The Kinetic Behavior and Thermochemical Properties of Phenoxy Radicals

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Abstract: The values of the absolute rate constants (k_i) and equilibrium constants (K_i) for reactions of a variety of phenoxy radicals at 60° in chlorobenzene solution, with organic hydroperoxides, 2,4,6-tri-*tert*-butylphenol, and their corresponding oxy radicals and hydrocarbons are obtained from the results of the present and earlier published work. Brønsted relationships of the form $\log k_i = a + b \log K_i$ are found to exist for hydrogen atom abstraction by 3- and 4-substituted phenoxy radicals from organic hydroperoxides, 2,4,6-tri-*tert*-butylphenol, and hydrocarbons. The values of a and b are strongly affected by the nature of the hydrogen atom donor molecule; for organic hydroperoxides, a is equal to 4.0, and b equals 0.51; for 2,4,6-tri-*tert*-butylphenol, a is equal to 5.65 ± 0.15, and b is equal to zero while, for hydrocarbons, a is equal to -1.2, and b is equal to 0.20. From these results and the differences in the heats of formation of organic hydroperoxides and 2,4,6-tri-*tert*-butylphenol and their oxy radicals, the Bond Dissociation Energies [BDE (O-H)] for a large number of phenols and hydroquinones are derived. Results of ancillary experiments are consistent with the view that phenols are stronger hydrogen bonding acids than organic hydroperoxides toward oxy radicals, and thus the observed rate differences, 6-10 in their transfer reactions, may be attributed to the occurrence of a prior equilibrium hydrogen bonding step in the hydrogen transfer between oxy radicals. The large rate differences, i.e., 10^4 to 10^5, between transfer from O-H and C-H bonds at the same values of K_i are correctly predicted by the energies of activation ($\Delta V^{\ddagger}$) calculated by the BEBO method of Johnston. The main source of the lower calculated activation energies for hydrogen atom transfer between oxy radicals is due to the low values of the potential energies of triplet repulsion between the oxygen moieties of the activated complex ($\Delta V_{\text{triplet}}$). Application of the BEBO method also leads to the correct prediction of the modes of hydrogen atom transfer, i.e., C-H vs. O-H, reactions of alkoxy radicals and the existence of the HBr catalysis of hydrocarbon oxidation. The rate constants at 60° for the bimolecular termination reactions of phenoxy radicals with peroxy radicals and with the 2,4,6-tri-*tert*-butylphenoxy radical are independent of substitution of the phenoxy radical and are in the range of 1 to 8×10^8 and 2×10^7 $(M\ \text{sec})^{-1}$, respectively. It is shown that the higher rate constants reported for reaction of peroxy radicals with 2,4,6-tri-*tert*-butylphenoxy [2×10^8 $(M\ \text{sec})^{-1}$] are due to steric effects; an unfavorable steric interaction of the phenoxy compared with peroxy moiety in the final products amounts to 5 kcal/mol. Finally as reported for related systems, the activation energies for the reaction of phenoxy radicals with the 2,4,6-tri-*tert*-butylphenoxy radical appear to be abnormally low, and it is suggested that the phenoxy radical systems should be subjected to the same theoretical treatment as those carried out for benzyl radicals. Such calculations may reveal the existence of metastable sandwich-like configurations as phenoxy radicals undergo bimolecular reactions.

For over a decade this laboratory has been engaged in systematic studies of the chemistry of phenoxy radicals in solution. From the results of our earliest work,[1] it was clear that the chemical systems in which phenoxy radicals are generated as reactive intermediates are dominated by reversible hydrogen atom transfers and complex equilibrium reactions. Moreover the rates of these reactions and positions of their final equilibria were apparently strongly influenced by the nature of the remote substitution of the phenolic moiety.[2] To provide a sound basis for analyses of the detailed mechanisms of these reactions, our efforts have been directed toward the systematic accumulation of kinetic and thermochemical data on these reactions as a function of substituent on the phenol and/or phenoxy radical derived from it.

