ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Nature of the Polar Effect in Reactions of Atoms and Radicals. II. Reactions of Chlorine Atoms and Peroxy Radicals[1,2]

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The attack of chlorine atoms upon substituted toluenes and of peroxy radicals upon substituted cumenes has been found to show a polar effect best correlated by σ^+-constants. Polar effects in the oxidation of substituted styrenes were found, but the rates of autoxidation of benzyl phenyl ethers were found to be insensitive to the nature of substituents. No polar effect could be found when the reactivities of styrenyl and *p*-nitrostyrenyl radicals toward molecular oxygen were compared.

Competitive photochlorinations of *m*- and *p*-substituted toluenes have been performed by Van Helden and Kooyman[4] and by Walling and Miller.[5] Although both groups of workers found the Hammett $\rho\sigma$-relationship to be obeyed, there were quantitative differences between the two sets of results. Depending upon how the data are treated, either a better σ- or σ^+-correlation can be shown.[6,7] Since the previous work involved different solvents as well as high concentrations of the toluene derivatives which might have influenced the relative reactivities by complexing the chlorine atom,[8] we have repeated the competitive photochlorinations in dilute carbon tetrachloride solution using several *p*-substituted toluenes wherein the substituents have significantly different σ- and σ^+-constants.

We have also repeated the autoxidation of a series of substituted cumenes[9] using the *p*-methoxy substituent to allow a distinction between σ- and σ^+-correlations. In addition, the oxidations of a number of alkyl benzyl ethers and substituted benzyl ethers were investigated as well as the co- and terpolymerization of oxygen with substituted styrenes.

Results

Photochlorination of Substituted Toluenes.—Table I lists the results obtained in the competitive photochlorination of a series of substituted toluenes. The disappearance of the hydrocarbons was determined by gas–liquid chromatography (g.l.c.) and relative reactivities calculated by the equation

$$k_A/k_B = \frac{\log([A]_f/[A]_i)}{\log([B]_f/[B]_i)}$$

where the subscripts refer to final and initial concentrations. The competitive chlorination of toluene and *p*-chlorotoluene was performed at several concentrations of aromatics, including benzene solution, to ascertain if the relative reactivities were solvent dependent. No dependence on solvent was noted. This result is contrary to an earlier report by Walling and Miller, who found an effect of benzene upon this competitive chlorination.[5] Nevertheless, the total initial aromatic hydrocarbon concentration in Table I was held at a constant and fairly low value (1 *M*) to minimize possible solvent effects.

When the data of Table I (with the exception of the *m*-phenoxy substituent for which a σ^+-constant is not available) were plotted as a function of σ- and σ^+-parameters, the best linear correlation with σ-constants[10] had a ρ of -0.76 with a std. dev. of 0.06 log unit, whereas the σ^+-correlation[11] had a ρ of -0.66 with a std. dev. of 0.02 log unit. Previous σ-correlations have given values of $\rho = -0.76$ at 70° (photochlorination, no added solvent)[5] and -1.50 at 80° (surfuryl chloride chlorination, benzene solution).[4]

TABLE I

COMPETITIVE PHOTOCHLORINATIONS AT 40° IN CARBON TETRACHLORIDE

Hydrocarbon A	$[A]_i$[a]	$[A]_f$[a]	$[B]_i$[b]	$[B]_f$[b]	k_A/k_B	Estimated uncertainty
p-Phenoxytoluene	0.204	0.113	0.806	0.636	2.50	±0.02
p-Phenyltoluene	.500	.290	.395	.278	1.55	± .01
p-Xylene	.807	.404	.660	.535	1.57[c]	± .01
m-Xylene	.763	.430	.654	.525	1.30[c]	± .02
m-Phenoxytoluene	.399	.226	.596	.307	0.86	± .01
p-Chlorotoluene	.667	.490	.333	.230	.79	± .01
p-Chlorotoluene	.266	.0196	.0133	.0092	.79	± .02
p-Chlorotoluene[d]	.667	.520	.333	.240	.79	± .01
m-Chlorotoluene	.582	.320	.330	.120	$.59_5$	± .005
p-Nitrotoluene	.734	.715	.294	.270	.32	± .01

[a] Initial and final concentration, mole l.$^{-1}$. [b] Toluene. [c] Statistically corrected. [d] Benzene solvent.

Autoxidation of Substituted Cumenes.—Table II summarizes the rates of autoxidation (R_o) of a series of cumene derivatives in the presence of azobisisobutyronitrile (AIBN) at 60° (e = efficiency of initiation).

$$\mathrm{AIBN} \xrightarrow{k_d} 2e\mathrm{R}\cdot \xrightarrow{\mathrm{O_2}} 2e\ \mathrm{RO_2}\cdot$$

$$\mathrm{C_6H_5C(CH_3)_2OO}\cdot + \mathrm{C_6H_5CH(CH_3)_2} \xrightarrow{k_p} \mathrm{C_6H_5C(CH_3)_2OOH} + \mathrm{C_6H_5(CH_3)_2}\cdot$$

$$2\mathrm{C_6H_5C(CH_3)_2OO}\cdot \xrightarrow{k_t} \text{nonradical products}$$

Relative values of $k_p/k_t^{1/2}$ were calculated from the equations[12]

$$R_o = k[\mathrm{RH}](R_i)^{1/2}/(2k_t)^{1/2} + R_i/2; \quad R_i = 2ek_d[\mathrm{AIBN}]$$

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(4) R. Van Helden and E. C. Kooyman, *Rec. trav. chim.*, **73**, 269 (1954).

(5) C. Walling and B. Miller, *J. Am. Chem. Soc.*, **79**, 4181 (1957).

(6) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

(7) P. D. Bartlett and C. Ruchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960).

(8) G. A. Russell, *ibid.*, **80**, 4987, 4997, 5002 (1958).

(9) G. A. Russell, *ibid.*, **78**, 1047 (1956).

(10) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(11) σ^+-Constants of H. C. Brown and Y. Okamoto (*J. Am. Chem. Soc.*, **80**, 4979 (1958)) were used for all substituents except *p*-phenoxy for which a value of -0.57 was derived by comparison of the rates of solvolysis of benzhydryl chlorides (J. Packer, J. Vaughan, and A. P. Wilson, *J. Org. Chem.*, **23**, 1215 (1958)) with twelve other σ^+-constants of Brown and Okamoto.

(12) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

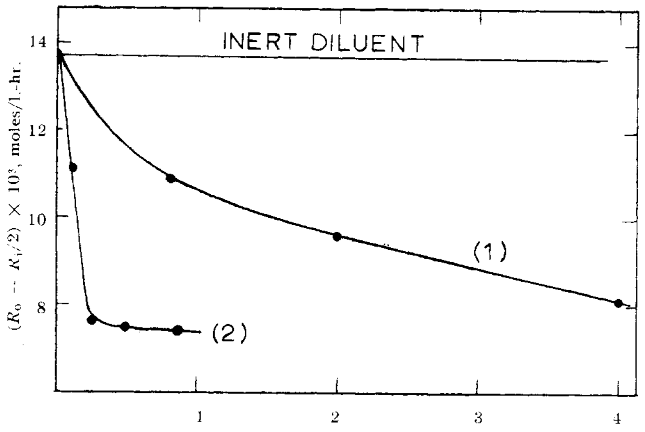

Fig. 1.—Effect of anisole (1) and diphenyl ether (2) on the rate of oxidation of 1.0 *M* cumene in chlorobenzene at 60°, 0.10 *M* AIBN.

