

(giving $a - x$), and the developing C_{12} -proton signal, at 401 Hz²¹ for IIIc, whose area was proportional to x . Plotting $\ln [a/(a - x)]$ vs. time gave first-order rate constants by graphical analysis. The data gave a nonlinear plot $[1/(a - x) \text{ vs. } t]$ when tested for a second-order reaction involving two molecules of IIc in the rate-determining step.

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Inhibition of Free Radical Reactions. III. Kinetic Study of the Reactions of Peroxy Radicals and Phenoxy Radicals in Hydrocarbon Systems

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Abstract: A systematic study has been made of the rates of oxygen absorption of solutions of 9,10-dihydroanthracene (DHA) and 2,2',3,3'-tetraphenylbutane containing a number of nonhindered phenols and varying amounts of hydroperoxide. The phenolic compounds studied were phenol, 3-hydroxyphenol, 4-methoxyphenol, 4-phenylphenol, 2-hydroxynaphthalene, and 3-hydroxypyrene. An analysis of the oxidation data has been carried out by means of a derived general rate expression I. The numerical results obtained by means of this analysis have yielded previously unattainable information regarding the relative rates of formation, of hydrogen abstraction, and of termination reactions of the phenoxy radicals. This information was then interpreted in terms of the energies of the HOMO of the phenols and hydroquinones as calculated by the Hückel technique. Although the log of the relative rates of reaction of the parent phenolic compound with the peroxy radical may be correlated for the simple phenol series and for the dioxyhydroquinone series, a variation of the values for the Coulomb and bond integrals failed to yield a single correlation for both series. This result was attributed to the difference in σ -bond energies of the two series. A variation of approximately 1000 in the ratio of the rate constant for the peroxy radical-phenoxy radical termination reaction to the square root of the rate constant for the bimolecular termination reaction of the phenoxy radical is observed. This variation was accounted for as arising from a decrease in the value of the bimolecular phenoxy termination rate as the phenoxy radical becomes more resonance stabilized. The smaller variation in the rate of the peroxy-phenoxy termination reaction was discussed in terms of polar stabilization of the transition for the reaction and the energy difference of the HOMO of the peroxy and phenoxy radicals. The relative rates of hydrogen abstraction from the hydroperoxide and from the hydrocarbon by the phenoxy radical were found to be relatively insensitive to the phenolic structure, indicating that both reactions are affected to the same extent by the stability of the phenoxy radical. The experimental rate data of earlier workers who utilized the tetralin-AIBN system for the study of phenol and 4-methoxyphenol have been subjected to the same analysis. From the curve fit of their data by means of eq I, the reactivity ratios for hydrogen abstraction from 9,10-dihydroanthracene and from tetralin at 60° were calculated to be 24 for the peroxy radical, 70 for the unsubstituted phenoxy radical, and larger than 200 for the 4-methoxyphenoxy radical. The significance of the high selectivity of the phenoxy radical in other chemical systems was then discussed.

Much of the present knowledge of the ease of formation and chemical reactivity of free radicals and atoms has been obtained from kinetic studies of chain reactions in which these species occur as reactive intermediates. A free-radical species of considerable interest in many areas of chemistry is the phenoxy radical.¹ A potentially useful system for the study of phenoxy radicals is the free-radical-initiated, liquid-phase oxidation of hydrocarbons containing small amounts of phenolic compounds.

In earlier work from this laboratory² the ideality of the experimental system consisting of the hydrocarbon, 9,10-dihydroanthracene (DHA), and the initiator, 2,2',3,3'-tetraphenylbutane (TPB), for the kinetic study of hydrocarbon inhibition by hydroquinones and hindered phenols was demonstrated. In the present study, the kinetically complex behavior of nonhindered

phenols is examined by means of this system. The work has several goals. The first is an analysis of the oxidation data by means of a generalized rate expression, avoiding the use of limiting rate expressions. The second is to use the numerical results obtained from this analysis to yield previously unattainable information regarding the relative rates of formation, of hydrogen abstraction, and of modes of destruction of phenoxy radicals. The third goal is to analyze the data of earlier workers by means of the same generalized rate expression in order to derive estimates of the reactivity ratios for peroxy and phenoxy radicals in hydrogen abstraction reactions.

Results

A. The General Rate Equation. The reactions of intermediate phenoxy radicals with hydroperoxides^{3,4}

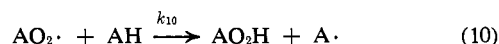
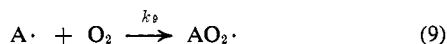
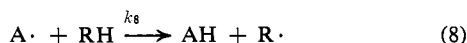
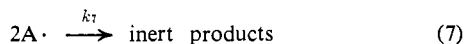
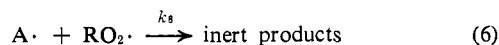
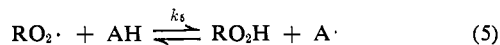
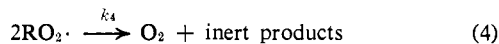
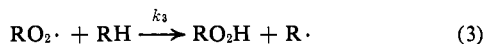
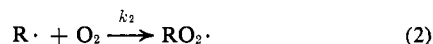
(1) Cf. J. H. I. Joschek and S. I. Miller, *J. Am. Chem. Soc.*, **88**, 3273 (1966), for an extensive list of references.

(2) L. R. Mahoney, *ibid.*, **88**, 3035 (1966).

(3) J. R. Thomas, *ibid.*, **85**, 2166 (1963).

(4) J. R. Thomas, *ibid.*, **86**, 4807 (1964).

and with hydrocarbons⁵⁻⁷ have been proposed to explain the nonideal kinetic behavior of hydrocarbon oxidations retarded by nonhindered phenols. In addition, reactions of these radicals with oxygen and with hydrocarbon free radicals are also possible.^{8,9} A scheme that includes all of these reactions is the following



where R-R is the source of free radicals; R· and RO₂· are the hydrocarbon and peroxy radicals; and AH and A· represent the parent phenol and phenoxy radicals.

The observed rates of oxygen absorption solutions of TPB in the presence of AH and in the absence of RH are first order in TPB (0.31×10^{-3} to 2.52×10^{-3} M), and independent of the concentration of the phenolic compound (0.5×10^{-3} M to 100×10^{-3} M) and oxygen pressure (above 200 mm). The first-order rate constant k_1 is equal to 2.0×10^{-4} sec⁻¹. This value is the same as that previously reported with hindered phenols^{2,5} and hydroquinones² as the peroxy radical scavengers. If reactions 9 and 10 were important, the measured value of k_1 would increase with increasing concentration of AH. The occurrence of reaction 11 would result in a decreased and oxygen-dependent value of k_1 . We therefore conclude that the reactions 9, 10, and 11 at 60° in chlorobenzene are unimportant for the compounds phenol, 4-phenylphenol, 2-hydroxynaphthalene, 3-hydroxypyrene, 4-methoxyphenol, and 3-hydroxyphenol. Therefore these reactions may be excluded from further consideration.

