Solvent Effects in the Reactions of Free Radicals and Atoms.   IX.   Effect of Solvent Polarity on the Reactions of Peroxy Radicals[1]

By Dale G. Hendry[2] and Glen A. Russell[3]

Received January 6, 1964

Small but significant effects of solvent polarity have been found in the autoxidation of a variety of olefins and aralkyl hydrocarbons. The solvent effect in the autoxidation of cyclohexene can be reasonably correlated with the dielectric constant of the solvent. Solvents of high polarity, such as nitromethane, favor the propagation reaction over the termination reaction. The rates of oxidation of a variety of alicyclic compounds are reported.

The kinetics of autoxidation of cyclohexene and cumene have been investigated in a number of solvents. In the presence of initiators such as azobisisobutyronitrile (AIBN) it is generally agreed that the rate is strictly first order in respect to hydrocarbon concentration.[4] However, plots of rates of oxidation at constant initiator concentration as a function of hydrocarbon concentration nearly always show some curvature,[4] presumably due to variations in the solvent composition. Figure 1 shows typical deviations from linearity for the oxidation of cyclohexene in benzene and cyclohexane solutions and the type of solvent effect observed when a polar solvent such as nitromethane is employed. Table I lists the observed rates of autoxidation of cyclohexene in a number of solvents.

TABLE I

Oxidation of Cyclohexene and Cumene in Various Solvents[a]

Solvent	Cyclohexene Rate $R_i/2$[b]	Cyclohexene $k_p/k_t^{1/2}$[c]	Cumene Rate $R_i/2$[b]	Cumene $k_p/k_t^{1/2}$[c]	Dielectric constant of solvent[d]
Cyclohexane	0.0306	0.48	....	...	2.0
t-Butylbenzene	.0315	0.54	0.0139	0.238	2.4
t-Butylnaphthalene	.0339	..	....	...	..
Benzene	.0342	0.54	....	...	2.3
Diphenyl ether	.0353	.67	0.0184	0.308	4.2
Carbon tetrachloride	.0364	.72	0.0158	0.255	2.2
Acetic acid	.0373	..	....	...	6.2
Benzotrifluoride	.0439	..	....	...	..
t-Butyl alcohol	.0445	..	....	...	11
Chlorobenzene	.0461	0.67	0.0187	0.274	5.6
1-Chloronaphthalene	.0464	0.75	....	...	5.0
m-Dichlorobenzene	.0480	..	....	...	5.0
3-Pentanone	.0500	..	....	...	17
2-Pentanol	.0520	..	....	...	..
2-Nitropropane	.0602	..	....	...	26
2-Propanol	.0613	..	....	...	18
Nitrobenzene	.0636	0.93	0.0237	0.346	35
Ethanol	.0693	..	....	...	24
Nitroethane	.0749	..	....	...	28
2-Butanone	.0752	..	....	...	19
Nitromethane	.0878	1.31	0.0233	0.338	36
Acetonitrile	.0921	1.28	0.0231	0.322	38
Dimethyl sulfoxide	.105	..	....	...	45

[a] 2.0 M hydrocarbon at 60° in the presence of 0.0504 M AIBN. [b] Mole/l.-hr. [c] (l./mole-hr.)$^{1/2}$; see text. [d] From "Technique of Organic Chemistry," Vol. 7, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1955.

(1) Directive Effects in Aliphatic Substitutions. XXVI. This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.
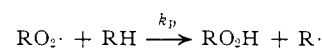(2) Ethyl Corporation Predoctoral Research Fellow, 1960–1961.
(3) Alfred P. Sloan Foundation Fellow, 1959–1963.
(4) G. A. Russell, J. Am. Chem. Soc., 79, 3871 (1957); H. S. Blanchard, ibid., 81, 4548 (1959); 82, 2014 (1960).
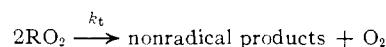
The accepted rate expression for the autoxidation of cyclohexene is

