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^{21}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 per-

formed 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]

(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]

BY GLEN A. RUSSELL[2a] AND ROGER C. WILLIAMSON, JR.[2b]

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

$$RO_2\cdot + RH \xrightarrow{k_p} RO_2H + R\cdot$$
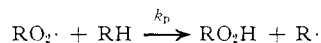
or addition to a double bond

$$RO_2\cdot + {>}C{=}C{<} \xrightarrow{k_a} RO_2\overset{|}{C}{-}\overset{|}{C}\cdot$$
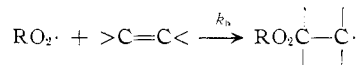
have been inferred.[3b] We thought it advisable to establish firmly the relative values of k_p and k_a for a series of aralkanes (cumene, tetralin, 2°-butylbenzene, bibenzenyl), aralkenes (styrene, substituted styrenes,[4] α-methylstyrene), and benzylic ethers (dibenzyl ether, benzyl ethyl ether, 2-phenyl-1,3-dioxolane). 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]

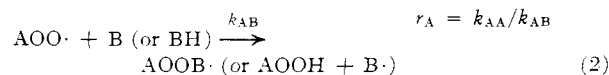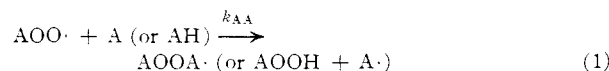(1) This research was supported by the Air Force Office of Scientific Research.

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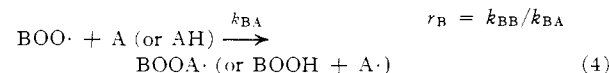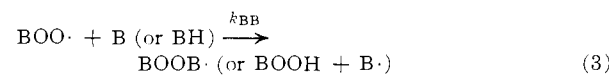
(4) G. A. Russell and R. C. Williamson, Jr., J. Am. Chem. Soc., 86, 2357 (1964).

(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 $k_{AB}/k_{BA} \cdot k_{BB} = k_{AA}(k_{tBB})^{1/2}/k_{BB}(k_{tAA})^{1/2}$, a linear relationship results when the rate of oxidation is plotted against [A] or [B]. Nonlinear relationships
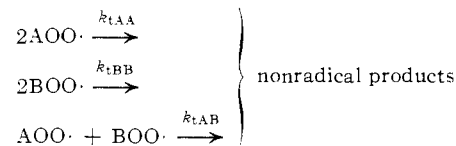
Propagation

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

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

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

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

Termination

$$2AOO\cdot \xrightarrow{k_{tAA}}$$
$$2BOO\cdot \xrightarrow{k_{tBB}} \Bigg\} \text{ nonradical products}$$
$$AOO\cdot + BOO\cdot \xrightarrow{k_{tAB}}$$

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

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 $k_{AA} \cdot k_{BB}$ 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 $\phi \gg 1$.

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

radicals are involved.[7] Presumably the rate minimum would have been more pronounced with *cis*-decalin if the presence of 2°-aliphatic peroxy radicals could have been excluded in the oxidation. The requirements for the sharp minimum, as observed with cumene–styrene mixtures, is that the retarding hydrocarbon should be much more reactive toward peroxy radicals than the hydrocarbon whose oxidation is being retarded and that the peroxy radicals formed from the retarder undergo self or crossed termination reactions much more readily than peroxy radicals derived from the substance being retarded.[3a]

To obtain reactivity data toward the peroxy radicals the disappearances of cooxidants were measured and the results subjected to kinetic analysis by the "Copolymerization" equation.[8] The results entered in the last two columns of Table I indicate considerable spread in the solutions of this equation. In some cases a negative intercept was observed. This must mean that either the analysis for substrate was not accurate or that the reactants are being consumed by some process in addition to reactions 1–4. Some of the negative solutions occurred when styrene was a cooxidant and would have been positive if less styrene had been consumed. It would appear that styrene may be consumed by some process in addition to the four propagation reactions, possibly by a reaction between styrene and some oxidation product.