Since reaction 2 is not rate controlling for 9,10-dihydroanthracene,² the rate of oxygen absorption observed in such a system is determined by the rates of reactions 1, 3, and 8, *i.e.*

$$d(\text{O}_2)/dt = 2k_1(\text{RR}) + k_3(\text{RO}_2\cdot)(\text{RH}) + k_8(\text{A}\cdot)(\text{RH})$$

Expressions for the concentration of A· and RO₂· may be obtained if two approximations are valid. The first approximation is that of the attainment of a steady-

(5) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2215 (1956).

(6) L. R. Mahoney and F. C. Ferris, *J. Am. Chem. Soc.*, **85**, 2345 (1963).

(7) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 2324 (1964).

(8) J. L. Bolland and P. TenHave, *Discussions Faraday Soc.*, **2**, 252 (1948).

(9) J. R. Dunn, W. A. Waters, and C. Wickham-Jones, *J. Chem. Soc.*, 2427 (1952).

state concentration for free radicals in the system, *i.e.*

$$2k_1(\text{RR}) = 2k_3(\text{RO}_2\cdot)^2 + 2k_6(\text{RO}_2\cdot)(\text{A}\cdot) + 2k_7(\text{A}\cdot)^2$$

Under conditions of sufficiently long kinetic chain length and highly efficient chain-transfer reactions of A·, then

$$k_5(\text{RO}_2\cdot)(\text{AH}) = k_{-5}(\text{A}\cdot)(\text{RO}_2\text{H}) + k_8(\text{A}\cdot)(\text{RH})$$

and we may write

$$\frac{1}{[2k_1(\text{RR})]^{1/2}(\text{RH})} \left[\frac{d(\text{O}_2)}{dt} - 2k_1(\text{RR}) \right] = \left\{ 1 + \left[\frac{(\text{AH})}{\frac{k_3}{k_5}(\text{RH}) + \frac{k_3 k_{-5}}{k_8 k_5}(\text{RO}_2\text{H})} \right] \right\}^{1/2} + \left\{ \frac{2k_4}{k_3^2} + \frac{2k_6}{k_3 k_8} \left[\frac{(\text{AH})}{\frac{k_3}{k_5}(\text{RH}) + \frac{k_{-5} k_3}{k_8 k_5}(\text{RO}_2\text{H})} \right] \right\} + \left\{ \frac{2k_7}{(k_8)^2} \left[\frac{(\text{AH})}{\frac{k_3}{k_5}(\text{RH}) + \frac{k_{-5} k_3}{k_8 k_5}(\text{RO}_2\text{H})} \right]^2 \right\} \quad (I)$$

The numerous limiting rate expressions employed by earlier workers⁴⁻⁷ for nonhindered phenols can be readily derived from these considerations by exclusion of the termination reactions 4 and 6 or 4 and 7 along with the exclusion of the chain-restarting reactions -5 or 8.

B. Rates of Oxidation of 9,10-Dihydroanthracene Retarded by Nonhindered Phenols. A systematic study was made of the rate of oxygen absorption on the TPB-initiated oxidation of 9,10-dihydroanthracene with and without added 9,10-dihydroanthryl hydroperoxide retarded by phenol, 4-phenylphenol, 2-hydroxynaphthalene, 3-hydroxypyrene, 4-methoxyphenol, and 3-hydroxyphenol. In all of the cases reported here the kinetic chain lengths are larger than or equal to 2.5. Typical results are presented in Tables I-III for phenol, 3-hydroxypyrene, and 4-methoxyphenol. The value of 1.1×10^{-4} M utilized for the hydroperoxide concentration corresponds to one-half the total amount of oxygen absorbed, *i.e.*, hydroperoxide formed, during the measurement.

The value of $2k_4/k_3^2$, determined from the rate of unretarded oxidation, has previously been reported. The other parameters are conveniently determined by curve fitting using computer techniques. A FORTRAN IV program compatible with the Ford Motor Co. Philco 212 computer installation was written by Mr. E. Ranke of the Computer Application Department of the Research and Engineering Staff. The principle of least-squares fit was applied to the experimental data to determine the unknown constants in eq I, utilizing ordinary hyperspace techniques. The first set of parameters was calculated from limiting rate expressions and the machine iteration process was initiated. The iteration procedure was continued until the successive values of all of the parameters changed by less than 10^{-5} , *i.e.*

$$\left| \frac{\left(\frac{k_5}{k_3} \right)_{n+1} - \left(\frac{k_5}{k_3} \right)_n}{\left(\frac{k_5}{k_3} \right)_n} \right| \leq 10^{-5}$$

where n is the n th iteration.

Table I. Rates of TPB-Initiated Oxidation of 9,10-Dihydroanthracene in Chlorobenzene at 60° Containing Phenol

AH × 10 ³ , M	TPB × 10 ³ , M	RH × 10 ² , M	RO ₂ H × 10 ⁴ , M	Rate × 10 ⁷ M sec ⁻¹		Dev, %
				Exptl	Calcd	
1.0	0.08	99	1.1	8.0	8.32	+4.00
2.0	0.08	99	1.1	7.0	7.34	+4.86
4.0	0.08	99	1.1	5.7	5.56	-2.52
8.0	0.08	99	1.1	4.9	4.49	-9.13
16.0	0.08	99	1.1	3.8	3.66	-3.28
32.0	0.08	99	1.1	3.2	3.24	-1.23
1.90	0.31	99	1.1	14.0	15.2	+7.90
4.75	0.31	99	1.1	10.9	10.98	-0.73
9.50	0.31	99	1.1	8.8	8.88	+0.91
14.25	0.31	99	1.1	8.0	7.98	-0.25
14.0	0.31	99	1.1	7.1	7.51	+5.32
23.75	0.31	99	1.1	7.1	7.50	+5.34
2.03	0.31	99	11.1	20.0	19.18	-4.27
2.03	0.31	99	21.1	21.95	21.82	-0.59
2.03	0.31	99	41.1	24.75	25.18	+1.71
4.06	0.31	99	11.1	15.20	14.98	-1.47
4.06	0.31	99	21.1	17.42	17.34	-0.46
4.06	0.31	99	41.1	20.20	20.54	+1.65
8.12	0.31	99	11.1	11.40	11.62	+1.89
8.12	0.31	99	41.1	13.50	13.50	0.00
8.12	0.31	99	41.1	16.05	16.58	+3.20
15.50	0.31	99	11.1	9.46	9.42	-0.42
15.50	0.31	99	21.1	10.12	10.72	+5.59
15.50	0.31	99	41.1	11.40	12.70	+10.24
24.25	0.31	99	11.1	8.66	8.30	-4.34
24.25	0.31	99	21.1	9.66	9.34	-3.85
24.25	0.31	99	41.1	10.65	10.35	-2.90
1.0	0.62	148	1.1	48.4	45.7	-5.91
2.0	0.62	148	1.1	38.9	36.18	-7.52
4.0	0.62	148	1.1	28.9	28.25	-2.30
10.0	0.62	148	1.1	20.6	20.55	-0.24
20.0	0.62	148	1.1	15.4	16.93	+9.04
1.0	1.24	148	1.1	66.0	67.16	+1.73
2.0	1.24	148	1.1	61.0	61.0	0.00
4.0	1.24	148	1.1	45.5	39.96	-13.85
10.0	1.24	148	1.1	32.4	30.56	-6.02
20.0	1.24	148	1.1	25.4	25.36	-1.58
1.0	0.08	195	1.1	21.5	22.50	+4.44
2.0	0.08	195	1.1	17.4	17.82	+2.36
4.0	0.08	195	1.1	12.5	13.82	+9.54
8.0	0.08	195	1.1	10.5	10.52	+0.19
16.0	0.08	195	1.1	8.4	8.32	-0.96
32.0	0.08	195	1.1	6.7	6.81	+1.61
1.0	0.31	195	1.1	44.2	44.8	+1.34
2.0	0.31	195	1.1	35.8	35.7	-0.28
Av % dev ± 3.54						