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

where R_i = rate of initiation = $2ek_d$[AIBN] and k_p and k_t are the rate constants for the propagation

$$RO_2\cdot + RH \xrightarrow{k_p} RO_2H + R\cdot$$

and termination reactions.[5]

$$2RO_2 \xrightarrow{k_t} \text{nonradical products} + O_2$$

Solvents could affect either the ratio $k_p/k_t^{1/2}$, the value of R_i, or the activity of cyclohexene. For a number of solvents the value of R_i was determined by the Hammond, Sen, and Boozer technique.[6]

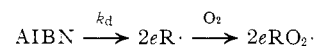$$AIBN \xrightarrow{k_d} 2eR\cdot \xrightarrow{O_2} 2eRO_2\cdot$$

Table II reports values of ek_d based on the assumption that 2,6-di-t-butyl-4-methylphenol reacts with 2.0 radicals when it is used as an inhibitor.

TABLE II

Inhibition Periods Observed in the Autoxidation of Cumene and Cyclohexene[a]

Solvent	Cyclohexene Inhibition period, min.	Cyclohexene $ek_d \times 10^6$, sec.$^{-1}$	Cumene Inhibition period, min.	Cumene $ek_d \times 10^6$, 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 ± .28	41.7 ± .7	4.00 ± .07
Chlorobenzene	25.7 ± 0.4	6.49 ± .09	25.5 ± .0	6.54 ± .00
Chloronaphthalene	28.5 ± 0.5	5.87 ± .10	31.7 ± .4	5.26 ± .07
t-Butylbenzene	33.8 ± 1.6	4.93 ± .21	35.1 ± .2	4.75 ± .03
Phenyl ether	40.5 ± 0.0	4.11 ± .00	42.8 ± 1.0	3.90 ± .10
Nitrobenzene	24.3 ± 2.5	6.87 ± .40	25.8 ± 0.7	6.46 ± .16
Nitromethane	14.0 ± 0.7	11.9 ± .5	25.6 ± 1.1	6.51 ± .26

[a] 1.9 M hydrocarbon at 60°, 0.0970 M AIBN, 1 × 10^{-3} M 2,6-di-t-butyl-4-methylphenol.

Agreement between ek_d values observed with cyclohexene and cumene was not good, particularly in the solvents which gave rise to the fastest oxidations, acetonitrile and nitromethane. The inhibition periods in nitromethane were poorly reproducible and depended on cyclohexene concentration. Table III lists some pertinent results.

The thermal decomposition of cyclohexenyl hydroperoxide in nitromethane [(ROOH)$_0$ = 0.085 M] gave a value for a first-order decomposition constant of 1.7 × 10^{-6} sec.$^{-1}$, $t_{1/2}$ = 110 hr. In acetonitrile solvent an

(5) D. G. Hendry and G. A. Russell, ibid., 86, 2371 (1964).
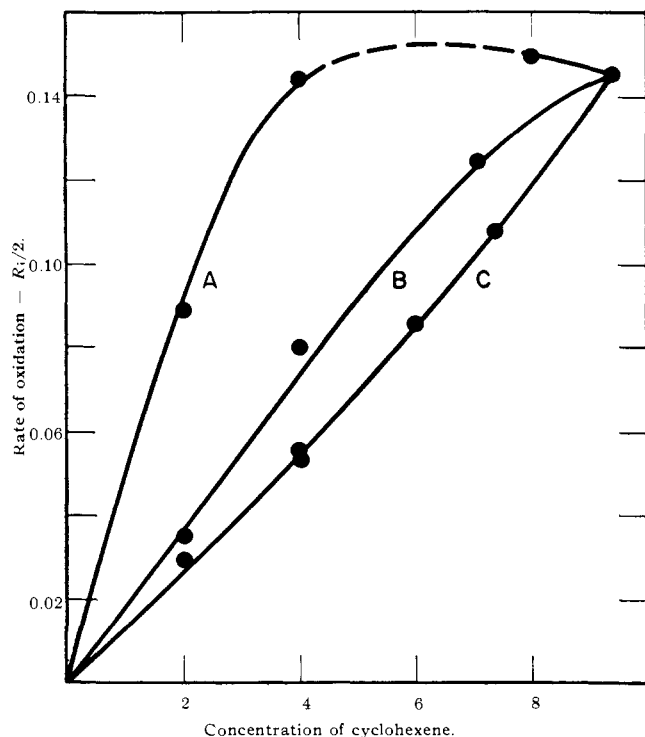(6) C. S. Hammond, J. N. Sen, and C. E. Boozer, ibid., 77, 3244 (1955).