The rates of oxidation of *p*-methoxy-, *p*-*t*-butoxy-, and *p*-phenoxycumene (Table II) were surprisingly low. We, therefore, investigated the effects of other aromatic ethers on the oxidation of cumene. Figure 1 shows that both anisole and diphenyl ether retard the oxidation of cumene more than would have been expected for an inert diluent. We feel this is a solvent effect which may be partially connected with the efficiency of initiation of the reactions.[13]

TABLE II

RATES OF OXIDATION OF CUMENES (1.0 *M*) AT 60°[a]

Substituent	Solvent	$(R_o - R_i/2) \times 10^3$[b]	$k_p/k_t^{1/2}$[c]	Rel. value $k_p/k_t^{1/2}$	
None	C_6H_5Cl	13.4	0.275	1.00[d]	
None	CH_3CO_2H	11.1	.23		1.0[d]
p-Methoxy	C_6H_5Cl	19.7	.405	1.47	
p-*t*-Butoxy	C_6H_5Cl	17.4	.358	1.30	
p-Phenoxy	C_6H_5Cl	16.5	.339	1.23	
p-Isopropyl	C_6H_5Cl	18.3[e]	.377[e]	1.37[e]	
p-Isopropyl	CH_3CO_2H	15.3[e]	.32[e]		1.4[e]
p-Bromo	C_6H_5Cl	11.3	.232	0.84	
p-Bromo	CH_3CO_2H	9.4	.19		0.83
p-Carbomethoxy	C_6H_5Cl	8.4	.17	0.62	
p-Carbomethoxy	CH_3CO_2H	8.2	.17		0.74
p-Nitro	C_6H_5Cl	6.5	.13	0.49	
p-Nitro	CH_3CO_2H	6.3	.13		0.56

[a] In the presence 0.10 *M* AIBN. [b] Mole/l.-hr.; $R_i = 1.31 \times 10^{-6}$ mole/l.-sec. (ref. 13). [c] $(\text{l./mole-hr.})^{1/2}$. [d] Assumed. [e] Statistically corrected.

TABLE III

COMPETITIVE AUTOXIDATION OF CUMENE, *p*-METHOXYCUMENE, AND *p*-NITROCUMENE[a]

Cumene[b]		*p*-Methoxy-cumene[b]		*p*-Nitrocumene[b]		Initial rate $(R_0 - R_i/2) \times 10^3$[c]
C_i	C_f	C_i	C_f	C_i	C_f	
1.000	...	...	...	...	...	13.7
0.800	0.630	0.200	0.129	...	...	..
.500	.390	.500	.294	...	...	15.8
.200	.160	.800	.300	...	...	..
...	...	1.000	...	...	...	19.7
0.800	0.618	...	...	0.200	0.171	..
0.500	0.385	...	...	0.500	0.435	10.1
...	...	...	...	1.000	...	6.75

[a] 0.10 *M* AIBN at 60°. [b] Moles/l., initial and final concentration in benzene solution. [c] Moles/l.-hr. in chlorobenzene solution.

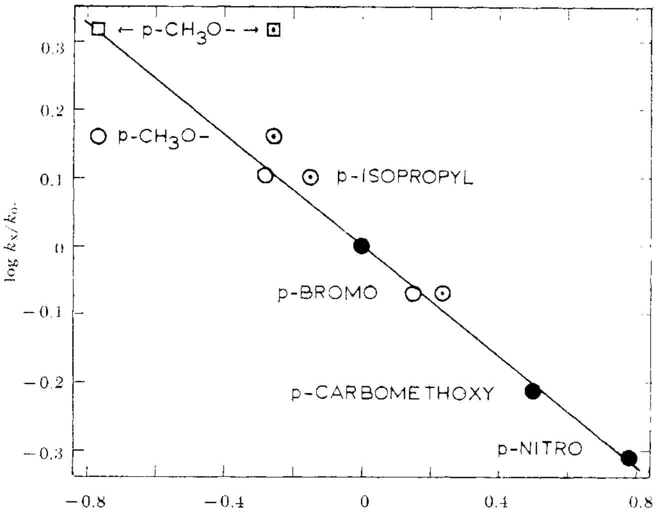

Fig. 2.—Correlation of reactivity of substituted cumenes (k_x) and cumene (k_o) toward peroxy radicals at 60°: ●, σ- = σ^+-constants; ○, σ^+-constant; ⊙, σ-constant; □, data from competitive oxidations in benzene. All other data for chlorobenzene solution.

Competitive autoxidations of cumene and *p*-methoxycumene were performed to ascertain relative values of k_p. We also performed competitive autoxidation of cumene and *p*-nitrocumene even though nitrobenzene does not retard the autoxidation of cumene in excess of that expected for an inert diluent. Pertinent data are summarized in Table III. Concentrations were determined by gas–liquid chromatography after column chromatography to remove oxidative products.

Treatment of the above data by the "Copolymerization" equation[14] demonstrates that toward the cumylperoxy radical, *p*-methoxycumene is 2.2 times as reactive as cumene while toward the *p*-methoxycumylperoxy radical, the relative reactivity is 2.1. The competitive experiments utilizing *p*-nitrocumene indicate that toward the cumylperoxy radical cumene is 1.5 times as reactive as *p*-nitrocumene. This value compares with relative $k_p/k_t^{1/2}$ values (Table II) of 2.2 in chlorobenzene and 1.6 in acetic acid for cumene and *p*-nitrocumene.

If it is assumed that values of k_t are independent of the substituent, relative values of k_p can be calculated from Table II which in conjunction with the cooxidation results (indicating a reactivity of *p*-methoxycumene 2.2 times that of cumene) lead to the σ- and σ^+-correlations shown in Fig. 2. A σ^+-correlation ($\log k_x/k_o = -0.41\sigma^+$, std. dev. < 0.01 log unit) is obviously preferred. The best σ-correlation has a std. dev. of 0.09 log unit. The rates in acetic acid also appear to fit a σ^+-correlation. However, oxidation rates of the *p*-alkoxycumenes could not be obtained in acetic acid since after a very brief period of oxygen absorption all oxidation ceased. Apparently the initially formed hydroperoxide underwent an acid-catalyzed decomposition to the corresponding *p*-alkoxyphenol which served as an effective oxidation inhibitor.

Autoxidation of Substituted Styrenes.—Competitive oxidations of styrene, *p*-nitrostyrene, and *p*-methoxystyrene were performed at 60° in benzene solution. The rates of oxidation were measured and the unreacted styrenes determined by g.l.c. at the end of the reaction. Table IV summarizes the results.

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(13) D. G. Hendry and G. A. Russell, *J. Am. Chem. Soc.*, **86**, 2368 (1964).

(14) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

TABLE IV

COMPETITIVE AUTOXIDATION OF STYRENES[a]

Styrene[b]		p-Methoxy-styrene[b]		p-Nitrostyrene[b]		$(R_o - R_i/2) \times 10^3$ [c]	$k_p/k_t^{1/2}$ [d]
C_i	C_f	C_i	C_f	C_i	C_f		
1.000	...	...	...	...	...	66.1	1.37
...	...	1.000	...	...	...	103	2.12
...	...	...	...	1.000	...	65.5	1.35
0.800	0.675	0.200	0.156	...	...	...	..
.500	.415	.500	.376	...	...	82.0	..
.200	.162	.800	.617	...	...	...	..
.800	.620	...	...	0.200	0.175	65.5	..
.500	.430	...	...	.500	.462	65.5	..
.200	.130	...	...	.800	.724	65.5	..
...	...	0.640	0.392	.200	.171	...	..
...	...	.400	.226	.500	.406	73.7	..
...	...	.160	.0615	.800	.691	...	..

