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Influence of solvent on free radical reactions

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INFLUENCE OF SOLVENT
ON FREE RADICAL REACTIONS

by

Dale Glenn Hendry

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Ames, Iowa

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GENERAL INTRODUCTION

The capability of the reaction media to influence the course or rate of free radical reactions has not been realized until recently (1a, p. 237; 1b, p. 35). The failure to acknowledge the possible importance of the solvent in these reactions rests on the fact that free radical intermediates do not usually have any positive or negative charge and therefore, should not be affected by such properties as the ionizing power of the solvent. There are cases where the solvent does appear to have only an insignificant effect on rate (2), and in a number of cases where there is a small variation in rate with change in solvent, relatively large but compensating changes in the entropy and enthalpy of activation have been reported (3). However, these latter effects have been seriously questioned, and they appear to be more a consequence of experimental error than actual phenomena (4).

One of the earliest indications that radical reactions could exhibit a polar nature was found in a study of the copolymerization of vinyl compounds (1b, p. 97). To explain the great tendency for alternation of the two monomer units in the polymer structure, it has been necessary to assume a polar transition state. If there were a highly polar transition state in these reactions, the solvent should be able to contribute to the stability of the transition state in accord with its polar nature. Thus a pronounced dependence of the reactivity of monomer on the dielectric constant of the solution would be expected. However, experimentation did not show such a dependence (2b, e). Apparently, the nature of the transition state is such that the lines of force between the charged portions of the transition state do not radiate appreciably into the solvent. Therefore, the solvent can contribute little in stabilization of the charges in the transition state.

Other properties besides the ionizing power of the solvent can be important in influencing radical reactions. The photolysis of aromatic disulfides shows a solvent dependence between the apparent rate of dissociation and the kinematic viscosity of the solvent. The apparent dissociation appears to depend on the ability of radical fragments to diffuse apart; as the viscosity increases and the rate of diffusion decreases more recombination and thus less apparent dissociation occurs (5).

The most striking solvent effect on a free radical reaction has been observed in competitive photochlorination of hydrocarbons and involves neither of the above mentioned factors (6). For example, the chlorination of 2,3-dimethylbutane in an aliphatic hydrocarbon solvent yields 60% 1-chloro-2,3-dimethylbutane and 40% 2-chloro-2,3-dimethylbutane, but if the solvent is 8 M benzene only 10% of the 1-isomer is obtained along with 90% of the 2-isomer (6a). It is believed that this decrease in reactivity of the chlorine atom is due to complexing with the aromatic ring of the aromatic solvent. The complex appears to be a Lewis acid-base type association, since the effect of solvent correlates with the relative basicity of various solvent as determined from the equilibrium constant for the interaction with hydrogen chloride.

Certain non-aromatic solvents also show a solvent effect in the photochlorination of 2,3-dimethylbutane. Solvents like ethers, organic halides, and organic sulfides appear to involve a pi-complex of the chlorine atom with the most electron rich atom in the solvent molecule. But other solvents such as carbon disulfide which produces an extremely large solvent effect probably involve a sigma-bond complex (6a). In either case and as with the aromatic solvents, the reactivity of the chlorine atom is decreased by some type of interaction with the solvent. Complexing reduces the electron deficiency of the chlorine atom resulting in a reduction in the reactivity.

The tertiary-butoxy radical appears to be subject to the same type of solvent effects as the chlorine atom; however, the effect is much less (7).

Data for other free radical reactions have been reviewed in the literature in an attempt to find additional cases where the solvent may alter the reactivity of a free radical (6a). In many reactions differences in either the rate or the course of the reaction have been observed in the presence of aromatic solvents as compared with the results in aliphatic hydrocarbon solvents, but the incompleteness of the data has not allowed definite conclusions to be made.

This study of effect of solvent in various free radical reactions has been undertaken, primarily, in an attempt to evaluate the general importance of the solvent in free radical reactions and to determine the nature of any effects that might be observed. Thus, three different reactions have been studied: the chlorination of aralkyl hydrocarbons, the methylation of both aliphatic and aromatic hydrocarbons with methylene, and the free radical oxidation of hydrocarbons.

In addition to the study concerning the importance of solvent in free radical oxidation reactions, the retardation caused by small amounts of highly reactive hydrocarbons also was investigated. Although the retardation effect can not be correctly classified as a result of the solvent, it remains a potential factor for controlling oxidation reactions. The investigation was undertaken because this effect is potentially important and because it involves the same system in which the influence of solvent had been evaluated.

PHOTOCHLORINATION OF ARALKYL HYDROCARBONS

Introduction

Competitive photochlorination offers a simple method for determining the relative reactivity of hydrogen atoms of various hydrocarbons toward the chlorine atom. For example the chlorination of 2,3-dimethylbutane (DMB) yields two monochlorinated products, 1-chloro-2,3-dimethylbutane and 2-chloro-2,3-dimethylbutane. In the following scheme the propagation reactions of the photochlorination reaction are shown.

$$(CH_3)_2CHCH(CH_3)_2 + Cl\cdot \xrightarrow{12k_1} (CH_3)_2CHCH(CH_3)CH_2\cdot + HCl$$

$$(CH_3)_2CHCH(CH_3)_2 + Cl\cdot \xrightarrow{2k_2} (CH_3)_2CH\dot{C}(CH_3)_2 + HCl$$

$$(CH_3)_2CHCH(CH_3)CH_2\cdot + Cl_2 \longrightarrow (CH_3)_2CHCH(CH_3)CH_2Cl + Cl\cdot$$

$$(CH_3)_2CH\dot{C}(CH_3)_2 + Cl_2 \longrightarrow (CH_3)_2CHCCl(CH_3)_2 + Cl\cdot$$

If all the alkyl radicals formed are assumed to react with molecular chlorine, then the rate at which the chlorine atom attacks one of the positions of the hydrocarbon is equal to the rate at which the corresponding chlorinated hydrocarbon is formed.

$$12k_1\,[DMB]\,[Cl\cdot] = \frac{d[\text{1-chloro-DMB}]}{dt}$$

$$2k_2\,[DMB]\,[Cl\cdot] = \frac{d[\text{2-chloro-DMB}]}{dt}$$

By dividing the first expression by the second and cancelling common terms, one obtains the following expression.

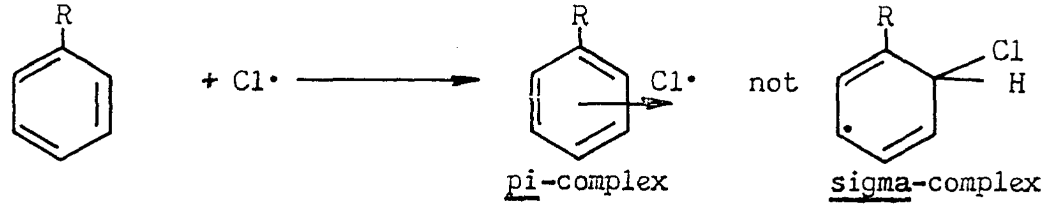
$$\frac{d[\text{1-chloro-DMB}]}{d[\text{2-chloro-DMB}]} = 6\,\frac{k_1}{k_2}$$

Integration over the period of the reaction yields:

$$\frac{\text{1-chloro-DMB-formed}}{\text{2-chloro-DMB-formed}} = 6\,\frac{k_1}{k_2}$$

Thus the relative reactivity (k_1/k_2) of the two different hydrogen atoms is equal to the ratio of the corresponding halide concentrations times a statistical correction for the relative number of the two hydrogen atoms.

This simple approach is complicated if the hydrocarbon that is being chlorinated is an aralkyl hydrocarbon since aromatic compounds are able to alter the reactivity of the chlorine atom by complexing (6). For example at 40° the relative reactivity of a tertiary and a primary hydrogen atom of DMB toward the chlorine atom is 3.9 if the solvent is the parent hydrocarbon. However, if the solution is 4.0 M chlorobenzene the relative reactivity is 13.5; a 4.0 M benzene solution of DMB produces a relative reactivity of 17.0. If the solution is made to be 8.0 M benzene, the reactivity increases to 40. The electron deficient chlorine atom forms a complex with the *pi*-electrons of the aromatic ring of the aromatic solvents, thereby making the chlorine atom less reactive and more selective.



The association is considered a *pi*-complex rather than a *sigma*-complex for several reasons. The data correlate with the basicity of the aromatic solvent and with the sigma (meta)- constants for the substituent of the aromatic solvent. However, they do not correlate with the relative phenylation rates of the solvent--a reaction which involves the formation of a sigma-complex. As is expected in the case of a pi-complex, the reactivity varies inversely with those factors that are a function of the electron density in the aromatic ring. As the electron density of the aromatic ring increases, the ring is able to form a more stable, but less reactive, pi-complex with the chlorine atom.

The degree to which the solvent effects the reactivity of a hydrogen atom depends on the nature of the carbon-hydrogen bond. If the relative reactivity of two different hydrogen atoms is controlled largely by inductive effects, the complexing ability of the solvent has little effect on the relative reactivity. But if the relative reactivity is controlled mainly by bond dissociation energy, a solvent effect generally is observed. For example, each hydrogen atom of tetramethylsilane is six times more reactive than a hydrogen atom of trimethylchlorosilane; the difference in reactivity of these hydrogens is due to inductive effects, and no solvent effect is observed. Although primary alkyl hydrogen atoms and alpha-hydrogen atoms of toluene show about equal reactivity to the chlorine atom in non-complexing solvents, toluene is much more reactive in a complexing solvent due to the resonance stabilization of the incipient benzyl radical. In regard to the importance of the nature of the carbon-hydrogen bond, it has been argued that the degree of bond breaking in the transition state is greater for the case of the complexed chlorine atom than for the uncomplexed atom (6a). This is in accord with the

Hammond postulate which states that less reactive a reagent is, the more the transition state will resemble the products (8). The resonance stabilization of the transition state will become more important as the complexing ability of the solvent increases since the chlorine atom becomes less reactive.

On the basis of the above generalities, care must be taken when measuring the relative reactives of two carbon-hydrogen bonds whose difference in reactivity is due to resonance factors. The presence of strongly complexing materials will greatly alter the apparent reactivity of such carbon-hydrogen bonds. In the chlorination of a compound like cumene, a large solvent effect should be observed in the relative reactivity of the alpha- and beta-hydrogen atoms since the difference in reactivity is governed mainly by differences in bond dissociation energy. Thus the chlorination of such compounds will be influenced by the complexing ability of the substrate itself.

According to the literature, chlorination of pure cumene leads mainly to the tertiary chloride even though there are six times as many primary hydrogen atoms as there are tertiary hydrogen atoms and ratios of alpha- to beta-chlorocumene reported vary from three to infinity (9). From these data it is not immediately clear whether the high reactivity of the tertiary hydrogen atom is due to the selectivity of the free chlorine atom or the complexed atom. The relative reactivity per hydrogen atom of toluene and cyclohexane to the chlorine atom has been reported to be 0.36 at 80°, and the value is independent of the toluene concentration (10). This low reactivity of the toluene benzylic hydrogen atom suggests that the phenyl group does not greatly activate the benzylic hydrogen atoms toward the chlorine atom. Quite different relative reactivities are observed when the bromine atom is the attacking species. The relative reactivity per hydrogen atom of toluene and cyclohexane to the bromine atom is 240 at 80° (10). The explanation for the low relative reactivity toward the chlorine atom compared with the high relative reactivity toward the bromine atom is that there is a much smaller degree of bond breaking in the transition state of the reaction with the chlorine atom; as the degree of bond-breaking decreases, the importance of resonance stabilization of the incipient free radical in the transition state by the phenyl group also decreases. The small degree of bond breaking in the transition state for the attack by chlorine atoms deemphasizes the importance of resonance stabilization.

From the above argument the true chlorinating agent in the photochlorination of pure cumene appears to be the more selective chlorine atom complex, and as stated previously any attempt to study the reactivity of the chlorine atom at high aromatic concentrations would be misleading. Recently Cerny and Hajek have reported the chlorination of equimolar mixtures of some aralkyl hydrocarbons and found relative reactivities which appear reasonable and correlate well with the values for the corresponding relative reactivities toward the peroxy radical (9d). However, these values were obtained at high aromatic concentration and undoubtedly involve a complexed chlorine atom not the uncomplexed atom. It is quite possible that with the compounds studied, the effect of the aromatic solvent is comparable, and the solvent effect on the reactivities in each case tend to cancel.

The chlorination studies that are reported in this section were designed to determine the importance of solvent in the chlorination of aralkyl hydrocarbons as well as to determine the reactivities of various aralkyl hydrocarbons to the uncomplexed chlorine atom. In order to accomplish this task it was necessary to chlorinate the aralkyl hydrocarbons at different concentrations using a noncomplexing solvent as diluent and to extrapolate these data to infinite dilution of the aralkyl hydrocarbon. The hydrocarbons studied by this technique were cumene, indan, and tetralin. Not only were the relative reactivities of the *alpha*- and *beta*-hydrogen atoms determined in each case but the reactivities of the *alpha*-hydrogen atoms relative to the hydrogen atoms of cyclohexane were determined by competitive chlorination with cyclohexane. These latter data are necessary for the comparison of the reactivities of the various *alpha*-hydrogen atoms.

Results and Discussion

Relative reactivity of alpha- and beta-hydrogen atoms

The relative reactivity of the alpha- and beta-hydrogen atoms of cumene, indan, and tetralin toward the chlorine atom are listed as a function of the substrate concentration in Table 1. Nitrobenzene was used as the solvent in the majority of these photochlorinations since this solvent is not a complexing solvent in the photochlorination of 2,3-dimethylbutane (6a). In addition the inertness of nitrobenzene as a solvent was shown in the chlorination of tetralin; the results obtained by using nitrobenzene as a solvent are in agreement with the results obtained by using cyclohexane which is not a complexing solvent. Mr. H. D. McBride of this laboratory has shown also that identical results are obtained in the chlorination of ethylbenzene with the solvents cyclohexane and nitrobenzene. All these results indicate that the chlorine atom does not complex significantly with nitrobenzene, and that this solvent is not causing electrophilic aromatic chlorination as a result of its high dielectric constant.

The same data found in Table 1 are presented in Figures 1 and 2. The relative reactivity of 42.2 in pure cumene corresponds to 87.5 percent alpha-chlorocumene which agrees with the results of Cerny and Hajek who obtained 91.3 percent alpha-chlorocumene (9d). The sweeping decrease in the relative reactivity with the decrease in the concentration of cumene illustrates that the cumene concentration indeed does affect the reactivity of the chlorine atom in the chlorination of cumene. The value for the relative reactivity obtained by extrapolating to infinite dilution

Table 1. Photochlorination of aralkyl hydrocarbons at 40°

Hydrocarbon	Mole	Conc.[a]	Solvent[b]	Mmole chloro-derivatives alpha	beta	k_α/k[c]
Cumene	0.105	7.05	none	3.75	0.549	42.2[d]
"	0.0756	5.04	NB	2.70	0.781	20.8
"	0.0450	3.00	NB	1.15	0.654	10.6
"	0.0224	1.49	NB	0.706	0.810	5.24
"	0.0000	0.00	NB	extrapolated		3.5[e]
Indan	0.119	7.96	none	3.96	0.310	6.39
"	0.0746	4.97	NB	1.87	0.250	3.73
"	0.0445	2.96	NB	0.846	0.173	2.46
"	0.0222	1.48	NB	0.379	0.106	1.78
"	0.0000	0.00	NB	extrapolated		1.2[f]
Tetralin	0.108	7.21	none	3.26	0.585	5.57
"	0.0741	4.94	CY	1.32	0.353	3.74
"	0.0449	2.99	NB	1.84	0.790	2.32
"	0.0220	1.47	NB	0.560	0.397	1.41
"	0.0218	1.45	CY	1.26	0.828	1.52
"	0.0000	0.00	NB or CY	extrapolated		1.15[f]

[a] Mole/lit. at 40°.

[b] NB = nitrobenzene, CY = cyclohexane.

[c] Per hydrogen atom.

[d] Average of 4 experiments.

[e] From Figure 1.

[f] From Figure 2.

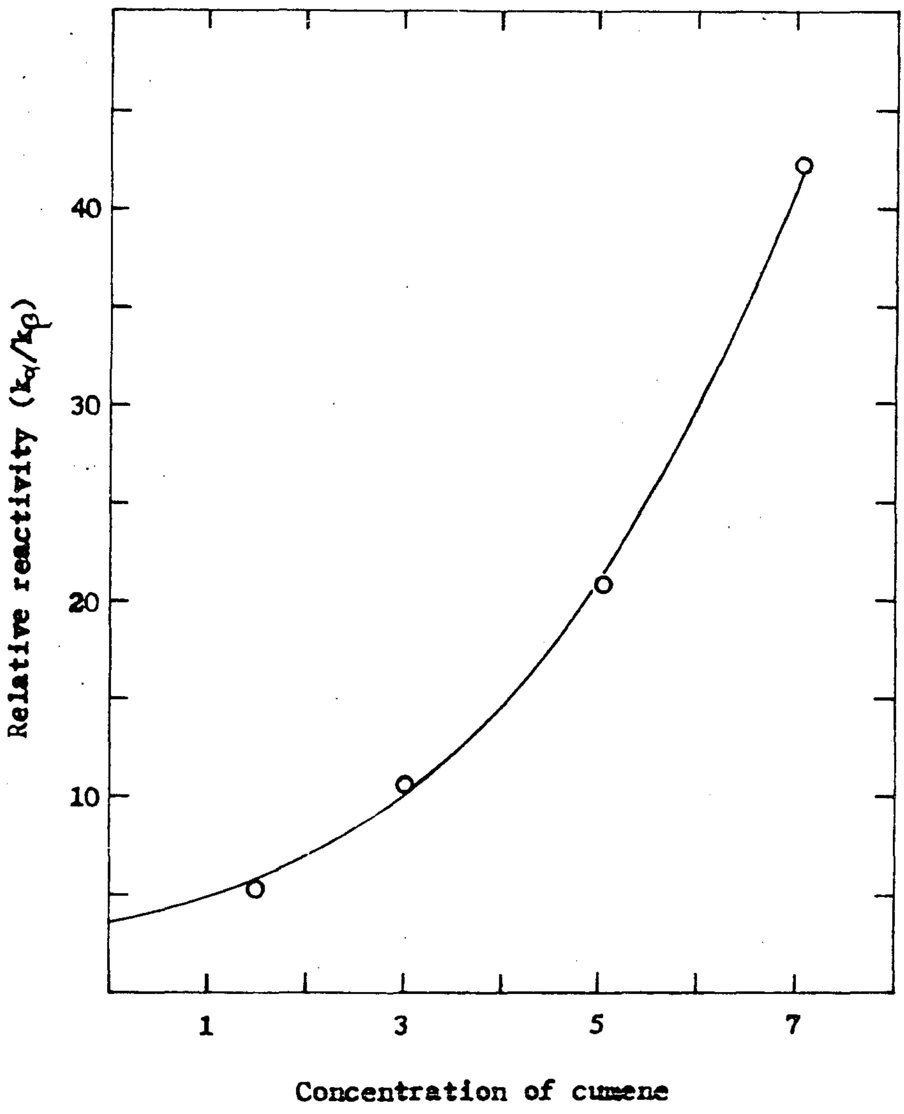


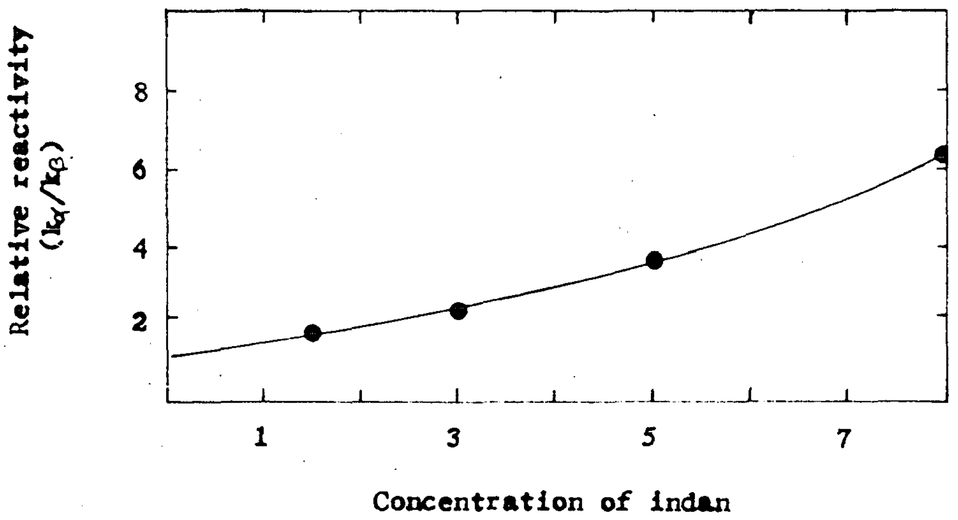
Figure 1. Effect of the concentration of cumene on the relative reactivity of the alpha- and beta-hydrogen atoms of cumene at 40° (inert diluent = nitrobenzene)

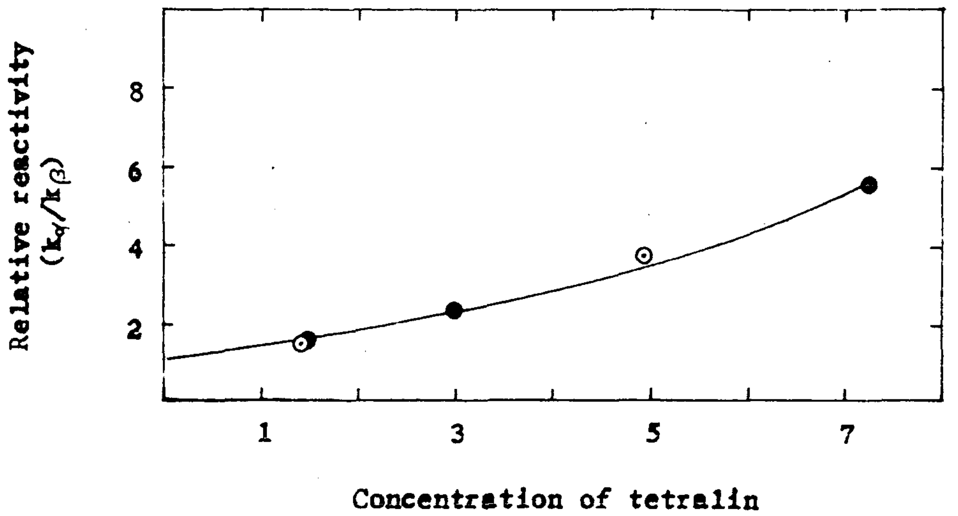
Figure 2a. Effect of the concentration of indan on the relative reactivity of the alpha- and beta-hydrogen atoms of indan at 40° in nitrobenzene

Figure 2b. Effect of the concentration of tetralin on the relative reactivity of the alpha- and beta-hydrogen atoms of tetralin at 40° in nitrobenzene and cyclohexane solutions

● : nitrobenzene solution

⊙ : cyclohexane solution


Relative reactivity
(k_α/k_β)
8
6
4
2
1
3
5
7
Concentration of indan


Relative reactivity
(k_α/k_β)
8
6
4
2
1
3
5
7
Concentration of tetralin

is 3.5 which should correspond to the relative reactivity toward the uncomplexed chlorine atom. There is some degree of uncertainty in this value, since it is not known how the curve should approach the ordinate; reasonable limits for this value would be 3.5 ± 1.0. The value is in agreement with the value of 3.9 reported for the relative reactivity of a tertiary and a primary hydrogen atoms of 2,3-dimethylbutane at the same temperature. However, there is no reason to expect that these two relative reactivities should show anything more than a qualitative agreement.