Fig. 1.—Rate of oxidation as a function of cyclohexene concentration: A, nitromethane solvent (dashed line indicated heterogeneous region); B, benzene solvent; C, cyclohexane solvent. All data at 60° in the presence of 0.0504 M AIBN.

experimentally measured value of k_d for AIBN was 9.93×10^{-6} sec.$^{-1}$ at 60°. It thus appears that the inhibitor was not appreciably consumed by radicals produced from the thermolysis of cyclohexenyl hydroperoxide. Nevertheless, the data of Table III demand

Table III

Effect of Hydrocarbon Concentration on Inhibition Periods in Nitromethane[a]

Hydrocarbon	Concn., moles/l.	Inhibition, min.
Cumene	1.4	49
Cyclohexene	0.24	45
Cyclohexene	.48	43
Cyclohexene	.96	38
Cyclohexene	1.92	31
Cyclohexene containing cyclohexenyl hydroperoxide[b]	0.48	28
No AIBN present		~20 hr.

[a] AIBN = 0.0970 M, 2,6-di-t-butyl-4-methylphenol = 2 × 10^{-3} M. [b] 0.012 M.

that this hydroperoxide must destroy the inhibitor. Possibly an induced reaction (IH = phenolic inhibitor) is involved

$$\text{ROOH} + \text{IH} \longrightarrow \text{RO} \cdot + \text{I} \cdot + \text{H}_2\text{O}$$
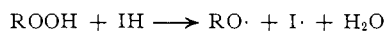
or cyclohexenyl hydroperoxide participates in a chain reaction with the inhibitor, for example

$$\text{I} \cdot + \text{ROOH} \longrightarrow \text{IOR} + \text{OH} \cdot$$

$$\text{OH} \cdot + \text{IH} \longrightarrow \text{H}_2\text{O} + \text{I} \cdot$$
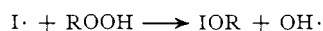
Similar reactions do not occur for cumene hydroperoxide.[7] In the present work the oxidation rate of cumene during the inhibition period was much less than that of cyclohexene and the concentration of hydroperoxide in solution must always have been less when

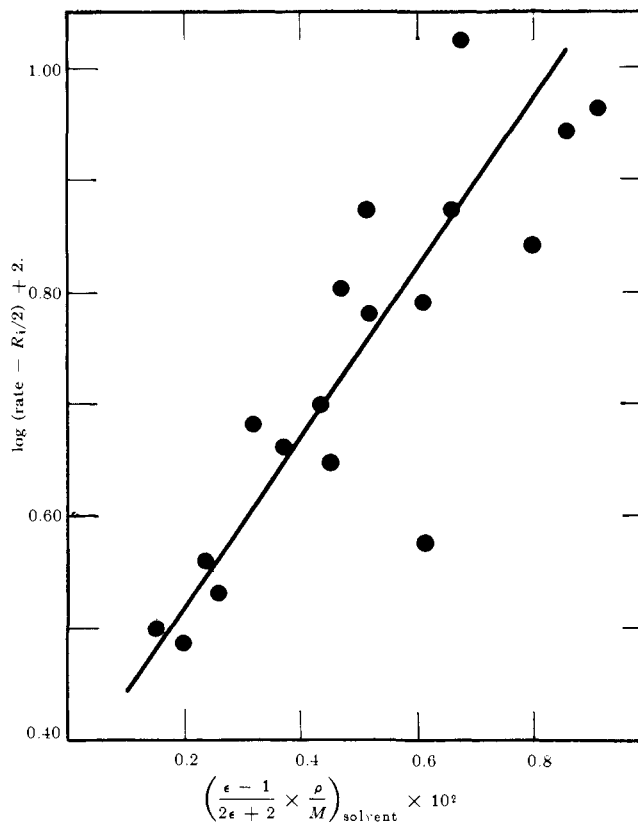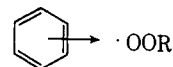(7) J. R. Thomas, *J. Am. Chem. Soc.*, **85**, 2166 (1963).