[a] Ten ml. of a benzene solution at 60° containing 0.10 M AIBN. [b] Moles/l., initial and final concentration. [c] Moles/l.-hr.; R_i taken as 1.31×10^{-6} moles/l.-sec. (ref. 13). [d] (l./mole-hr.)$^{1/2}$.

Solutions of the "Copolymerization" equation using the data of Table IV are summarized in Table V.

TABLE V

RELATIVE PROPAGATION CONSTANTS BETWEEN STYRENYLPEROXY RADICALS AND STYRENES

M_1	M_2	k_{11}/k_{12}[a]	k_{22}/k_{21}[a]
p-Methoxy-styrene	p-Nitrostyrene	3.2, 2.8, 1.4, *2.3*	0.45, 0.08, 0.05, *0.17*
Styrene	p-Methoxy-styrene	0.70, 0.64, 0.39, *0.55*	1.62, 1.18, 1.10, *1.2*
Styrene	p-Nitrostyrene	1.90, 1.69, 1.00, *1.5*	0.52, 0.10, 0.07, *0.22*

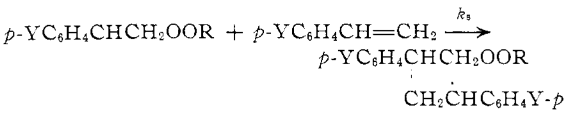
Radical	Substrate	Rel. react.
p-Methoxystyrenylperoxy	p-Methoxystyrene	1.2 ± 0.2
	Styrene	1.0[b]
	p-Nitrostyrene	0.5 ± 0.2
Styrenylperoxy	p-Methoxystyrene	1.8 ± 0.2
	Styrene	1.0[b]
	p-Nitrostyrene	0.6 ± 0.2
p-Nitrostyrenylperoxy	p-Methoxystyrene	1.2 ± 1
	Styrene	1.0[b]
	p-Nitrostyrene	0.2 ± 0.1

[a] $M_1OO\cdot + M_1 \xrightarrow{k_{11}} M_1OOM_1\cdot$, etc. The "Copolymerization" equation has been solved by machine to give an equation, $k_{11}/k_{12} = a + bk_{22}/k_{21}$. Three experiments yield three lines and three intersections when k_{11}/k_{12} and k_{22}/k_{21} are plotted against each other. The intersections are given together with the center of gravity (in italic type) for the triangle thus formed. [b] Assumed.

The data of Table V show a consistent qualitative trend. The limited data indicate that toward the styrenylperoxy radical a σ^+-correlation ($\rho = -0.3$) is preferred, but toward the p-methoxystyrenylperoxy radical a σ-correlation ($\rho = -0.4$) gives better agreement.

Polar Effects in the Reactions of Styrenyl Radicals with Oxygen.—Another polar effect was investigated in the autoxidation of p-nitrostyrene, namely, the question of whether a polar effect exists in the very rapid reaction

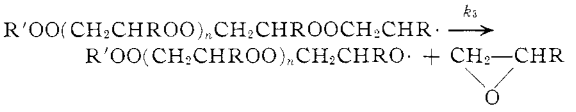
$$p\text{-}YC_6H_4CHCH_2OOR + O_2 \xrightarrow{k_o} p\text{-}YC_6H_4CH(O_2\cdot)CH_2OOR \quad (1)$$



$$p\text{-}YC_6H_4CHCH_2OOR + p\text{-}YC_6H_4CH{=}CH_2 \xrightarrow{k_s} p\text{-}YC_6H_4\underset{\underset{CH_2\dot{C}HC_6H_4Y\text{-}p}{\vdots}}{C}HCH_2OOR$$

(2)

Comparison of k_o with k_s was attempted by analysis of the polymeric peroxides formed, but for Y = hydrogen[15] and nitro an exact 1:1 copolymer (within analytical limits) was formed at 60° in a solution saturated with oxygen at a pressure of 1 atm. A more sensitive test for a polar effect of Y on reaction 1 appeared to be an analysis of the benzaldehydes formed by the spalation reaction (4)[16]



(3)

$$R'OO(CH_2CHROO)_nCH_2CHRO\cdot \xrightarrow{k_4} R'O\cdot + (n + 1)CH_2O + (n + 1)RCHO \quad (4)$$

A polar effect lowering the magnitude of k_o might be expected to increase the probability of occurrence of reactions 3 and 4. Table VI shows that at high oxygen pressures reactions 3 and 4 do have a higher probability when Y is nitro, but at lower oxygen pressures reactions 3 and 4 are actually less favored when Y is nitro. The data thus gave no evidence of a polar effect in the peroxidation step (reaction 1) when Y is a powerful electron-withdrawing group.

TABLE VI

BENZALDEHYDES FORMED IN THE OXIDATION OF STYRENE AND p-NITROSTYRENE[a]

	Mole aromatic aldehyde / Mole oxygen absorbed[b]	
Oxygen press., mm.	Styrene	p-Nitrostyrene
50	0.700	0.458
100	.592	.350
250	.390	.319
500	.200	.268
710	.160	.220
2280	.103	.154

[a] 1 M in m-dichlorobenzene solutions containing 0.10 M AIBN at 60°. [b] Approximately 1 mmole of oxygen absorbed per 10 ml. of solution.

Autoxidation of Benzyl Ethers.—Polar effects were also investigated in the oxidation of benzyl ethers. Results of rate studies are summarized in Table VII.

TABLE VII

RATES OF OXIDATION OF BENZYL ETHERS[a]

Entry no.	Ether ($YC_6H_4CH_2OR$) Y =	R =	$(R_o - R_i/2) \times 10^3$ [b]	$k_p/k_t^{1/2}$ [c]	Rel. value of $k_p/k_t^{1/2}$
1	p-CH$_3$O	C_6H_5	4.6	0.095	0.46
2	p-CH$_3$	C_6H_5	8.5	.175	.85
3	m-CH$_3$	C_6H_5	7.8	.161	.78
4	H	C_6H_5	7.2	.148	.72
5	p-Cl	C_6H_5	7.0	.144	.70
6	m-Cl	C_6H_5	6.6	.136	.66
7	p-NO$_2$	C_6H_5	7.5	.155	.75
8	m-NO$_2$	C_6H_5	5.7	.118	.57
9	H	p-CH$_3$C$_6$H$_4$	8.1	.167	.81
10	H	p-NO$_2$C$_6$H$_4$	8.1	.167	.81
11	H	$CH_2C_6H_5$	67.6	.695[d]	3.4[d]
12	H	$C(CH_3)_3$	29.4	.605	2.9
13	H	CH_2CH_3	21.6	.445	2.2
14	H	CH_3	20.1	.415	2.0
15	H	H	10.0	.206	1.0
16	m-CH$_3$	CH_3	20.1	.415	2.0
17	p-Cl	CH_3	20.1	.415	2.0

[a] In chlorobenzene solution at 60° containing 0.10 M AIBN. [b] Moles/l.-hr.; R_i taken as 1.31×10^{-6} mole/l.-sec. (ref. 13). [c] (l./mole-hr.)$^{1/2}$ [d] Statistically corrected.

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(15) A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.*, **78**, 1017 (1956).

(16) F. R. Mayo, *ibid.*, **80**, 2465 (1958).