In Figure 2 the relative reactivity of the alpha- and beta-hydrogen atoms of indan and tetralin are shown graphically as a function of the concentration of aromatic hydrocarbon. The observed curves are similar to that found for cumene except that the solvent effects are not as large. This reduction in the solvent effect is expected as the alpha- and beta-positions for both indan and tetralin are secondary positions although the alpha-positions are adjacent to a benzene ring; the relative reactivity of the alpha- and beta-positions at infinite dilution for each case agree surprisingly well. This value is 1.2 ± .1 for indan and 1.15 ± .1 for tetralin. Not only do the extrapolated values agree for both indan and tetralin but it is interesting that the values at higher concentrations do also.

The conclusion that the benzene ring only slightly activates the alpha-position above the reactivity of the beta-position toward the chlorine atom supports the previously suggested interpretation that little bond breaking occurs in the transition state for the reaction of an uncomplexed chlorine atom with a hydrocarbon (10). As was discussed earlier, if the degree of bond breaking in the transition state for a carbon-hydrogen bond activated by an aromatic ring decreases, the importance of resonance stabilization and the degree of activation by the aromatic group also decreases.

Reactivity of alpha- and beta-hydrogen atoms relative to cyclohexane

It is not satisfactory to assume that the reactivity of hydrogen atoms in the *beta*-positions of these hydrocarbons will be identical to those of the corresponding primary and secondary hydrogen atoms in aliphatic systems. For example the primary hydrogen atoms of tertiary-butylbenzene are reported to be about 0.6 times as reactive as the primary hydrogen atoms of 2,3-dimethylbutane (6a). In order to compare the reactivities of the hydrogen atoms of cumene, indan, and tetralin to each other and to the hydrogen atoms of aliphatic compounds, each hydrocarbon was chlorinated competitively with cyclohexane. Cyclohexane was chosen because of its ideal physical properties and because its reactivity is known relative to many other aliphatic hydrocarbons.

The data for competitive chlorinations with cyclohexane as a function of the aromatic concentration are in Table 2. These data are shown graphically in Figures 3 and 4. Because of the experimental error in these cases as well as the lack of a large solvent effect, the curves have been approximated by straight lines. The extrapolated values are also in Table 3 along with some other relative reactivities from the literature.

From Figure 3 it can be seen that cumene exhibits essentially no solvent effect in the reactivity of the *alpha*-position relative to cyclohexane. Since a large solvent effect is observed between the *alpha*- and

Table 2. Competitive photochlorination of cyclohexane and aralkyl hydrocarbons at 40°

Aralkyl hydrocarbon (mole)	Cyclohexane (mole)	Conc. aralkyl hydrocarbon[a]	Added solvent[b]	Chlorination products, mmole chlorocyclohexane	Chlorination products, mmole alpha-chloro aralkyl	k_{α}/k_{CY}[c]
Cumene						
0.0000	--	0.00	NB, CY or Cl_4	extrapolated		2.9[d]
0.0229	0.00379	1.53	NB	0.183	0.288	3.12
0.0447	0.00745	2.98	NB	0.495	0.786	3.18
0.0455	0.00759	3.03	NB	0.297	0.456	3.07
0.0450	0.00750	3.00	CCl_4	0.135	0.200	2.96
0.0755	0.0126	5.04	CCl_4	0.149	0.246	3.31
0.0944	0.0158	6.29	none	0.516	0.816	3.16
Indan						
0.0000	--	0.00	NB or CY	extrapolated		2.2[e]
0.0222	0.110	1.48	none	0.396	0.805	3.02
0.0422	0.0399	2.81	NB	0.985	1.290	3.71
0.0443	0.0857	2.95	none	2.45	1.44	3.41
0.0740	0.0518	4.93	none	0.429	0.952	4.63
Tetralin						
0.0000	--	0.00	NB or CY	extrapolated		2.1[e]
0.221	0.107	1.47	none	4.53	0.845	2.72
0.0445	0.0445	2.97	NB	0.551	0.579	3.16
0.0445	0.0795	2.97	none	0.158	0.102	3.46
0.0741	0.0429	4.94	none	0.336	0.795	4.11

[a] Mole/lit. at 40°.

[b] NB = nitrobenzene, CY = cyclohexane.

[c] Per hydrogen atom.

[d] From Figure 3.

[e] From Figure 4.

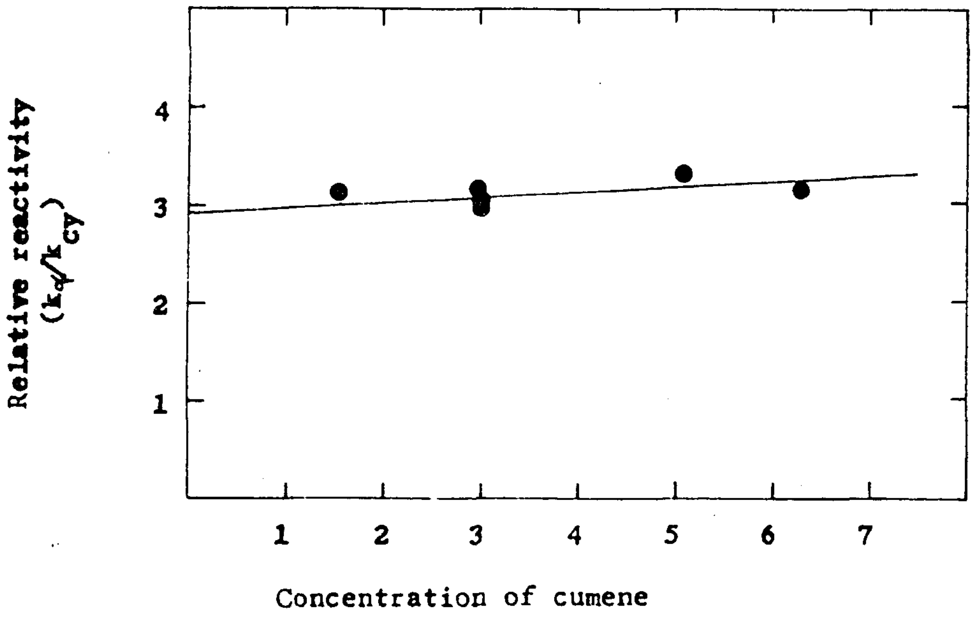


Figure 3. Effect of concentration of cumene on the reactivity of the alpha-hydrogen atom of cumene compared to the reactivity of a hydrogen atom of cyclohexane at 40° (inert diluent = nitrobenzene)

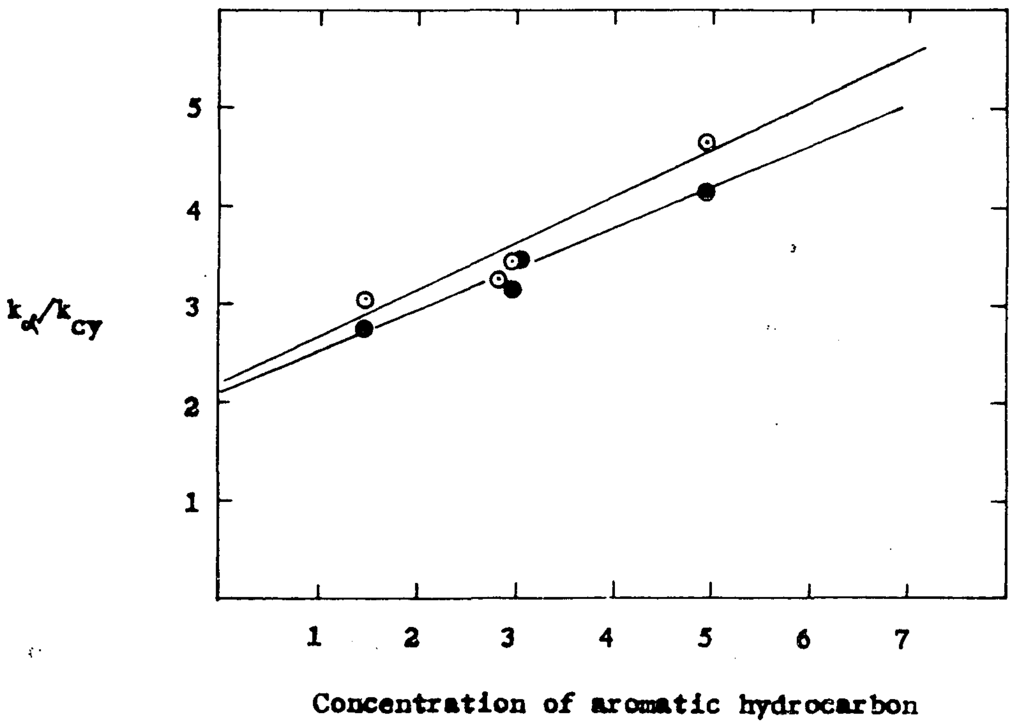


Figure 4. Effect of aromatic concentration on the reactivities of an *alpha*-hydrogen atom of indan and tetralin relative to a hydrogen atom of cyclohexane

⊙ : indan

● : tetralin

beta-positions, there must be a large solvent effect in the reactivity of cyclohexane relative to the beta-position. In illustration the relative reactivity of a cyclohexane hydrogen atom and a primary hydrogen atom of cumene can be determined from the data in Figure 1 and Figure 3 and is about 4.8 in 4.0 M cumene. The value of 6.9 for the reactivity of a cyclohexane hydrogen atom relative to a primary hydrogen atom of 2,3-dimethylbutane was found in 4.0 M tertiary-butylbenzene at 40° (6a). The difference is explainable by two factors: first, tertiary-butylbenzene is a slightly better complexing agent than cumene, and second, the reactivity of the beta-position of cumene is not identical to that of a primary hydrogen atom of 2,3-dimethylbutane. For example, from the data in Table 3 a beta-position of cumene is about 2.2 times more reactive than a primary hydrogen atom of 2,3-dimethylbutane at infinite dilution.

The lack of a solvent effect in the reactivity of the alpha-position of cumene relative to cyclohexane should be rationalized. In this case a rather large solvent effect, at least one of the order found between the beta-position and cyclohexane, would be expected. This result can be considered consistent with the results of Mr. A. Ito of this laboratory who found in the competitive chlorinations of cyclopentylbenzene and cyclohexylbenzene with cyclohexane an inverse solvent effect where the reaction of the more reactive alpha-hydrogen atom is more favorable at a lower aromatic concentration. The only reasonable explanation for this effect in his two systems appears to be that the chlorine atom complex is bulkier and is hindered in attacking the alpha-hydrogen atom while the uncomplexed chlorine atom is not. The results for cumene appear to be

Table 3. Reactivities of some carbon-hydrogen bonds toward chlorine atoms at 40°

Hydrocarbon	Position	Relative reactivity (per hydrogen atom)
Cyclopentane (6a)	secondary	1.04
Cyclohexane	secondary	1.00[a]
2,3-Dimethylbutane (6a)	primary	0.37
	tertiary	1.44
Toluene[b]	alpha	0.52
Ethylbenzene[c]	alpha	1.30
	beta	0.67
Cumene	alpha	2.85
	beta	0.82
Tertiary-butylbenzene (6a)	beta	0.23
Tetralin	alpha	2.14
	beta	2.04
Indan	alpha	2.26
	beta	1.74

[a] Assumed.

[b] Results of Mr. A. Ito of this laboratory.

[c] Results of Mr. H. D. McBride.

between what normally would be expected and that observed for the two cycloalkylbenzenes; thus the possibility exists that there are steric interactions in the reaction for the complexed chlorine atom with the *alpha*-position of cumene. These interactions would tend to cancel the normal solvent effect. Electronic interactions between the *pi*-electron clouds of the aromatic ring of cumene and the complex also might aid to decrease the expected reactivity of the complexed chlorine atom toward these *alpha*-hydrogen atoms. This latter suggestion would explain the reason why a solvent effect is observed between *tertiary*-hydrogen atoms of 2,3-dimethylbutane and hydrogen atoms of cyclohexane (6a) since one would not expect a smaller steric interaction between an isopropyl group of 2,3-dimethylbutane than a phenyl group of cumene.

The curves for the reactivity of the *alpha*-position of indan and tetralin relative to cyclohexane show more slope than is observed for cumene. The comparison of Figures 2 and 4 reveal that there is no significant solvent effect in the relative reactivities of the *beta*-positions of indan and tetralin and cyclohexane. Since there is little difference in the resonance stability of the two resulting radicals, these results are reasonable. The slopes found in Figure 4 are in agreement with the argument for the lack of solvent effect in the similar case for cumene. Since the *alpha*-carbon is substituted to a lesser degree, the *alpha*-position of both indan and tetralin would be easily approached by the chlorine complex, and the solvent effect should not be suppressed by any steric or electronic interactions.

From the data in Table 3 it is seen that the *alpha*-position of cumene is activated in comparison to the tertiary-position of 2,3-dimethylbutane. This two-fold rate enhancement is probably the result of the resonance stabilizing effect of the phenyl group on the transition state, although it is much less than that which appears in other free radical reactions. In the free radical bromination this enhancement has been observed to be about 120 by Mr. C. D. DeBoer of this laboratory. The small degree of activation for attack by the chlorine atom again testifies to the small amount of bond breaking in the transition state.

From vapor phase data in the literature it is possible to estimate the relative reactivities of a primary hydrogen atom of ethane, a secondary hydrogen atom of propane, and the tertiary hydrogen atom of isobutane to the chlorine atom at 40° (11). These relative reactivities are 1:4:6, respectively. If one of the methyl groups is replaced in this series by a phenyl group the series toluene, ethylbenzene, cumene is obtained and the relative reactivities of the corresponding primary, secondary, and tertiary hydrogen atoms of these hydrocarbons are 1.0:2.6:5.8. The comparison of these two different series shows that the methyl group activates to about the same degree in each case. Although the aromatic series seems to show slightly less activation by the methyl group, the differences are probably within experimental error.

Szwarc and coworkers have recently argued the importance of steric interactions in the transition state of reactions between the methyl radical with certain aralkyl hydrocarbons, and they state that these steric interactions prevent the phenyl group from rotating to a position in which maximum resonance stabilization of the free electron may be obtained (12). The radical which results from the reaction of the methyl radical with either ethylbenzene or cumene obtains maximum resonance stability only when the methyl group or groups on the *alpha*-carbon are in the same plane as the aromatic ring. However, in such a configuration there are steric interactions between the methyl groups on the *alpha*-carbon atom and the *ortho*-hydrogen atoms of the aromatic ring, and in order to reduce these steric interactions the phenyl group assumes a position where it is not coplanar with the rest of the radical. In this configuration the contribution of the phenyl group to the resonance stability of the radical is less than the contribution made by the phenyl group in the benzyl radical. The importance of these steric interactions may be seen by comparing the relative reactivities of toluene, ethylbenzene, and cumene toward the methyl radical with the relative reactivities of aliphatic primary, secondary, and tertiary hydrogen atoms of ethane, butane, and isopropane, respectively. For the aliphatic series in the vapor phase this sequence is 1.0:17:180 at 65° (13) and for the aromatic series at the same temperature as reported by Szwarc, the sequence is 1.0:4.1:13. In the aromatic series the substitution of a methyl group for an *alpha*-hydrogen atom does not activate the remaining *alpha*-hydrogen atom to the same degree as it does in the aliphatic series, presumably due to steric interactions in the transition state which prevent the phenyl group from participating as fully as possible in stabilizing the radical.

The steric interactions as described by Szwarc apparently are not as important in the photochlorination of aralkyl hydrocarbons as they are for the reactions of the methyl radicals since in the chlorinations the methyl group enhances the rate to the same degree in the aromatic and aliphatic systems. If steric inhibition of resonance in the transition state were importance for the reaction of the chlorine atom with ethylbenzene and cumene, the enhancement would not be as great as in the aliphatic system.

Data for the relative reactivities of a number of aralkyl hydrocarbons toward various free radicals are listed for comparison in Table 4. The alpha-hydrogen atoms of ethylbenzene, indan, and tetralin are all secondary hydrogen atoms. There is some discrepancy in their relative reactives since indan and tetralin are both about 1.7 times more reactive than ethylbenzene. However, a similar reactivity sequence has been observed with other free radicals as may be seen in Table 4; generally the spread in the reactivities is greater, with tetralin being much more reactive than indan. Szwarc and coworkers has reported the relative reactivities per alpha-hydrogen atom of ethylbenzene, indan, and tetralin toward the methyl radical to be 1.0:4.2:12.5 (12), and explain this order of reactivities partly by the degree of inhibition of resonance due to steric interactions in the transition state; thus the low reactivity of ethylbenzene is due to the interactions between the methyl group and an ortho-hydrogen atom. In the case of indan and tetralin this type of interaction would not be present in the reaction, and these authors accept the explanation given earlier in the literature for difference in the reactivities of indan and tetralin (14) which states that more strain is added to the ring of indan in forming the radical than in the formation of the radical from tetralin. This strain is said to retard the reaction

Table 4. Relative reactivities of some aralkyl hydrocarbons toward various radicals

Hydrocarbon	Cl· 40°	ROO· (14) 90°	CCl_3· (15) 91.5°	<u>t</u>-BuO· (16) 135°	CH_3· (12) 65°
Toluene	1.00[a]	1.00[a]	1.00[a]	1.00[a]	1.00[a]
Ethylbenzene	2.50	7.72	4.6	3.2	4.14
Cumene	5.50	13.3	12.5	5.1	12.9
Indan	4.35	37.	7.1	...	8.3
Tetralin	4.15	67.	12.8	7.6	11.5

[a] Assumed.

of indan relative to tetralin.

The saturated ring of tetralin is reported to assume a conformation similar to the chair form of cyclohexane (17). This conformation produces two distinct <u>alpha</u>-hydrogen atoms, axial and equatorial, where the axial carbon-hydrogen bond will be closer to being parallel to the <u>pi</u>-orbitals of the aromatic ring than the equatorial. Szwarc and coworkers believe that no further strain is involved in attaining the transition state when this bond participates in the reaction. Thus they feel that the axial hydrogen atoms would be significantly more reactive than the equatorial hydrogen atoms, and only axial hydrogen atoms should be considered as reacting. With these assumptions the relative reactivity of the tetralin hydrogen atoms becomes 23 times more reactive per reacting hydrogen atom than toluene toward the methyl radical, and all the reactivities in

Table 4 for tetralin should be multiplied by two.

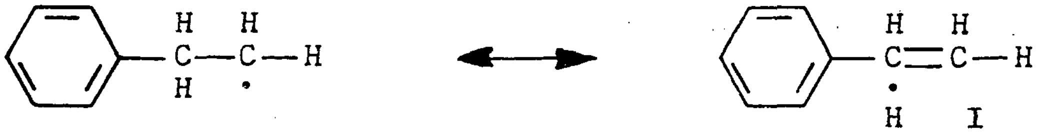
Observation of models of tetralin and the corresponding radical indicates that these assumptions may be over simplifications since it is unnecessary for the chair conformation of tetralin to interconvert to the other chair conformation as an original equatorial hydrogen atom reacts. If it were necessary for the interconversion to occur, and if the energy of activation for the process was greater than the energy of activation for hydrogen abstraction, there would be a significant difference in the reactivities of these two hydrogen atoms.

In the reaction of the axial hydrogen atom of tetralin the assumption that no additional strain develops due to the fact that the axial carbon-hydrogen bond is already in position for maximum resonance interaction with the aromatic ring is not necessarily correct. Although the carbon-hydrogen bond does not have to rotate to achieve maximum resonance interaction, the bond angle in the ring will increase in going from the reactant to the _alpha_-tetralyl radical and a fraction of this increase will be felt in going from the ground state to the transition state. In the case of tetralin no strain develops because the puckered ring can easily accommodate this increase in bond angle in both the transition state and the final product. The reactivity of the _alpha_-hydrogen atoms of indan is lower than that of the corresponding hydrogen atoms of tetralin because the bond angles are smaller than normal carbon-carbon bond angles, and the change of hybridization adds to the strain of the ring. It is not reasonable to assume that the axial bond of tetralin should be much more reactive than the equatorial bond since the same changes in the bond angles are involved in going from reactants to radical. The only difference is in the degree to which the orbitals of the carbon atom rotate, which is slightly larger in the case of an equatorial hydrogen atom.

If the transition state is close to the reaction products, extensive bond rupture and change in bond hybridization will have occurred and the energy contents of the transition states for attack on the equatorial and axial hydrogen atoms will be nearly equivalent. On the other hand, if there is very little bond-breaking in the transition state with little change in bond hybridization and bond angle, then appreciable overlap of the bond being broken with the pi-orbitals of benzene ring, can occur only for axial attack. The chlorine atom is well known to involve little bond-breaking in its transition state for hydrogen abstraction (10), in fact, it is one of the least selective radical species known, thus the observation that the alpha-hydrogen atoms of tetralin and indan have nearly equivalent reactivity is not in agreement with analysis given above and suggests that orientation of the carbon-hydrogen bond relative to the benzene ring in the ground state has little to do with the reactivity of that bond toward a free radical.

If steric interactions are not important in the chlorination of ethylbenzene, as was concluded earlier, it is necessary to explain the observation that indan and tetralin are more reactive than ethylbenzene. In the reaction of all radicals with these two hydrocarbons the inductive effect of the alkyl chain can not be ignored. Indan and tetralin should be expected to have the reactivity of a compound like para-diethylbenzene rather than ethylbenzene. The reactivity of this compound is not known but Mr. R. C. Williamson of this laboratory has shown that a methyl group in the *para*-position of toluene activates the benzylic hydrogens by a factor of 1.5. If the activation of a *para*-methyl group in toluene is comparable for that in ethylbenzene, one would expect a value of 3.8 for the relative reactivity of benzylic hydrogen atoms in the ethyl group of a *para*-substituted ethylbenzene. This value is quite close to that observed for the relative reactivities of the benzylic hydrogen atoms of indan and tetralin 4.35 and 4.15, respectively.

In Table 3 the primary hydrogen atoms of cumene as well as those of ethylbenzene have a greater reactivity than the primary hydrogen atoms of 2,3-dimethylbutane. To explain the increased reactivity of these primary hydrogen atoms it is tempting to consider the hyperconjugation resonance structures (I) important in stabilizing the transition state.



I

The importance of such structures wherein the double bond is conjugated with aromatic ring may be greater than in a case where it is not conjugated. Consistent with this idea is the low reactivity of the primary hydrogen atoms of *tertiary*-butylbenzene where there are no *alpha*-hydrogen atoms available for hyperconjugation.

The *beta*-hydrogen atoms of indan and tetralin show an increased reactivity over the hydrogen atoms of cyclohexane--a fact which is in agreement with the hyperconjugation explanation given above.

Quantitatively the data is not consistent since one would expect on the basis of the above explanation that indan should be more reactive in the *beta*-position than tetralin. Twice as many hyperconjugation structures exist wherein the double bond is conjugated with the benzene ring for indan as for tetralin, but both compounds exhibit about the same reactivity in this position.

The above explanation for the enhancement in the reactivity of the *beta*-position of indan and tetralin appears to be in disagreement with some of the principles discussed concerning solvent effects. If the *beta*-position is activated by this type of resonance stabilization, it would be expected that the solvent effect should not be very great when the *alpha*- and *beta*-positions are compared but significant when the *beta*-position and cyclohexane are compared. The experimental data do not agree with these conclusions.

Another reason for questioning this explanation is that if the activation is important for reaction with a chlorine atom other radical reactions should also produce significant amounts of *beta*-substituted products; however, this fact does not appear to be the case for the bromine atom (10) or for the peroxy radical (1a, p. 406). In support of the explanation it may be argued that these hyperconjugation structures are important only in cases wherein a small amount of bond breaking occurs in the transition state; as the bond breaking becomes more important the interaction of an adjacent phenyl group also may become more important, and predominately *alpha*-substitution occurs.