In Tables I-III the experimental rates of oxidation (column 5) are compared with the calculated rates of oxidation (column 6). In the last column of the tables are given the percentage deviations of the experimental rates from the calculated ones. The values of the parameters used to fit all of the experimental data for each compound as well as the average percentage deviation of the experimental rates of oxidation from the calculated rates are given in Table IV. The average percentage deviations ($\pm 3-6\%$) compare favorably with an experimental uncertainty in the measurement of $\pm 0.3 \times 10^{-7} M \text{ sec}^{-1}$ or 3%, whichever is larger. The experimental data are, therefore, accurately described by the general rate equation I.

Discussion

A. Correlation of the Values of k_5/k_3 with Energy of HOMO of the Parent Phenol. Successful correlations of polarographic oxidation-reduction potentials with

Table II. Rates of Initiated Oxidation of 9,10-Dihydroanthracene in Chlorobenzene at 60° Containing 1-Hydroxypyrene

AH × 10 ³ , M	TPB × 10 ³ , M	RH, M	RO ₂ H × 10 ⁴ , M	Rate × 10 ⁷ M sec ⁻¹		Dev, %
				Exptl	Calcd	
0.05	0.30	0.242	1.1	3.9	3.28	-8.35
0.10	0.30	0.242	1.1	3.4	3.34	-1.79
0.20	0.30	0.242	1.1	3.9	3.68	-5.63
0.50	0.30	0.242	1.1	4.8	4.59	-4.48
1.00	0.30	0.242	1.1	5.3	5.71	+7.18
2.00	0.30	0.242	1.1	8.1	7.31	-9.45
4.00	0.30	0.242	1.1	9.4	9.46	+0.63
0.10	0.29	0.458	1.1	5.7	4.98	-14.45
0.20	0.29	0.458	1.1	5.3	5.18	-2.32
0.50	0.29	0.458	1.1	6.6	6.20	-6.45
1.00	0.29	0.458	1.1	7.3	7.64	+4.45
2.00	0.29	0.458	1.1	9.3	9.80	+5.10
4.00	0.29	0.458	1.1	12.3	12.88	+4.50
0.2	0.29	0.458	41.1	5.4	5.56	+2.88
0.4	0.29	0.458	41.1	5.9	5.52	-6.89
1.0	0.29	0.458	41.1	7.5	6.96	-7.20
2.0	0.29	0.458	41.1	8.6	8.84	+2.72
4.0	0.29	0.458	41.1	11.7	11.52	+1.56
0.01	0.08	1.04	1.1	11.2	11.87	+5.65
0.05	0.08	1.04	1.1	5.8	6.29	+7.79
0.50	0.08	1.04	1.1	5.5	5.19	-5.97
1.00	0.08	1.04	1.1	6.0	6.09	+1.47
2.00	0.08	1.04	1.1	6.4	7.69	+16.75
4.00	0.08	1.04	1.1	10.3	10.09	-2.09
0.10	0.32	1.04	1.1	12.0	11.43	-4.98
0.50	0.32	1.04	1.1	11.6	11.03	-5.66
1.00	0.32	1.04	1.1	11.9	12.83	+7.25
1.00	0.32	1.04	1.1	11.9	12.83	+7.25
2.00	0.32	1.04	1.1	15.4	16.01	+3.82
4.00	0.32	1.04	1.1	18.5	20.8	+12.30
Av % dev ± 6.23						

the energies of the HOMO and lowest unoccupied molecular orbitals of aromatic hydrocarbon calculated by the Hückel technique have been frequently reported.¹⁰ These results have stimulated attempts to correlate the relative reactivities, k_5/k_3 , of phenols toward oxidation by peroxy radicals with the energies of the HOMO of the phenolic compounds.^{11,12}

However, in these previous attempts the reactivities were determined assuming that $d(O_2)/dt$ was inversely proportional to k_5/k_3 , which this work shows only to have limited validity. Because of the importance of reactions -5 and 8, this relationship appears to be valid only for the hindered phenols and hydroquinones reported in earlier work from this laboratory. In the present work reliable values of k_5/k_3 for nonhindered phenols have been obtained for the first time, and they are summarized in Table V as are also the k_5/k_3 values for hydroquinones.² The energies of the HOMO of all the compounds included in Table V, calculated by the Hückel technique, utilizing two sets of values for the Coulomb and bond integrals are also given. A plot of $\log k_5/k_3$ vs. the energy of the HOMO with $\alpha_0 = \alpha_{CC} + \beta_{CC}$ and $\beta_{CC} = \beta_{CO}$ is shown in Figure 1. This correlation results in two lines, one for the simple monohydroxy compound, with a correlation coefficient, r , equal to 0.934 and a second line with r equal to 0.972 for 3-hydroxyphenyl, 4-methoxyphenol, and the hy-

(10) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 173-187.

(11) D. S. Davis, H. L. Goldsmith, A. K. Gupta, and G. R. Lester, *J. Chem. Soc.*, 4926 (1956).

(12) T. Fueno, T. Ree, and H. Eyring, *J. Phys. Chem.*, **63**, 1940 (1959).