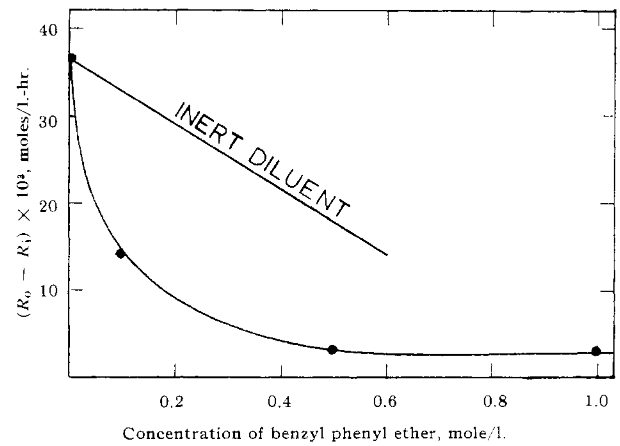


Fig. 3.—Rates of oxidation of mixtures of dibenzyl ether and benzyl phenyl ether in chlorobenzene at 60°; total concentration of benzylic methylene groups held constant at 1.0 *M*; 0.10 *M* AIBN.

A comparison of entries 2–7 in Table VII leads to the conclusion that attack of peroxy radicals on $Y-C_6H_4-CH_2OC_6H_5$ is rather insensitive to the nature of Y. Entries 16 and 17 show the same lack of polar sensitivity for $Y-C_6H_4CH_2OCH_3$. Entries 9 and 10 in the table suggest that benzylic attack on $C_6H_5CH_2OC_6H_4-Y$ by peroxy radicals is also quite insensitive to the nature of Y. However, there is a variation in rate of autoxidation of compounds of the type $C_6H_5CH_2OR$ as R is varied from hydrogen to phenyl or alkyl (entries 4, 11–15). The rate of oxidation of dibenzyl ether and the benzyl alkyl ethers appeared too large in view of the rates observed for other ethers, particularly when considered in view of reasonable inductive parameters for R. We therefore investigated the oxidation of dibenzyl ether with the idea that for some reason k_t might be less for dibenzyl ether and the benzyl alkyl ethers than for the benzyl phenyl ethers. One test to determine qualitatively significant differences in termination rate constants in competitive autoxidations involves the shape of plots of oxidation rates *vs.* composition of a two-component (plus solvent) mixture.[12] If values of k_t are nearly the same an additive rate should result, while if values of k_t differ greatly the observed rates should be less than the additive value. Figure 3 shows that this is indeed the case when dibenzyl ether and benzyl phenyl ether are competitively oxidized. Benzyl phenyl ether in 0 to 0.6 *M* concentrations depresses the rate of oxidation of a 1 *M* mixture of dibenzyl and benzyl phenyl ether below that expected if an inert diluent had been substituted for the benzyl phenyl ether. Dibenzyl ether and benzyl ethyl ether were each competitively autoxidized with styrene in a separate study.[17] Solution of the "Copolymerization" equation showed that both ethers had about the same reactivity per benzylic methylene group toward styrenylperoxy radicals (dibenzyl ether = 0.85, benzyl ethyl ether = 0.75, tetralin = 1.00).

Discussion

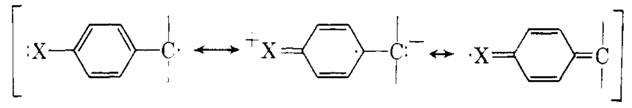
The results summarized in the previous section have demonstrated that: (a) in carbon tetrachloride solution the attack of chlorine atoms on benzylic hydrogen atoms follows the σ^+-rather than the σ-constants of substituents in the aromatic ring, (b) a σ^+-correlation is preferred in the attack of peroxy radicals upon substituted cumenes, (c) electron-withdrawing substituents deactivate and electron-supplying substituents activate substituted styrenes in addition reactions involving peroxy radicals, (d) the reactivities of a variety of benzyl and phenyl ethers toward peroxy radicals are rather insensitive to polar substituents in the benzyl or phenyl nucleus, (e) the reactivity of substituted styrenyl radicals toward oxygen does not show a pronounced polar effect.

All electron-poor radicals or atoms display pronounced polar effects in their attack on carbon–hydrogen bonds. This is undoubtedly due to contributions to the transition state of resonance structure I.

$$[\text{R-H X}\cdot \leftrightarrow \text{R}\cdot\overset{+}{\text{H}}\ \text{X:}^- \leftrightarrow \text{R}\cdot\text{H-X}]$$

I

For attack on benzylic hydrogen atoms all or nearly all electron-seeking radicals or atoms give rise to rate data best correlated by σ^+-parameters.[18] When the attacking radical or atom has a low electron affinity, for example, the phenyl radical[19] and presumably the methyl radical, no polar effect exists, even though the energy of activation and hence the degree of bond breaking is greater for the phenyl radical than for the highly reactive but electron-seeking chlorine atom.[19] This rules out the explanation[20] that the polar effect results from resonance structures for the incipient aralkyl radical of the type



That is, the polar effect in reactions of this type is concerned with the nature of the attacking radical and not with the resonance stabilization of the resulting benzylic radical.

It is interesting to compare the magnitude of the polar effect in the attack of radicals and atoms upon benzylic hydrogen atoms. It has been emphasized that the magnitude of this effect for attack upon a given substrate or group of similar substrates is best understood by considering two factors: (a) the electron affinity of the attacking atom or radical and (b) the degree of bond breaking in the transition state.[6] In general, substitutions at benzylic hydrogen atoms involve a variable degree of bond breaking and any increase in bond breaking (through a decrease in the reactivity of the attacking radical) will favor polar and other resonance contributions to the transition state (resonance structure I). Table VIII summarizes those substitutions wherein clearly defined ρ's are now available. In every case but for the *t*-butoxy radical a better fit with σ^+-constants than for σ-constants is observed. For the *t*-butoxy radical the proper substituents have not been examined to distinguish clearly between a σ- and a σ^+-correlation.

Some data for phenols have been included in Table VIII since it now appears that the initial reaction be-

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(17) G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2364 (1964).

(18) For a summary of numerous correlations of this type see J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

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

(20) R. W. Taft, I. R. Fox, and I. C. Lewis, *ibid.*, **83**, 3349 (1961).

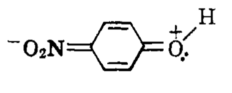
TABLE VIII

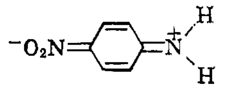
MAGNITUDE OF POLAR EFFECT IN SELECTED RADICAL REACTIONS

Attacking radical	Substrate	Solvent	Temp., °C.	ρ	Reference
$C_6H_5\cdot$	Toluenes	CCl_4	60	0	19
$RO_2\cdot$	Cumenes	Chlorobenzene	60	−0.41	This work
$RO_2\cdot$	Styrenes	Benzene	60	−0.3 to −0.4	This work
$RO_2\cdot$	Phenols	Styrene	65	−1.49	18
$RO_2\cdot$	Benzyl phenyl ethers	Chlorobenzene	60	0	This work
$C_6H_5CO_2\cdot$	Dibenzyl ethers	Reactants	80–90	−0.65	21
$Cl\cdot$	Toluenes	CCl_4	40	−0.66	This work
$Br\cdot$	Toluenes	Reactants	80	−1.46	22
$(CH_3)_3CO\cdot$	Toluenes	Reactants	40	−0.83	23
$(CH_3)_3CO\cdot$	Phenols	CCl_4	122	−1.19	24
$CCl_3\cdot$	Toluenes	Chlorobenzene	80	−1.46	25
DPPH·	Phenols	CCl_4	30	−4.54	26

tween peroxy[27a] or other radicals[27b] and a phenol involves abstraction of the phenolic hydrogen atom. Toward the peroxy or alkoxy radicals, a greater polar effect is observed in attack upon phenols than upon cumenes. We feel that bond breaking is probably greater for attack upon the cumenes and that the difference in values of ρ reflect different electron-donating abilities of the two classes of compounds. The large ρ observed for diphenylpicrylhydrazyl in attack on phenols (−4.5) is probably connected with a higher degree of bond breaking as well as a different electron affinity of the attacking radical than for attack by a peroxy radical (ρ = −1.5).

