with 10% sodium bicarbonate solution, dried over sodium sulfate, excess benzene stripped off and a crude distillation performed with a twelve inch silver jacketed column. This was followed by two careful distillations on the spinning band column, neither of which was able to remove all of the unreacted benzaldehyde. Analysis by g.l.c. showed a 99% purity with the one percent impurity consisting of benzaldehyde. The material had a b.p. of 78° at 2.5 m.m., $\underline{n}_D^{20}$ 1.5269; reported b.p. 240° at 760 m.m., $\underline{n}_D^{20}$ 1.5270 (78).

The g.l.c. columns used in the analysis for these autoxidations are the same as those listed in the first portion of this thesis.

Table 17. Conditions for g.l.c. analysis of competitive oxidations not previously mentioned

Compound[a]	Temperature	Column	Helium flow (c.c./min.)	Retention time (minutes)
Styrene	145	4	50	3.3
Cumene	"	"	"	2.5
Anisole(IS)	"	"	"	4.6
Styrene	140	4	50	3.6
Benzyl ethyl ether	"	"	"	7.2
Anisole(IS)	"	"	"	5.0
Styrene	145	4	50	3.3
Tetralin	"	"	"	9.3
Anisole(IS)	"	"	"	4.5
Styrene	130	4	45	5.0
α-Methylstyrene	"	"	"	6.4
Cumene(IS)	"	"	"	3.7
Styrene	140	4	50	3.3
Dibenzyl ether	190	2	70	5.9
Anisole(IS)	140	4	50	4.6
<u>p</u>-Nitrocumene(IS)	190	2	70	2.5
Cumene	140	4	50	2.7
<u>sec</u>-Butylbenzene	"	"	"	3.5
Anisole(IS)	"	"	"	5.0
Cumene	145	4	50	2.5
Tetralin	"	"	"	9.1
Anisole(IS)	"	"	"	4.5
Cumene	155	5	55	5.0
<u>cis</u>-Decalin	"	"	"	10.7
Anisole(IS)	"	"	"	6.3

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[a] IS stands for internal standard. When two are given, the first is for the first compound in the series.

Table 17. (Continued)

Compound[a]	Temperature	Column	Helium flow (c.c./min.)	Retention time (minutes)
Cumene	140	4	40	2.9
Benzyl ethyl ether	"	"	"	7.6
Anisole(IS)	"	"	"	5.3
Cumene	140	4	50	2.6
Bibenzyl	200	3	60	8.6
Anisole(IS)	140	4	50	4.7
p-Nitrocumene(IS)	200	3	60	6.3
Tetralin	140	4	50	9.6
α-Methylstyrene	"	"	"	4.1
Cumene(IS)	"	"	"	2.6
Tetralin	140	4	50	10.0
Benzyl ethyl ether	"	"	"	7.0
Anisole(IS)	"	"	"	4.9
Tetralin	145	4	50	9.3
cis-Decalin	"	"	"	3.4
Anisole(IS)	"	"	"	4.5
Styrene	140	4	50	3.3
2-Phenyl-1,3-dioxolane	200	3	60	3.2
Anisole(IS)	140	4	50	4.6
p-Nitrocumene(IS)	200	3	60	6.1

SUMMARY

The relative reactivities of *meta* and *para* substituted toluenes toward the chlorine atom in carbon tetrachloride at 40° has been shown to be better correlated by σ^+ than by σ constants with the following equation: $\log \frac{k}{k_o} = -0.663\ \sigma^+ + 0.014$, std. dev. ± 0.02 log units. It was also shown that the relative reactivities of *p*-chlorotoluene and toluene did not change when benzene was used as the solvent. A σ^+ correlation also holds for the relative reactivities of substituted cumenes toward the peroxy radical in chlorobenzene solution at 60°. This correlation fits the following equation: $\log \frac{k}{k_o} = -0.375\ \sigma^+ + 0.009$; std. dev. ± 0.015 log units. Competitive autoxidation was employed to obtain the relative reactivity of *p*-methoxycumene and cumene due to the fact that the methoxycumene retards the rate of oxidation of cumene.

A series of *meta*- and *para*-substituted benzyl phenyl ethers were autoxidized but abnormally slow rates and no substituent effect were observed. *p*-Nitrophenyl and *p*-tolyl benzyl ether showed no substituent effect. *p*-Chloro- and *m*-methylbenzyl methyl ether showed no substituent effect on their rates of oxidation even though they did oxidize some three times faster than the benzyl phenyl ethers. This indicated that no substituent effects were observed due to the ethereal oxygen atom stabilizing the transition state to such an extent that substituents located on the benzene ring had little influence on the transition state. The slowness of the rate of oxidation of the benzyl phenyl ethers was attributed to a combination of a high termination rate constant and other factors.

A series of benzyl ethers and benzyl alcohol was autoxidized and the relative reactivities of _t_-butyl, ethyl and methyl benzyl ethers, along with benzyl alcohol were shown to correlate with Taft's σ^* values while dibenzyl ether was more reactive and benzyl phenyl ether less reactive than this correlation predicts.

Styrene, _p_-nitrostyrene and _p_-methoxystyrene were competitively autoxidized. The relative reactivities of these substrates were shown to be dependent upon the structure of the peroxy radical. The relative reactivities obtained by attack of a _p_-nitrostyrenyl peroxy radical gave a correlation with σ constants with a larger ρ than that found for the σ correlation involving the _p_-methoxystyrenyl peroxy radical. However, a σ^+ correlation was found for the relative reactivities towards the styrenyl peroxy radical.

A number of hydrocarbons were oxidized competitively and the relative reactivities where possible were obtained toward each of the corresponding peroxy radicals. For example, the relative reactivities of 2-phenyl-1,3-dioxolane, styrene, alpha-methylstyrene, p-nitrostyrene, p-methoxystyrene, dibenzyl ether, benzyl ethyl ether, tetralin and cumene were all obtained in respect to the tetralyl peroxy radical.

It was noted that the structure of the peroxy radical was important in determining the relative values of propagation rate constants in co-oxidation studies. This variation with structure was partially explained on steric requirements.

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