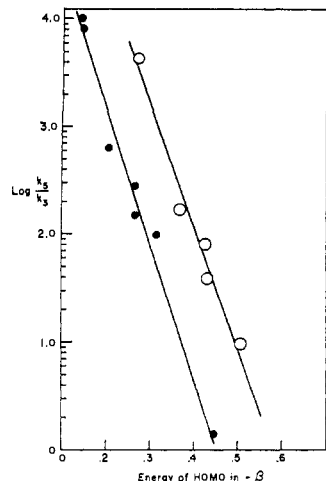


Figure 1. Plot of $\log k_5/k_3$ vs. energy of the HOMO of the phenol. The value of the Coulomb and bond integrals correspond to $\alpha_0 = \alpha_{CC} + \beta_{CC}$ and $\beta_{CO} = \beta_{CC}$.

droquinones. Similar results are obtained utilizing the parameters $\alpha = \alpha_{CC} + 2\beta_{CC}$, $\beta_{CO} = \sqrt{2}\beta_{CC}$, although the least-squares fit becomes worse for the monohydroxy compounds with r equal to 0.900 and improves for the dioxy compounds with r equal to 0.994. As is observed in the polarographic oxidations of aromatic hydrocarbons, the phenol derived from the nonalternate hydrocarbon fluoranthene falls far from both correlation lines and was not included in the least-squares fit.

The expectation of a correlation of the $\log k_5/k_3$ vs. the HOMO is based on the following argument.¹⁰ In a given series of phenolic compounds the rate of reaction 5 should depend on the disassociation energy D of the OH bond of the phenol, *i.e.*



A separation of D into σ and π energy terms may be made and the π energy term is then related to the energy of the HOMO of the phenol. If the σ energy term for a series of phenols is the same, then a single correlation should be expected. In the present study a satisfactory correlation is observed within a given series of phenolic compounds. Since a variation of values for the Coulomb and bond integrals has little effect on this result, we conclude that the source of the two correlation lines finds its origin in the difference in the σ energy terms for the monoxy and the dioxy compounds.

B. Interpretation of the Values of $0.5k_6/[(k_4)^{1/2}(k_7)^{1/2}]$. The values of $0.5k_6/[(k_4)^{1/2}(k_7)^{1/2}]$, the ratio of the rate constant for the cross-termination reaction 6 to the geometric mean of the rate constants for the homotermination reactions 4 and 7 of the peroxy and phenoxy radical are seen to be very sensitive to the structure of the phenoxy radicals. Since k_4 is a constant for a given hydrocarbon this quantity represents the ratio of the rate constant for reaction 6, the peroxy radical-phenoxy radical termination, to the square root of the rate constant for reaction 7, the bimolecular termination reaction of phenoxy radicals. The variation of this ratio by a factor of 1000 is most easily accounted for as arising from a decrease in the value of k_7 as the phenoxy radical becomes more resonance stabilized.

Table III. Rates of TPB-Initiated Oxidation of 9,10-Dihydroanthracene in Chlorobenzene at 60° Containing 4-Methoxyphenol

AH × 10 ³ , M	TPB × 10 ³ , M	RH × 10 ³ , M	RO ₂ H × 10 ⁴ , M	Rate × 10 ⁷ M sec ⁻¹		Dev, %
				Exptl	Calcd	
0.1	0.31	99.0	1.1	5.6	5.00	-10.70
0.2	0.31	99.0	1.1	4.6	4.46	-3.20
0.5	0.31	99.0	1.1	4.3	4.31	+0.21
1.0	0.31	99.0	1.1	4.5	4.57	+1.55
1.0	0.31	99.0	1.1	4.6	4.57	-0.65
1.0	0.31	99.0	1.1	4.2	4.57	+8.80
2.0	0.31	99.0	1.1	5.5	5.10	-7.30
3.0	0.31	99.0	1.1	5.4	5.49	+1.67
4.0	0.31	99.0	1.1	5.5	5.80	+5.45
8.0	0.31	99.0	1.1	6.6	6.53	-1.06
10.0	0.31	99.0	1.1	7.1	6.74	-3.80
12.0	0.31	99.0	1.1	6.9	7.00	+1.45
20.0	0.31	99.0	1.1	7.3	7.29	-0.14
40.0	0.31	99.0	1.1	7.5	7.97	+6.30
100.0	0.31	99.0	1.1	7.7	7.94	+3.10
0.05	0.31	242.0	1.1	18.6	17.90	-3.70
0.1	0.31	242.0	1.1	14.4	13.76	-4.80
0.2	0.31	242.0	1.1	10.9	11.00	+0.91
0.5	0.31	242.0	1.1	8.1	9.02	+11.10
2.0	0.31	242.0	1.1	8.0	9.10	+13.40
5.0	0.31	242.0	1.1	10.3	10.70	+3.90
10.0	0.31	242.0	1.1	12.6	12.46	-1.50
20.0	0.31	242.0	1.1	15.0	14.25	-5.00
40.0	0.31	242.0	1.1	15.0	15.80	+5.30
0.05	0.075	242.0	1.1	9.1	8.61	-5.40
0.1	0.075	242.0	1.1	6.0	6.55	+9.10
0.5	0.075	242.0	1.1	3.8	4.21	+10.60
1.0	0.075	242.0	1.1	3.6	4.02	+11.60
2.0	0.075	242.0	1.1	4.4	4.23	-3.90
5.0	0.075	242.0	1.1	5.0	5.00	0.00
20.0	0.075	242.0	1.1	7.3	6.83	-6.45
40.0	0.075	242.0	1.1	7.8	7.60	-2.56
0.05	0.31	99.0	21.1	7.0	6.63	-5.30
0.10	0.31	99.0	21.1	4.9	5.41	+10.40
1.0	0.31	99.0	21.1	4.2	4.44	+5.85
5.0	0.31	99.0	21.1	6.0	5.68	-5.34
10.0	0.31	99.0	21.1	6.1	6.41	+5.07
20.0	0.31	99.0	21.1	6.9	7.05	+2.27
40.0	0.31	99.0	21.1	7.6	7.61	+0.13
0.05	0.31	99.0	41.1	7.1	7.20	+1.41
0.10	0.31	99.0	41.1	5.3	5.78	+9.00
0.20	0.31	99.0	41.1	4.9	4.89	-0.20
0.50	0.31	99.0	41.1	3.6	4.32	+20.30
1.00	0.31	99.0	41.1	3.6	4.32	+20.30
10.0	0.31	99.0	41.1	5.9	6.20	+5.10
20.0	0.31	99.0	41.1	6.5	6.84	+5.20
40.0	0.31	99.0	41.1	7.5	7.63	+1.73
Av % dev						± 5.41

Although systematic determinations of the dimerization rates of phenoxy radicals have not been reported, estimates of k_7 for the radicals derived from phenol and 3-hydroxypyrene may be made. The values of k_7 for the simple, unsubstituted, phenoxy radical generated photochemically in water and in CCl₄ at room temperature are in the range of 10⁹ M⁻¹ sec⁻¹.^{13,14} In contrast, very low rates of dimerization of perinaphthyl free radicals may be inferred or have been reported. The value of k_7 for the parent radical I at room temperature is sufficiently low so that strong esr signals are observed for periods of several months in CCl₄ solution.¹⁵ Recently Rabold, *et al.*,¹⁶ reported

(13) G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.*, **61**, 708 (1960).

(14) E. J. Land, G. Porter, and E. Strachen, *ibid.*, **59**, 2016 (1963).