Another polar effect that may be important in reactions of phenols or anilines should be considered. Resonance interaction of the nonbonding electron pairs on the oxygen or nitrogen atom with the substituent will favor conformations in which the OH or NH bonds are coplanar with the aromatic ring for powerful electron-withdrawing *p*-substituents

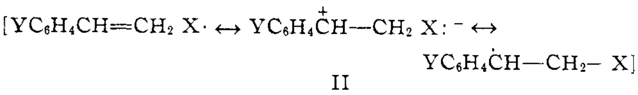




The O–H or N–H bonds are in these cases poorly situated (not perpendicular to the plane of the ring) from a stereoelectric viewpoint for benzylic-type resonance stabilization of the incipient phenoxy or anilino radicals.

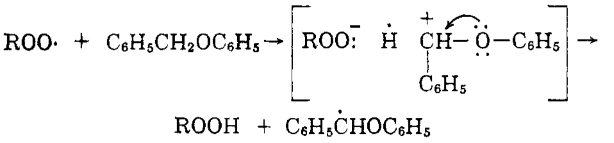
The electron affinities of the five radicals and atoms studied in attack on substituted toluenes are in the order $Cl\cdot > Br\cdot > (CH_3)_3CO\cdot > CCl_3\cdot > C_6H_5\cdot$.[28] The magnitude of the polar effects observed are $Br\cdot \sim CCl_3\cdot > (CH_3)_3CO\cdot > Cl\cdot > C_6H_5\cdot$. We believe the discrepancies between these two series are best explained by a consideration of the amount of bond breaking in the transition states. The electron affinity of chlorine and bromine atoms are rather similar and the widely different values of ρ are consistent with a considerably greater bond-breaking in the transition state for attack by bromine atoms. Despite the low electron affinity of the trichloromethyl radical, its low reactivity gives rise to a transition state with extensive bond breaking, and a fairly large polar effect (ρ = −1.46) results. The more reactive *t*-butoxy radical displays a smaller polar effect (ρ = −0.83) despite higher electron affinity because of the lower degree of bond breaking in the transition state and a smaller contribution from the dipolar resonance structure I.

Polar effects were also observed in the terpolymerization reaction between oxygen, styrene, and substituted styrenes (Table V). Qualitatively these results parallel those observed in benzylic substitution and are consistent with the occurrence of resonance structure II in the transition state for the addition reaction of the peroxy radical.



$$[YC_6H_4CH{=}CH_2\ X\cdot \leftrightarrow \underset{\text{II}}{YC_6H_4\overset{+}{C}H{-}CH_2\ X:^-} \leftrightarrow YC_6H_4\dot{C}H{-}CH_2{-}\ X]$$

The results of autoxidation of substituted benzyl phenyl ethers and benzyl alkyl ethers lead to the conclusion that attack by peroxy radicals is insensitive to polar effects of substituents in either the phenyl or benzyl group. It is believed that this insensitivity results from the fact that the ether oxygen atom acts as a powerful electron-supplying group in both the substituted and unsubstituted compounds. This effect



$$ROO\cdot + C_6H_5CH_2OC_6H_5 \rightarrow \left[ROO\overset{-}{:}\ \ \dot{H}\ \ \underset{C_6H_5}{\overset{+}{C}H}{-}\ddot{\underset{..}{O}}{-}C_6H_5\right] \rightarrow ROOH + C_6H_5\dot{C}HOC_6H_5$$

apparently overshadows effects of polar substitutions in either of the phenyl rings. In view of this conclusion the semiquantitative relationships reported between reactivities and substituent constants for several substituted benzyl ethers ($RC_6H_4CH_2OCH_2C_6H_5$) toward *t*-butoxy ($\rho \sim 0.5$) and benzoyloxy radicals (ρ = −0.65)[21] appear surprising. However, Table VIII does indicate that in reactions with benzylic hydrogen atoms that *t*-butoxy radicals show a considerably greater polar effect than do peroxy radicals and the reported results are consistent with a decreasing polar effect and decreasing electron affinity in the order, $C_6H_5CO_2\cdot > (CH_3)_3CO\cdot > RO_2$

From the present work it would appear that the reaction of oxygen with substituted styrenyl radicals is independent of substituents in the styrenyl ring. However, when radicals of more widely different electron-donating properties are compared, such as styrenyl and phenyl radicals,[19] it does appear that polar structures

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(21) R. L. Huang, H. H. Lee, and S. H. Ong, *J. Chem. Soc.*, 3336 (1962).

(22) R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354 (1963).

(23) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6113 (1960).

(24) K. U. Ingold, *Can. J. Chem.*, **41**, 2816 (1963).

(25) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960).

(26) M. P. Godsoy, D. H. Lohman, and K. E. Russell, *Chem. Ind.* (London), 1603 (1959).

(27) (a) L. R. Mahoney and F. C. Ferris, *J. Am. Chem. Soc.*, **85**, 2345 (1963); (b) K. U. Ingold, *Can. J. Chem.*, **41**, 2807 (1963).

(28) H. O. Pritchard, *Chem. Rev.*, **52**, 529 (1953).

do make important contributions to the transition states and to the rates of the reactions. Thus, resonance structure III is much more important for R =

$$[R\cdot\cdot O\text{–}O\cdot \leftrightarrow R^{+}:\bar{O}\text{–}O\cdot \leftrightarrow R\sim OO\cdot]$$

III

styrenyl than for R = phenyl or phenoxy.[19]

Experimental

Apparatus and Procedure for Competitive Photochlorinations.—The photochlorination apparatus was designed so that the carrier gas (prepurified nitrogen) after entering the system could be directed by the manipulation of a three-way Teflon 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 (approximately 30-ml. in volume) through a finely drawn inlet tube which reached nearly to the bottom of the flask. The exit gas passed through an ice-water condenser and a trap containing a 10% sodium hydroxide solution before entering the atmosphere. The reaction flask was mounted in a 40° water thermostat and placed approximately 3 cm. from a 200-watt unfrosted tungsten light bulb.

The procedure used for the photochlorination involved first sweeping carrier gas through the sample to remove traces of oxygen. When it was desired to start the chlorination the stopcock was adjusted to allow nitrogen to pass over the liquid chlorine. The liquid chlorine was then allowed to warm to its boiling point. After the proper amount of chlorine had evaporated, as determined by the calibration on the liquid reservoir, the liquid chlorine remaining in the reservoir was gradually cooled. After the liquid chlorine was sufficiently cool, the stopcock was adjusted so that nitrogen again bypassed the reservoir. Generally the flow of nitrogen was regulated so all the chlorine was added to the reaction mixture in about 2 hr. After the addition was complete, nitrogen was allowed to pass through the reaction mixture to remove traces of hydrogen chloride.