Fig. 2.—Correlation of oxidation of 2.0 M cyclohexene at 60° in various solvents and in the presence of 0.0504 M AIBN with Kirkwood–Onsager parameter according to the method of Powling and Bernstein.

cumene was used in the inhibition reaction. Values of $k_p/k_t^{1/2}$ entered in Table I were calculated using the ek_d values measured with cumene as a substrate.[8]

It is seen that the same solvent effect exists whether the rates of oxidation are considered or whether only the values of $k_p/k_t^{1/2}$ of Table I are considered. It seems certain that the observed solvent effect is connected mainly with a change in the ratios of $k_p/k_t^{1/2}$ rather than in changes of R_i. Plots of the rates of oxidation (or $k_p/k_t^{1/2}$) $vs.$ $(D - 1)/(2D + 1)$ for the solvent give a fairly smooth curve with no indication of specific solvent effects for compounds which could form π-complexes with peroxy radicals. The major effect involved seems to be a general solvent effect involving dielectric constant. Figure 2 shows the correlation of the log oxidation rate and the Kirkwood–Onsager parameter treated according to the method of Powling and Bernstein.[9] The rates of oxidation in acetic acid and ethanol appear to be 57 and 74% of that predicted by the correlation, respectively. Possibly the reactivity of the peroxy radical is reduced by hydrogen bonding. A

$$\text{ROO}\cdots\text{HX}$$
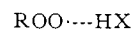
similar effect of acetic acid has been reported in the oxidation of cumene,[4] and hydrogen bonding has been

(8) Using inhibition times measured with cyclohexene as the substrate and with k_d = 9.6 × 10^{-6} sec.$^{-1}$ (J. P. Van Hook and A. V. Tobolsky, *ibid.*, **80**, 779 (1958)) leads to values of e greater than 1 in nitromethane and acetonitrile solution.

(9) J. Powling and H. J. Bernstein, *ibid.*, **73**, 1815, 4353 (1951).

suggested to be important in other autoxidation reactions.[10]

The rates of oxidation of several other hydrocarbons were measured in a "slow" solvent, chlorobenzene, and a "fast" solvent, nitromethane. Table IV lists pertinent results.

TABLE IV
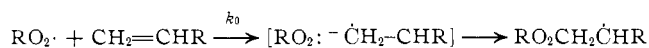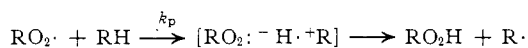OXIDATION OF HYDROCARBONS IN CHLOROBENZENE AND NITROMETHANE SOLUTION[a]

Hydrocarbon	Rate − $R_i/2$[b] Chlorobenzene	Nitromethane	Rate CH_3NO_2 Rate C_6H_5Cl
Cyclopentene	0.0718[c]	0.1088[c]	1.51
Cyclohexene	.0461	.0879	1.91
Cycloheptene	.0311	.0526	1.70
Cyclooctene	.0123	.0294[c]	2.41
1,5-Cyclooctadiene	.0596	.0931	1.56
1,3-Cyclohexadiene	2.06[d]	3.67[d]	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	.00732[e]	.0101[e]	1.38

[a] 2.0 M at 60° in presence of 0.0504 M AIBN.   [b] Moles/l.-hr.
[c] 2 × rate of 1.0 M solution.   [d] 11.8 × rate of 0.17 M solution.
[e] 1.33 × rate of 1.5 M solution.