Other suggestions can be made to rationalize the increased reactivity of the *beta*-positions in these compounds. Because its electron affinity is large the chlorine atom is attracted to the high electron density of the aromatic rings of the aralkyl hydrocarbons as illustrated by the complexing of the atom with aromatic rings. If the chlorine atom tends to be drawn to these molecules, the hydrogen atoms in the attracting molecule have greater opportunity to react with the chlorine atom than hydrogen atoms in a non-complexing molecule. The reactivity of both the *alpha*- and the *beta*-positions should be favored by this factor. Radicals with lower electron affinities would not be affected to such an extent by the electron density of the aromatic ring; therefore, only the chlorine atom would be expected to exhibit these high reactivities in the *beta*-position relative to normal aliphatic systems. Once complexed by one aromatic ring, the reactivity of a chlorine atom toward another indan or tetralin molecule should not reflect an activation other than that connected with bond dissociation energy for benzyl type carbon-hydrogen bonds.

The fact that the primary hydrogen atoms of *tertiary*-butylbenzene do not show any activation over the reactivity of the primary hydrogen atoms of 2,3-dimethylbutane is evidence against the above interpretation. In fact these hydrogen atoms are deactivated to the extent 0.6 of the reactivity of the primary hydrogen atoms of 2,3-dimethylbutane, an effect generally ascribed to the inductive effect of the phenyl group.

Experimental

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 stopcock 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 $\frac{1}{4}$ inch "Tygon" tubing which directed the carrier gas to the chlorine reservoir when the reservoir was not being by-passed. The three-way stopcock which was used to direct the gas either through or around the chlorine reservoir was equipped with a "Teflon" stopcock 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 stopcock 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 stopcock was adjusted so the nitrogen again by-passed 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.

Analysis procedure

The alpha-chloride in the chlorination mixtures was determined by selectively hydrolyzing aliquots of the reaction mixture in 80% alcohol and titrating the free chloride potentiometrically with silver nitrate. In order to insure the complete hydrolysis of the alpha-chloride, the hydrolysis was followed by directly titrating with sodium hydroxide the hydrogen chloride formed; once the formation of acid ceased the hydrolysis was stopped.

The total chlorine content of the mixtures determined by decomposing aliquots of the mixtures by the method of Rauscher (18) and titrating the free chloride potentiometrically. The amount of beta-chloride was assumed to be the difference of the total chloride and the alpha-chloride in the cases where there were no other chloride present. In the competitive chlorinations with cyclohexane, the chlorocyclohexane was determined by gas liquid chromatography using toluene for the internal standard. The separations were made by the use of a 2-meter Perkin-Elmer "B" column (reportedly di-2-ethylhexylsebacate) at 110°.

Reagents

99 Mole percent minimum purity cumene obtained from Phillips Petroleum Company was used. Indan was prepared from indene by hydrogenating over a 5% paladium-on-charcoal catalyst. The traces of unreacted indene were removed by washing the filtered reaction mixture with neutral potassium permanganate. After washing several times with water, the material was dried and fractionally distilled, b.p. 78-9°, n_D^{20} 1.5390. Matheson practical grade tetralin was purified by repeated washing with both 90% sulfuric acid and water, dried, and distilled, n_D^{20} 1.5416. Both spectrograde Eastman-Kodak cyclohexane and Phillips Petroleum 99 mole percent minimum purity cyclohexane were used. The nitrobenzene that was used was the center portion obtained in a simple distillation of Matheson practical grade nitrobenzene; it was further purified, as were all the other liquids, by passage over activated silica gel in a nitrogen atmosphere and stored under nitrogen.

METHYLATION OF HYDROCARBONS

Introduction

At the time this study was undertaken some discrepancy appeared in the literature concerning the reactivity of methylene. Frey and Kistiakowsky generated methylene from ketene by photolysis in the vapor phase and found that at room temperature methylene was 1.7 times more reactive toward the secondary hydrogen atom of butane than toward the primary hydrogen atoms (19). Doering *et al*. earlier had reported the relative reactivity of secondary and primary hydrogen atoms of pentane toward methylene formed by photolysis of diazomethane in the liquid phase to be 1.04 at 15° (20). These workers also studied the reaction of cyclohexene with methylene and reported the relative reactivities are 1:1.2:1.2 for a vinyl hydrogen atom, an allylic, secondary hydrogen atom and a non-allylic secondary hydrogen atom. Because of this extremely high reactivity and low selectivity it was suggested that "methylene must be classed as the most indiscriminate reagent known in organic chemistry.

Frey and Kistiakowsky state that the discrepancy in the reactivity of methylene prepared by these two different methods is the result of excess energy with which the methylene is formed. They feel that the methylene as it is first formed in photolysis of diazomethane has excess energy compared with any thermal equilibrium value and thus is more reactive than any methylene at thermal equilibrium. The selectivities show that the methylene formed from ketene is not as "hot" as that from diazomethane and in support of this hypothesis Frey and Kistiakowsky show that increasing the relative amount of inert gas decreases the reactivity of the methylene formed from ketene. They interpret this observation as indicating that methylene generated from ketene is to a degree also a "hot" reagent, i.e., has more vibrational energy than would be found at thermal equilibrium; the presence of an inert gas gives the "hot" methylene an opportunity to dissipate some of its excess energy with inert collisions before reacting, producing a less reactive methylene (19).

Methylene can exist in two electronic states, and methylene generated from diazomethane appears to react as expected for a singlet electronic state, even though Herzberg has shown that the molecule exists as a triple in the ground state (21). Woodworth and Skell reported that the addition of methylene from diazomethane to cis- or trans-2-butene gives stereospecific products, cis- or trans-1,2-dimethylcyclopropane, respectively (22). The stereospecific product that is obtained in each case indicates that no open chain, long lived intermediate is involved which could lose the stereospecificity; such an intermediate would not be expected if the methylene is in a singlet state since singlet methylene can add directly to a double bond. However, Frey has decomposed diazomethane in the presence of cis-2-butene and a large amount of inert gas and found nearly equal amounts of cis- and trans-1,2-dimethylcyclopropane (23). This fact indicates that methylene obtained from diazomethane will convert to a singlet electronic state if provided with a sufficient number of inert collisions.

The experimentation of this section was undertaken in the attempt to alter the reactivity of methylene by the use of aromatic solvents. Since methylene is an electron deficient reagent it could form a complex with aromatic solvents similar to that of the chlorine atom; this complex of a "hot" methylene would quickly lose its excess energy and perhaps convert to a triplet state. Therefore, if methylene does form a complex with aromatic solvents, a different reactivity should be observed.

2,3-Dimethylbutane was used as the substrate for investigating the possibility of a solvent effect in the reactivity of methylene with carbon-hydrogen bonds. The relative reactivity can be determined directly from the ratio of the products--2,3-dimethylpentane and 2,2,3-trimethylbutane. The reactivity of the primary hydrogen atom relative to the tertiary hydrogen in 2,3-dimethylbutane has been previously measured and found to be 0.813 with excess hydrocarbon as solvent (20).

A complicating factor in this problem is the reaction of methylene with aromatic compounds such as benzene. If diazomethane is decomposed in benzene, cycloheptatriene and toluene are obtained (24). Thus if benzene is used as a solvent in the methylation of 2,3-dimethylbutane, cycloheptatriene and toluene will also appear as products. The ratio of these products also was determined at different aromatic concentrations in order to examine the possibility of a solvent effect in the reaction of methylene with benzene.

Results and Discussion

Solutions of 2,3-dimethylbutane containing 0, 2, and 4 M benzene were treated with diazomethane and irradiated with ultraviolet light until the yellow color of the diazomethane had disappeared. At the completion of each photolysis, the resulting mixture was analyzed quantitatively by gas-liquid chromotography for 2,2,3-trimethylbutane and 2,3-dimethylpentane. Both the ratio of products and the corresponding relative reactivity for a primary and a tertiary hydrogen atom of the hydrocarbon are given with the corresponding 95% confidence intervals for each experiment in Table 5. While the data do show some small variation, the conclusion must be drawn that aromatic solvents are unimportant in influencing the reactivity of methylene toward simple carbon-hydrogen bonds.

By the data in Table 6 some variation of product ratios is indicated for the reaction of methylene with benzene in the vapor phase and in various solvents. In pure benzene solution, decomposition of the diazomethane gives cycloheptatriene and toluene in the ratio of 4.76 ± .20, while in the vapor phase, the ratio is 3.23 ± .07. The reaction of methylene with pure benzene has been studied previously, but the ratio of products reported is smaller than reported here; however, the analysis in these other cases was obtained by isolation of the products and some of the cycloheptatriene could have been lost due to its instability in the presence of air. The vapor phase experiments were performed at higher temperatures than those in solution, but the product ratio shows no temperature dependence in the range of temperature studied. Lack of temperature dependence in a reaction of methylene formed from diazomethane

Table 5. Methylation of 2,3-dimethylbutane in the presence of benzene at 25°

Concentration of benzene[a]	$\frac{\text{2,3-DMP}^b}{\text{2,2,3-TMB}}$	$\frac{k_p{}^c}{k_t}$
0.00	4.83 ± .39	0.805 ± .065
1.97	5.12 ± .09	0.854 ± .015
3.93	5.08 ± .13	0.847 ± .021
Average	5.01 ± .48	0.835 ± .080

[a] Concentration in mole/lit.

[b] Ratio of the concentrations of 2,3-dimethylpentane and 2,2,3-trimethylbutane in the reaction product.

[c] Relative reactivity of the primary hydrogen atoms and the tertiary hydrogen atoms.

has been reported previously by Doering _et_ _al_. (20); they observed no change in the relative reactivities of the primary and secondary hydrogen atoms of pentane between the temperatures of 15° and -75°.

In the various solvents other than benzene the reaction yields values for the ratio of products between those of the reaction in pure benzene and the vapor phase. The observed order for the decreasing ability of the aromatic solvent to give cycloheptatriene compared with toluene is 11.2 _M_ benzene, 4.0 _M_ _tertiary_-butylbenzene plus 2.0 _M_ benzene, 4.0 _M_ chlorobenzene plus 2.0 _M_ benzene, 2.0 _M_ benzene, vapor phase. This sequence is identical to that observed for the decrease in formation of 2-chloro-2,3-dimethylbutane, or the increase of 1-chloro-2,3-dimethylbutane in photochlorination of 2,3-dimethylbutane. To assume that the

Table 6. Methylation of benzene with diazomethane

Solvent	Concentration of benzene[a]	Temperature	$\frac{\text{CHT}}{\text{Toluene}}$[b]
Benzene	11.4	25° C	4.76 ± .40
4 *M* *t*-butylbenzene[c]	2.0	25	4.38 ± .30
4 *M* chlorobenzene[d]	2.0	25	3.64 ± .36
7.5 *M* cyclohexane	2.0	25	3.72 ± .22
Vapor phase	-	155	3.31 ± .21
Vapor phase	-	180	3.12 ± .22
Vapor phase	-	200	3.30 ± .19
Vapor phase	Average		3.23 ± .25

[a] Concentration in mole/lit.

[b] Molar ratio of cycloheptatriene and toluene in reaction product.

[c] 2,3-dimethylbutane (3.6 *M*) used as a co-solvent.

[d] 2,3-dimethylbutane (3.2 *M*) used as a co-solvent.

aromatic solvents affect the reactivity of methylene by the formation of *pi*-complex appears reasonable due to this agreement with the photochlorination data.

The simplest explanation of the data would assume the formation of a *pi*-complex between methylene and benzene; this complex can collapse to either product in the same ratio obtained from the vapor phase, or it may react with another molecule of benzene to give the same products in a different ratio. A higher yield of cycloheptatriene would be demanded in the second case. Since the electron deficiency of the methylene would be satisfied to a greater extent when it is associated with two benzene molecules, the complexed methylene would exhibit more selectivity in the reaction with another benzene molecules and give more cycloheptatriene than observed in the direct reaction. Therefore, as the concentration of benzene increases the ratio of cycloheptatriene and toluene also increases since the reaction of benzene with the complex would be first order with respect to benzene.

If both benzene and tertiary-butylbenzene are present in the reaction mixture, cycloheptatriene and toluene will be formed by the reaction of a complex of methylene and tertiary-butylbenzene with benzene. This reaction should yield a higher cycloheptatriene toluene ratio than the one of the benzene complex since the tertiary-butylbenzene complex would be stronger due to higher electron density of the aromatic ring. However, the concentration of the complexing solvent is important, and while tertiary-butylbenzene should yield more cycloheptatriene than would benzene, the lower concentration of tertiary-butylbenzene tends to cancel this effect. Chlorobenzene has a much lower electron density in the aromatic ring, and its methylene complex would not be as strong as the other two complexes mentioned and should not give as much cycloheptatriene; the ratio of products obtained in chlorobenzene solution is essentially the same as obtained with no added aromatic solvent.

The low degree of selectivity exhibited by methylene when generated from diazomethane indicates the tendency of methylene to react upon every collision; thus in a mixture of benzene and 2,3-dimethylbutane, the methylene will not be selective and either will react with the butane upon collision or complex with benzene. The solvent will obviously have no effect on the relative reactivity of the hydrogen atoms of the butane molecule if the methylene reacts directly with it. The majority of the methylene-benzene complex would give toluene and cycloheptatriene, but some of the complex would react with 2,3-dimethylbutane. However, if the amount of methylene in the complex form which reacts with the butane is small compared to that which reacts directly or if the solvent effect is not significantly large, no solvent effect will be measured.

Should the methylene formed from diazomethane be "hot" as suggested, the formation of the complex with an aromatic solvent would allow the extra energy to be first distributed though the complex and then though the solution provided the complex is sufficiently long lived. But to assume that a difference of reactivity in the various solvents is due to mere deactivation of the methylene is not sufficient since a graded change in reactivity is observed with the changed availability of pi-electrons of the solvent. If complexing did not affect the reactivity of the deactivated methylene, 4 M chlorobenzene should be as efficient in altering the reactivity of methylene as 4 M tertiary-butylbenzene.

The above discussion has been employed to explain a small solvent effect and while the data are consistent with earlier photochlorination work, they are insufficient to consider the explanation unequivocally proven. Because of the small influence of solvent observed and the experimental difficulties involved in obtaining satisfactory data, this problem was abandoned at this point in search of a system exhibiting more dramatic solvent effects.

Experimental

Apparatus and procedures for methylation reactions

Diazomethane was generated in a 125-ml. distillation flask fitted with a small addition funnel and modified with a nitrogen inlet tube which extended to the bottom of flask; immediate formation of diazomethane occurred upon the dropwise addition of a carbitol solution of 1 M N-methyl-N-nitrosotoluenesulfonamide solution to 50 ml. of 50% aqueous potassium hydroxide which had been preheated to about 55°. As the diazomethane was formed it was carried by nitrogen to the reaction vessel through the sidearm of the distillation flask and through a second inlet tube that extended to the bottom of the reaction vessel. The reaction vessel was constructed from a quartz tube 1.2-cm. x 8-cm. and had a test tube bottom and a ground glass joint at the top for connection of the vessel to a condenser. The second inlet tube and the condenser were of one construction so the inlet tube entered the reaction vessel through the center of the glass joint. After the nitrogen passed through the ice-water condenser from the reaction vessel, it was allowed to bubble through a phenol solution before entering the atmosphere in order to remove any diazomethane which had escaped the reaction mixture.

The system was swept with nitrogen prior to each experiment to remove any oxygen that might have been present. After the diazomethane was generated and almost completely transferred to the reaction vessel, irradiation with ultraviolet energy from a General Electric UA-2 lamp was begun. The irradiation was continued until the yellow color of the diazomethane had disappeared; generally this was about an hour except when large amounts of aromatic compounds were present as solvents. Control experiments indicated that the cycloheptatriene-toluene ratio was stable to irradiation for the period of time during which the actual irradiations were made. However, other control experiments indicated these ratios were not reproducible when oxygen was present; the presence of oxygen always resulted in a loss of cycloheptatriene. Experiments using sunlight and tungsten light to catalyze the decomposition of the diazomethane gave slightly higher cycloheptatriene-toluene ratios (5.0 ± .2) although the difference is hardly significant. The relative reactivity of benzene and 2,3-dimethylbutane toward methylene generated by decomposition of ultraviolet radiation was approximately 1.5 on a molecular basis.

The vapor phase reactions were carried out in a tube constructed of a pyrex tube 1.7-cm. x 35-cm.; the heated portion of the tube was 25-cm. in length. The diazomethane was generated in the same apparatus as was used above; the benzene was allowed to enter the reaction tube as the vapor from boiling benzene. The reaction products were collected in an ice-trap connected to the exit of the reaction tube. A control experiment showed that the cycloheptatriene-toluene ratios were stable under the conditions of the reaction. Temperatures were measured with an iron-constantan thermocouple.

Analysis

In all cases, gas-liquid chromotography was used for analyzing the reaction products of each methylation reaction. Correction factors were determined to convert product area ratios obtained in the analysis to molar ratios. Since control experiments showed that passing a benzene solution of diazomethane through the gas-liquid chromotography unit gave cycloheptatriene and toluene all unreacted diazomethane was removed or destroyed before analysis. The ratio of products in these control experiments was greater than 30, but attempts to reproduce this high ratio on a synthetic scale were unsuccessful. If the diazomethane were destroyed in the benzene solution with phenol or hydrochloric acid, no cycloheptatriene nor toluene was obtained upon injecting a sample in the unit.

Reagents

Phillips Petroleum 2,3-dimethylbutane (99 mole %) and redistilled Mallinckrodt benzene (thiophene free) were the substances used for the methylations. Tertiary-butylbenzene (99 mole %), redistilled Eastman-Kodak chlorobenzene, and Eastman-Kodak cyclohexane (spectro grade) were used as solvents. For the determination of correction factors used in the analysis, Phillips Petroleum toluene (99.9 mole %) and samples of 2,3-dimethylpentane (99.6 mole %) and 2,2,3-trimethylbutane (99.6 mole %) from National Bureau of Standards were obtained; the cycloheptatriene was prepared by using conditions reported by Woods (25) from bicyclo (2.2.1) heptadiene which was a gift from Shell Chemical Co.

OXIDATION OF HYDROCARBONS

Introduction

The reaction of oxygen with hydrocarbons in the presence of free radical initiators has been studied extensively in recent years, and most of the mechanistic features of the reaction are well understood (26). The mechanism is generally expressed as

$$\text{Initiator} \longrightarrow R\cdot$$

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

$$ROO\cdot + RH \xrightarrow{k_p} ROOH + R\cdot$$

$$2\ R\cdot \longrightarrow R\text{-}R$$

$$ROO\cdot + R\cdot \longrightarrow ROOR$$

$$2\ ROO\cdot \xrightarrow{k_t} \text{Non-radical products}$$

The initiator may be hydroperoxides which are often present as impurities in the hydrocarbon or it may be an added compound which decomposes to give free radicals at the temperature of the reaction. The non-radical products are oxidized forms of the hydrocarbon, i.e., aldehyde or ketone, alcohol, and/or olefin.

At high oxygen pressures the last reaction is the only important termination step since oxygen reacts readily with the radical formed from the hydrocarbon and no significant amount of the non-oxygenated radical is allowed to build up. The rate expression which is derived from this mechanism and which is consistent with experimentation in those cases where the initiator radical reacts with oxygen before attacking the hydrocarbon is

$$\text{Rate} = -d\ O_2\ /dt = k_p R_i^{\frac{1}{2}}[RH]/(2k_t)^{\frac{1}{2}} + R_i/2$$

R_i is the rate of initiation of free radicals and is the product of the rate of decomposition of the initiator and an efficiency factor which accounts for the destruction of the initiator radicals before they react with oxygen.

The reaction may be used as a means to study the influence of solvent on the reactivity of a peroxy radical since the ratio of rate constants $k_p/k_t^{\frac{1}{2}}$ may be easily obtained, providing R_i is known, by measuring the absorption of oxygen as a function of time. The propagation rate constant, k_p, contains the activity coefficient of the peroxy radical, and the termination rate constant, k_t, contains the square of the activity coefficient of the peroxy radicals; thus in the ratio of rate constants the terms for the activity coefficient will not appear since they cancel in the expression. Factors which govern the activity of the peroxy radical, such as interactions between the radical and solvent, may not effect the rate of the two competing reactions in the same manner. Probably solvent interactions would not affect the reactivity of the peroxy radical toward the hydrocarbon in the same degree as the reactivity toward another peroxy radical. It is conceivable that increasing the solvent interaction would increase the relative amount of the termination reaction. Therefore, one might observe in the ratio of rate constants the effect of solvent interaction on the peroxy radical although this effect is not predictable.

Since the concentration of the hydrocarbon appears in the rate expression, the interaction of solvent with the hydrocarbon may also effect the rate; but there is no reason to believe that the activity coefficient of the hydrocarbon, as measured by physical methods, will be proportional to this effect since the solvent interaction may either enhance or retard the reactivity of the hydrocarbon.

A solvent effect on the rate of initiation may also influence the overall rate of oxidation, but the importance of this effect may be evaluated directly by experimental measurements. From their study of hydrocarbon oxidation, Hammond *et al.* have devised a technique for determining the rate of initiation from induced inhibition periods (27), and their results indicate that the solvent does affect the rate of initiation by influencing both the rate of decomposition and the efficiency factor when the initiator is azodiisobutyronitrile (AIBN).

According to transition state theory the possibility of solvent affecting the activity of the transition states for the propagation and termination steps exists (28, p. 128); therefore, solvents which mainly decrease the activity of the transition state for the propagation reaction will enhance the rate of the reaction. The prediction of how the solvent affects the activity of the transition state is not readily made unless one has a certain knowledge about the nature of the transition state. However, the activity of a transition state would be expected to decrease with increased polarity of the solvent if the transition state had some degree of polar character.

Boozer *et al.* have studied the oxidation of tetralin in seven common solvents and in most cases found only a slight variation in the rate; although in nitromethane, a 50% rate enhancement did occur compared to chlorobenzene, carbon tetrachloride, and diphenyl ether (29). They offer no explanation for the abnormal rate in nitromethane. Frye *et al.* have studied the oxidation of several hydrocarbons in the presence of simple alcohols, but due to the complexities of their method, their results are ambiguous (30). In some cases they found it necessary to assume that the peroxy radical removed the hydroxyl hydrogen atom of the solvent in preference to reacting with the hydrocarbon. Since the energy required to remove a hydrogen atom from an alcohol is at least 20 kcal. greater than that required to remove the hydrogen atom from a hydrocarbon of the type like tetralin or cyclohexene (1a, p. 49), this process is unlikely.

For an extensive study of the influence of solvent on free radical oxidations, cyclohexene was chosen as the hydrocarbon since it oxidizes at a reasonable rate and gives 3-cyclohexenyl hydroperoxide in high yields (26b). In a limited number of solvents, other hydrocarbons were oxidized to investigate the generality of the effects observed with cyclohexene. These efforts have led to the study of the reactivity of various hydrocarbons toward the peroxy radical.

Results and Discussion

Oxidation kinetics of cyclohexene

In order to verify the assumption that the oxidation of cyclohexene follows the kinetic expression given in the previous section, experiments were performed varying separately the concentration of initiator and cyclohexene. Since the rate of oxidation is expected to depend on the one-half power of the rate of initiation, the rate should be proportional to the one-half power of the AIBN concentration. The data for this series of experiments are in Table 7, and the dependence of the rate (minus $R_i/2$) on the one-half power of initiator is shown graphically in Figure 5.