Analysis of Photochlorination Products.—A known amount of an internal standard was added to the reaction mixture in the reaction flask after completion of the photochlorination. This ensured against errors caused by loss on transfer. The unreacted toluene and substituted toluene were then analyzed by a g.l.c. unit equipped with a hot wire detector. In all determinations, a correction factor was determined to account for the difference in thermal conductivity between the substrates and the standard. In several instances two internal standards were added and each substrate analyzed at a different temperature.

Apparatus and Procedure for Autoxidation.—The oxidation reactions were carried out in a reaction flask that was about 20 in. in length. The bottom of the flask was constructed from a 50-ml. erlenmeyer flask and joined to a standard tapered joint by approximately 16 in. of 8–10 mm. glass tubing jacketed by an outside jacket of 20 mm. tubing. The standard tapered joint fitted an adaptor which was connected to a gas buret by a short length of rubber tubing. When AIBN was used as the catalyst it was added to the flask in a benzene solution and the benzene removed at a pressure of 20–30 mm. Solutions that were to be oxidized were added by pipet to the reaction flask and the mixture cooled by Dry Ice. The entire system was alternately evacuated and filled with oxygen several times, the flask warmed to room temperature, and fastened to a reciprocating rack in a 60.00 ± 0.15° oil thermostat. After allowing the temperature of the contents in the reaction flask to equilibrate to the temperature of the oil bath, the gas buret was adjusted, the reciprocation started, and readings were taken periodically. The volume of oxygen absorbed was corrected for nitrogen evolution from the AIBN. A correction factor of 1.50 ml. of nitrogen (25°, 740 mm.) per min. per l. was used for 0.10 M solutions of AIBN. The reciprocating rack was powered by a $^1/_3$ horse powermotor and operated between 145 to 150 c.p.m. The rate of oxidation did not change when the rate of shaking was increased by a factor of two. When competitive autoxidations were performed, the length of time required for 15–20% reaction varied from 4 hr. for the styrenes to 20 hr. for the cumenes.

Solutions were ordinarily prepared and pipetted at known concentrations at the reaction temperature. In some cases, solutions were prepared at room temperature and pipetted at room temperature. In these cases the volume and concentration of the solution at the reaction temperature were computed and the rates calculated on this basis.

Method of Analysis of Competitive Autoxidations.—The reaction mixture was added to a silica gel chromatography column and eluted by a 20-fold excess of benzene. When the highly polar substrate *p*-nitrostyrene was involved the eluting solvent was a 1% solution of diethyl ether in benzene. A known quantity of an internal standard was then added to the eluted solution for g.l.c. analysis. This procedure was proved to be quantitative in eluting the substrates cumene, styrene, *p*-nitrostyrene, and benzyl phenyl ether by absorbing a solution containing a known amount of each of these substrates on the column and eluting with a 20-fold excess of solvent. The amount of substrate in the eluent was shown to be the same as that added by g.l.c. analysis. *p*-Methoxycumene and *p*-methoxystyrene were shown to be eluted quantitatively after oxidation by following the 20-fold excess of solvent with an additional 100 ml. of solvent. This 100 ml. of solution was then concentrated to about 5 ml. and this solution was tested for traces of the substrate by g.l.c. analysis. In all cases this test was negative. The products of oxidation and unreacted AIBN, which could later interfere with the g.l.c. analysis, were retained quantitatively on the silica gel column.

Analysis of Benzaldehydes Formed in the Oxidation of Styrenes.—Solutions of benzaldehyde and *p*-nitrobenzaldehyde in a 1:4 mixture of *m*-dichlorobenzene and pentane followed Beer's law (5.93 μ for benzaldehyde and 5.96 μ for *p*-nitrobenzaldehyde) below 1×10^{-2} M. Solutions of styrene and *p*-nitrostyrene (10 ml. of a 1 M solution containing 0.10 M AIBN) were oxidized at a variety of pressures and the oxygen uptake measured (see Table VII). For oxidations above 1 atm. a Paar shaker was used and oxygen uptake approximated by assuming that the rate of oxidation was the same as measured at 710 mm. pressure. After the absorption of about 1 mmole of oxygen the oxidates were diluted to 50 or 100 ml. with pentane and stored at 0° until the precipitation of polymer ceased. The resulting clear solutions were analyzed for carbonyl using a Perkin–Elmer Model 21 spectrometer.

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

Azobisisobutyronitrile (AIBN) obtained from Chemical Intermediates and the Bordon Monomer–Polymer division was recrystallized from methanol and dried under vacuum, m.p. 101.5–102° dec.

Toluene (Fisher reagent grade) was rectified. The minimum purity was 99.9% by g.l.c. analysis.

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

p-Phenoxytoluene was prepared by treating the potassium salt of *p*-cresol with a slight excess of bromobenzene in the presence of catalytic amount of powdered copper at 270° for 3 hr.[29] The potassium salt was prepared by treating 2 moles of *p*-cresol with 1 mole of potassium hydroxide at 150°. This melt was then cooled and benzene added to azeotrope on the water formed in the reaction. The excess cresol then served as a solvent for the potassium salt in the reaction with bromobenzene. The reaction mixture containing the ether was washed with 15% aqueous sodium hydroxide (to remove the unreacted *p*-cresol), water, dried over sodium sulfate, and distilled. The fraction used had b.p. 110–111° at 2 mm., lit.[29] b.p. 292° at 1 atm. pressure. The complete absence of other materials was shown by g.l.c. analysis.

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

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

m- and *p*-xylene (Phillips 99 mole %) was rectified to remove a lower boiling constituent and ethylbenzene. The fraction used was one showing no other peaks on g.l.c. analysis, n^{20}D 1.4915.

p-Methoxycumene was prepared by treating 55 g. of *p*-isopropylphenol dissolved in 150 ml. of a 1:1 water–ethanol mixture containing 25 g. of potassium hydroxide with 51 g. of methyl

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(29) F. Ullmann and P. Sponagel, *Liebigs Ann.*, **350**, 83 (1906).

sulfate. Thirty minutes after the dropwise addition of the methyl sulfate, 200 ml. of a 1:1 methanol–concentrated ammonium hydroxide solution was added to destroy any unreacted methyl sulfate. The reaction mixture was then extracted with ether and the ether layer washed with 10% potassium hydroxide solution, water, dried over sodium sulfate, and the ether distilled. Rectification of the remaining material gave 37 g. of the desired product, b.p. 85° at 10 mm., $n^{20}\mathrm{D}$ 1.5033.

p-*t*-Butoxycumene, b.p. 111.7° at 12 mm., $n^{20}\mathrm{D}$ 1.4860, was prepared by the addition of isobutylene to *p*-isopropylphenol in the presence of a catalytic amount of sulfuric acid.[30]

p-Phenoxycumene and *m*-phenoxycumene were prepared from the *p*- and *m*-isopropylphenols by the procedure described for the phenoxytoluenes. The *m*-isopropylphenol was a gift from the Hercules Powder Co. The *p*-isomer had b.p. 150° at 7 mm., lit.[31] b.p. 288.9° at 760 mm. The *m*-isomer had b.p. 144° at 7 mm., $n^{20}\mathrm{D}$ 1.5570; g.l.c. analysis showed both compounds to be greater than 99.8% pure.

p-Bromocumene was prepared by the bromination of cumene in the dark using iodine as a catalyst. To 100 g. of cumene dissolved in 100 ml. of a 1:1 mixture of carbon tetrachloride and acetic acid was added one large crystal of iodine and 150 g. of bromine in 150 ml. of carbon tetrachloride. The reaction was allowed to proceed overnight with gentle refluxing. The mixture was then washed with 10% sodium hydroxide solution, water, and then dried over sodium sulfate. A crude distillation through a Vigreux column was followed by a careful rectification through a Todd column packed with glass helices to give material, b.p. of 110° at 22 mm., $n^{20}\mathrm{D}$ 1.5360; lit.[9] b.p. 123.5° at 53 mm., $n^{20}\mathrm{D}$ 1.5363.

p-Nitrocumene was prepared by the procedure of Brown and Bonner[32]; b.p. 110° at 5 mm., $n^{20}\mathrm{D}$ 1.5369, lit.[32] $n^{20}\mathrm{D}$ 1.5369.