Of the compounds listed in Table IV, 1,3-cyclohexadiene and bicyclo[2.2.1]heptadiene formed polymeric peroxides whereas all the other substrates formed hydroperoxides. However, the magnitude of the solvent effect is the same whether a hydroperoxide or a polymeric peroxide is the reaction product.

Discussion

The results presented demand that either the propagation or termination reaction of the autoxidation sequence are sensitive to the nature of the solvent. Possibly both reactions are sensitive to solvent. The effect is small but can be important in synthetic reactions. The propagation reaction involving either attack of a peroxy radical or saturated carbon–hydrogen bonds or addition to a conjugated olefin is known to involve a polar effect of the following type.[11]

$$RO_2\cdot + RH \xrightarrow{k_p} [RO_2: {}^-H\cdot {}^+R] \longrightarrow RO_2H + R\cdot$$

$$RO_2\cdot + CH_2{=}CHR \xrightarrow{k_0} [RO_2: {}^-\dot{C}H_2{-}CHR] \longrightarrow RO_2CH_2\dot{C}HR$$

It would be reasonable to attribute the increase in $k_p/k_t^{1/2}$ when the solvent polarity is increased to solvation of the polar transition state for the propagation reaction. Several of the experiments listed in Table IV were designed to test this idea. Thus, the polar nature of the transition state should be greater for allylic attack on cycloheptatriene than upon cycloheptene (due to the stability of the tropylium cation). A small effect in the right direction was observed (Table IV) with the autoxidation of cycloheptatriene being increased by 100% (nitromethane vs. chlorobenzene as solvent), whereas the same change in solvents only increased the rate of oxidation of cycloheptene by 70%. On the other hand, the transition state for attack of peroxy radicals on p-nitrocumene should possess less polar character than for attack on cumene but the solvent effect observed (Table IV) was 40% for p-nitrocumene and 26% for cumene.

Effects of changes in the dielectric constant of the solvent have been examined in the competitive attack of chlorine atoms upon saturated carbon–hydrogen bonds and no appreciable effect observed.[12] Effects of solvents on alternating tendencies in the copolymerization of styrene–methyl methacrylate and α-methylstyrene–maleic anhydride, systems where strong polar effects are believed to occur in the propagation reactions, have been studied and little, if any, effect observed.[13] In view of these observations, the solvent effect observed in the present study may be connected with the termination process wherein peroxy radicals with some polar character in their ground state

$$R{-}\ddot{O}{-}\ddot{O}\cdot \leftrightarrow R{-}\ddot{O}{-}\overset{+}{O}\cdot{}^-$$
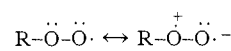
are converted to nonpolar products, possibly via a tetroxide. In this regard Cook and Norcross found significant solvent polarity effects in the disproportionation of 2,6-di-t-butyl-4-isopropylphenoxy radicals.[14] Phenoxy radicals are recognized to have polar states[15] due to resonance of type
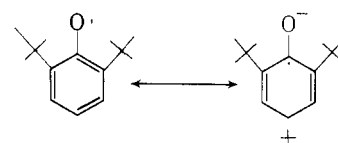
If it is assumed that the oxidation rates summarized in Table IV reflect only changes in k_p (i.e., k_t constant) it follows that in chlorobenzene solution at 60° the relative reactivities of cyclopentene:cyclohexene:indan:tetralin are 1:0.6:0.5:0.6 per α-hydrogen atom. Toward the phenyl radical at 60° the observed reactivity series is not significantly different, 1.0:1.2:0.8:1.3.[16] However, toward the bromine atom the cycloalkenes are much more reactive than the aralkanes, 1.0:0.2:0.07:0.06,[17] while toward the methyl radical the aralkanes are more reactive than the cycloalkenes in hydrogen abstraction, 1.0:0.2:8:12.[18] Since the electron affinity of the radicals involved are Br· > RO₂· > C₆H₅· > CH₃·, it would appear that the peculiar reversal in the reactivity series is due to a polar effect. As the attacking radical (X·) increases in electron affinity, the cycloalkenes become more reactive relative than their benzo analogs apparently because the contribution from resonance structure I is more important than the contribution from II.