Table II lists the reactivity data calculated from Table I. Column 2 lists the values of $k'_p/k_t^{1/2}$ calculated from the rates of oxidation of the pure substrates, where k'_p is equal to k_p or k_a depending on whether hydrogen abstraction or addition is involved. Columns 3–8 of Table II list the reactivities observed toward the specific peroxy radicals as calculated by the "Copolymerization" equation.

Discussion

The data summarized in Table II present a reasonably consistent picture. There are no major differences revealed in the reactivity series when the peroxy radical is varied from styrenyl to α-methylstyrenyl, tetralyl, or cumyl. The available data for α-ethoxybenzyl and decalyl peroxy radicals are also included in Table II, but we consider these data less reliable than those for the other four peroxy radicals. The agreement between the present study and a previous one[3a] on the relative reactivity of cumene and tetralin is not particularly good (see Table II).

We conclude from Table II that peroxy radicals have about the same reactivity irrespective of the nature of the alkyl substituent. However, termination rate constants for peroxy radicals certainly vary with the nature of the alkyl substituent. In the over-all rate expressions for oxidation this variation appears as an inverse square-root dependence and hence the effect of variation of the termination rate constant on over-all rate is reduced. Nevertheless, several examples of variation in k_t are obvious in Table II in addition to the cumylperoxy–tetralylperoxy radicals discussed previously.[3a] Styrene is about 10–20 times as reactive as cumene toward peroxy radicals such as tetralyl- or cumylperoxy, but the oxidation rate of styrene is only

(7) F. R. Jaffee, T. R. Steadman, and R. W. McKinney, *J. Am. Chem. Soc.*, **85**, 351 (1963).

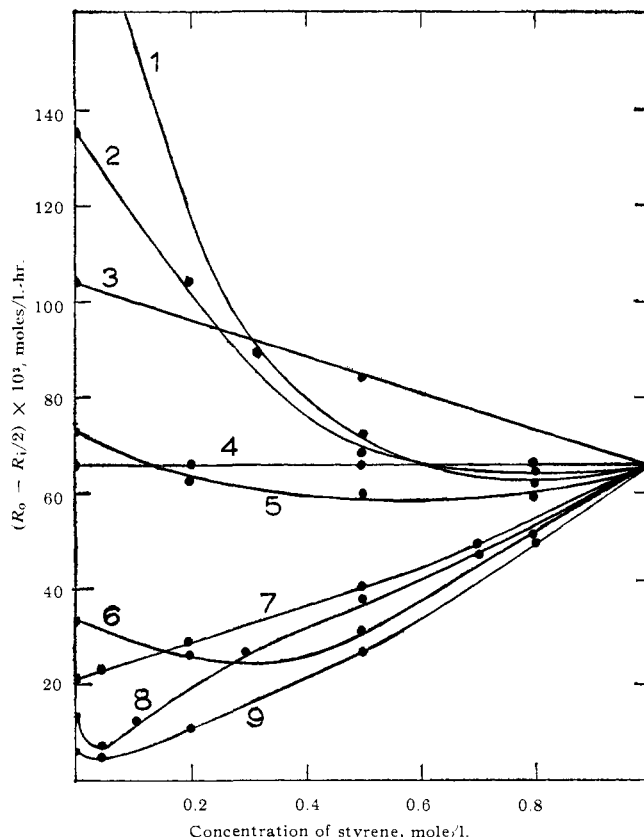(8) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

Fig. 1.—Rates of oxidation of binary mixtures of various hydrocarbons and styrene in benzene solution at 60°, 0.10 *M* AIBN; total substrate concentration = 1.0 *M*: 1, 2-phenyl-1,3-dioxolane; 2, α-methylstyrene; 3, *p*-methoxystyrene; 4, *p*-nitrostyrene; 5, dibenzyl ether; 6, tetralin; 7, benzyl ethyl ether; 8, cumene; 9, *cis*-decalin.