Methyl *p*-isopropylbenzoate was synthesized by converting *p*-isopropylbenzoic acid to the acid chloride with thionyl chloride followed by treatment with excess methanol in pyridine[33]; b.p. 118–119° at 12 mm., $n^{20}\mathrm{D}$ 1.5108, lit.[9] $n^{20}\mathrm{D}$ 1.5108.

p-Diisopropylbenzene (Aldrich Chemical Co.) was distilled through a glass helices packed Todd column; b.p. 112.3° at 3 mm., $n^{20}\mathrm{D}$ 1.4896, lit.[34] $n^{20}\mathrm{D}$ 1.4898.

The substituted-benzyl phenyl ethers were prepared by treating equal molar quantities of potassium phenoxide with the corresponding benzyl chloride or bromide (the bromide was used when it was commercially available) in a 1:1 mixture of ethanol and tetrahydrofuran. The potassium phenoxide was freshly prepared by treating equal molar quantities of phenol and potassium hydroxide in a melt at about 150°. Enough solvent was then added to the cooled salt to give a saturated solution. The benzyl halide was then added dropwise over a period of approximately 2 hr. with stirring and the resulting solution stirred under reflux overnight. Solvent was then removed with a rotating evaporator until crystals began to form in the solution or until most of the solvent had been removed in instances where the product was a liquid. All solutions containing solid products were then cooled in an ice bath and the solids filtered and recrystallized from ethanol. Liquids were rectified and fractions chosen having a constant boiling point and refractive index. Special care had to be taken, however, in the preparation of *p*-methoxybenzyl phenyl ether. As little ethanol as possible should be used to dissolve the potassium phenoxide in tetrahydrofuran and this solution added dropwise to a concentrated solution of *p*-methoxybenzyl chloride in tetrahydrofuran. If the normal procedure is followed the major product formed is *p*-methoxy-*p*′-hydroxydiphenylmethane. Table IX lists the physical properties of the benzyl phenyl ethers. All new compounds had n.m.r. spectra consistent with their structures.

p-Nitrophenyl benzyl ether (m.p. 105–105.5°) and *p*-tolyl benzyl ether (m.p. 39–40°) were synthesized by adding benzyl chloride dropwise to a saturated solution of the potassium salt of the corresponding phenol in a 1:1 ethanol–tetrahydrofuran solution followed by stirring under reflux overnight. Both of these potassium salts were prepared by treating potassium *t*-butoxide with the phenols in 150 ml. of tetrahydrofuran. Ethanol (150 ml.) was then added to dissolve the salt. The same work-up procedure employed for the preparation of the substituted-benzyl phenyl ethers was used. Both solids were recrystallized from ethanol.

TABLE IX

PHYSICAL CONSTANTS OF SOME BENZYL PHENYL ETHERS ($C_6H_5OCH_2C_6H_4X$)

	Found			Literature	
X =	M.p., °C.	B.p., °C. (mm.)	$n^{20}\mathrm{D}$	M.p., °C.	B.p., °C. (mm.)
Hydrogen	39.0–39.2			39[35]	
p-Nitro-	90.3–90.7			91[36]	
m-Nitro-		163 (1.5)	1.5980		182 (2)[37]
p-Chloro-	85.0–85.5			85.5–86.5[38]	
m-Chloro-	36.0–36.5			36–36.4[38]	
m-Methyl-		160 (0.5)	1.5731		168–170 (17)[39]
p-Methyl-	81.5–82.0				
p-Methoxy-	89.5–90.5				

Benzyl methyl ether was prepared by adding 20 g. (0.5 g.-atom) of potassium in small pieces to 300 ml. of a 1:1 methanol–tetrahydrofuran solution. After the last of the potassium had reacted, 63 g. (0.5 mole) of benzyl chloride was then added slowly and the resulting solution was stirred and heated under reflux overnight. This solution was then washed with 10% sodium hydroxide solution, water, and dried over sodium sulfate. Solvent was then distilled off and the remaining liquid rectified through a 15-in. spinning band column. The fraction used showed no impurities by g.l.c. analysis; $n^{20}\mathrm{D}$ 1.5028, lit.[40] $n^{20}\mathrm{D}$ 1.5022.

Benzyl ethyl ether (Eastman) was distilled through a 15-in. spinning band column; $n^{20}\mathrm{D}$ 1.4950.

Benzyl *t*-butyl ether was prepared by the reaction of potassium *t*-butoxide with benzyl chloride in a *t*-butyl alcohol–tetrahydrofuran solution at room temperature with stirring for 7 days; b.p. 39–40° at 0.5 mm., $n^{20}\mathrm{D}$ 1.4858.

m-Methylbenzyl methyl ether was synthesized from *m*-methylbenzyl bromide and potassium methoxide using the same method and work-up procedure as in making benzyl methyl ether. Analysis by g.l.c. showed 99% purity with the impurity being the *m*-methylbenzyl bromide; b.p. 47° at 2 mm., $n^{20}\mathrm{D}$ 1.5003. *p*-Chlorobenzyl methyl ether was prepared from *p*-chlorobenzyl bromide in the same manner as the *m*-methyl isomer; b.p. 60° at 2 mm., $n^{20}\mathrm{D}$ 1.5467.

Commercial styrene containing inhibitor was distilled through a silver jacketed, glass helices packed, 10-in. column; $n^{20}\mathrm{D}$ 1.5467.

p-Nitrostyrene was prepared according to the procedure of Walling and Wolfstirn[41]; m.p. 21.2–21.5°, lit.[41] 21.4°.

The copolymer of *p*-nitrostyrene with oxygen was a solid that could be precipitated from acetone by benzene; m.p. (decomposition) 120–122°.

Anal. Calcd. $C_8H_7NO_4$: C, 53.22; H, 4.11; N, 7.92. Found: C, 53.04; H, 3.86; N, 7.73.

In a typical preparation 20 ml. of a 1 *M* solution of *p*-nitrostyrene in benzene containing 0.1 *M* AIBN was shaken in a 1 atm. pressure of oxygen for 20 hr. at 60°. At this time 1.65 g. of solid peroxide (55% based on oxygen absorbed) was removed by filtration and the filtrate added to cold methanol and an additional 0.90 g. (30%) of peroxide collected. After precipitation, this sample could not be redissolved in benzene. Both samples were swollen with benzene at 50°, cooled, and filtered. This process was repeated; the samples were dried at 15 mm. for 24 hr. and analyzed.

p-Methoxystyrene was prepared by the procedure of Walling and Wolfstirn.[41] This compound contained an autoxidation inhibitor which could not be removed by distillations, by washing with acid or base, or by passage through alumina or silica gel. It was finally removed by treating 15 g. of *p*-methoxystyrene with 0.08 g. of AIBN and oxygen at 60°. Upon observing oxygen uptake the reaction was stopped and passed through a silica gel column to remove any unreacted AIBN and oxidized products. The

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(30) D. R. Stevens, *J. Org. Chem.*, **20**, 1232 (1955).