(15) P. B. Sago, M. Nakazaki, and M. Calvin, *J. Chem. Phys.*, **26**, 1343 (1957).

(16) G. Rabold, K. H. Bar-Eli, E. Reid, and K. Weiss, *ibid.*, **42**, 2438 (1965).

Table IV. Summary of Parameters Utilized to Fit Experimental Data to Eq I

Compound	k_3/k_5	$2k_6/(k_3k_8 \times 10^{-4}), M \text{ sec}^{-1}$	k_3k_{-5}/k_3k_8	$2k_7/(k_3^2 \times 10^3), M \text{ sec}^{-1}$	Av % dev ^a
Phenol	0.103	0.342	11.3	0.584	±3.54
2-Hydroxynaphthalene	0.0318	2.31	1.69	17.8	±5.55
4-Phenylphenol	0.0128	0.76	0.763	1.20	±4.50
3-Hydroxypyrene	0.000216	70.2	0.0067	0.118	±6.23
3-Hydroxyphenol	0.362	2.12	17.8	50.0	±5.03
4-Methoxyphenol	0.00353	4.96	0.0618	0.254	±5.41

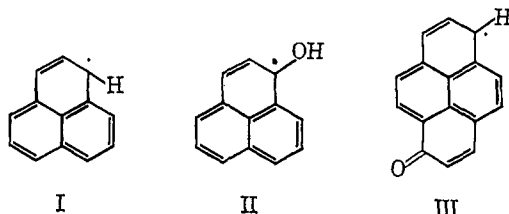
^a Average per cent deviation = $(\sum[(k_{\text{calc}} - k_{\text{expt}})/k_{\text{calc}}]/n) \times 100$ where n is equal to the number of experimental rates determined for the compound.

Table V. Comparison of Kinetic Parameters with Energy of HOMO of the Phenols and Hydroquinones

Compound	k_5/k_3	k_{-5}/k_3	$k_6/[2(k_4)^{1/2}(k_7)^{1/2}]$	Energy of HOMO in terms of $-\beta$
Phenol	9.7	110	2.2	0.6070 ^b
2-Hydroxynaphthalene	39.0	53	2.7	0.4823
4-Phenylphenol	78.0	59.5	3.5	0.48616
1-Hydroxynaphthalene	163.0	0.4058
3-Hydroxypyrene	4400	31.0	1020	0.2966
3-Hydroxyphenol	1.38	49.1	1.5	0.5293
4,4'-Dihydroxybiphenyl	97 ^a	0.3615
1,4-Dihydroxybenzene	147 ^a	0.3216
4-Methoxyphenol	284	17.5	49.0	(0.3216)
1,5-Dihydroxynaphthalene	650 ^a	0.2735
3,10-Dihydroxypyrene	8000 ^a	0.1645
3,8-Dihydroxypyrene	10000 ^a	0.1639
3-Hydroxyfluorene	1090	0.4065

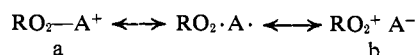
^a Experimental k_5/k_3 corrected for statistical factor of 2. ^b Coulomb and bond integrals, $\alpha_0 = \alpha_{\text{CC}} + 2\beta_{\text{CC}}, \beta_{\text{CO}} = \sqrt{2}\beta_{\text{CC}}$. ^c Coulomb and bond integrals, $\alpha_0 = \alpha_{\text{CC}} + \beta_{\text{CC}}, \beta_{\text{CO}} = \beta_{\text{CC}}$.

a value of k_7 equal to $300 M^{-1} \text{ sec}^{-1}$ for the photochemically generated hydroxyperinaphthenyl radical II in benzene at 25° . The phenoxy radical derived from 3-hydroxypyrene (III) possesses such a perinaph-



thenyl structure and thus the source of the variation in the value of $k_6/(k_7)^{1/2}$ may be accounted for by a decrease of 10^4 – 10^6 in the value of k_7 in going from the phenoxy to the pyrenoxy radical. However, this explanation implies that the value of k_6 remains relatively constant¹⁷ or, equivalently, that the energy of the transition state for reaction 6 is lowered relative to reaction 7 in the same series of phenoxy radicals.

A possible explanation for the smaller variation of k_6 in these systems may be found in the concept of "donor-acceptor" radicals. This concept was first utilized¹⁸ to account for the values of $k_6/[2(k_4)^{1/2}(k_7)^{1/2}]$ extracted from the kinetics of the copolymerization of vinyl compounds. Polar contributions such as a and b lower the energy of the transition state for the radical-radical reactions, *i.e.*



(17) An increase of a factor of ca. 10 in the value of k_5 is possible since k_5 for the phenoxy radical is calculated as $4.0 \times 10^8 M^{-1} \text{ sec}^{-1}$ utilizing k_4 equal to $10^7 M^{-1} \text{ sec}^{-1}$ and k_7 equal to $10^9 M^{-1} \text{ sec}^{-1}$.

(18) C. Walling, "Free Radicals in Solution," John Wiley and Sons Inc., New York, N. Y., 1957, p 144.

The relative importance of such effects in reaction 6 may be estimated since the magnitude of their contribution should be proportional to the difference in the energy of the HOMO of the "donor" and "acceptor" radicals.¹⁹

There are three cases of interest: when the energy of the HOMO of the phenoxy radical is (i) higher than, (ii) lower than, and (iii) equal to that of the peroxy radical. In case i, the energy of the transition state for reaction 6 will be lowered by polar contributions such as a, while in case ii, stabilization would result from polar contributions of the type b. When the energies are equal, case iii, there will be no polar stabilization of the transition for reaction 6 compared to reaction 7. Thus a minimum would occur in the magnitude of such stabilization when the HOMO of the phenoxy radical and peroxy radical are equal. It is of interest in this regard to note that $k_6/[2(k_4)^{1/2}(k_7)^{1/2}]$ passes through a minimum value when the energy of the HOMO of the phenoxy radical is -0.4β to -0.5β , suggesting that the HOMO of the peroxy radical has an energy in this range.

C. Values of k_5/k_3 . In contrast to the values of k_5/k_3 and $k_6/[2(k_4)^{1/2}(k_7)^{1/2}]$, the ratio of rate constants for hydrogen abstraction from hydroperoxide and from hydrocarbon, k_{-5}/k_8 , is relatively insensitive to the structure of the phenoxy radical. This ratio varies by a factor of only 4 in the monoxy series and by a factor of only 3 in the dioxy series. Thus both reac-

(19) This statement is valid in the case of charge-transfer complex interactions; *cf.* ref 10, pp 199–201. Although not previously drawn, the analogy between charge-transfer complexes and polar contributions to transition states is reasonable: the electron affinity of the "acceptor" and ionization potential of the "donor" affect both phenomena in the same manner.