five times that of cumene under comparable conditions at 60°. We believe this is due to the fact that styrenylperoxy radicals terminate about ten times as fast as cumylperoxy radicals.[9] Styrene and α-methylstyrene have nearly the same reactivity toward peroxy radicals and the 2-fold difference in rates of oxidation is thus attributed to an enhanced rate of termination of styrenylperoxy radicals. *cis*-Decalin, whose rate of autoxidation is only about one-half that of cumene, is actually more reactive than cumene toward each of the three peroxy radicals studied. Here it is believed that 2°-alkylperoxy radicals derived from *cis*-decalin[7] lead to a more rapid termination process than that observed for the 3°-peroxy radicals from cumene.[10a] In the present work, cumene was found to be 0.6 as reactive as *cis*-decalin toward a cumylperoxy radical. Utilizing another experimental approach Alagy, Clement, and Balacéanu had previously reported that cumene was 0.5 times as reactive as decalin (presumably a mixture of *cis* and *trans* isomers.)[3b]

Experimental

(9) The assumption is made that since $k_{BA}/k_{BB} \approx k_{CA}/k_{CB} = 15$ that $k_{AA}/k_{BB} = 15$ where A is styrene, B is cumene, and C is tetralin. The best fit with curve 8, Fig. 1, occurs when θ (ref. 3a) $= k_{tAB}'/(k_{tAA}k_{tBB})^{1/2} = 2$–3.

(10) (a) Suggestions concerning the details of the termination process consistent with 2°- and 1°-alkylperoxy radicals terminating more readily than 3°-alkylperoxy radicals have been made.[3a,4] See also P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963). (b) A. Rieche, E. Schmitz, and E. Beyer, *Ber.*, **91**, 1935 (1958).

TABLE I

AUTOXIDATION OF ARALKANES, ARALKENES, AND BENZYLIC ETHERS AT 60°[a]