Experimental

Oxidation Procedure.—The general procedure has been described elsewhere.[11] Oxidates were analyzed for hydroper-

(10) E. T. Denisov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 53 (1960); F. F. Rust and E. A. Youngman, J. Org. Chem., 27, 3778 (1962).
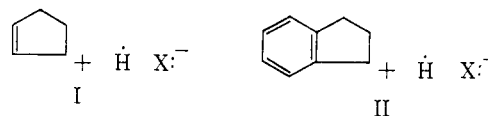
(11) G. A. Russell and R. C. Williamson, Jr., J. Am. Chem. Soc., 86, 2357 (1964).

(12) G. A. Russell, ibid., 80, 4987 (1958).

(13) C. Walling and F. R. Mayo, J. Polymer Sci., 3, 895 (1948); C. C. Price and J. G. Walsh, ibid., 6, 239 (1951).

(14) C. D. Cook and B. E. Norcross, J. Am. Chem. Soc., 81, 1176 (1959).

(15) E. Mueller, K. Ley, and W. Kiedaisch, Ber., 88, 1819 (1955).

(16) R. F. Bridger and G. A. Russell, J. Am. Chem. Soc., 85, 3754 (1963).

(17) G. A. Russell and K. M. Desmond, ibid., 85, 3139 (1963).

(18) J. Gresser, A. Rajbenbach, and M. Szwarc, ibid., 83, 3005 (1961); J. A. Meyer, V. Stannett, and M. Szwarc, ibid., 83, 25 (1961).

oxide by the procedure of Barnard and Hargrave.[19] In this analysis nitromethane interfered slightly and a blank correction obtained using the same amount and concentration of nitromethane was applied. Table V summarizes typical hydroperoxide yields. It is not believed that the solvents employed (Table I) were involved in a cooxidation sequence. In the absence of cyclohexene or cumene the solvents themselves did not undergo oxidation at a significant rate. Moreover, many of the solvents would be inert to peroxy radical attack because of the polar effect of electron-withdrawing functional groups such as nitro, cyano, sulfoxide, carbonyl, and carboxyl substituents. Substituents such as ethers, sulfides, amines, or amides were not employed because of the possible complications from cooxidation.

TABLE V

Hydroperoxide Yields in Autoxidation of Cyclohexene[a]

Hydrocarbon	Solvent	% of absorbed O_2 found as ROOH
Cyclohexene	CH_3NO_2	101
Cyclohexene	$(CH_3)_2CHOH$	104
Tetralin	CH_3NO_2	93
Cycloocta-1,5-diene	CH_3NO_2	90
Cycloheptene	CH_3NO_2	65
Cycloheptatriene	CH_3NO_2	47
Cycloheptatriene	C_6H_5Cl	36
Cyclooctene	C_6H_5Cl	62
Cyclopentene[b]	CH_3NO_2	70
Norbornadiene	CH_3NO_2	9

[a] 2.0 M hydrocarbon at 60° in presence of 0.0504 M AIBN. [b] 1.0 M hydrocarbon.

(19) D. Barnard and K. Hargrave, Anal. Chem. Acta, 5, 476 (1951).