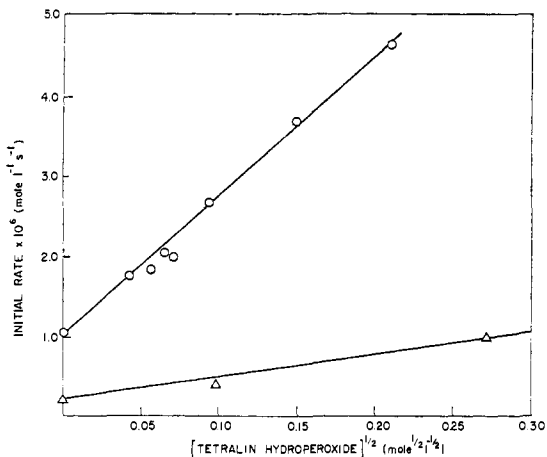


Figure 2. Plot of initial rate of oxygen absorption vs. concentration of [tetralin hydroperoxide]^{1/2}: Δ, 4-methoxyphenol, 1.73×10^{-4} M, tetralin, 7.35 M, and AIBN 9.76×10^{-4} M; O, phenol, 4.92×10^{-3} M, tetralin, 7.35 M, and AIBN, 1.23×10^{-3} M.

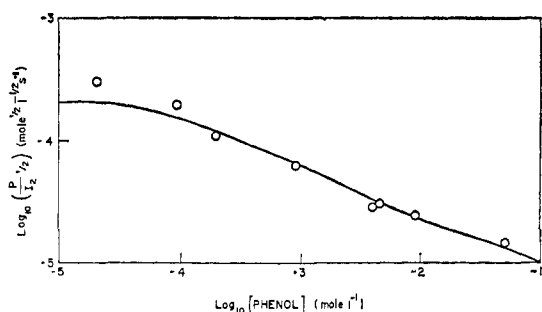


Figure 3. Plot of $\log(P/[I_2]^{1/2})$ vs. $\log[\text{phenol}]$.

tions are affected to approximately the same extent by the phenoxy radical stability.

Thomas⁴ has previously estimated a value of k_{-5} equal to 2.0×10^5 l. mole⁻¹ sec⁻¹ for the simple unsubstituted phenoxy radical. Although this value may be an order of magnitude too large,²⁰ the large value of the ratio k_{-5}/k_8 is in itself surprising. It would appear that bond energies are very poor indices for the relative rates of such processes since the bond energy of the benzylic type C-H of 9,10-dihydroanthracene should be less than 78 kcal²¹ mole⁻¹ while the bond energy for the OH bond of the hydroperoxide is estimated to be 90 kcal²¹ mole⁻¹. The elegant work of Kreilick and Weissman²² on the hydrogen atom exchange reactions of hindered oxy radicals indicates that the rates of these processes are frequently large. From their work they detected the existence of a short-lived (10^{-9} sec) intermediate complex in such reactions. An explanation for the source of facile hydrogen atom transfer in oxyhydroxy systems compared to those in oxyhydrocarbon systems may ultimately be found from the results of such experiments.

D. Reactivity Ratio for the Peroxy, Phenoxy, and 4-Methoxyphenoxy Radicals. In section B of the

(20) The value was calculated from a scheme which neglected the occurrence of reaction 7 and assumed that the value of k_8 was the same for the phenoxy and tri-*t*-butylphenoxy radical used in the calculation was that obtained in CCl₄ solution. The values of k_{-5} , hydrogen atom transfers from stable phenoxy radicals, are faster (three times) in CCl₄ than in benzene or chlorobenzene.

(21) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(22) R. W. Kreilick and S. I. Weissman, *J. Am. Chem. Soc.*, **88**, 2645 (1966).

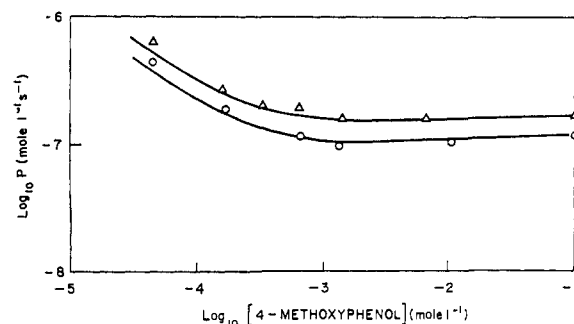


Figure 4. Plot of $\log P$ vs. $\log[4\text{-methoxyphenol}]$: Δ, tetralin, 7.35 M, AIBN, 1.95×10^{-3} M; O, tetralin, 7.35 M, AIBN, 9.76×10^{-4} M.

present work the variation in the values of $k_6/[2(k_4)^{1/2}(k_7)^{1/2}]$ in the unsubstituted phenoxy-3-pyrenoxy series could be accounted for as arising from a decrease of 10^4 to 10^6 in the values of k_7 . If this interpretation is correct the values of k_8 , the rate constant for the hydrogen abstraction by the phenoxy radical from 9,10-dihydroanthracene, must also decrease by two orders of magnitude, since the values of $k_8/(2k_7)^{1/2}$ for the two extreme numbers of the series are approximately equal.

A more elegant technique to determine the sensitivity of reaction 8 to the structure of the phenoxy radical is to obtain the reactivity ratio $(k_8)_{\text{DHA}}/(k_8)_{\text{RH}_2}$ for a given phenoxy from 9,10-dihydroanthracene and from a second hydrocarbon, RH₂. Equation I derived in the present work may be utilized to describe the rate data obtained from systems in which other hydrocarbons are employed as the oxidizable substrates. Such an analysis has been made for the previously reported rates of oxidation of the hydrocarbon, tetralin, containing the initiator, AIBN, and the phenolic compounds, phenol^{4,7} and 4-methoxyphenol.⁷ Curve fits²³ of the experimental points where the kinetic chain length is larger than 5.0 were made by means of eq I. The results are presented in Figures 2-7. For Figures 2-4 (data of Howard and Ingold for tetralin at 65°), the parameters utilized to calculate solid curves from eq I of the present work are as follows: for phenol, $2k_4^2/k_8 = 2.97 \times 10^4$ l. mole⁻¹ sec⁻¹, $k_3/k_5 = 0.005$, $k_3k_{-5}/k_5k_8 = 25.0$, $2k_6/k_3k_8 = 1.0 \times 10^7$ l.⁻¹ mole sec, and $2k_7/k_8^2 = 2.1 \times 10^8$ l. mole⁻¹ sec⁻¹; for 4-methoxyphenol, $k_3/k_5 = 0.000167$, $k_3k_{-5}/k_5k_8 = 0.533$, $2k_6/k_3k_8 = 3.0 \times 10^8$ l.⁻¹ mole sec, and $2k_7/k_8^2 = 8.26 \times 10^7$ l. mole⁻¹ sec⁻¹. For Figures 5-7 (data of Thomas for tetralin at 57°), the parameters utilized to calculate solid curves from eq I of the present work are as follows: $2k_4/k_3^2 = 4.35 \times 10^4$ l. mole⁻¹ sec⁻¹, $k_3/k_5 = 0.004$, (k_3/k_5) .