Substrate A	Substrate B	$[A]_0$	$[B]_0$	Init. rate of oxid.[b] Benzene	Chloro-benzene	$[A]_f$	$[B]_f$	r_A[c]	r_B[c]
Styrene	. . .	1.000	. . .	25.4	26.8	. . .	. . .	. . .	. . .
	α-Methylstyrene	. . .	1.000	51.6	. . .	. . .	. . .	. . .	. . .
Styrene	α-Methylstyrene	0.200	0.800	39.4	. . .	0.153	0.570	0.9 ± 0.1	1.2 ± 0.1
Styrene	α-Methylstyrene	.500	.500	26.5	. . .	.405	.397	1.18	1.40
Styrene	α-Methylstyrene	.800	.200	24.8	. . .	.608	.141	0.71, 0.78	0.87, 1.26
Styrene	α-Methylstyrene	.900	.100	24.4	. . .	. . .	. . .	. . .	. . .
Styrene	α-Methylstyrene	.950	.050	25.4	. . .	. . .	. . .	. . .	. . .
	2-Phenyl-1,3-dioxolane	. . .	1.000	77.4	. . .	. . .	. . .	. . .	. . .
Styrene	2-Phenyl-1,3-dioxolane	0.300	0.700	34.1	. . .	0.186	0.388	0.2 ± 0.2	1.5 ± 1
Styrene	2-Phenyl-1,3-dioxolane	.500	.500	26.6	. . .	.377	.230	−.20	0.66
Styrene	2-Phenyl-1,3-dioxolane	.800	.200	24.0	. . .	.730	.162	.56, 0.30	3.50, 0.95
	Dibenzyl ether	. . .	1.000	28.1	26.1	. . .	. . .	. . .	. . .
Styrene	Dibenzyl ether	0.200	0.800	25.8	. . .	0.162	0.740	1.65 ± 0.05	0.26 ± 0.03
Styrene	Dibenzyl ether	.500	.500	24.0	. . .	.417	.460	1.79	.29
Styrene	Dibenzyl ether	.800	.200	23.0	. . .	.685	.183	1.58, 1.61	.20, 0.28
	Benzyl ethyl ether	. . .	1.000	8.7	8.74	. . .	. . .	. . .	. . .
Styrene	Benzyl ethyl ether	0.050	0.950	9.6	. . .	. . .	. . .	. . .	. . .
Styrene	Benzyl ethyl ether	.200	.800	11.6	. . .	0.118	0.740	3.8 ± 0.3	0 ± 0.2
Styrene	Benzyl ethyl ether	.500	.500	15.4	. . .	.302	.456	5.04	0.098
Styrene	Benzyl ethyl ether	.700	.300	19.2	. . .	.439	.267	3.60, 3.13	0.054, −0.17
	Tetralin	. . .	1.000	13.2	. . .	. . .	. . .	. . .	. . .
Styrene	Tetralin	0.200	0.800	10.5	. . .	0.167	0.728	2.8 ± 0.5	1.2 ± 0.6
Styrene	Tetralin	.500	.500	12.4	. . .	.413	.439	1.07	0.42
Styrene	Tetralin	.800	.200	21.6	. . .	.656	.186	2.94, 4.3	0.65, 2.58
	cis-Decalin	. . .	1.000	3.3	. . .	. . .	. . .	. . .	. . .
Styrene	cis-Decalin	0.050	0.950	2.6	. . .	. . .	. . .	. . .	. . .
Styrene	cis-Decalin	.200	.800	6.1	. . .	. . .	. . .	. . .	. . .
Styrene	cis-Decalin	.500	.500	11.6	. . .	. . .	. . .	. . .	. . .
Styrene	cis-Decalin	.800	.200	19.4	. . .	. . .	. . .	. . .	. . .
Styrene	Cumene	.700	.300	18.3	. . .	0.594	0.294	6.5 ± 1	−0.2 ± 0.2
Styrene	Cumene	.500	.500	15.0	. . .	.424	.490	8.1	.11
Styrene	Cumene	.300	.700	10.5	. . .	.234	.695	6.6, 4.5	−.27, −0.30
Styrene	Cumene	.100	.900	5.7	. . .	. . .	. . .	. . .	. . .
Styrene	Cumene	.050	.950	3.3	. . .	. . .	. . .	. . .	. . .
Cumene		1.000	. . .	5.8	5.70	. . .	. . .	. . .	. . .
Cumene	Benzyl ethyl ether	0.930	0.070	2.9	. . .	. . .	. . .	. . .	. . .
Cumene	Benzyl ethyl ether	.800	.200	3.9	. . .	0.749	0.134	0.1 ± 0.1	2.1 ± 0.2
Cumene	Benzyl ethyl ether	.500	.500	5.7	. . .	.455	.360	.41	2.54
Cumene	Benzyl ethyl ether	.200	.800	8.1	. . .	.186	.680	.02, −0.11	1.99, 1.90
Cumene	Benzyl ethyl ether	.100	.900	10.0	. . .	. . .	. . .	. . .	. . .
Cumene	Benzyl ethyl ether	.030	.970	10.7	. . .	. . .	. . .	. . .	. . .
	2°-Butylbenzene	. . .	1.000	3.7	3.58	. . .	. . .	. . .	. . .
Cumene	2°-Butylbenzene	0.100	0.900	3.6	. . .	. . .	. . .	. . .	. . .
Cumene	2°-Butylbenzene	.200	.800	3.8	. . .	0.163	0.764	1.15 ± 0.05	0.025 ± 0.01
Cumene	2°-Butylbenzene	.500	.500	4.2	. . .	.432	.468	1.31	0.06
Cumene	2°-Butylbenzene	.800	.200	4.8	. . .	.625	.164	1.00, 0.96	0.04, −0.09
Cumene	2°-Butylbenzene	.900	.100	5.4	. . .	. . .	. . .	. . .	. . .
Cumene	Dibenzyl ether	.950	.050	3.7	. . .	. . .	. . .	. . .	. . .
Cumene	Dibenzyl ether	.900	.100	4.8	. . .	. . .	. . .	. . .	. . .
Cumene	Dibenzyl ether	.500	.500	12.9	. . .	. . .	. . .	. . .	. . .
	Bibenzyl	. . .	1.000	3.0	. . .	. . .	. . .	. . .	. . .
Cumene	Bibenzyl	0.200	0.800	. . .	. . .	0.147	0.785	. . .	. . .
Cumene	Bibenzyl	.500	.500	. . .	. . .	.410	.476	2.42	−0.12
Cumene	Bibenzyl	.800	.200	. . .	. . .	.650	.168	0.89, 0.78	−0.14, −0.50
Cumene	Tetralin	.800	.200	. . .	. . .	.730	.134	0 ± 0.2	2.5 ± 1
Cumene	Tetralin	.500	.500	. . .	. . .	.482	.408	0.33	6.44
Cumene	Tetralin	.200	.800	. . .	. . .	.177	.662	.07, −0.56	1.32, 1.06
Cumene	cis-Decalin	.200	.800	3.8	. . .	.192	.750	.58	1.56
Cumene	cis-Decalin	.500	.500	3.7	. . .	.466	.446	.58	1.56
Cumene	cis-Decalin	.800	.200	4.4	. . .	.726	.170	.58, 0.58	1.56, 1.56
Tetralin	Benzyl ethyl ether	.930	.070	11.0	. . .	. . .	. . .	. . .	. . .
Tetralin	Benzyl ethyl ether	.800	.200	8.8	. . .	0.600	0.152	0.88 ± 0.02	0.48 ± 0.02
Tetralin	Benzyl ethyl ether	.500	.500	9.1	. . .	.399	.418	.94	0.55
Tetralin	Benzyl ethyl ether	.200	.800	10.2	. . .	.163	.710	.92, 0.82	.47, 0.46
Tetralin	Benzyl ethyl ether	.100	.900	12.4	. . .	. . .	. . .	. . .	. . .
Tetralin	Benzyl ethyl ether	.030	.970	10.3	. . .	. . .	. . .	. . .	. . .