Our approach has been to utilize a variety of experimental techniques to examine a number of different but interrelatable chemical systems. Initial studies were carried out on systems in which both peroxy and phenoxy radicals are generated as reactive intermediates. The rates of oxidation of the 9,10-dihydroanthracene (DHA), 2,2′,3,3′-tetraphenylbutane (TPB) system inhibited by a variety of 3- and 4-substituted phenols were shown to be consistent with the complex kinetic scheme 1-8, where R·, RO_2·, and A· are the free radicals derived from DHA or TPB, hydroperoxide, and nonhindered phenol, respectively.[3] In the same work, the rates of oxidation reported by workers in other laboratories utilizing different hydrocarbon-initiator systems were similarly shown to be consistent with the kinetic scheme 1-8, and the rate data from all these works were quantitatively fitted to the general rate equation I derived from reactions 1-8:

$$\text{R-R} \xrightarrow{k_1} 2\text{R}\cdot \tag{1}$$

$$\text{R}\cdot + \text{O}_2 \xrightarrow{k_2} \text{RO}_2\cdot \tag{2}$$

$$\text{RO}_2\cdot + \text{RH} \xrightarrow{k_3} \text{RO}_2\text{H} + \text{R}\cdot \tag{3}$$

$$2\text{RO}_2\cdot \xrightarrow{k_4} \text{O}_2 + \text{inert products} \tag{4}$$

$$\text{RO}_2\cdot + \text{AH} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \text{RO}_2\text{H} + \text{A}\cdot \tag{5, -5}$$

$$\text{A}\cdot + \text{RO}_2\cdot \xrightarrow{k_6} \text{inert products} \tag{6}$$

$$2\text{A}\cdot \xrightarrow{k_7} \text{inert products} \tag{7}$$

$$\text{A}\cdot + \text{RH} \xrightarrow{k_8} \text{AH} + \text{R}. \tag{8}$$

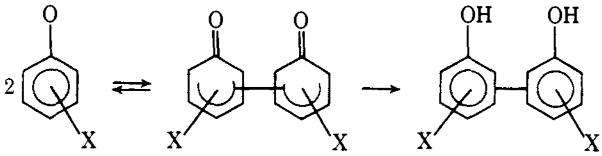
$$\frac{1}{[2k_1(\text{RR})]^{1/2}(\text{RH})}\left[\frac{d(\text{O}_2)}{dt} - 2k_1(\text{RR})\right] = \frac{1 + \alpha}{\left[\dfrac{2k_4}{k_3^2} + \dfrac{2k_6}{k_3k_8}\alpha + \dfrac{2k_7}{(k_8)^2}\alpha^2\right]^{1/2}} \tag{I}$$

where

$$\alpha = (\text{AH})/[(k_3/k_5)(\text{RH}) + (k_{-5}k_3/k_8k_5)(\text{RO}_2\text{H})]$$

Utilizing the directly measured values of $k_3/(2k_4)^{1/2}$ and $k_8/(2k_7)^{1/2}$ determined in the absence of and in the presence of high concentrations of the phenol, a computer fit of the experimental rates of oxygen absorption to the general rate expression I was carried out for the determination of the values of $2k_6/k_3k_8$, k_5/k_3, and k_{-5}/k_8.

An analysis of the relative magnitudes of these rather tenuously derived computer values of ratios of rate constants as a function of substitution of AH revealed that, as the values of k_5/k_3 increased, there occurred a corresponding increase in the values of $k_6/(k_7)^{1/2}$. This finding led to the "radical" proposal that the values of the rate constants for the bimolecular termination reaction of A· (k_7) were *not*, in general, ***diffusion controlled*** but varied by several orders of magnitude as a function of the substituent on AH (A·). That proposal has been quantitatively confirmed by our recent independent determination of the absolute values of k_7 for a large number of substituted phenoxy radicals by an ESR photochemical stationary state method.[4-6] It was also shown[5] that the values of k_7 determined by the photochemical stationary state method were directly applicable to the values of k_7 manifested during the phenolic inhibited oxidation of hydrocarbons in the liquid phase. From the results of a number of ancillary experiments, these variations in the values of k_7 were shown to be consistent with the occurrence of the reversible dimerization of the phenoxy radical followed by an irreversible enolization of the initially formed dimer, i.e.