(23) The value of $k_3/(2k_4)^{1/2}$, 5.8×10^{-3} l.^{1/2} mole^{1/2} sec^{-1/2}, for tetralin at 65° is that reported by Howard and Ingold.⁷ Utilization of a slightly larger value (7.3×10^{-3} l.^{1/2} mole^{1/2} sec^{-1/2}) for this ratio yields a better fit of the data as $[\text{AH}] \rightarrow 0$. However, the use of the different values modifies only the arguments made in regard to the reactivity ratio for the peroxy radical. An increase in the value of k_4 by 40% for the 9,10-dihydroanthracylperoxy radical compared to the value of k_4 for the tetralylperoxy radical would accommodate the conclusions drawn below. The value at 57° was estimated from data reported at lower temperatures. The concentration of RO₂H used for the calculation was 2×10^{-4} M. Experimental points with phenol concentrations higher than 0.1 M were not considered in the calculated curves, since hydrogen-bonded species of phenol and hydroperoxide would predominate under such conditions. The least reliable values are $k_8/(2k_7)^{1/2}$ for phenol in tetralin since the per cent of oxidation at 0.1 M phenol and 5.62 M tetralin at 57° due to reaction 8 is calculated as 82% via eq I.

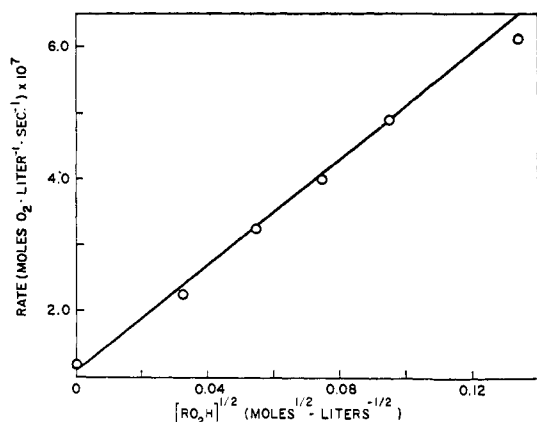


Figure 5. Rate of oxygen absorption vs. $[\text{RO}_2\text{H}]^{1/2}$: tetralin, 1.41 M, AIBN, 4×10^{-3} M, and phenol, 3×10^{-3} M.

$(k_{-5}/k_8) = 52.0$, $2k_6/k_3k_8 = 3 \times 10^7 \text{ l.}^{-1} \text{ mole sec.}$, and $2k_7/k_8^2 = 6 \times 10^7 \text{ l. mole}^{-1} \text{ sec}^{-1}$.

An estimate of the value of the reactivity ratio for the peroxy radical, $(k_3)_{\text{DHA}}/(k_3)_{\text{tetralin}}$, may be made by comparing the ratios $[k_3/(2k_4)^{1/2}]_{\text{DHA}}/[k_3/(2k_4)^{1/2}]_{\text{tetralin}}$ and $(k_3/k_5)_{\text{DHA}}/(k_3/k_5)_{\text{tetralin}}$. In Table VI these ratios

Table VI. Reactivity Ratios for the Peroxy, Phenoxy, and 4-Methoxyphenoxy Radicals

Hydrocarbon	Temp, °C	$k_3/(2k_4)^{1/2}$ (M sec) ^{1/2}	Reactivity ratio	k_3/k_5	Reactivity ratio
Peroxy radical					
9,10-Dihydroanthracene	60	100	...	0.102	...
Tetralin	65	5.8	17.2	0.005 ^a	20.4
Tetralin	57	4.8	20.6	0.0040 ^a	25.5
				0.000167 ^b	21.2
Hydrocarbon	Temp, °C	k_3/k_8	Reactivity ratio	$k_8/(2k_7)^{1/2}$ (M sec) ^{1/2}	Reactivity ratio
Phenoxy radical					
9,10-Dihydroanthracene	60	100	...	13.1×10^{-3}	...
Tetralin	65	5000	45.5	2.18×10^{-4}	60.0
Tetralin	57	13000	117.0	1.29×10^{-4}	102.0
4-Methoxyphenoxy radical					
9,10-Dihydroanthracene	60	18.0	...	19.8×10^{-3}	...
Tetralin	65	3200	178	1.1×10^{-3}	180

^a Phenol as the inhibitor. ^b 4-Methoxyphenol as the inhibitor.

are given and their values vary from 17 to 25. The constancy of the values of the ratios are thus consistent with the view that the values of k_4 and k_5 are relatively insensitive to the structure of the secondary peroxy radical. The absolute values of k_3 for these two hydrocarbons have recently been determined by the rotating sector technique. The reactivity ratio $(k_3)_{\text{DHA}}/(k_3)_{\text{tetralin}}$ at 30° in chlorobenzene is 27,²⁴ using these absolute values.

The value of $(k_8)_{\text{DHA}}/(k_8)_{\text{tetralin}}$ for this imple unsubstituted phenoxy radical is obtained by comparison of the ratio $(k_{-5}/k_8)_{\text{tetralin}}/(k_{-5}/k_8)_{\text{DHA}}$ and $[k_8/(2k_7)^{1/2}]_{\text{DHA}}/[k_8/(2k_7)^{1/2}]_{\text{tetralin}}$. From the consistency of these ratios, 45–60 at 65° and 102–117 at 57°, we conclude

(24) Personal communication to the author by Dr. K. U. Ingold.

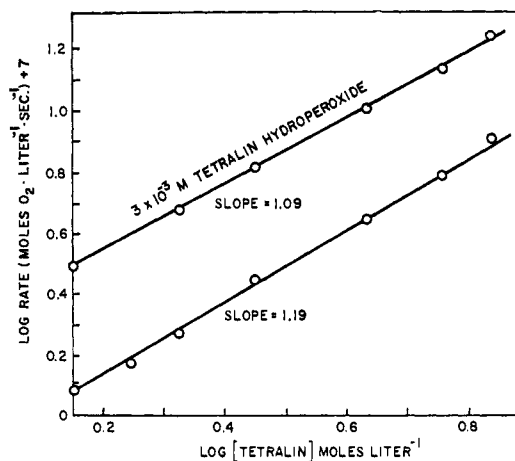


Figure 6. Log of the rate of oxygen absorption vs. log of tetralin concentration: phenol, 3×10^{-3} M; AIBN, 4×10^{-3} M.