TABLE I (Continued)

Substrate A	Substrate B	[A]$_0$	[B]$_0$	Init. rate of oxid.[b] Benzene	Chloro-benzene	[A]$_f$	[B]$_f$	r_A[c]	r_B[c]
Tetralin	cis-Decalin	0.800	0.200	9.5	...	0.600	0.175	1.89 ± 0.01	0.01 ± 0.002
Tetralin	cis-Decalin	.500	.500	6.5	...	.365	.450	1.88	.004
Tetralin	cis-Decalin	.200	.800	4.1	...	.133	.750	1.89, 1.91	.009, 0.015
Tetralin	α-Methylstyrene	.200	.800	..	...	.136	.458	0.85 ± 0.1	1.3 ± 0.2
Tetralin	α-Methylstyrene	.500	.500	..	...	.354	.335	1.31	1.69
Tetralin	α-Methylstyrene	.800	.200	..	...	.574	.123	0.69, 0.59	1.44, 0.84

[a] Cooxidations performed in benzene solution. Subscripts 0 and f refer to initial and final concentration in moles/l. [b] Ml. of oxygen (STP) per 100 min. for 10 ml. of a solution containing 0.10 M AIBN, corrected for nitrogen evolution. [c] From solution of the "Copolymerization" equation. The first experiment of each set determines a straight line when r_A is plotted as a function of r_B (r_A = k_{AA}/k_{BB}; r_B = k_{BB}/k_{BA}; AOO· + A $\xrightarrow{k_{AA}}$ AOOA·, etc.). The second experiment determines another straight line which intersects the first at the values listed. The third experiment defines a third line which intersects the first two at the points shown. The center of gravity of the triangle thus formed is given in italic type. A reasonable experimental uncertainty has been estimated.