At zero AIBN concentration some oxidation was detected, but the rate obtained appeared to be dependent on the purity of cyclohexene. The values reported were obtained with cyclohexene that had been freshly purified by passage through silica gel under a nitrogen atmosphere. The fact oxidation did occur under these conditions suggests the possibility that oxygen can react directly with cyclohexene (26c). There are two conceivable processes by which this could occur; the oxygen could either abstract an allylic hydrogen atom or add directly to the double bond. Both of these cases would result in the formation of radicals which would start the normal chain process. However, the decomposition of trace amounts of hydroperoxide which could be present would have the same effect. No definite conclusion can be drawn concerning the direct reaction because the difficulty encountered in obtaining samples of hydrocarbon absolutely free of hydroperoxides is too great; it may be said that if this reaction occurs the rate is extremely slow.

Table 7. Oxidation of cyclohexene at 60° in the presence of AIBN

Concentration of cyclohexene (mole/lit.)	Solvent	Concentration of AIBN (mole/lit.)	Rate - $R_i/2$ (mole/lit.-hr.)
9.4	None	0.0933	0.199
9.4	None	.0504	.145
9.4	None	.0332	.123
9.4	None	.0094	.070
9.4	None	.0000	.0074
9.4	None	.0000	.0054
7.34	Cyclohexane	.0504	.107
5.99	Cyclohexane	.0504	.0885
3.98	Cyclohexane	.0504	.0520
3.93	Cyclohexane	.0504	.0532
1.99	Cyclohexane	.0504	.0306
7.07	Benzene	.0504	.125
3.99	Benzene	.0504	.0795
1.98	Benzene	.0504	.0342
8.00	Nitromethane	.0504	.150
4.00	Nitromethane	.0504	.145
2.00	Nitromethane	.0504	.0879

The dependence of rate on the cyclohexene concentration was studied in three solvents, cyclohexane, benzene, and nitromethane. Cyclohexane was used because its structure is similar to that of cyclohexene, benzene was used since it is a simple aromatic solvent, and nitromethane was used because it is a highly polar solvent. Nitromethane proved not to be a satisfactory solvent in the region of 5 to 7 M cyclohexene since the components were immiscible. The data for these oxidations are also in Table 7 but are shown graphically in Figure 6. In the figure the approximately linear dependence of the rate on the concentration of cyclohexene

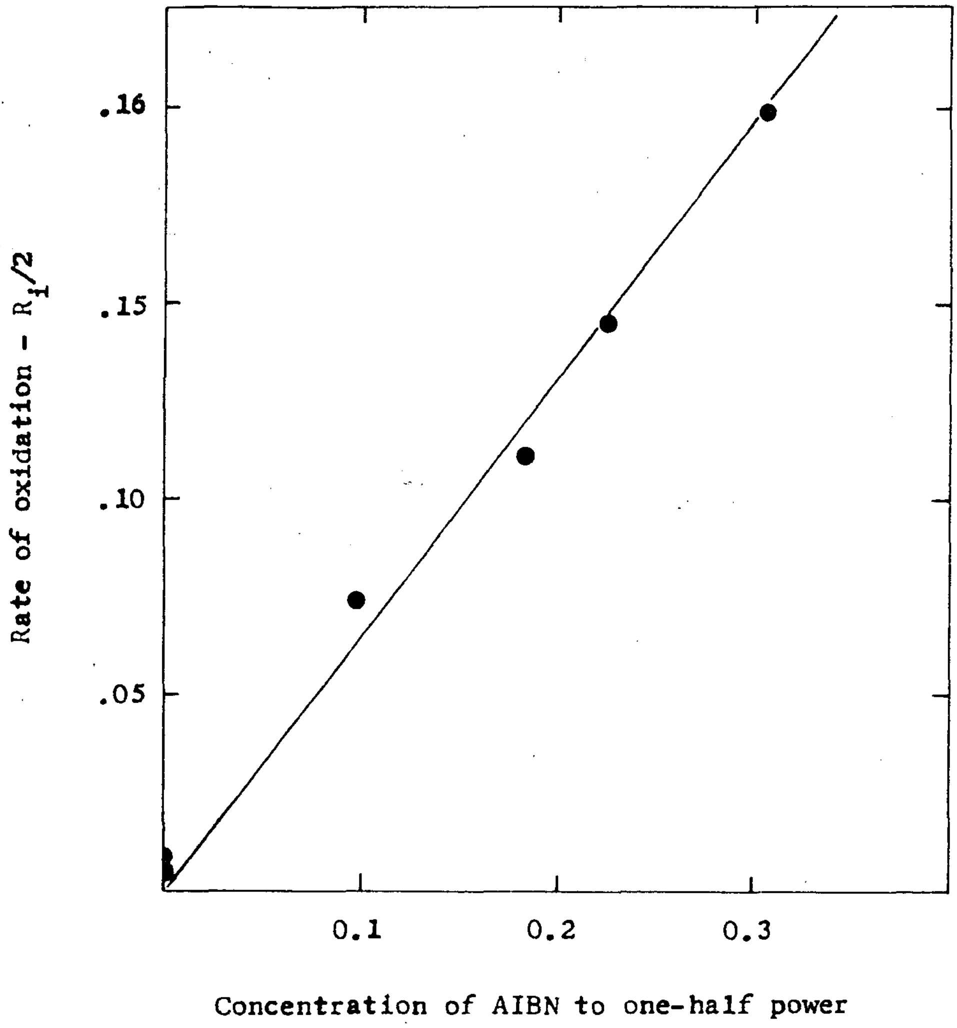


Figure 5. Oxidation of 9.4 M cyclohexene as a function of the one-half power of AIBN (no added solvent)

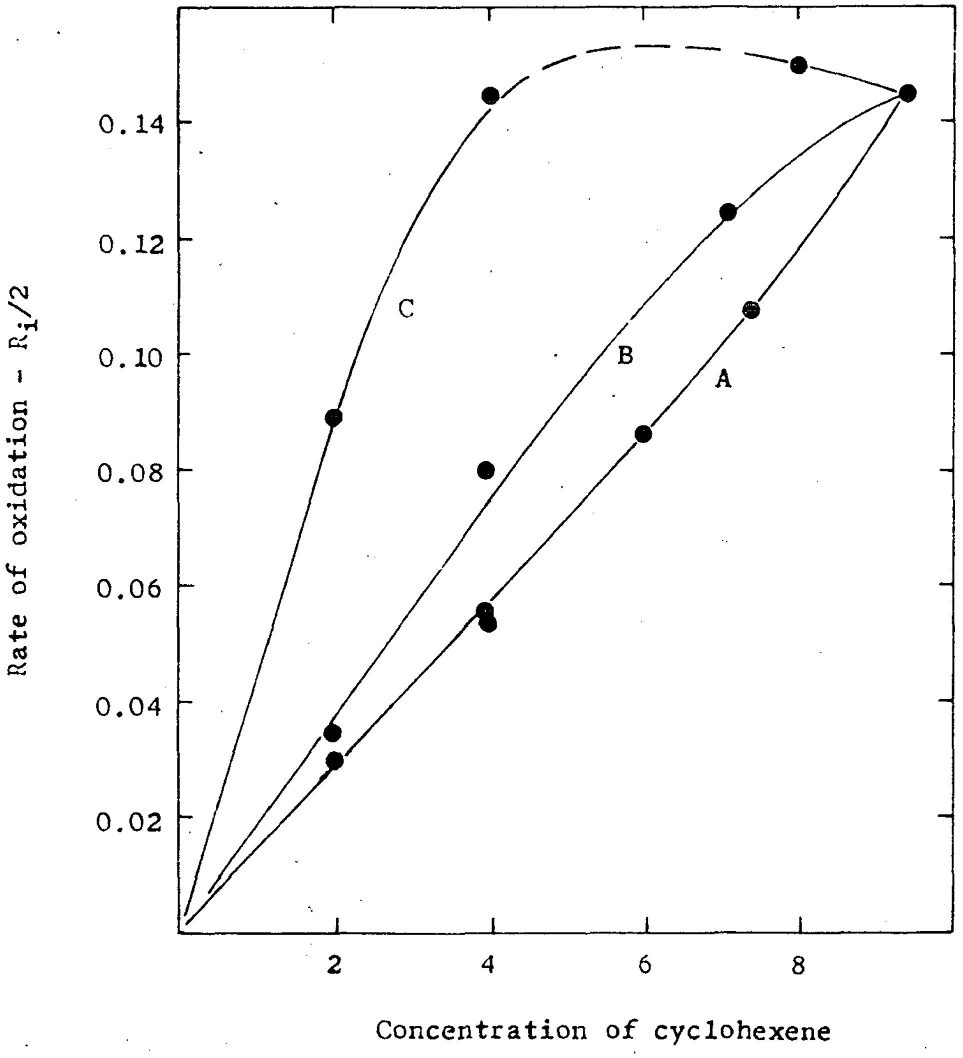


Figure 6. Rate of oxidation as a function of cyclohexene concentration

A: cyclohexane solvent
B: benzene solvent
C: nitromethane solvent (dashed line indicates heterogeneous region)

can be seen at the lower concentrations. The initial slopes must reflect some properties of the solvent. The curvatures at the higher concentrations of cyclohexene are the result of the large change in the nature of the solution. It is interesting to note that even the dilution of cyclohexene with cyclohexane does cause a slight amount of curvature; this fact is indicative of the sensitivity of the reaction to the nature of the solution, although the means by which the solvent affects the rate is not apparent.

Study of rate of initiation in various solvents

Since the solvent affects both the rate of decomposition of AIBN, k_d, and the efficiency factor, e, the product of these two terms, ek_d, was determined in a number of solvents. Both polar solvents and free radical complexing solvents were included with the compounds in which decomposition was studied.

The method used to determine ek_d was the same as developed by Hammond *et al*. (27) and later used by Blanchard (31). The method involves measuring the inhibition time caused by a specific amount of the inhibitor 2,6-di-*t*-butyl-4-methyl-phenol. This phenol readily traps two peroxy radicals per molecule (32), and the following equation is the relationship which relates the rate of initiation with the inhibition time, t, and with the concentration of phenol.

$$R_i = 2ek_d[\text{AIBN}] = 2[\text{Phenol}]/t$$

First the rates of initiation were determined using 1.9 *M* cyclohexene as the oxidant. The data for these experiments are in Table 8, in which a large difference in the ek_d term is seen in acetonitrile and nitromethane

Table 8. Inhibited oxidation of cyclohexene and cumene at 60° in the presence of inhibitor[a] and 0.0970 M AIBN

Solvent	Cyclohexene Inhibition period (min.)	 $ek_d \times 10^6$ (sec.$^{-1}$)	Cumene Inhibition period (min.)	 $ek_d \times 10^6$ (sec.$^{-1}$)
Acetonitrile	16.0 ± 0.5	10.4 ± 0.3	23.5 ± 0.0	7.09 ± 0.00
Carbon tetrachloride	33.0 ± 2.0	5.05 ± 0.28	41.7 ± 0.7	4.00 ± 0.07
Chlorobenzene	25.7 ± 0.4	6.49 ± 0.09	25.5 ± 0.0	6.54 ± 0.00
Chloronaphthalene	28.5 ± 0.5	5.87 ± 0.10	31.7 ± 0.4	5.26 ± 0.07
tertiary-Butylbenzene	33.8 ± 1.6	4.93 ± 0.21	35.1 ± 0.2	4.75 ± 0.03
Phenyl ether	40.5 ± 0.0	4.11 ± 0.00	42.8 ± 1.0	3.90 ± 0.10
Nitrobenzene	24.3 ± 2.5	6.87 ± 0.40	25.8 ± 0.7	6.46 ± 0.16
Nitromethane	14.0 ± 0.7	11.9 ± 0.5	25.6 ± 1.1	6.51 ± 0.26

[a] Inhibitor was 10^{-3} M 2,6-di-*t*-butyl-4-methylphenol.

solvent compared to the other solvents; the result in nitrobenzene is intermediate. A reasonable value for the rate of decomposition of AIBN under the conditions is 9.6×10^{-6} sec^{-1} (33) which would mean that the efficiency term is greater than 1.0 in nitromethane. The efficiency term, e, is the fraction of radicals generated from the initiator which do not couple before reacting with oxygen; therefore, it must always be between 1 and 0. From the data obtained and using the above value for the rate constant not only is the nitromethane value greater than 1.0 but the value in acetonitrile is 1.0 and in nitrobenzene .77; Hammond, et al., reports values of .73 for both nitromethane and nitrobenzene (27). In order to check the rate of decomposition of AIBN the rate of nitrogen evolution was measured from the decomposition of a 0.054 M AIBN solution in nitromethane; the value obtained for the rate constant at 60° was 9.93×10^{-6} sec^{-1}. The conclusion was made that under the conditions employed something was destroying the inhibitor other than the radicals from the initiator. One possible source of radicals could be the result of the direct reaction of oxygen with the hydrocarbon; this reaction has been shown in the previous section not to be important in a hydrocarbon solvent, but the possibility exists that nitromethane accelerates the reaction. This hypothesis was shown to be incorrect by studying the effect of 0.002 M inhibitor on a 4.0 M solution of cyclohexene in nitromethane with no AIBN present; if there was an appreciable amount of the reaction occurring an inhibition time of a few hours would have been expected. The length of the inhibition period was approximately 20 hours which corresponds to a rate of initiation of 5×10^{-8} sec^{-1}; if this direct process does occur it does not account for more than 0.5% of the rate of initiation observed in the presence of AIBN.

During the measurement of the inhibition periods for the determination of ek_d in nitromethane, it was observed that the initial slopes were greater than with any of the other solvents. This indicates that cyclohexene in nitromethane competes more favorably with the inhibitor for the peroxy radical than it does in other solvents, and a larger amount of cyclohexenyl hydroperoxide is formed in nitromethane than in the other solvents during the inhibition period. If the peroxide is not stable in nitromethane the decomposition of the peroxide will result in another source of initiation. This possibility was tested by studying the stability of cyclohexenyl hydroperoxide in nitromethane under the conditions of the inhibited oxidation; the data for this experiment are in Table 9. From the first order rate constant for the decomposition, it is possible to estimate the amount of hydroperoxide necessary to cause sufficient initiation to account for the large value of ek_d. This concentration is approximately 0.5 M which is too large to be reasonable, and the conclusion must be drawn that decomposition of the hydroperoxide in solution is not contributing significantly to the overall rate of initiation.

There remains two possibilities which could account for the unreasonably high apparent rate of initiation in nitromethane. K. U. Ingold has reported that the reaction between 2,6-di-t-butyl-4-methyl-phenol and alkylhydroperoxide is slow (34); however, in the presence of a polar solvent like nitromethane this reaction may become significant. In addition, McGowan and Powell have concluded that the phenoxy radical from

Table 9. Stability of cyclohexenyl hydroperoxide in nitromethane at 60°

Time in minutes	Concentration of hydroperoxide (mole/lit.)
0	_circa_ 0.085
85	.0838
172	.0820
512	.0796
1235	.0734
1582	.0696

$k_d = 1.7 \times 10^{-6}$ sec.$^{-1}$

$t_{\frac{1}{2}} = 110$ hours

tri-_t_-butylphenol will react with _t_-butyl hydroperoxide (35); since a significant amount of oxygen is absorbed during the inhibition period (1×10^{-4} mole of oxygen is not uncommon) one of these two reactions may serve to shorten the induction period by destroying inhibitor. The exact nature of the inhibition reaction is not fully understood; however, the existence of phenoxy radicals has been questioned in some cases. The peroxy radical-phenol complex which has been suggested as the intermediate also could be reactive toward hydroperoxides.

To test the importance of these factors during the inhibited oxidation in nitromethane, the inhibition period was studied as a function of the cyclohexene concentration. The information from these experiments are given in Table 10; four different concentrations of cyclohexene have been

Table 10. Effect of hydrocarbon concentration on inhibited oxidation at 60° in nitromethane and in the presence of 0.002 M inhibitor and 0.0970 M AIBN

	Concentration of hydrocarbon (mole/lit.)	Inhibition time (min.)	Rate after inhibition period[a] (mole/lit.-hr.)
Cyclohexene	1.92	31	0.23
Cyclohexene	0.96	38	.11
Cyclohexene	.48	43	.049
Cyclohexene	.24	45	.03[b]
Cumene	1.39	49	.023
Cyclohexene[c]	0.48	28	.052

[a] In the cases for cyclohexene the rates are greater than those observed in the uninhibited experiments; the reason for this phenomena is unknown.

[b] Initial rate; gradual rate decrease was observed due to the low concentration of cyclohexene.

[c] Solution contained 0.12 mmole of cyclohexenyl hydroperoxide.

used plus one concentration of cumene. As the concentration of cyclohexene is decreased the inhibition time increases, even the experiment with the lowest concentration of cyclohexene gives a shorter inhibition period than the same experiment with cumene. These results are what would be expected if hydroperoxides were interfering, since more hydroperoxides would be formed during the inhibitor period of the greater concentrations of cyclohexene. Cumene oxidizes much slower than cyclohexene, thus less hydroperoxide is formed during the inhibition period. It does not appear possible to differentiate between the two reactions given above since both can account for the apparent loss of inhibitor.

To insure the assumption that hydroperoxide interferes with the reaction, an experiment which is included in Table 10 was performed with a known amount of cyclohexenyl hydroperoxide present at the start of the inhibited reaction. The amount of hydroperoxide corresponds about to the amount which is formed during a normal inhibition period in nitromethane solvent. The added hydroperoxide shortens the inhibition period by about 35%, thus proving the interference of the hydroperoxide.

In order to obtain satisfactory rates of initiation in the various solvents the inhibition studies were again performed but using cumene in place of cyclohexene. Since cumene is less reactive than cyclohexene toward the peroxy radical, cumene does not compete with inhibitor to the same degree as cyclohexene; therefore, during the inhibition period less hydroperoxide is formed which can interfere. These data are also in Table 8. There is a smaller spread in ek_d values obtained using cumene as substrate; moreover, in no case does e exceed 1.

Solvent effect on oxidation of hydrocarbons

The solvents first used to investigate the influence of solvent on the rate of oxidation of cyclohexene were those within which the rate of formation of free radicals from azo-bisisobutyronitrile had been determined previously. In these solvents 2.0 $\underline{M}$ cyclohexene was oxidized to the extent of about one percent while the absorption of oxygen was followed at constant pressure. During the initial 100 minutes the rate of the reaction was generally constant although after that time a gradual decrease was noted. In some cases during the initial 20 minutes the rate appeared significantly faster than that observed in the following 80 minutes; for such cases the latter rate has been reported as the rate of the reaction. The rates of cyclohexene oxidation which have been corrected by subtraction of $R_i/2$ are given in Table 11 with corresponding values of $k_p/k_t^{\frac{1}{2}}$; the series of values for ek_d in Table 8 which were evaluated with cumene have been used to determine the ratio of rate constants.

From the data in Table 11 a solvent effect may be seen in the rate of oxidation. Changing the solvent from cyclohexane to acetonitrile causes a 300% increase in the rate; little effect is observed when the solvent is changed to aromatic solvents from cyclohexane. In the photochlorination of 2,3-dimethylbutane where the formation of a pi-complex between the chlorine atom and aromatic solvent is important, aliphatic solvents and nitrobenzene give similar product ratios, but the other aromatic solvents exhibit varying results (6). In addition, no correlation is observed between the values of $k_p/k_t^{\frac{1}{2}}$ and the photochlorination data and from these results the conclusion must be made that in the oxidation of cyclohexene the reactivity of the radical is not influenced by the formation of pi-complexes.

The nature of the solvent effect was further studied by oxidizing cyclohexene in a greater variety of solvents. The rate data from these experiments and those in Table 11 with the dielectric constant of the solvents at room temperature are in Table 12. In general an increase in rate of oxidation occurs with an increase of the dielectric constant of the solvent.

Table 11. Oxidation of 2.0 M cyclohexene at 60° in various solvents and in the presence of 0.0504 M AIBN; effect of solvent on overall rate and on $k_p/k_t^{\frac{1}{2}}$

Solvent	Rate - $R_i/2$ mole/lit.-hr.	$k_p/k_t^{\frac{1}{2}}$ (mole/lit.-hr.)$^{\frac{1}{2}}$
Cyclohexane	0.0306	0.48
t-Butylbenzene	.0315	.54
Benzene	.0342	.54
Diphenyl ether	.0353	.67
Carbon tetrachloride	.0364	.72
Chlorobenzene	.0461	.67
1-Chloronaphthalene	.0464	.75
Nitrobenzene	.0636	.93
Nitromethane	.0878	1.31
Acetonitrile	.0921	1.28

Laidler and Eyring have considered the effect of solvents on the rate of chemical reactions and have shown that the logarithm of the rate should be related to the function, $(D - 1)/(2D + 1)$ where D is the dielectric constant of the solvent (38). According to these workers the free energy change required to transfer a dipole with moment u from a vacuum to a medium with a dielectric constant D is

$$\Delta F = kT \ln f = -(u^2/a^3)(D - 1)/(2D + 1) + \phi$$

where f is the activity coefficient of the molecule with reference to the dilute gas and the term a is the radius of the molecule within which the

Table 12. Oxidation of 2.0 M cyclohexene at 60° in various solvents and in the presence of 0.0504 M AIBN; correlation between rate and dielectric constant of solvent

Solvent	Rate $R_i/2$ mole/lit.-hr.	Dielectric constant of solvent (36,37)
Cyclohexane	0.0306	2.02
t-Butybenzene	.0315	2.38
t-Butylnaphthalene	.0339	--
Benzene	.0342	2.28
Diphenyl ether	.0353	4.22
Carbon tetrachloride	.0364	2.24
Acetic acid	.0373	6.15
Benzotrifluoride	.0439	--
t-Butyl alcohol	.0445	10.9
Chlorobenzene	.0461	5.62
1-Chloronaphthalene	.0464	5.04
m-Dichlorobenzene	.0480	5.04
3-Pentanone	.0500	17.0
2-Pentanol	.0520	--
2-Nitropropane	.0602	25.52
2-Propanol	.0613	18.3
Nitrobenzene	.0636	34.82
Ethanol	.0693	24.30
Nitroethane	.0749	28.06
2-Butanone	.0752	18.51
Nitromethane	.0878	35.87
Acetonitrile	.0921	37.5
Dimethyl sulfoxide	.105	45.

charge is symmetrically distributed. The term ϕ is a correction factor for nonelectrostatic effects which are the results of forces between the dipole and solvent molecules such as those resulting from re-orientation of the neighboring solvent molecules. Kirkwood originally suggested the above equation but did not add the non-electrostatic term (39).

The rate constant, k', for a reaction in solution is equal to the rate constant, k_o', in dilute gas phase corrected by the activity coefficient in solution of the reactants (A and B) and the activated complex (M^*) relative to the dilute gas phase.

$$k' = k_o'(f_A f_B / f_{M^*})$$

By converting the expression to logarithms and substituting the proper expressions for the activity coefficient as derived from the former expression, Laidler and Eyring obtained

$$\ln k' = \ln k_o' - (u_A^2/a_A^3 + u_B^2/a_B^3 - u_{M^*}^2/a_{M^*}^3)(D - 1)/(2D + 1)kT + (\phi_A + \phi_B - \phi_{M^*})/kT$$

Since the non-electrostatic terms depend on the solvent, plotting $\ln k'$ verse $(D - 1)/(2D + 1)$ will give a straight line only when the sum of these terms is significant compared with the interaction of the dipole with the dielectric constant of the medium. In some ionic reactions a linear relationship is observed between these two terms; an example is the formation of a quaternary ammonium salt from benzyl bromide and either pyridine or triethylamine in alcohol-benzene solvent mixtures (40). However, in benzene-nitrobenzene solvent mixtures the same reactions do not give linear plots which indicate that the non-electrostatic term becomes important when nitrobenzene is present.