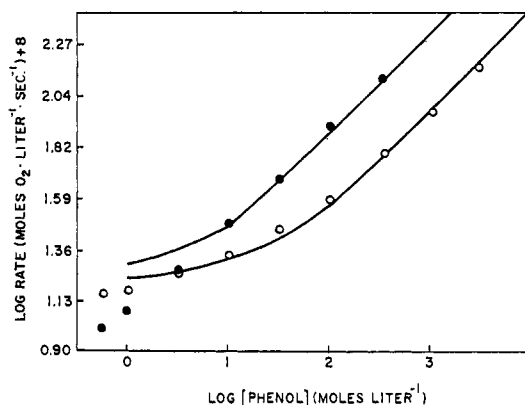


Figure 7. Log of the rate of oxygen absorption vs. log of the phenol concentration: tetralin, 5.35 M; AIBN, 4×10^{-3} M. O, no added hydroperoxide; ●, 3×10^{-3} M hydroperoxide added.

that k_{-5} is insensitive to the structure of the secondary hydroperoxide and further that k_7 is not severely affected by the solvent change. A value of $(k_8)_{\text{DHA}}/(k_8)_{\text{tetralin}}$ for the unsubstituted phenoxy radical at 60° is then approximately 70. By means of an analogous procedure the reactivity ratio for the 4-methoxyphenoxy radical, $(k_8)_{\text{DHA}}/(k_8)_{\text{tetralin}}$, at 60° is calculated to be somewhat larger than 200.

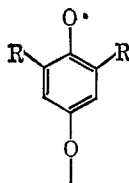
These values of the reactivity ratios for the two phenoxy radicals are consistent with the view that the phenoxy radical is highly selective in hydrogen abstraction reactions, and this selectivity may be further enhanced by suitable substitution. Knowledge of the reactivities of phenoxy radicals in the hydrogen abstraction reactions 8 and -5 is vital to the understanding of not only the mechanism of the inhibition of hydrocarbon oxidation but is of equal importance to such diverse areas as the formation of linear polyphenylene oxide polymers²⁵ and in the elucidation of the mechanism of various enzymatic oxidations.²⁶ In these later two systems phenoxy radicals have been postulated as important intermediates. With the exception of a study of the 2,4,6-tri-*t*-butylphenoxy radical carried out in this lab-

(25) G. D. Cooper, H. S. Blanchard, G. F. Erdes, and H. Finkbeiner, *J. Am. Chem. Soc.*, **87**, 3996 (1965).

(26) "Oxygenases," O. Hayaishi, Ed., Academic Press Inc., New York N. Y., 1962; A. H. Mehler, Chapter 3; D. Kartesz and R. Zito, Chapter 8.

oratory²⁷ there have been no reports concerning the reactivities of phenoxy radicals although their possible physiological importance requires that they be highly selective in their reactions.

The complex, low molecular weight mixtures obtained on the oxidative polymerization of 2,6-diisopropylphenol²⁸ compared to the linear polymers obtained from 2,6-dimethylphenol may be due to the high selectivity of the intermediate phenoxy radicals IV. From



IV

the reactivity ratio for the 4-methoxyphenoxy radical, the relative rates of hydrogen abstraction from a tertiary $\geq\text{CH}$ (isopropylbenzene) *vs.* a primary C-H (toluene) is calculated as 50.²⁹ Therefore, this reaction, leading to complex C-C and C-O compounds, would be of much greater importance in the case of the isopropyl compounds.

Kartesz and Zito²⁶ have reported that the relative rate of reaction of the reactive intermediate in the enzymatic oxidation of hydroquinone compared to phenol is 52. For the peroxy radical in the present study the ratio of rate constants for the same compounds in reaction 5 is 30. This result is not inconsistent then

(27) M. A. DaRooge and L. R. Mahoney, submitted for publication.

(28) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959).

(29) Calculated on the basis that $(k_2)_{\text{cumene}}/(k_2)_{\text{toluene}}$ is 5.0; *cf.* G. A. Russell, *ibid.*, **78**, 1047 (1956).

with the intervention of phenoxy radicals or semiquinones as intermediates in the reaction.

Experimental Section

Materials. The oxidizable hydrocarbon 9,10-dihydroanthracene was obtained from Henley and Co. (98% minimum). This material after three recrystallizations from ethanol had mp 109.5–110.0° (corrected) (lit.⁸ 109–110.5°). Periodically during use, the hydrocarbon was subjected to iodometric analysis and contained less than 0.02% (limit of detection) hydroperoxide. Spectrophotometric analysis revealed an impurity of 0.08% anthracene.

2,2,3,3-Tetraphenylbutane was synthesized by the method of Müller and Roscheisen,³⁰ mp 122–123° (lit.³⁰ 122–123°).

9,10-Dihydro-9-anthryl hydroperoxide was prepared according to the procedure of Bickel and Kooyman.⁵ Two recrystallizations from toluene–pentane yielded a material, mp 109–110°; iodometric analysis gave a value of 95% peroxide. The material contained a 4.8% impurity of anthracene as determined by spectrophotometric analysis.

3-Hydroxypyrene was prepared according to the procedure of Tietze and Bayer³¹ and Vollman, *et al.*,³² mp 180° (lit.³² 179–180°).

Anal. Calcd: C, 88.05; H, 4.62. Found: C, 88.03; H, 4.74.

The other phenols were obtained from commercial sources and purified by recrystallization and sublimation to yield materials which gave melting points which agreed with published literature values. Another criterion of purity was the single spot obtained by thin layer chromatography on silica plates on elution with benzene followed by 20% chloroform–benzene mixtures.

Rate measurements were carried out by means of the apparatus described in earlier publications from this laboratory.²

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(30) E. Müller and G. Roscheisen, *Ber.*, **90**, 543 (1957).

(31) E. Tietze and O. Bayer, *Ann.*, **539**, 207 (1939).

(32) H. Vollman, H. Becker, M. Corell, and H. Streeck, *ibid.*, **531**, 1 (1937).

Carbon Monoxide Reactions. II. The γ Radiation Initiated Chlorocarbonylation of Paraffins

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Contribution from the Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey 07036. Received December 15, 1966

Abstract: The synthesis of acid chlorides by means of a radical chain reaction utilizing carbon tetrachloride and carbon monoxide as reagents has been extended to include a variety of hydrocarbons. The problems encountered when peroxide initiation was used have been traced to initiator-destroying products formed from the interaction of the metal reactor surface with acid chlorides. This difficulty has been circumvented by using γ radiation to initiate chlorocarbonylations. The γ radiation provides the added advantage of temperature-independent initiation. Acid chlorides have been produced from some representative paraffins ranging from ethane to hexadecane. Some approximate *G* values have been determined and used to estimate the magnitude of the kinetic chain length.

A novel route to acid halides, from paraffins *via* halogenation in the presence of carbon monoxide, is being investigated in this laboratory. The *peroxide-initiated* synthesis of cyclohexanecarboxylic acid chloride from cyclohexane, which was used as a model reaction to demonstrate the feasibility of this technique, was the subject of a previous communication.¹

Our initial attempts to achieve this halocarbonylation with a variety of the more commonly used radical halogenating agents were unsuccessful and gave cyclohexyl halides exclusively. The synthesis of acid halide (eq 6) as opposed to alkyl halide (eq 5) involves a competition between CO and halogenating reagent for alkyl radi-

(1) W. A. Thaler, *J. Am. Chem. Soc.*, **88**, 4278 (1966).