TABLE II

RELATIVE REACTIVITIES OF PEROXY RADICALS TOWARD ARALKANES AND ARALKENES, 60°, BENZENE SOLUTION

Substrate	$k_p'/k_t^{1/2a}$	Styrenyl	α-Methyl-styrenyl	Attacking peroxy radical Tetralyl	Cumyl	α-Ethoxybenzyl	Decalyl
2-Phenyl-1,3-dioxolane	6.2	14					
α-Methylstyrene	4.1	3.1	1.2	1.2			
p-Methoxystyrene	3.2[b]	4.0[b]					
Styrene	2.0	2.8	1.1	0.8	~1	~10	
p-Nitrostyrene	2.0[b]	1.7[b]					
Benzyl ethyl ether	0.63	0.75		1.1	1.0	0.48	
Dibenzyl ether	2.2	1.7					
Tetralin	1.00	1.0	1.0	1.0	1.0	1.0	1.0
Cumene	0.40			0.40, 0.06,[c] 0.10[d]	0.10, 0.04[c]	0.48	0.006
2°-Butylbenzene	0.21				0.09		
Bibenzyl	0.17				~0		
cis-Decalin	0.19			0.53	0.17		0.01

[a] Relative values; from Table I using the expression, $-d[O_2]/dt = k'_p[RH](R_i)^{1/2}/(2k_t)^{1/2} + R_i/2$ (ref. 6); $R_i = 1.31 \times 10^{-8}$ mole/l.-sec. (D. G. Hendry and G. A. Russell. J. Am. Chem. Soc., **86**, 2368 (1964)). [b] Ref. 4. [c] Ref. 3a, 90°. [d] Ref. 3d.

Materials.—The solvents, AIBN, styrene, and cumene employed have been described.[4] α-Methylstyrene showed a purity of greater than 99% by g.l.c. It was chromatographically filtered through silica gel before use. Tetralin (Eastman Kodak Co.) was rectified with a spinning band column to remove a lower boiling component and decalin. The fraction used contained a trace of decalin but had a purity greater than 99.7% by g.l.c. It was passed through silica gel before use. cis-Decalin was a gift from W. R. Grace Co. Rectification through a Todd column gave a fraction greater than 99% pure with the major impurity being tetralin. It was passed through silica gel before use. 2°-Butylbenzene (Eastman Kodak Co.) was rectified through a spinning band column to give material. n^{20}D 1.4898. Bibenzyl (Eastman Kodak Co.) was recrystallized from ethanol: m.p. 52.8–53.1°. 2-Phenyl-1,3-dioxolane was prepared from equal molecular amounts of benzaldehyde and ethylene glycol in the presence of a trace of p-toluenesulfonic acid. Benzene was employed to azeotrope water which was collected in a Dean–Stark trap. When 80% of the theoretical water had been collected the reaction was stopped and the product washed with 10% sodium

bicarbonate solution, dried. and a crude vacuum distillation performed. This was followed by two careful rectifications with a 15-in. spinning band column. The fraction. b.p. 78° at 2.5 mm., n^{20}D 1.5270 1.5269, lit.[10b]. consisted of 99% 2-phenyl-1,3-dioxolane and 1% benzaldehyde as analyzed by g.l.c. The autoxidation of 2-phenyl-1,3-dioxolane showed a decreasing rate with time. presumably from the ionic decomposition of the hydroperoxide to form phenol.

Analytical Procedure.—The oxidates were first chromatographed to remove oxidation products as described previously.[4] Elution with a 20-fold excess of benzene was proved to elute quantitatively the substrates employed. The concentrations of reactants were determined after oxidation by use of a number of different g.l.c. columns. conditions, and internal standards.[11]

(11) R. C. Williamson, Jr., Ph.D. Dissertation, Iowa State University, 1963.