In the propagation reaction of the cyclohexene oxidation, the reactants have relatively small dipole moments and their interaction with the solvent would be due partly to electrostatic effects but non-electrostatic effects will probably be more important.

If the transition state for the oxidation of cyclohexene exhibits a polar character, the dipole moment would not be as great as that found in ionic reactions. Thus, the effect of the dielectric constant would not be as large in the free radical reaction as commonly encountered in ionic processes. In addition, non-electrostatic forces would be expected to be relatively more important because of the small dipole moment in the transition state for the radical reaction. The plotting of the oxidation data by the method of Laidler and Eyring is shown in Figure 7. In preparing this figure the overall corrected rate has been used instead of a specific rate constant. Since the overall rate is given by $(k_p/k_t^{\frac{1}{2}})R_i^{\frac{1}{2}}[RH]$ it follows that the rate will be directly proportional to k_p as solvent is changed provided $[RH]$ is held constant, R_i does not vary and k_t is independent of solvent. Experimentally for the data in Figure 7, $[RH]$ was held constant, limited data show R_i does not vary significantly (see Table 8), it seems reasonable that k_p would be more susceptible to this kind of a solvent effect than k_t. The latter conclusion is based on the assumption that the transition state for the propagation reaction is more polar than the transition state for the termination reaction.

The upward swing at higher dielectric constants is as expected on the basis of the relative importance of the electrostatic and non-electrostatic terms. A number of factors contribute to the wide dispersion of the data in the plot. First, since the dielectric constant for each solvent is not directly related to the ability of one molecule to solvate a dipole, one would not expect the non-electrostatic forces to change evenly with the dielectric constant. Second, the values for the dielectric constant are

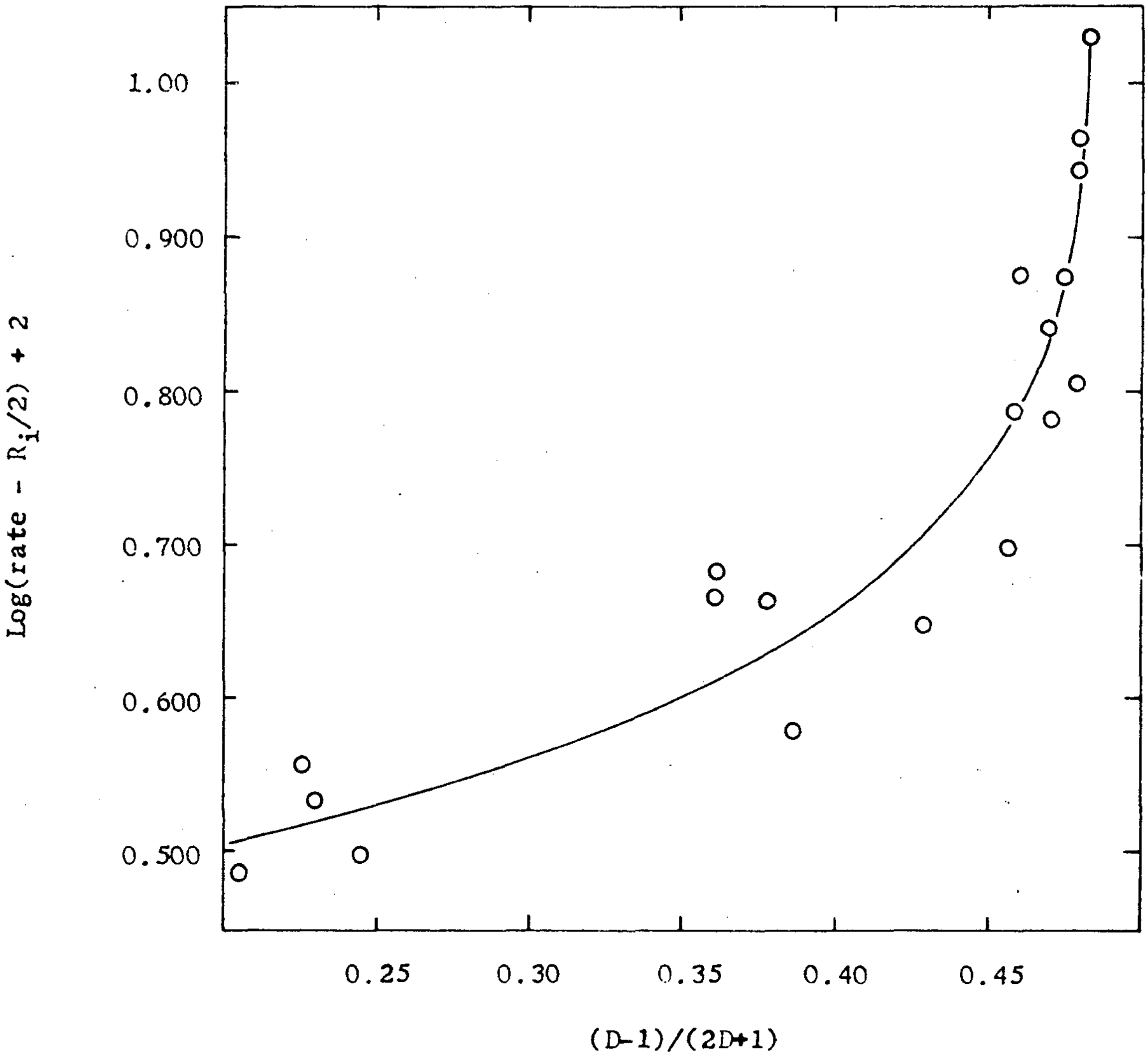


Figure 7. Correlation of oxidation of 2.0 $\underline{M}$ cyclohexene at 60° in various solvents and in the presence of 0.0504 $\underline{M}$ AIBN with Kirkwood-Onsanger parameter according to Laidler and Eyring

those for pure solvents at room temperature while the rates refer to reactions in solvents at a temperature of 60° which are about 80% pure due to the presence of cyclohexene. In addition, while for each solvent the propagation rate constant is roughly proportional to the rate, slight variation in the rates of initiation may be occurring.

The data of Menschutkin (41) and Grimm et al. (42) who have studied the reaction of ethyl iodide and triethyl amine show the same type of curvature for solvents with high dielectric constants, with a large amount of dispersion when plotted by the method of Laidler and Eyring. The dispersion found in their work supports the first explanation given for the dispersion, although the number of solvents which are identical in the two reactions are too limited for comparison of their relative deviations. Winstein and co-workers have studied the solvolysis of p-methyoxyneophyl toluenesulfonate in a large number of solvents, and their data correlate poorly with $(D - 1)/(2D + 1)$—the rates in hydroxylic solvents are as much as 10^3 times faster than non-hydroxylic solvents with comparable dielectric constant (37). In this case the non-electrostatic forces are such that the dielectric constant becomes a poor guide for relating the rates. However, the data of Winstein correlate with some other ionic reactions, i.e., rearrangements of 9-decalyl perbenzoate (43), 1-phenylallyl-3,4,5-tribromobenzoate (44), and benzoyl azide (45), and with the effect of solvent on the charge-transfer absorption maximum of 1-methyl-4-carbo-methoxy pyridinium iodide (46).

In the method of Laidler and Eyring the term a is considered the radius of the reactant and is assumed to be independent of the solvent.

However, other workers have related this term to the radius of the cavity in the solvent that contains the molecule of reactant and consider it to depend on the molar volume of the solvent (47). The data for the oxidation of cyclohexene is plotted verses $(d/M)(D - 1)/(2D + 1)$ in Figure 8 where d is the density (48) and M molecular weight of the pure solvent. In this plot the points are scattered but a linear relationship appears to be involved. The deviations are most likely the result of the fact that the physical constants (d, M, and D) of the 2 M cyclohexene solutions in which the reactions were carried out were approximated by the constants of the pure solvents.

In this oxidation study the hydroxylic solvents show no special effect on the rate when compared on the basis of dielectric constant with the other solvents. The difference in this reaction and the solvolysis reaction is the result of a difference in the amount of charge and charge separation in the transition states. Since in the solvolysis reaction the initial products have full positive charges, the transition state would have more ionic character than that for the free radical reaction. The greater the charge in the transition state the greater is the role of the solvent in stabilizing the charge; as the charge increases the possibility of stabilization by direct interaction in the case of the hydroxylic solvents becomes important because of the nucleophilic character of these compounds and their ability to hydrogen bond. In the transition state for the oxidation reaction the dipole may not be large enough for the hydroxylic solvents to participate by a direct interaction, thus no unusual solvent effect is observed.

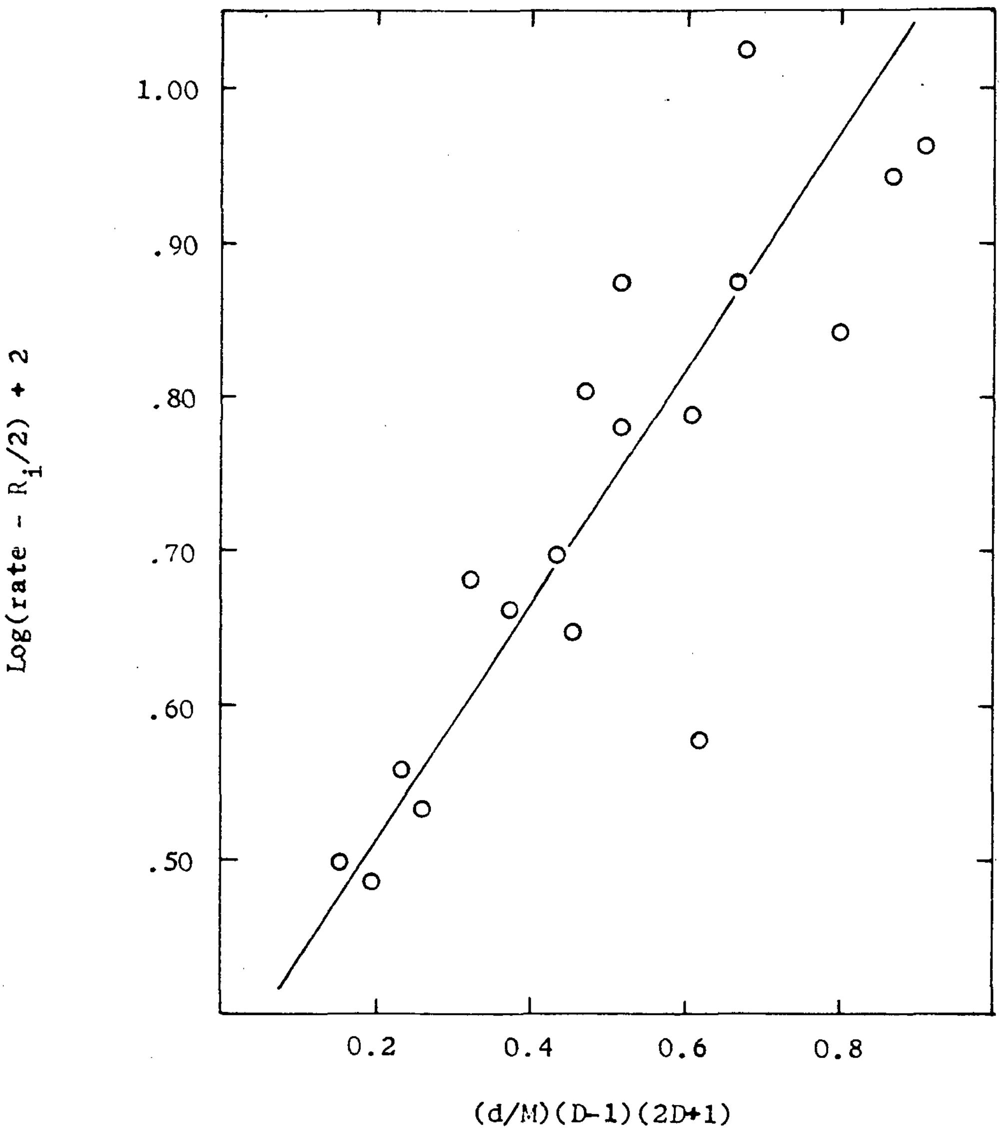


Figure 8. Correlation of oxidation of 2.0 $\underline{M}$ cyclohexene at 60° in various solvents and in the presence of 0.0504 $\underline{M}$ AIBN with Kirkwood-Onsanger parameter according to the method of Powling and Bernstein

Since the dielectric constant of the solvent is important in the oxidation of cyclohexene, water might be expected to have a large accelerating effect on the rate; however, water can not be used as a solvent in the reaction because neither cyclohexene nor AIBN are soluble in it. The effect of water was studied by using mixtures of water and some other compound as the solvent of the reaction; the data for these experiments are given in Table 13. These data show that water markedly retards the rate in all the solvent systems studied.

Before considering the effect of water on the oxidation reaction, the nature of the transition state found in the oxidation of hydrocarbons should be discussed. Important resonance structures contributing to the stability of the transition state have been suggested to be the following (14):

$$\underset{\text{I}}{R{:}H\ \cdot X} \qquad \underset{\text{II}}{\overset{+}{R}\cdot\ H\ \overset{-}{:X}} \qquad \underset{\text{III}}{R\cdot\ H{:}X}$$

The importance of structure II in some radical reactions is supported by the correlation of the relative reactivities of substituted toluene and cumene derivatives. These relative reactivities toward certain radicals are better correlated by the use of sigma-plus constants, although which of these constants give the best correlation for attack by peroxy radicals has not been concluded at this time. However, the small rho value for the reaction indicates that polar factors are only slightly important, which is consistent with the relatively small dependence of the rate of cyclohexene oxidation on the dielectric constant of the solvent.

Since the transition state does appear to show some polar character,

Table 13. Oxidation of 2.0 M cyclohexene in mixed solvents at 60° in the presence of 0.0504 M AIBN

Solvent_1	Solvent_2	$n_2/(n_1 + n_2)$	Rate - $R_i/2$ mole/lit.-hr.
Ethanol	- - -	0.000	0.0693
Ethanol	Water	.142	.0670
Ethanol	Water	.263	.0568
Ethanol	Water	.359	.0357
Ethanol	Water	.445	.0284
2-Propanol	- - -	.000	.0613
2-Propanol	Water	.375	.0265
2-Butanone	- - -	.000	.0752
2-Butanone	Water	.115	.0436
Acetic acid	- - -	.000	.0373
Acetic acid	Water	.103	.0371
Acetic acid	Water	.368	.0299
Acetic acid	Formic acid	.122	.0310
Acetic acid	Formic acid	.223	.0312
Acetic acid	Formic acid	.396	.0378
Acetic acid	Formic acid	.524	.0403
Acetic acid	Nitromethane	.092	.0362
Acetic acid	Nitromethane	.434	.0431
Acetic acid	Nitromethane	.852	.0640
- - -	Nitromethane	1.000	.0878
Acetic acid	Cyclohexane	0.092	.0368
Acetic acid	Cyclohexane	.778	.0314
- - -	Cyclohexane	1.000	.0306

one might expect that a strongly solvating molecule (S) could stabilize it through direct interaction with the charge. Obviously this does not occur with any of the solvents used since all the rates are relatively consistent when compared on the basis of the dielectric constant of the solvent in which they were obtained. Solvents which most likely would be able to stabilize the transition intermediate in this manner would be acetic acid and ethanol, but the position of these solvents in Figure 7 is not unusual. The occurance of this type of interaction would not necessarily accelerate the rate of the reaction. Since the products are not ionic fragments, this solvation can hinder the decomposition of the transition state to form products. Therefore, an increase in activation energy due to this type of solvation can cause a retardation in the rate of the reaction. Such a phenomena does not occur in solvolysis reactions because charge stabilization in the transition state by the solvent can be carried over to stabilize the ionic products and in these cases the participation causes a rate enhancement.

From the retarding effect that it produces, water may be sufficient to participate directly in the transition state of the oxidation reaction as discussed above. The data from Table 13 for the solvent pairs acetic acid-water and ethanol-water are presented graphically in Figure 9 with data for the solvent pairs acetic acid-formic acid and acetic acid-nitromethane. The two systems with water in the solvent mixture approach the same rate at near 50 mole % water, which is consistent with the above explanation for the retardation. The data in Table 13 for 2-propanol-water and 2-butanone-water solvent pairs also appear to approach this same value although the data are not as complete. The decrease in rate with addition of water occurs fastest in the ketone-water system possibly because hydrogen bonding between a ketone and water is less than in the case of an alcohol or acid with water; the less the water forms hydrogen bonds with the other solvent, the more readily the water may participate

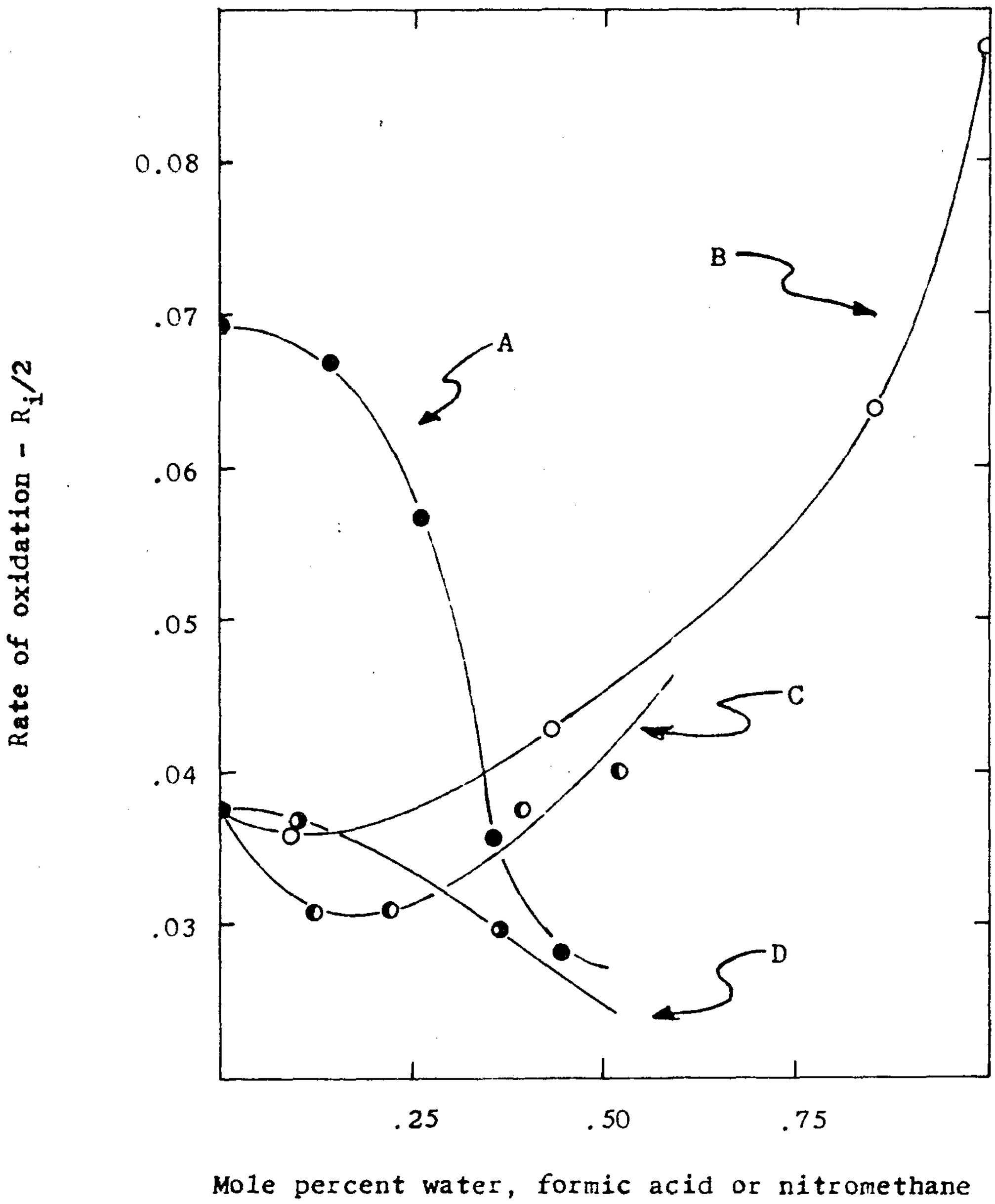


Figure 9. Oxidation of 2.0 M cyclohexene at 60° in mixtures of two solvents and in the presence of 0.0504 M AIBN

A: ethanol-water solvent pair
B: acetic acid-nitromethane
C: acetic acid-formic acid
D: acetic acid-water

with the transition state.

Since the dielectric constant of formic acid is greater than that of the other pure solvents used, the effect of this acid on the reaction is important; however, cyclohexene is not sufficiently soluble in formic acid to prepare a 2 *M* solution. To determine whether formic acid accelerates the reaction, mixtures of this acid and acetic acid were used as the solvent for a series of cyclohexene oxidations; the data are in Table 13 and shown in Figure 9. The presence of a small amount of formic acid in the acetic acid solution causes a slight retardation in the rate of oxidation, but if the composition of the solvent mixture is increased to about 18 mole % formic acid, the rate starts to increase. The reason for the minimum is unknown, but presumedly it is the result of strong interactions between the two solvents. In Figure 9 the data for the solvent pair acetic acid-nitromethane also show a minimum but much smaller than in the previous case. The data in Table 13 for the solvent pair acetic acid-cyclohexane produce a straight line with no minimum.

The study of the influence of solvent on free radical oxidation reactions was continued by oxidizing other hydrocarbons in various solvents. From the data for the oxidation of cumene in eight different solvents given in Table 14 the effect of solvent may be seen. The effect is of equal importance in both the rate of oxidation and $k_p/k_t^{\frac{1}{2}}$ for this system, but the overall effect is less than observed in the oxidation of cyclohexene. The most rapid rate obtained is 70% greater than the slowest rate; between the same two solvents in the oxidation of cyclohexene, a 100% rate increase is observed. In the oxidation of cumene, nitrobenzene produces the same result as acetonitrile and nitromethane, although cyclohexene oxidizes considerably slower in nitrobenzene than in acetonitrile or nitromethane.

A number of hydrocarbons were oxidized in both chlorobenzene and nitromethane to determine the generality of the observed solvent effect. These two solvents were used since in them the rates of initiation are the same, while the oxidation rates of cyclohexene are much different. The data in Table 15 includes examples where addition of a peroxy radical to a double bond occurs as well as ones involving hydrogen atom abstraction by the peroxy radical. In all cases changing the solvent from chlorobenzene to nitromethane produces about the same degree of rate enhancement.

Table 14. Oxidation of 2.0 M cumene at 60° in various solvents and in the presence of 0.0504 M AIBN

Solvent	Rate - $R_i/2$ mole/lit.-hr.	$k_p/k_t^{\frac{1}{2}}$ (mole/lit.-hr.)$^{\frac{1}{2}}$
t-Butylbenzene	0.0139	0.238
Carbon tetrachloride	.0153	.305
1-Chloronaphthlene	.0158	.255
Diphenyl ether	.0184	.308
Chlorobenzene	.0187	.274
Acetonitrile	.0231	.322
Nitromethane	.0233	.338
Nitrobenzene	.0237	.346

Table 15. Oxidation of 2.0 M hydrocarbon in chlorobenzene and nitromethane solution at 60° and in the presence of 0.0504 M AIBN

Hydrocarbon	Rate in chlorobenzene mole/lit.-hr.	Rate in nitromethane mole/lit.-hr.	Column 3 / Column 2
Cyclopentene[a]	0.0718	0.1088	1.51
Cyclohexene	.0461	.0879	1.91
Cycloheptene	.0311	.0526	1.70
Cycloöctene[b]	.0123	.0294	2.41
Cycloöcta-1,5-diene	.0596	.0931	1.56
Cyclohexa-1,3-diene[c]	2.06	3.67	1.78
Cycloheptatriene	0.0465	0.0946	2.03
Bicyclo-(2.2.1)-heptadiene	.212	.257	1.28
Indan	.0342	.0585	1.71
Tetralin	.0402	.0672	1.67
Cumene	.0187	.0233	1.26
p-Nitrocumene[d]	.00732	.0101	1.38

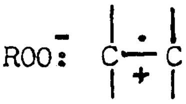
[a] Rates estimated from oxidation of 1.0 M hydrocarbon solutions.