(31) R. A. Smith, *J. Am. Chem. Soc.*, **56**, 717 (1934).

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(40) W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, and L. C. Gibbons, *J. Am. Chem. Soc.*, **69**, 2451 (1947).

(41) C. Walling and K. B. Wolfstirn, *ibid.*, **69**, 852 (1947).

resulting liquid was then flash distilled at 0.1 mm. This liquid was carefully distilled, giving a pure compound, b.p. 54–55° at 2 mm., n^{24}_D 1.5618; lit.[41] b.p. 53–54° at 2 mm., n^{20}_D 1.5612, 1.5608, and 1.5620.

Gas–Liquid Chromatographic Analysis.—Solutions of mixtures of hydrocarbons for competitive oxidation or chlorination were prepared, then aliquots mixed with an aliquot of a standard solution of the internal standard and triplicate g.l.c. analyses performed to provide calibration factors to convert area ratios into mole ratios. After chlorination or oxidation, analyses were again performed at least in triplicate. A number of different column substrates, conditions, and internal standards were employed. Pertinent details are summarized elsewhere.[42]

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[42] R. C. Williamson, Jr., Ph.D. Dissertation, Iowa State University Library, 1963.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Directive Effects in Aliphatic Substitutions. XXV. Reactivity of Aralkanes, Aralkenes, and Benzylic Ethers toward Peroxy Radicals[1]

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RECEIVED JANUARY 18, 1964

The competitive oxidation of a number of aralkanes, aralkenes, and benzyl ethers has been performed and their reactivities toward the derived peroxy radicals measured. The reactivities are fairly independent of the structure of R in ROO·. To explain the rates of oxidation of the pure compounds, it must be assumed that termination rate constants are dependent upon the structures of the peroxy radicals. This observation is consistent with the rate minima observed in the autoxidation of numerous binary mixtures.

The rates of autoxidation of numerous substances capable of yielding benzylic-type radicals have been reported in the literature.[3] From these rates the relative values of rate constants for the attack of peroxy radicals upon benzylic hydrogen atoms

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

or addition to a double bond

$$RO_2\cdot + {>}C{=}C{<} \xrightarrow{k_a} RO_2\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot$$

have been inferred.[3b] We thought it advisable to establish firmly the relative values of k_p and k_a for a series of aralkanes (cumene, tetralin, 2°-butylbenzene, bibenzenyl), aralkenes (styrene, substituted styrenes,[4] α-methylstyrene), and benzylic ethers (dibenzyl ether, benzyl ethyl ether, 2-phenyl-1,3-dioxolane). We have therefore measured the rates of autoxidation of the above compounds at 60° in chlorobenzene and benzene solution containing 0.1 *M* azobisisobutyronitrile (AIBN) as well as the rates of oxidation of various binary mixtures. In addition, the relative rates of disappearance of substrates in the cooxidation of binary mixtures was measured by gas–liquid chromatography (g.l.c.). Table I lists the pertinent results.

Table I indicates that in many instances rate minima were observed in the oxidation of binary mixtures. This reflects differences in the termination rate constants as well as possibly favored cross termination reactions in the cooxidations.[3a,5]

Propagation

$$AOO\cdot + A\ (\text{or } AH) \xrightarrow{k_{AA}} AOOA\cdot\ (\text{or } AOOH + A\cdot) \qquad (1)$$

$$AOO\cdot + B\ (\text{or } BH) \xrightarrow{k_{AB}} AOOB\cdot\ (\text{or } AOOH + B\cdot) \qquad r_A = k_{AA}/k_{AB} \qquad (2)$$

$$BOO\cdot + B\ (\text{or } BH) \xrightarrow{k_{BB}} BOOB\cdot\ (\text{or } BOOH + B\cdot) \qquad (3)$$

$$BOO\cdot + A\ (\text{or } AH) \xrightarrow{k_{BA}} BOOA\cdot\ (\text{or } BOOH + A\cdot) \qquad r_B = k_{BB}/k_{BA} \qquad (4)$$

Termination

$$\left.\begin{array}{l} 2AOO\cdot \xrightarrow{k_{tAA}} \\ 2BOO\cdot \xrightarrow{k_{tBB}} \\ AOO\cdot + BOO\cdot \xrightarrow{k_{tAB}} \end{array}\right\} \text{nonradical products}$$

This phenomenon has been previously discussed in connection with the cooxidation of mixtures of cumene–tetralin, cumene–indan, and cumene–dibenzyl ether.[3a,b] Figure 1 shows the effects of several cooxidants on the rate of oxidation of binary mixtures containing styrene. Curves such as 3 (p-methoxystyrene), 4 (p-nitrostyrene), or 7 (benzyl ethyl ether) indicate that peroxy radicals formed from these substrates have termination rate constants approximately the same as those for termination of styrenylperoxy radicals. This seems reasonable since all the radicals involved are 2°-benzylic radicals.[6] Apparently, styrenylperoxy radicals terminate more readily than cumylperoxy radicals as indicated by the sharp minimum in the rate (curve 8, Fig. 1) of oxidation of mixtures of cumene and styrene. The same effect is observed with *cis*-decalin (curve 9, Fig. 1) where a mixture of 3° and 2°-aliphatic peroxy

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[2] (a) Alfred P. Sloan Foundation Fellow, 1959–1963; (b) N.I.H. Predoctoral Fellow, 1960–1963.

[3] (a) G. A. Russell, *J. Am. Chem. Soc.*, **77**, 4583 (1955); (b) G. A. Russell, *ibid.*, **78**, 1047 (1956); (c) F. R. Mayo, A. A. Miller, and G. A. Russell, *ibid.*, **80**, 2500 (1958); (d) J. Alagy, G. Clement, and J. C. Balaceanu, *Bull. soc. chim. France*, 1325 (1959); 1495 (1960); 1792 (1961).

[4] G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

[5] The over-all rate expression applicable to a competitive oxidation has been developed (ref. 3a). The presence of a rate minimum in a binary (A + B) mixture where [A] + [B] = constant is the result of the values of the ratios, k_{AA}/k_{AB}, k_{BA}/k_{BB}, $k_{AA}/(k_{tAA})^{1/2}$, $k_{BB}/(k_{tBB})^{1/2}$, and $\phi = k_{tAB}/(k_{tAA}k_{tBB})^{1/2}$. It can be shown that when $\phi = 1$ and $k_{AA}/k_{AB} = k_{BA}/k_{BB} = k_{AA}(k_{tBB})^{1/2}/k_{BB}(k_{tAA})^{1/2}$, a linear relationship results when the rate of oxidation is plotted against [A] or [B]. Nonlinear relationships can be observed even when $\phi = 1$ and $k_{tAA} = k_{tBB}$ if the values of k_{AA}/k_{AB}, k_{BA}/k_{BB}, and k_{AA}/k_{BB} are quite different. Although values of ϕ can be obtained from plots of oxidation rate *vs.* [A] or [B] by curve fitting, values of k_{tAA}/k_{tBB} cannot be obtained unless the ratio k_{AA}/k_{BB} can be independently measured. However, the presence of a sharp minimum in the rate curve seems fairly diagnostic of large differences in the values of k_{tAA}, k_{tBB}, and/or $\phi >> 1$.

[6] G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).