Reagents.—Research grade cyclopentene (99.89 mole %), cyclohexene (99.98 mole %), and cumene (100.0 mole %) were obtained from Phillips Petroleum Co. Cycloheptene was prepared by the reduction of cycloheptanone by lithium aluminum hydride followed by elimination of water catalyzed by naphthalenesulfonic acid. Cyclooctene and cycloocta-1,5-diene were gifts from Cities Service Research and Development Co., while cycloheptatriene and norbornadiene were gifts from Shell Chemical Co. Indan (Aldrich Chemical Co.) and tetralin (Matheson, Coleman and Bell) were shaken with sulfuric acid, washed, and dried. Cyclohexa-1,3-diene was prepared by bromination of cyclohexene with N-bromosuccinimide followed by quinoline-catalyzed dehydrobromination.[20] The preparation of p-nitrocumene has already been described.[11]

The hydrocarbons other than those of research grade were rectified in a Todd column with a monel spiral and center fractions selected having constant boiling points and having no impurities detectable by gas chromatography. The purified hydrocarbons were passed through silica gel under a dry nitrogen atmosphere and stored under nitrogen prior to use. Cyclohexenyl hydroperoxide was prepared by oxidizing a large volume of cyclohexene to the extent of a few per cent with AIBN and oxygen. The excess cyclohexene was removed at reduced pressure and the hydroperoxide fractionated in vacuo. Purity by hydroperoxide analysis was 82.5%.

Solvents.—Commercial solvents were distilled prior to use and where possible passed through a silica gel column prior to use. t-Butylnaphthalene was prepared by the reaction of t-butyl alcohol with naphthalene in the presence of boron trifluoride and phosphoric anhydride. Distillation gave material, b.p. 84–89° (1 mm.), $n^{20}D$ 1.5694, which was passed through silica gel before use.

(20) G. S. Hammond and J. Warkentin, J. Am. Chem. Soc., 83, 2554 (1961).

[Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa]

Retarding Effects of Polyarylmethanes in Autoxidation Reactions[1,2]

### By Dale G. Hendry[3a] and Glen A. Russell[3b]

Received January 6, 1964

The retarding effect of polyarylmethanes or polyarylalkenes on the autoxidation of cyclohexene or cumene has been established to be due to the low reactivity of the polyarylmethyl radicals formed by attack of peroxy radicals. The polyarylmethyl radicals can persist in the presence of oxygen and retard the reaction by trapping peroxy radicals to give nonradical products. Abilities of polyarylmethanes to inhibit autoxidation reactions parallel and are a measure of the resonance stabilization of the polyarylmethyl radicals. Inhibition of this type becomes more pronounced as the temperature is raised.

The rate of autoxidation is generally retarded by materials which destroy the chain-propagating free radical intermediates. The effectiveness of phenols and anilines as inhibitors depends on the reactivity of these substances with peroxy radicals and the inability of the resulting phenoxy or anilino radicals to carry on effectively the chain oxidation.[4]

The presence of substances which give rise to peroxy radicals which readily terminate can bring about a retardation of the autoxidation of substances which yield peroxy radicals that terminate at a slower rate.[5] Thus small amounts of tetralin drastically retard the oxidation of cumene even though tetralin is more reactive than cumene toward peroxy radicals.[5,6] In this competitive oxidation it can be proved that only peroxy radicals are involved in the termination process.[5]

We herein describe another type of retardation in the cooxidation of hydrocarbons (RH and AH). When one of the hydrocarbons (AH) forms an alkyl radical which reacts only slowly with oxygen, retardation can result from the sequence of reactions

$$\text{ROO} \cdot + \text{AH} \longrightarrow \text{ROOH} + \text{A} \cdot$$

$$\text{ROO} \cdot + \text{A} \cdot \longrightarrow \text{ROOA}$$
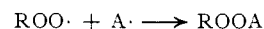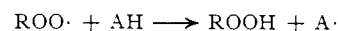
Such retardation is apparently widespread in high temperature vapor phase autoxidations. Thus, toluene, ethylbenzene, or cumene retard the oxidation of alkanes in the vapor phase at 250° with the formation of dimers and disproportionation products derived from the resulting benzyl radicals.[7] Propylene retards the oxidation of propane presumably through the formation of the relatively stable allyl radical,[8] and diisobutylene inhibits the high temperature oxidation of heptane.[9]