[b] Rate in nitromethane estimated from oxidation of 1.0 M hydrocarbon solution.

[c] Rates estimated from oxidation of 0.17 M hydrocarbon solutions.

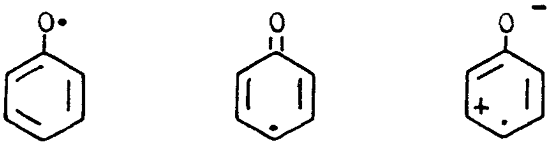
[d] Rates estimated from oxidation 1.5 M hydrocarbon solutions.

Since a solvent effect is observed in the addition reaction of the peroxy radical to both cyclohexa-1,3-diene and bicyclo-(2,2,1)-heptadiene, interactions similar to those for the abstraction reaction must occur, and the transition state also for this reaction may be assumed to have some polar character. An important contributing resonance structure would be, therefore,



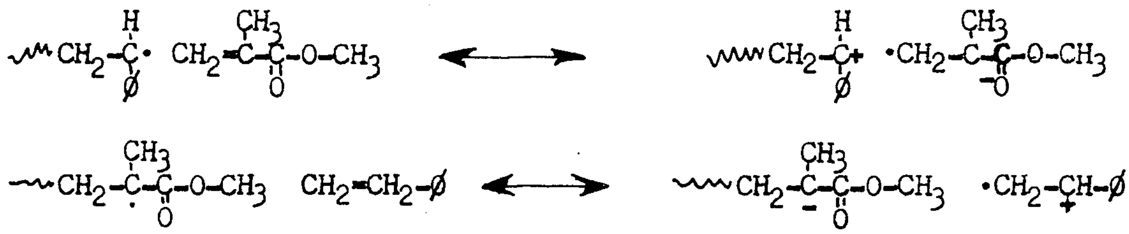
$$\mathrm{RO}\overset{-}{\mathrm{O}}\!:\ \overset{|}{\underset{|}{\mathrm{C}}}\overset{\cdot}{\underset{+}{-}}\overset{|}{\underset{|}{\mathrm{C}}}$$

Cook and Norcross have studied the disproportionation of the 2,6-di-t-butyl-4-isopropyl phenoxy radical and found no significant dependence of the rate on the dielectric constant of the solvent, but a relationship between the enthalpy of activation and the dielectric constant was found to exist (49). In this reaction the phenoxy radical appears to be highly solvated due to its ionic character that is illustrated by the ionic reaction with hydrogen chloride (53); as the reactants proceed to the transition state the solvation decreases. The important resonance structures for the radical are



The observation was made that the greater the ability of the solvent to solvate the starting phenoxy radical, the greater the enthapy of activation which was required for desolvation. This reaction differs from an oxidation reaction in that the phenoxy radical, the reactant, is more polar than the transition state while for the propagation step of the oxidation reaction the transition state is more polar than the reactants.

Other radical reactions where the transition state is more polar than the reactants are found in the copolymerization of vinyl compounds. For example, in the copolymerization of styrene and methyl methyarcylarte, a styrene radical reacts with methylmetharcylate about twice as rapidly as with styrene while the methyl methyarcylate radical reacts about twice as rapidly with styrene as with methyl metharcylate (51). The best explanation of this tendency of alternation has been given by Walling *et al.*, who suggest that ionic resonance structures contribute to the stability of the transition states of the preferred cross reactions (52). The important structures for the transition states of the cross reactions are



$$\sim CH_2-\overset{H}{\underset{\phi}{C}}\cdot \quad CH_2=\overset{CH_3}{C}-\underset{O}{\overset{\|}{C}}-O-CH_3 \longleftrightarrow \sim CH_2-\overset{H}{\underset{\phi}{C}}{+} \quad \cdot CH_2-\overset{CH_3}{C}=\underset{^{-}O}{C}-O-CH_3$$

$$\sim CH_2-\overset{CH_3}{\underset{\cdot}{C}}-\underset{O}{\overset{\|}{C}}-O-CH_3 \quad CH_2=CH_2-\phi \longleftrightarrow \sim CH_2-\overset{CH_3}{\underset{-}{C}}=\underset{O}{C}-O-CH_3 \quad \cdot CH_2-\underset{+}{CH}-\phi$$

where ø signifies a phenyl group. Similar structures can not be written for the reaction of each radical with its corresponding monomer and employ a carbonyl group and a phenyl group to stabilize the negative and positive charges, respectively.

Attempts to increase the tendency toward alternation in this copolymerization reaction (2b, e) and in the copolymerization of *alpha*-methylstyrene with maleic anhydride (2e) by increasing the dielectric constant of the solvent were not successful; no change greater than experimental error was observed when the solvent was changed from benzene to acetonitrile in either case. Therefore, while the tendency of alternation in copolymerization strongly suggests a polar transition state, no influence of solvent was detected.

A simple explanation may be given for the lack of solvent effect in this reaction. In the transition state for both steps of the copolymerization reaction, the atoms between which the electron transfer occurs are well shielded from solvent by alkyl and aryl groups. The dipole of the transition state is thus surrounded by a hydrocarbon layer which would have a low microscopic dielectric constant. Interaction between charges in a medium of low dielectric constant is much greater than in a medium of high dielectric constant. The effect of the alkyl group shielding is reminiscent of the effect of alkyl substitution on the second ionization constant (K_2) of carboxylic acids (53). For example in the case of malonic acid, K_2/K_1 is 1.36×10^{-3} while this ratio is 0.83×10^{-5} for diethylmalonic acid (54). Thus, the carboxylate anion has a much larger effect on the second ionization constant when separated from the ionizing carboxylic acid group by nonpolar alkyl groups in the substituted compound than by primarily polar solvent molecules in the unsubstituted compound.

Consistent with the above reason for the lack of solvent effect in copolymerization of vinyl compounds is the low solvent effect observed in the oxidation of cumene, p-nitrocumene, and bicyclo-(2.2.1)-heptadiene. In each of these cases the positive charge of the transition state is shielded by hydrocarbon groups as in the copolymerization transition states. Another factor which contributes to prevent a solvent effect in the copolymerization is the greater degree of charge stabilization by resonance; increasing the stabilization of the charge corresponds with decreasing the charge density, which results in less interaction with the solvent.

Detection of a solvent effect in copolymerization studies is more difficult due to inaccuracy in the values for the relative reactivity of the monomers to each radical; these values are seldom accurate to within ± 10%. If more accurate data could be obtained, influences of solvent might be detected.

Relative reactivity of cyclic hydrocarbons toward the peroxy radical

The co-oxidation of aralkyl hydrocarbons has shown that all secondary peroxy radicals interact to form non-radical products at approximately the same rate, and on this basis the relative reactivity of various benzylic secondary hydrogen atoms toward a peroxy radical has been estimated (14). Robb and Shahin have determined the rate constants of the propagation and termination step for the oxidation of cyclohexene and methyl substituted cyclohexenes (55), and their data show that the variation in propagation rate constants exceeds the variation of the termination rate constants. In addition to this, since the rate of oxidation varies inversely to the square root of the termination rate constant, the smaller variation of this constant with structure tends to have a comparatively little effect on the overall rate. On this basis, an approximation of the relative reactivities of the cyclic olefin toward a peroxy radical may be made by assuming that the rates of termination for the peroxy radicals of the various cyclic olefins are the same. The relative reactivities determined in this manner are given in Table 16 along with data for the corresponding relative reactivities toward the methyl radical (56).

In both reactions reported in Table 16 cyclopentene is more reactive

Table 16. Relative reactivity per hydrogen atom of some cyclic hydrocarbons toward a peroxy radical and a methyl radical

Hydrocarbon	Peroxy radical[a] 60°	Methyl radical (55) 65°
Cyclopentene	5.85	2.0
Cyclohexene	3.74	0.38
Cycloheptene	2.53	1.6
Cyclöoctene	1.00[b]	1.00[b]
Cyclöocta-1,5-diene	2.42	--
Cycloheptatriene	7.57	4.2

[a] Calculated from data found in Table 15 for chlorobenzene solvent assuming k_t is equal for the hydrocarbons studied.

[b] Assumed.

than cyclohexene. This result is unexpected since tetralin is more reactive than indan--as seen in Table 4; one might expect these two systems to be similar in their order of reactivity. A factor contributing to a difference in these two systems is the greater inflexibility of the aromatic system. Because of the more rigid system, one would expect strain to be greater in the hybridization of the alpha-carbon atom in the indanyl radical than in cyclopentenyl radical, and thus while strain is important in decreasing the relative reactivity of indan compared to tetralin, it is not sufficiently important in the case of cyclopentene compared to cyclohexene.

While the order of decreasing reactivity for cycloalkanes is C_8, C_7,

C_5, and C_6 (6a, 57), the cycloalkenes may be different since from inspection of the models for the 3-cycloalkenyl radicals, the order of decreasing ability of the free electron to interact with the double bond is C_5, C_6, C_7, and C_8. This latter factor has been suggested to control the relative reaction rates of 1,2-benzcycloalkenes for processes where in the transition state the resonance interaction between the ring and an adjacent carbonium ion is involved (58). For example the alpha-chloride of indan is four times more reactive to hydrolysis in aqueous alcohol than the corresponding chloride of tetralin, and as the side ring is increased in size to seven and eight membered rings, the rates of hydrolysis of the chloride decreases.

The greater activity of indan compounds compared to corresponding tetralin compounds in these ionic reactions appear contradictory to the greater reactivity of tetralin as compared with indan in free radical abstraction. However, the importance of resonance stabilization by an aromatic ring is greater in ionic reactions than in radical reactions. This is seen by comparing the relative rates of hydrolysis at 25° in ethanol-ether solution for benzyl chloride, diphenylmethyl chloride, and triphenylmethyl chloride which are $1:2 \times 10^3:3 \times 10^7$, respectively (59), with the relative rates of hydrogen atom abstraction from the corresponding parent hydrocarbon by the highly selective polystyrene radical at 60° which are 1:28.2:85, respectively (2a). The difference in the relative reactivities of these two systems is too great to be explained by the difference in degree of bond breaking and must be attributed to a greater ability of phenyl groups to stabilize an adjacent positive charge than an adjacent free electron. In section one the lower reactivity of indan as compared to tetralin toward reactions with free radicals was related to the increased strain in the transition state of indan; apparently the greater resonance stabilization expected in the indan radical is not sufficient to overcome the deactivation by the increase in strain. But in the ionic reactions of indan and tetralin derivatives the greater stabilization resulting from the interaction of the aromatic ring with a carbonium ion is enough to compensate for the ring strain in the case of the indan derivative, and the reaction occurs more rapidly in this case.

If strain is not as important in free radical reactions of cycloalkenes as for the benzocycloalkenes, due to the less rigid system, resonance stabilization should be more important, and the expected rates of hydrogen abstraction should depend on the degree of stability of the radical. In the cycloalkene series, the sequence where the reactivities corresponding with the stability of the resulting cycloalkene radical is observed for the peroxy radical. Since the degree of bond breaking is often not great in some free radical reactions, the stabilization obtained by resonance in the transition state may not always be important. Apparently in the case for the methyl radical, bond breaking is not sufficiently great to allow significant resonance stabilization in the transition state, and some other factor is important in controlling the relative rates. The reactivity of cyclohexene to the methyl radical appears low; however, Miss K. Desmond of this laboratory has found the reactivity toward the succinimidyl radical for cyclohexene to be lower than for either cyclopentene or cycloheptene, although Walling and Thaler have reported the relative reactivity of cyclopentene and cyclohexene toward a t-butoxy radical to be 1.0 (60). Another factor which may be important in addition to the resonance stabilization in the resulting radical is the loss or gain of hydrogen-hydrogen interactions as the reactants approach the transition state. If qualitatively, hydrogen-hydrogen interactions are as important in the radical reaction of cycloalkenes as there are in the reactions of cycloalkanes then the low reactivity of cyclohexene would not be surprising. This low reactivity would be found in cases where the bond breaking would be small, since in these cases the hydrogen-hydrogen interactions would dominate.

Experimental

Oxidation 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 $60.00 \pm 0.15^{\circ}$ 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. In the cases where the inhibition time was measured the reciprocation was started at the time the flask was fastened to the rack. 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.

Analysis for hydroperoxide were made by the stannous chloride procedure of Barnard and Hargrave (61). Control experiments showed that nitromethane interferes with the analysis unless the analysis blanks contain the same amount of nitromethane as the hydroperoxide sample. The following hydroperoxide yields were obtained in nitromethane: 2 M cyclohexene, 101%; 2 M tetralin, 93%; 2 M cycloöcta-1,5-diene, 90%; 2 M cycloheptene, 65%; 2 M cycloheptatriene, 47%; 1 M cyclopentene, 70%; 2 M bicyclo-(2.2.1)-heptadiene, 9.0%. In chlorobenzene solution yields of 62% and 36% were obtained for 2 M cycloöctene and 2 M cycloheptatriene, respectively, while 2 M cyclohexene in 2-propanol solution gave 104%.

Reagents

Research grade cyclopentene (99.89 minimum mole %), cyclohexene (99.98 minimum mole %), and cumene (100.0 minimum mole %) were obtained from Phillips Petroleum Co. Cycloheptene was prepared by reduction of cycloheptanone with lithium alumnim hydride followed by elimination of water catalyzed by naphthalene sulfonic acid. Cycloöctene and cycloöcta-1,5-diene were obtained as gifts from City Service Research and Development Co., while cycloheptatriene and bicyclo-(2.2.1)-heptadiene were gifts from Shell Chemical Co. Indan from Aldrich Chemical Co. and tetralin from Matheson Coleman and Bell were shaken with sulfuric acid, washed, and dried for further purification. Cyclohexa-1,3-diene was prepared by bromination of cyclohexene with N-bromosuccinimide followed by quinoline catalyzed elimination of hydrogen bromide (62). The hydrocarbons except those which were research grade were fractionated and center fractions having constant boiling points and refractive indices were used. p-Nitrocumene which had been prepared earlier in these laboratories by nitration of cumene was redistilled before it was used. All hydrocarbons were passed through activated silica gel in a dry nitrogen atmosphere and stored under dry nitrogen prior to the study of their oxidation.

<u>t</u>-Butylnaphthalene was prepared by the reaction of <u>t</u>-butyl alcohol with naphthalene in the presence of boron trifluoride and phosphoric anhydride, distilled, and passed through silica gel. Other solvents were obtained from the normal commercial sources and were purified by accepted methods. If possible the solvents were passed through silica gel. N-Methylpropionamide was prepared by addition of propionyl chloride to 40% aqueous methylamine (63); this amide and dimethyl formamide were used as solvents for the oxidation of cyclohexene, but the rates of oxidation were extremely slow, apparently the result of inhibition.

OXIDATION OF HYDROCARBONS IN THE PRESENCE OF TRIPHENYLMETHANE AND SIMILAR TYPE COMPOUNDS

Introduction

The most satisfactory retarding agents for free radical oxidation reactions are substances capable of trapping peroxy radicals--the radicals necessary for the propagation reaction. Substituted phenols and anilines commonly have been used as retarding agents and the processes by which these compounds retard oxidation reactions have been extensively studied (64). Some hydrocarbons are known to act as retarders in the oxidation of certain hydrocarbons, and two possible mechanisms appear to be involved.

Tetralin oxidizes considerably faster than cumene, but the overall rate of oxidization for cumene containing a small amount of tetralin is considerably slower than that of pure cumene (65a). The relative reactivity of tetralin is greater toward the peroxy radical than cumene, and the rates of termination involving two <u>alpha</u>-tetralyl radicals or one <u>alpha</u>-tetralyl radical and one <u>alpha</u>-cumyl radical are greater than that involving two <u>alpha</u>-cumyl radicals. Thus in the oxidation of cumene with small amounts of tetralin present, relatively large amounts of <u>alpha</u>-tetralyl peroxy radicals are formed due to the greater reactivity of tetralin. With the increase in the concentration of <u>alpha</u>-tetralyl peroxy radicals, termination occurs more readily, and therefore, the overall rate is slower (65a). Thus the ability of one hydrocarbon to retard the oxidation of another hydrocarbon depends on the relative rates of termination involving the corresponding peroxy radicals. A number of combinations of hydrocarbons has been investigated in this light (65).

In high temperature oxidation reactions, hydrocarbons which yield benzyl or allyl radicals upon hydrogen atom abstraction act as inhibitors. Thus toluene, ethylbenzene, and cumene serve as inhibitors for the vapor phase oxidation of alkanes at 350° (66), while olefinic hydrocarbons such as propylene and diisobutylene are reported to inhibit the high temperature oxidation of alkanes (67). These oxidation retarders oxidize readily at room temperature, and in order for them to act as inhibitors in the vapor phase, the reaction of the corresponding allyl or benzyl radicals with oxygen must be reversible at high temperatures. In this case these radicals would be able to act as traps for other radicals. Consistent with this explanation, Szwarc has reported that oxygen does not destroy benzyl radicals at 500° (68).

Competitive oxidations of various aralkyl hydrocarbons have revealed that triphenylmethane effectively retards the rate of oxidation of cumene at 90° (14). The mechanism of this retardation has not been studied and possibly could involve a process similar to one of the above mechanism. Thus the effect of triphenylmethane and similar type compounds on the oxidation of cyclohexane was investigated.

Results and Discussion

Mixtures of cyclohexene and triphenylmethane having a total hydrocarbon concentration of 2.0 M were oxidized at 60° in chlorobenzene solution, at a total pressure of 710 mm. of mercury. The data obtained in this series of experiments are summarized in Table 17 and given graphically in Figure 10. The strongly concave curve obtained is the same type of curve that was observed previously (14). The observation suggests the possibility of using triphenylmethane to retard other free radical oxidations even though triphenylmethane is generally considered more reactive in free radical processes than hydrocarbons like cumene or cyclohexene. For example from polymerization studies of styrene at 60°, the relative reactivity of triphenylmethane and cumene toward a polystyrenyl radical is reported to be 4.7 (2a); Walling and Jacknow have reported a value of 1.4 for the relative reactivity of triphenylmethane and cumene toward a t-butoxy radical at 40° (7b). From the chlorination results reported in the first section and the work of Mr. A. Ito in this laboratory, the relative reactivity of these hydrocarbons toward the more reactive chlorine atom is determined to be only 1.3. To compare the relative reactivity of triphenylmethane and cyclohexene toward the chlorine atom is more difficult; but from the data in the previous section, the relative reactivity of cyclohexene and tetralin toward a peroxy radical may be estimated. By using the relative reactivity of triphenylmethane and tetralin toward the chlorine atom, one may estimate a minimum value of about 1.6 for the relative reactivity of triphenylmethane and cyclohexene toward a peroxy radical. The actual value may be larger than

Table 17. Oxidation of cyclohexene-triphenylmethane mixtures in chlorobenzene solution and in presence of 0.0504 M AIBN at 60°

Concentration of cyclohexene mole/lit.	Concentration of triphenylmethane mole/lit.	Rate - $R_i/2$ mole/lit.-hr.
	711 mm. total pressure	
2.0	0.0	0.0472
2.0	.02	.0394
1.9	.1	.0252
1.5	.5	.0100
0.0	2.0	.0022
	300 mm. total pressure	
2.0	0.0	.0482
2.0	.0	.0476
1.9	.1	.0194
1.5	.5	.0071

1.6, but in any case triphenylmethane also is more reactive than cyclohexene.

Once the ability of triphenylmethane to retard the oxidation of cyclohexene was established, the possibility of other hydrocarbons acting as retardants was investigated. A number of experiments were performed in chlorobenzene solution where the effect of triphenylethene, 1,1-diphenyl-ethene, 1-naphthyldiphenylmethane, 9-phenylfluorene and, for comparison, triphenylmethane were studied. Solutions of various concentrations of these hydrocarbons with 2.0 M cyclohexene were oxidized; the data are presented in Table 18 and given graphically in Figure 11. Pentaphenylethane was also tested as a retarder; the results were

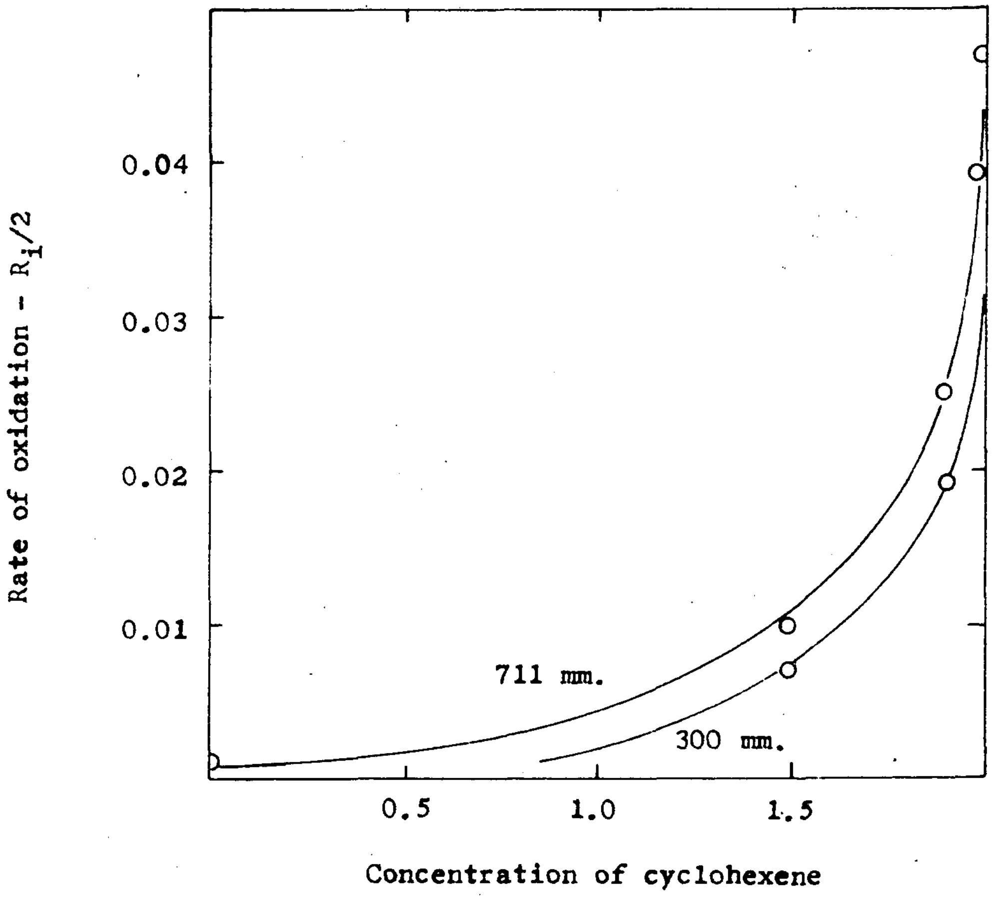


Figure 10. Effect of triphenylmethane on the oxidation of cyclohexene at 60° in the presence of 0.0504 M AIBN (total hydrocarbon concentration = 2.0 M)

Table 18. Oxidation of 2.0 M cyclohexene at 60° with various added hydrocarbons in chlorobenzene solution and in the presence of 0.0504 M AIBN

Added hydrocarbon	Concentration mole/lit.	Total pressure mm.	Rate - $R_i/2$ mole/lit.-hr.
None	--	711	0.0472
None	--	300	0.0482
9-Phenylfluorene	0.01	711	0.0266
9-Phenylfluorene	0.01	300	0.0202
9-Phenylfluorene	0.1	711	0.0043
9-Phenylfluorene	0.5	711	0.0034
Triphenylmethane	0.1	711	0.0254
Triphenylmethane	0.5	711	0.0123
α-naphthyldiphenylmethane	0.1	711	0.0295
α-naphthyldiphenylmethane	0.1	300	0.0271
Triphenylethene	0.5	711	0.0462
1,1-diphenylethene	0.5	711	0.0415

misleading due to dissociation of the ethane into triphenylmethyl and diphenylmethyl radicals, as was demonstrated by a blank experiment where pentaphenylethane in chlorobenzene solution was shaken with oxygen at 60°C. A significant oxygen absorption indicated that dissociation into radicals was occurring; this dissociation is well known at higher temperatures (69).

The curves in Figure 11 show that other hydrocarbons retard the rate

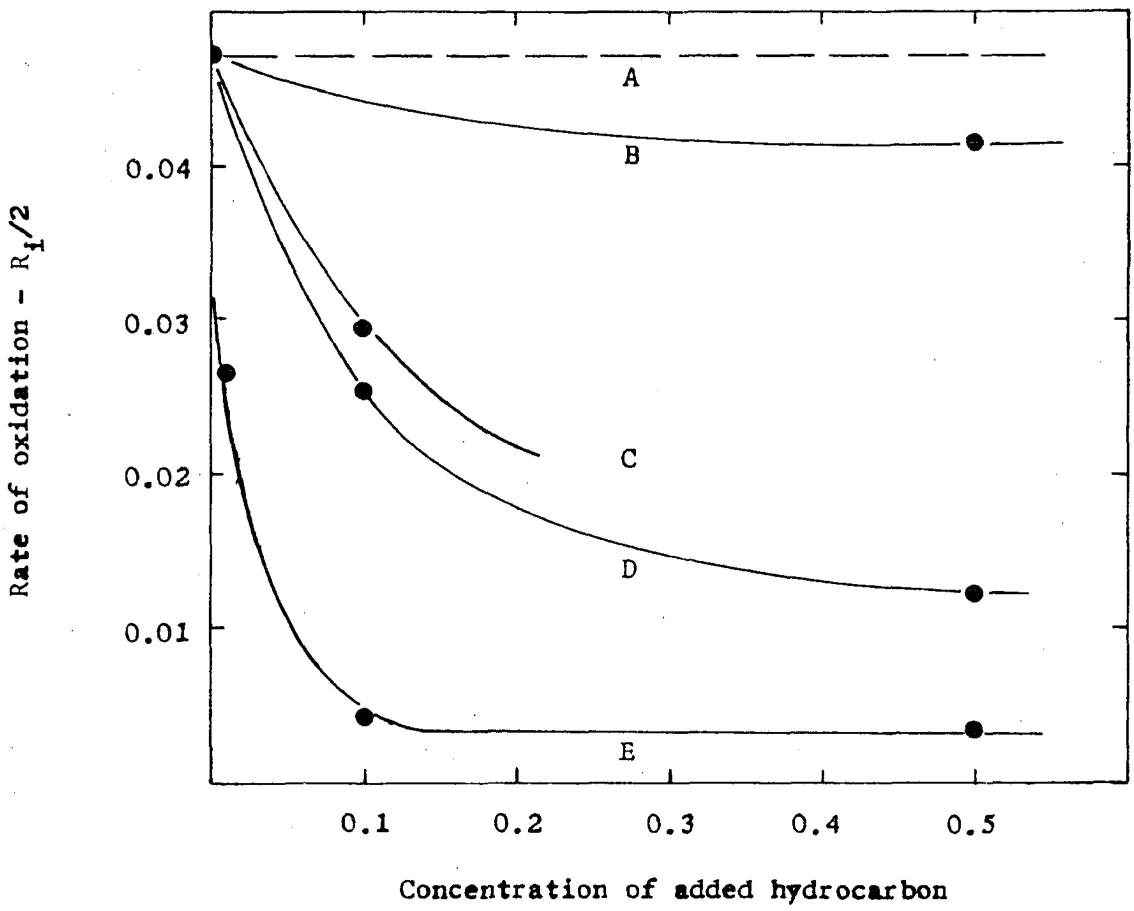


Figure 11. Effect of various hydrocarbons on the oxidation of 2.0 M cyclohexene at 60° in the presence of 0.0504 M AIBN

A: inert hydrocarbon
B: 1,1-diphenylethene
C: 1-naphthyldiphenylmethane
D: triphenylmethane
E: 9-phenylfluorene

of oxidation to various degrees. 9-Phenylfluorene is strikingly efficient in the retardation, and the presence of fluorene to the extent of three-quarters mole percent of the total hydrocarbon concentration produces fifty percent retardation. All these hydrocarbons form relatively stable radicals when they react with a peroxy radical.

The competitive oxidation of two hydrocarbons has been suggested to be in accord with the following scheme (65a).

Initiation: $\text{Catalyst} \xrightarrow{k_d} 2eR\cdot$

$R'\cdot + O_2 \xrightarrow{\text{very fast}} R'OO\cdot$

$R'OO\cdot + R_IH \longrightarrow R'OOH + R_I\cdot$

$R'OO\cdot + R_{II}H \longrightarrow R'OOH + R_{II}\cdot$

Propagation: $R_I\cdot + O_2 \xrightarrow{\text{very fast}} R_IOO\cdot$

$R_{II}\cdot + O_2 \xrightarrow{\text{very fast}} R_{II}OO\cdot$

$R_IOO\cdot + R_IH \xrightarrow{k_1} R_IOOH + R_I\cdot$

$R_IOO\cdot + R_{II}H \xrightarrow{k_2} R_IOOH + R_{II}\cdot$

$R_{II}OO\cdot + R_IH \xrightarrow{k_3} R_{II}OOH + R_I\cdot$

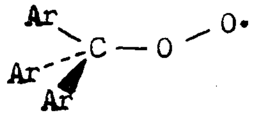
$R_{II}OO\cdot + R_{II}H \xrightarrow{k_4} R_{II}OOH + R_{II}\cdot$

Termination: $2R_IOO\cdot \xrightarrow{k_5} \text{non-radical products}$

$2R_{II}OO\cdot \xrightarrow{k_6} \text{non-radical products}$

$R_IOO\cdot + R_{II}OO\cdot \xrightarrow{k_7} \text{non-radical products}$

At least two explanations may be given for the retardation in the rate of oxidation by these reactive hydrocarbons. First, the triphenylmethyl peroxy radical and the peroxy radicals from these other hydrocarbons could be intrinsically less reactive than the 3-cyclohexenyl and the cumyl peroxy radicals; as the concentration of these reactive hydrocarbons is increased a larger percent of the peroxy radicals would be the less reactive peroxy radical from these hydrocarbons. But there is no apparent reason for this low reactivity; steric interactions are not a reasonable explanation. The free electron of the peroxy radical is two oxygen atoms plus one carbon atom away from the aryl groups (Ar-); these groups are directed away from the oxygen atoms and the free electron at an angle of about 120°. These relationships can be seen in the following drawing.



The other explanation involves the assumption that the radicals generated from these hydrocarbons do not react rapidly and completely with oxygen to give peroxy radicals. These more stable radicals possibly do not react rapidly with oxygen as do the less stable radicals, e.g., 3-cyclohexenyl and *alpha*-cumyl radicals. If this consideration were true, the concentration of these fairly stable radicals would become significant, and the radicals would be able to trap other peroxy radicals. In this case two more termination steps would be important in the overall oxidation.

$$R_{II}\cdot + R_{I}OO\cdot \xrightarrow{k_8} R_{II}OOR_{I}$$
$$R_{II}\cdot + R_{II}OO\cdot \xrightarrow{k_9} R_{II}OOR_{II}$$

The symbol R_I signifies the 3-cyclohexenyl or the *alpha*-cumyl radical, and R_{II} indicates the radical from the added hydrocarbon, e.g., triphenylmethyl radical. These additional termination mechanisms would tend to reduce the concentration of peroxy radical--the radical which continues the kinetic chain—and reduces the oxidation rate.

The oxidation of cumene (70) at 65°C, tetralin (65a, 71) at both 45° and 90°C, and diphenylmethane (72) at 115°C all involve only the termination between two peroxy radicals at pressures of the order of one atmosphere. Generally in the oxidation of olefins, only termination between peroxy radicals in involved at atmosphere pressure, but Bateman *et al.*, have observed at lower pressures a correlation between the reactivity of various olefinic hydrocarbons with the oxygen pressure at which pressure dependence becomes zero (73). As the olefins become more reactive, they observed that a higher pressure of oxygen was required to prevent the occurrence of termination processes other than the one involving only the peroxy radical. An extreme example has been observed in the case of 2,6-dimethylhepta-2,5-diene where termination involving both an alkyl radical and a peroxy radical is important even at atmospheric pressure (74). Therefore, while most radicals apparently react readily with oxygen at atmospheric pressure, the more stable radicals may not react as readily.

Pressure dependence studies were undertaken to test the possibility of the retardation being the result of these additional termination steps. A significant oxygen pressure dependence in a retarded system would indicate that the reaction between the aralkyl radical and oxygen is incomplete and additional termination processes are important. The absence of an oxygen pressure dependence would indicate that the reaction of the radical with oxygen is going to completion and that these other possible termination processes are not involved.

Triphenylmethane-cyclohexene mixtures were again oxidized but at a lower pressure--300 mm. total pressure. These data are in Table 17 with the corresponding work at 711 mm. and shown in Figure 10. The actual corresponding oxygen pressure, obtained by correcting the total pressure for the vapor pressure of the cyclohexene and the chlorobenzene was 170 mm. verse 580 mm. in the earlier experiments. Thus a 70 percent oxygen pressure decrease caused about a 25 percent decrease in the rate. This type of non-linear oxygen pressure dependence is normal since the rate of oxidation is not proportional to a simple function of oxygen pressure.

For a more complete study of the oxygen pressure dependence in this system, a search was made to find a hydrocarbon which would not cause a significant retardation at atmospheric pressure but would at lower pressures. Fluorene proved satisfactory for these experiments; it was oxidized with cyclohexene (total hydrocarbon concentration equal to 2.0 $\underline{M}$) in chlorobenzene solution under the usual conditions and the results are listed in Table 19 and shown graphically in Figure 12. Oxygen pressure dependence is not observed for the oxidation of 2.0 $\underline{M}$ cyclohexene--where there is no fluorene; but as the cyclohexene is gradually replaced with fluorene a very pronounced retardation becomes apparent which does show a significant pressure dependence. These data have been replotted in Figure 13 with the rate a function of pressure instead of the hydrocarbon concentration. In this figure, a series of curves is obtained which approach zero rate at zero oxygen pressure. An exception is in the case of the 2.0 $\underline{M}$ cyclohexene curve where no pressure dependence was observed over the pressure range studied. Some rates for the oxidation of ethyl linolenate (at 45°C) are included on the graph for comparison (26b); these rates have

Table 19. Oxidation of cyclohexene-fluorene mixtures at various pressures at 60° in chlorobenzene solution and in the presence of 0.0504 M AIBN; total hydrocarbon concentrations = 2.0 M

Cyclohexene concentration mole/lit.	Fluorene concentration mole/lit.	Total pressure mm.	Rate mole/lit.-hr.
2.0	0.0	711	0.0472
1.9	0.1	711	0.0429
1.5	0.5	711	0.0376
0.0	2.0	711	0.0220
1.9	0.1	503	0.0409
1.5	0.5	503	0.0354
1.9	0.1	400	0.0380
1.5	0.5	400	0.0309
2.0	0.0	300	0.0482
2.0	0.0	300	0.0476
1.9	0.1	300	0.0340
1.5	0.5	300	0.0246
0.0	2.0	300	0.0178

been multiplied by a factor for better comparison.

Since a pressure dependence is observed in these systems, the reaction of the triphenylmethyl radical or the fluorenyl radical can not be rapid and complete with oxygen. Due to this incomplete reaction a significant concentration of the stable radical develops. The

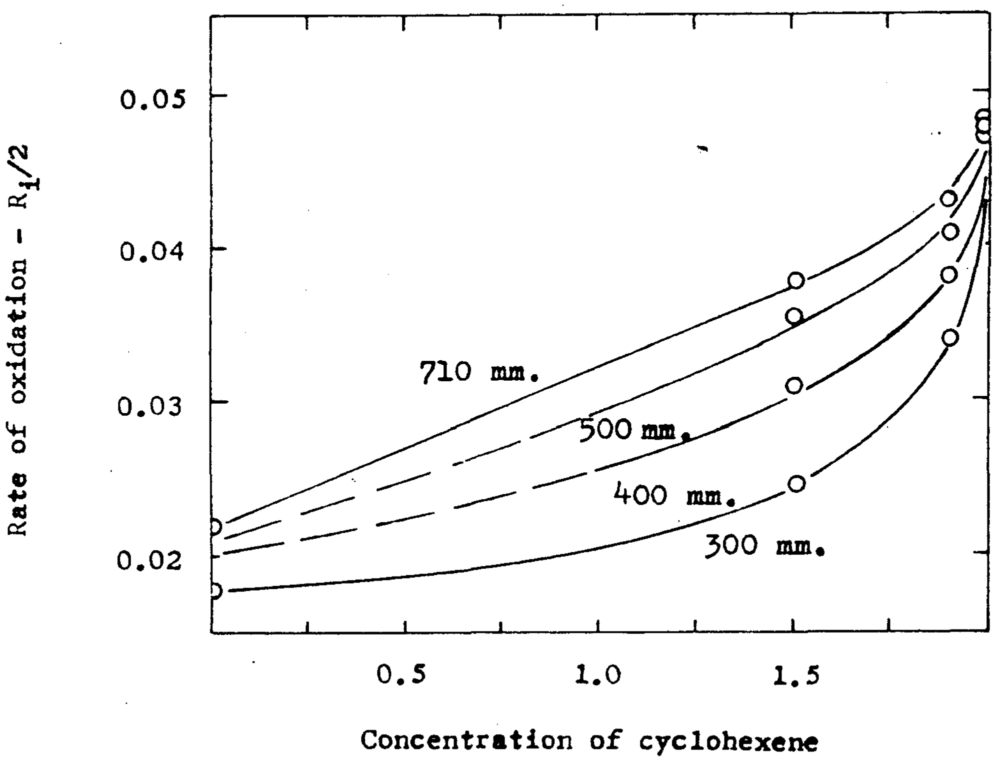
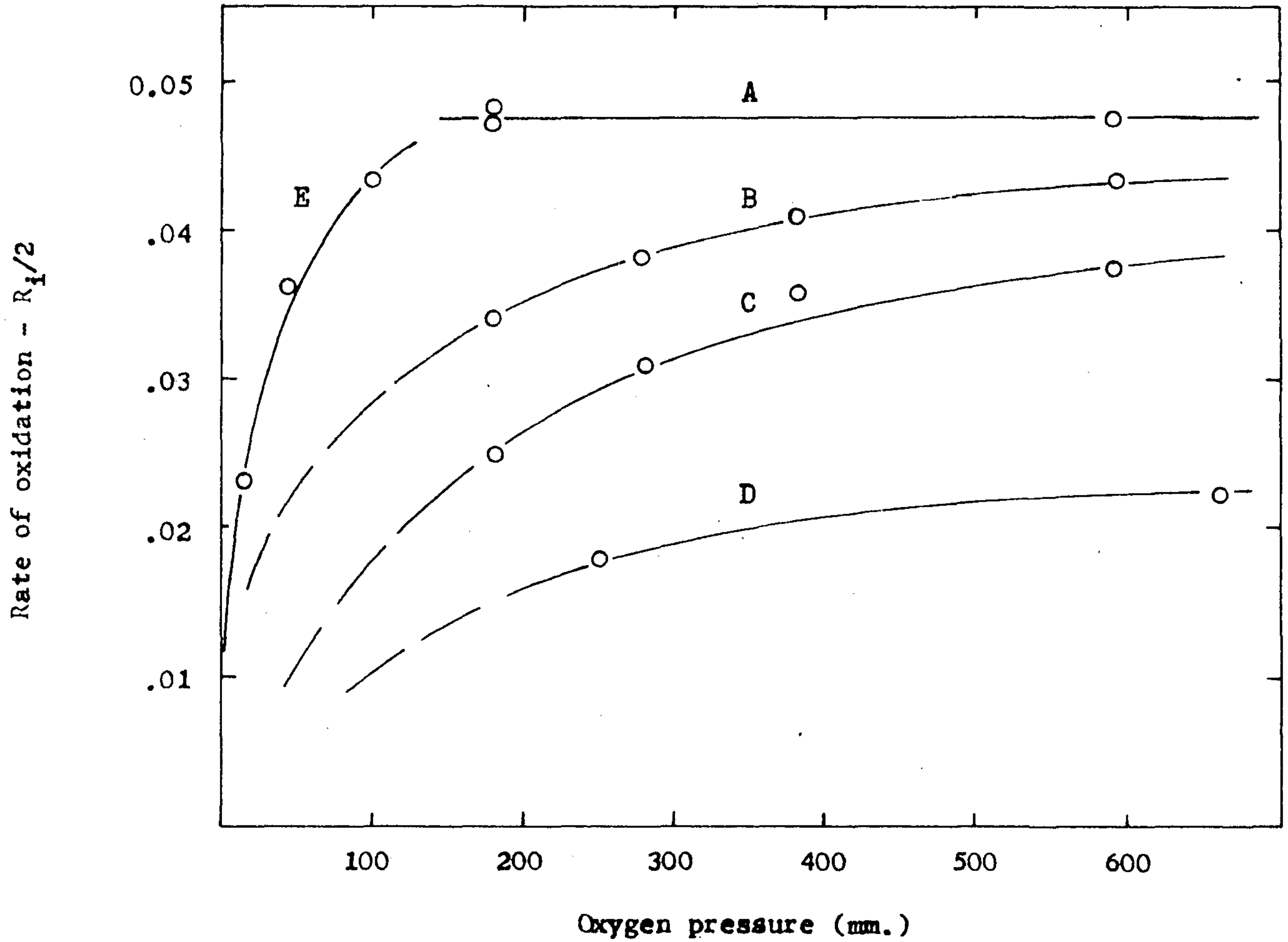


Figure 12. Effect of pressure on the rate of competitive oxidation of cyclohexene and fluorene (total hydrocarbon concentration = 2.0 *M*)

Figure 13. Effect of oxygen pressure on the oxidation of fluorene-cyclohexene mixtures in the presence of 0.0504 M AIBN at 60°

A: 2.0 M cyclohexene
B: 1.9 M cyclohexene--0.1 M fluorene
C: 1.5 M cyclohexene--0.5 M fluorene
D: 2.0 M fluorene
E: 3.0 M ethyl linoleate at 45°C


0.05
.04
.03
.02
.01
100
200
300
400
500
600
A
B
C
D
E
Rate of oxidation - $R_{i}/2$
Oxygen pressure (mm.)

rate now will be reduced by additional termination processes between the stable radical and a peroxy radical.

A test of this phase of the mechanism would be a comparison of the reactivity of these special hydrocarbons, or the stability of their corresponding radical with their ability to retard oxidation. If the principles discussed above are correct, the more stable radical will be more effective in retarding the oxidation.

On the basis of the number of resonance structures that can be written it would seem likely that a phenyl group stabilizes an electron on an adjacent atom to a greater degree than an alkyl group, an 1-naphthyl group stabilizes more than a phenyl group, and a fluorenyl group stabilizes more than two phenyl groups. Thus, the expected order of reactivity should lead to a order of decreasing retardation of 9-phenylfluorene, 1-naphthyldiphenylmethane, triphenylmethane, 1,1-diphenylethene. The observed order, as seen in Figure 11, differs with the compounds 1-naphthyldiphenylmethane and triphenylmethane, where their order is reversed. This variance best can be explained by considering the contribution of steric factors on the radical stability. If a phenyl group of the triphenylmethyl radical is replaced by an 1-naphthyl group, a loss in coplanarity of the phenyl and naphthyl groups may occur due to steric interactions. The second ring of the naphthyl group will interact with the neighboring phenyl group. The loss of coplanarity would result in a loss of more resonance stability than is gained by the replacement of a phenyl group with a naphthyl group. Figure 14 has been prepared by assuming a planar structure for the radical. The interaction of the <u>ortho</u>-hydrogens on the

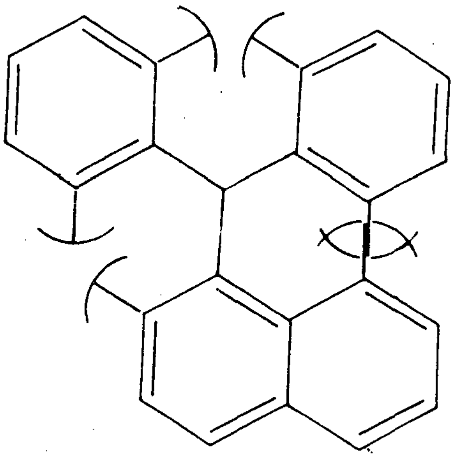


Figure 14. Drawing showing hydrogen-hydrogen interactions in the 1-naphthyldiphenylmethyl radical

two phenyl groups can not be readily seen in the figure, but this type of interaction is large enough to prevent complete planarity of the phenyl groups of the triphenylmethyl radical (75). From the figure, the interaction between the hydrogen atom bonded to the eight carbon of the naphthyl group and the _ortho_-hydrogen of the neighboring phenyl group can be seen to interact to a much larger extent than do the two _ortho_-hydrogens of neighboring phenyl groups. Thus one would expect this radical to be less planar than the triphenylmethyl radical and, correspondingly, less stable due to the loss of resonance energy.

With this correlation between degree of retardation and reactivity, apparently this type of system would be useful for determining, at least qualitatively, reactivities of hydrocarbons similar to that of triphenylmethane toward the peroxy radical. If this method is to be used for this purpose, two factors contributing to the concentration of the stable radical and to the overall retardation should be recognized. The more stable radical is formed faster since the corresponding hydrocarbon is more reactive, and the more stable radical disappears more slowly since it reacts more slowly with oxygen. These two factors do compliment each other, and they tend to magnify any difference in reactivity and make it easier to detect smaller changes.

Additional information in support of a second termination process which does involve the triphenylmethyl radical was obtained from the study of the temperature dependence of the retardation. 2.0 _M_ cumene was oxidized with various concentrations of triphenylmethane at both 60° and 90°. The data is in Table 20 and shown visually in Figure 15. For comparison

Table 20. Effect of triphenylmethane on the oxidation of 2.0 M cumene at 60° and 90° in bromobenzene solution

Concentration of triphenylmethane mole/lit.	Rate - $R_i/2$ mole/lit.-hr.
	60°C; catalyst 0.0504 M AIBN; 650 mm. total pressure
0.000	0.0144
.002	.0157
.020	.00691
.10	.0034
	90°C; catalyst 0.04 M t-butyl perbenzoate; 720 mm. total pressure
.000	.00954
.002	.00723
.020	.00145
.10	.00147

of the two systems in the figure, the rates are expressed in terms of percent retardation relative to the corresponding run with no triphenylmethane. The total pressure used in each series of experiments was chosen so that the partial pressures of oxygen was the same in both cases.

It is seen in the figure that triphenylmethane is more efficient at retarding the oxidation of cumene at 90°C than at 60°. This fact is interpreted as meaning that the triphenylmethyl radical contributes to a higher percentage of the total radical concentration at the higher

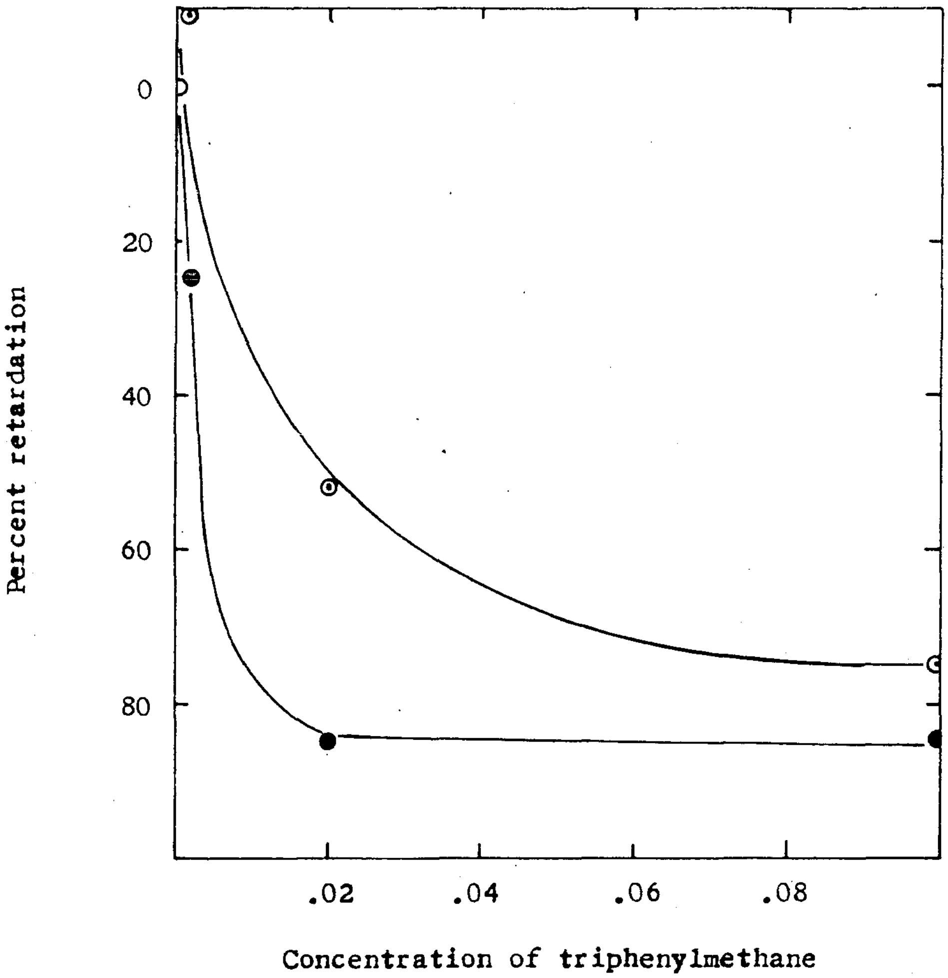


Figure 15. Effect of triphenylmethane on the oxidation of 2.0 M cumene in bromobenzene solution

⊙ : in the presence of 0.0504 M AIBN at 60°

● : in the presence of 0.04 M t-butylperbenzoate at 90°

percentage of the total radical concentration at the higher temperature. This is the same type of phenomenon observed by Bateman in his study of pressure dependence on the rate of oxidation of ethyl linolenate as a function of temperature (26b). Increased pressure dependence occurs at higher temperatures which indicates that greater concentrations of ethyl linolenate radical were present. The explanation given, which is applicable to the data in this section, is that the propagation step, wherein the peroxy radical attacks the hydrocarbon, shows more temperature dependence than the reaction of the radical with oxygen. Thus the rate of formation of the radical increases more with temperature than the rate of disappearance. The application of this explanation to the triphenylmethane system is best seen by considering the expression for the triphenylmethyl radical concentration derived from steady state assumptions. The rate of formation of the stable radical must equal the sum of the rates of disappearance by the reaction with oxygen and with peroxy radical. If the rate constant for the formation of the radical is the only rate constant significantly increased by an increase in temperature, the concentration of stable radical must increase. Since the same trend is observed with an increase in the temperature of the oxidation as was observed by Bateman, the proposed termination reaction is reasonable.

Since the triphenylmethyl radical is involved in the termination, the reaction between the radical and oxygen must be considered. This reaction could involve one of two distinct processes: the process may be a slow irreversible reaction, or it may be a fast reaction complicated by a fast reverse reaction.

$$R_{II}\cdot + O_2 \xrightarrow[\text{slow}]{k_{O_2}} R_{II}OO\cdot$$

or

$$R_{II}\cdot + O_2 \underset{k_{-O_2}}{\overset{k_{O_2}}{\rightleftharpoons}} R_{II}OO\cdot$$

If it is assumed that the reaction under consideration has a small energy of activation as in the reaction of a simple alkyl radicals and oxygen (26b), it is difficult to conceive reasons why the reaction would proceed at a slower rate for the more stable radical. Thus a fast equilibrium would be more reasonable than a slow irreversible reaction. However, the energy of activation for the reaction with oxygen may increase as the radical becomes more stable. To form the carbon-oxygen bond of the peroxy radical the free electron must be localized. The energy for this process will depend on the degree of stability of the radical and will appear, at the least, in part in the energy of activation. Thus in this case the reaction is expected to be a slow reaction and governed by the energy of activation.

To differentiate between these two mechanisms seems possible if there were a way of trapping the peroxy radical. If the reaction is fast and reversible, trapping the triphenylmethyl peroxy radical will reduce the concentration of triphenylmethyl radical by the mass law effect. If the reaction with oxygen is not reversible, reducing the triphenylmethyl peroxy radical concentration will have little effect on the triphenylmethyl radical concentration. It is difficult to devise a method in which the peroxy radical is trapped but where no destruction of radicals occurs. The most suitable trapping agent appears to be hydrogen bromide, which has been used as a catalyst in the vapor phase oxidations of alkanes (76). With this catalyst, oxidization of isobutane at temperatures as low as 160° is possible with the main product being t-butyl hydroperoxide. Without the hydrogen bromide much higher temperatures are required for the oxidation. It is thought that hydrogen bromide functions in this oxidation as follows:

$$ROO\cdot + HBr \longrightarrow ROOH + Br\cdot$$

$$Br\cdot + RH \longrightarrow HBr + R\cdot$$

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

In the liquid phase certain heavy metal salts in the presence of bromide ion have been observed to serve as catalyst or as a co-catalyst for free radical oxidations (77). The best system appears to be one in which manganous or colbaltous ion plus some bromide salt is used in glacial acetic acid solution; in this system hydrogen bromide is present as a result of the equilibrium:

$$MBr(OAc) + HOAc \rightleftharpoons M(OAc)_2 + HBr$$

There are some discrepancies in the references concerning the role of the hydrogen bromide. According to Ravans who has studied the oxidation of p-toluic acid in this system, hydrogen bromide is involved solely in the initiation step (77e). In his kinetic derivation he makes a number of unlikely assumptions, one of which is that in the oxygen pressure range studied (128-265 mm.) the p-toluic acid radical reacts immediately with oxygen. In view of previously stated data concerning the reactivity of radicals with oxygen this assumption appears incorrect. Another questionable assumption is the complete reaction of hydrogen bromide with oxygen forming a hydroperoxy radical and a bromine atom in the presence of peroxy and hydroxy radicals. This assumption is in disagreement with the vapor phase oxidation of alkanes in the presence of hydrogen bromide (76). If the hydrogen bromide does not react with the peroxy radical as is suggested by Ravans, there is no explanation for the high yield of hydroperoxide product in the vapor phase reaction. Under the conditions of the vapor phase reaction, the reaction of peroxy radical with unreacted alkane occurs too slowly to be considered important. H. S. Blanchard privately has indicated that he has studied the oxidation of cumene in a similar system by using AIBN as the catalyst and colbalt bromo acetate as a co-catalyst. The product from this oxidation is mainly the hydroperoxide while in the work of Ravens, the first detectable product is the aldehyde which undergoes further oxidation to the acid. The evidence of Blanchard indicates that the main role of the hydrogen bromide is similar to the role in the vapor phase oxidation where it is involved in the propagation step; therefore, it does appear that in this liquid phase system hydrogen bromide is an excellent trap for peroxy radical. The presence of this trapping agent does not stop the oxidation since the bromine atom which is generated in the trapping step continues the kinetic chain.

In order to differentiate between the two possible mechanisms for the reaction of the triphenylmethane radical with oxygen, the retarding effect of 0.1 M triphenylmethane was compared in two systems. The first system

Table 21. Effect of triphenylmethane and cobalt salts on the oxidation of 2.0 M cumene at 60° in acetic acid solution and in the presence of 0.0504 M AIBN

Concentration of triphenylmethane mole/lit.	Cobalt compound	Concentration compound cobalt mole/lit.	Rate - $R_i/2$ mole/lit.-hr.
0.00	None	---	0.0151
.10	None	---	.0028
.00	Bromoacetate	0.019	.160
.10	Bromoacetate	.019	.0424
.00	Diacetate	.020	.0581
.50	Diacetate	.020	.0027
.50	Bromoacetate	.019	.0014

was 2.0 M cumene plus 0.0504 M AIBN in acetic acid solution; the second system was the same as the previous system except 0.02 M cobalt (II) bromoacetate was added as a co-catalyst. In these two systems the triphenylmethane caused the same retardation, 75-80 percent. The data for these experiments are given in Table 21 and shown graphically in Figure 16. The experiments with cobalt ion present show varying degrees of autocatalysis; in the cases where a large effect is noticeable, the initial slope is indicated with a dashed line. In a second series of experiments the retarding effect of 0.5 M triphenylmethane was studied in a system consisting of 2.0 M cumene, 0.0504 M AIBN, and 0.02 M cobalt (II) acetate in acetic acid solution. In separate experiments the cobalt (II) acetate

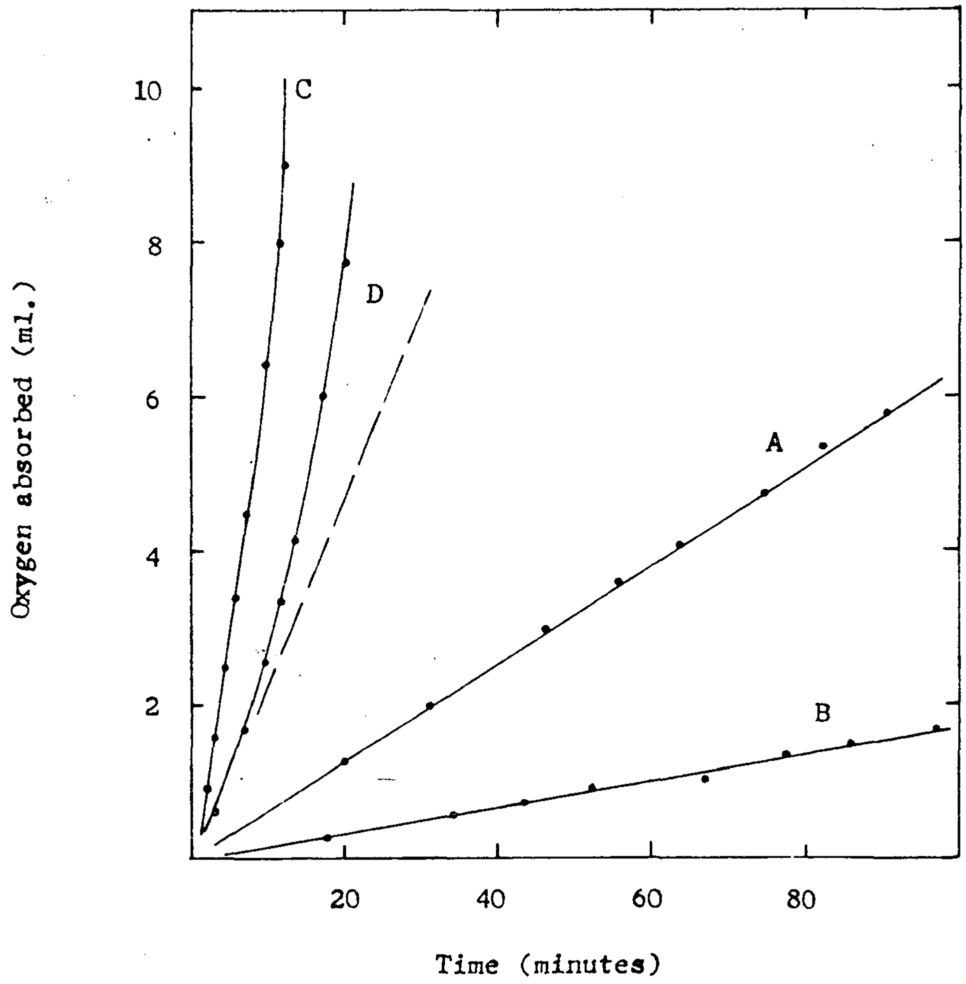


Figure 16. Effect of 0.1 M triphenylmethane and 0.02 M cobalt (II) bromoacetate on the oxidation of 2.0 M cumene at 60° in the presence of 0.0504 M AIBN

A: no added materials
B: 0.1 M triphenylmethane
C: 0.02 M cobalt (II) bromoacetate
D: 0.02 M cobalt (II) bromoacetate + 0.1 M triphenylmethane

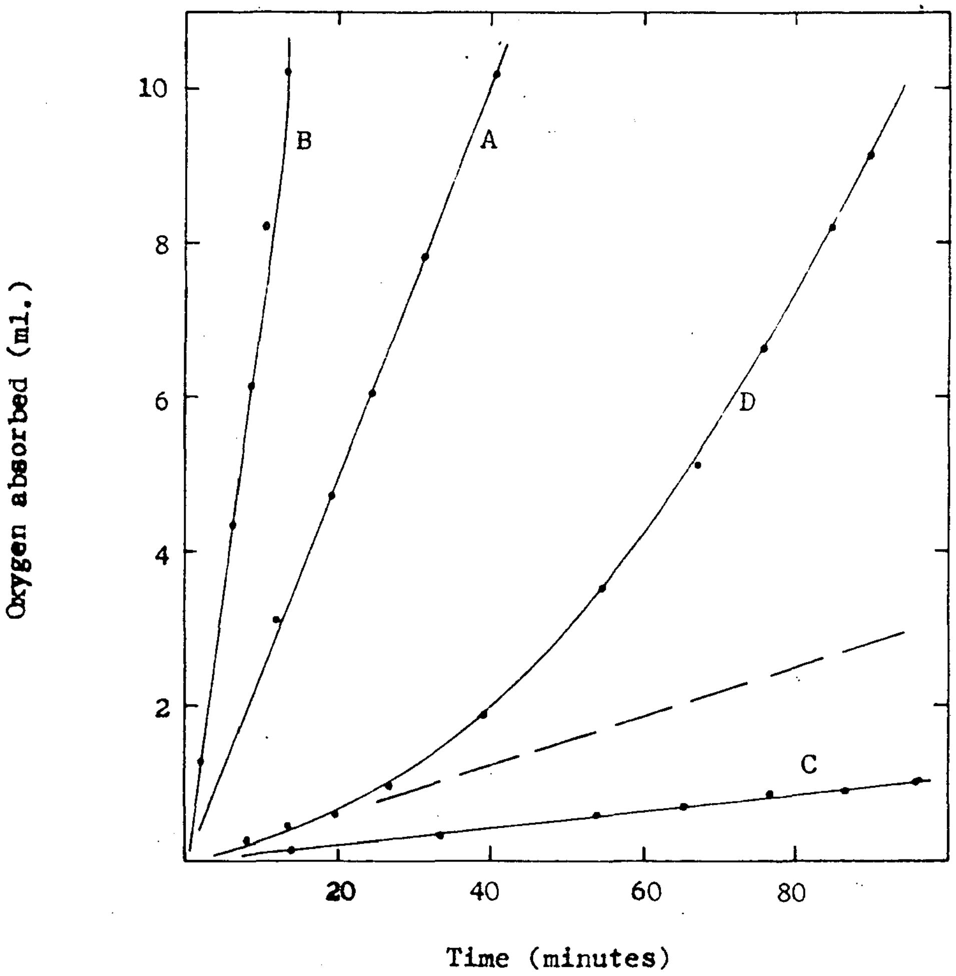


Figure 17. Effect of 0.5 M triphenylmethane and 0.02 M bromide ion on the oxidation of 2.0 M cumene at 60° in the presence of 0.0504 M AIBN and 0.02 M cobalt (II) ion

A: 0.02 M cobalt (II) acetate
B: 0.02 M cobalt (II) bromoacetate
C: 0.02 M cobalt (II) acetate + 0.5 M triphenylmethane
D: 0.02 M cobalt (II) bromoacetate + 0.5 M triphenylmethane

was replaced with the same concentration of cobalt (II) bromoacetate. By comparing the experiments in each of these systems it can be seen that the catalysis is not due solely to the cobalt ion; in addition the triphenylmethane has approximately the same retarding effect in the presence of 0.05 M triphenylmethane in the presence of either cobalt (II) acetate or cobalt (II) bromoacetate, about 91-95 percent retardation (Table 21 or Figure 17). Since about the same retardation is observed in the presence or absence of hydrogen bromide the reverse step must be slow and of little importance; therefore, one must conclude that the presence of significant amounts of the stable radicals during these competitive oxidation results from their slow reaction with oxygen. The reaction of oxygen with these radicals depends on the energy of activation which involves the necessary energy required to localize the free electron of the radical. The more stable the radical, the more the electron is spread through the molecule and the greater is the energy required to localize the electron for the formation of the bond.

From the results obtained above a mechanism for the retardation of the rate of oxidation of cyclohexene by triphenylmethane may be stated. For simplification all peroxy radicals are considered equal in reactivity, and cyclohexene and triphenylmethane are represented by R_IH and $R_{II}H$, respectively.

Initiation: $\text{Initiator} \xrightarrow{2ek_d} R'\cdot \xrightarrow[\text{very fast}]{O_2} ROO\cdot$

Propagation: $ROO\cdot + R_IH \xrightarrow{k_1} ROOH + R_I\cdot$

$ROO\cdot + R_{II}H \xrightarrow{k_2} ROOH + R_{II}\cdot$

$R_I\cdot + O_2 \xrightarrow{\text{very fast}} ROO\cdot$

$$R_{II}\cdot + O_2 \xrightarrow{k_3} ROO\cdot$$

Termination:

$$R_{II}\cdot + ROO\cdot \xrightarrow{k_4} R_{II}OOR$$

$$2ROO\cdot \xrightarrow{k_5} \text{non-radical products} + O_2$$

The expression for the disappearance of oxygen according to this mechanism is:

$$-\frac{dO_2}{dt} = R_i + k_1[ROO\cdot][R_IH] + k_3[R_{II}\cdot][O_2] - k_5[ROO\cdot]^2.$$

The following steady state equation may be given since the rate of initiation (R_i) is equal to the rate of termination (R_t) and the rate of formation of $R_{II}\cdot$ is equal to the rate of disappearance of $R_{II}\cdot$

$$R_i = R_t = 2k_4[R_{II}\cdot][ROO\cdot] + 2k_5[ROO\cdot]^2$$

$$k_2[ROO\cdot][R_{II}H] = k_4[R_{II}\cdot][ROO\cdot] + k_3[R_{II}\cdot][O_2]$$

The above expressions can be simplified by considering only the case where $R_{II}H$ is sufficiently large so that the termination between two peroxy radicals is unimportant. With this assumption the term $k_5\ ROO\cdot^2$ may be dropped from the rate and steady state expressions. Solving these two simplified steady state expressions gives:

$$[ROO\cdot] = \frac{k_4R_i + \sqrt{k_4^2R_i^2 + 8k_4k_2k_3R_i[O_2][R_{II}H]}}{4k_4k_2[R_{II}H]}$$

$$[R_{II}\cdot] = \frac{2R_ik_2[R_{II}H]}{k_4R_i + \sqrt{k_4^2R_i^2 + 8k_4k_2k_3R_i[O_2][R_{II}H]}}$$

Substitution of these values in the expression for the disappearance of oxygen and simplification give the following rate expression which agrees qualitatively with the results but which has not been tested experimentally:

$$-\frac{dO_2}{dt} - R_i = \frac{k_1[R_IH]}{2k_2[R_{II}H]} R_i + \sqrt{R_i^2 + 8k_2k_3/k_4R_i[O_2][R_{II}H]} + \frac{2k_2k_3/k_4\,[O_2][R_{II}H]}{R_i + \sqrt{R_i^2 + 8k_2k_3/k_4R_i[O_2][R_{II}H]}}$$

The apparatus required to test this expression must be more sensitive than the apparatus with which the preceding data has been obtained. However, if the proper equipment was at hand and the rate expression proved to be valid, the equation would provide a relatively simple method for obtaining the relative reactivities of highly reactive hydrocarbons such as triphenylmethane. At the present time there is no other method by which this information may be obtained.

Experimental

Procedure

The oxidation procedure has been described in the previous section.

Reagents

Triphenylmethane and fluorene were obtained from Matheson, Coleman and Bell, while triphenylethylene and 1,1-diphenylethylene were secured from Aldrich Chemical Co. Pentaphenylethane was prepared by the addition of diphenylbromomethane to triphenylmethyl sodium (78), and 1-naphthaldiphenylmethane was obtained by reduction of the corresponding carbinol which was prepared by the addition of 1-naphthylmagnesium bromide to benzophenone (79). 9-Phenylfluorene was of an unknown source (melting point after recrystalization, 145-7°). The solids were recrystalized until the melting points corresponded with literature values. The 1,1-diphenylethylene was distilled before use.

Bromobenzene from Matheson, Coleman and Bell was passed through silica gel before use. Other materials used have been mentioned in the previous experimental section.

SUMMARY

The relative reactivity of the alpha- and beta-hydrogen atoms of aralkyl hydrocarbons in photochlorination has been shown to be dependent on the concentration of the aromatic substrate. For example at 40° the relative reactivity of the alpha- and beta-hydrogen atoms of cumene is 42.2 for the photochlorination of the pure compound whereas at infinite dilution and in an inert solvent it is 3.5. At high aromatic concentrations the reacting radical is a complex between a chlorine atom and the aromatic substrate, but at low aromatic concentrations the uncomplexed and nonselective chlorine atom is responsible for reaction. The reactivity values obtained by extrapolation to infinite dilution of the hydrocarbon represents the true reactivity for the various positions of these compounds toward the chlorine atom.

The reaction of methylene with 2,3-dimethylbutane indicates no dependence on the solvent, although the reaction with benzene appears to depend on the aromatic character of the solution. The concentration ratio of products for the reaction of methylene with benzene, moles cycloheptatriene per mole toluene, may be varied from 3.2 to 4.8 by changing the solvent. The change may be explained through complexing of methylene with the aromatic compounds present in solution; nevertheless, it is questionable whether the small degree of variation with the nature of the solution warrants an explanation.

The rates of oxidation of hydrocarbons in the presence of oxygen and free radical initiators depends on the solvent; however, there is no correlation of the reaction rates with the ability of the solvent to form

pi-complexes, as found in photochlorination. Rather, the data correlate with the dielectric constant of the solvent.

A study concerning the effect of triphenylmethane and similar reactive compounds on the rate of oxidation of hydrocarbons such as cyclohexene and cumene indicates these materials can effectively retard free radical oxidations. The retardation is caused by the radical which results through abstraction of an hydrogen atom from the added hydrocarbon by a peroxy radical. Under the conditions of the reaction these relatively stable radicals react slowly with oxygen. However, they couple rapidly with peroxy radicals causing a reduction in the chain length of the propagation reaction and thus a decrease in the rate of oxidation.

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