(7a)

The degree of reversibility depends, as does the value of k_5/k_3, on the thermochemical stability of the phenoxy radical.

In addition to the correct prediction of the values of k_7 as a function of phenoxy radical substitution, our confidence in the validity of this overall procedure for the determination of the absolute values of the rate constants by computer fitting method is strengthened by values of k_5 obtained from the results of two other types of experiments which we will now describe.

By means of a direct ESR experimental method,[7,8] the absolute values of k_5 have recently been determined for the reaction of the *tert*-butylperoxy radical with phenol and 2-hydroxynaphthalene over the temperature range of −90 to 40°[9] As those workers pointed out, our earlier computer-derived values of k_5 for these two phenols were in strikingly good agreement with the values obtained by their direct measurement technique.

A second source of experimental verification comes from the results of our study of the synergistic effects of mixtures of hindered and nonhindered phenols as inhibitors of hydrocarbon oxidations.[10] In that work, it was shown that the occurrence of the transfer reactions by phenoxy radicals, i.e., reactions −5 and 8, could be completely surpressed by the addition of 2,6-di-*tert*-butylphenols. Under these conditions, the rates of oxidation were found to be quantitatively accounted for by the reaction scheme:

$$\mathrm{A\cdot + BH \xrightarrow{k_9} AH + B\cdot} \qquad (9, -9)$$

$$\mathrm{RO_2\cdot + BH \xrightarrow{k_{5'}} RO_2H + B\cdot} \qquad (5')$$

$$\mathrm{A\cdot + B\cdot \xrightarrow{k_{10}}} \qquad (10)$$

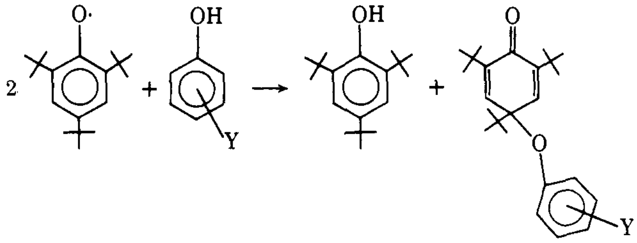
$$\mathrm{RO_2\cdot + B\cdot \xrightarrow{k_{11}}} \qquad (11)$$

where BH and B· represent the 2,6-di-*tert*-butylphenol and corresponding phenoxy radical. The measured rates of oxidation in such systems is given by the simple expression in II. The value of q would equal unity if termination is exclusively by means of reaction 10. If reaction 11 is the sole mode of termination, then the value of q would equal 2. Since the value of $k_{5'}/k_3$ may be directly and independently measured,[11] values of qk_5/k_3 and hence of qk_5 may be obtained by this method. As previously reported,[10] the values of qk_5/k_3 derived by this method are consistent with the value of k_5/k_3 determined by the computer fitting method.

$$\frac{\mathrm{d(O_2)}}{\mathrm{d}t} = 2k_1(\mathrm{RR}) + 2k_1(\mathrm{RR})\frac{k_3(\mathrm{RH})}{qk_5(\mathrm{AH}) + qk_{5'}(\mathrm{BH})} \qquad \text{(II)}$$

Based upon the above, we now feel confident in reporting the values of the absolute rate constants for the reactions 5, −5, 6, 7, and 8 at 60° in chlorobenzene solution for a wide variety of nonhindered phenols. The absolute values of k_8 and k_{-5} are derived from the values of the ratios $k_8/(2k_7)^{1/2}$ and the computer-derived ratios k_{-5}/k_8. Utilizing the independently determined value of k_3 equal to 850 $(M\ \mathrm{sec})^{-1}$ for DHA at 60°,[12] the absolute values of k_5 and k_6 are then calculated from the computer derived values of k_5/k_3 and k_6/k_3k_8.

The results of kinetic and thermochemical studies utilizing the stable 2,4,6-tri-*tert*-butylphenoxy radical allowed an extension to an interrelation to systems involving stable phenoxy, peroxy, and simple phenoxy radicals as reactive intermediates. Thus the values of the strongly substituent-dependent absolute rate constants for the hydrogen atom abstraction reaction by the 2,4,6-tri-*tert*-butylphenoxy radical from a variety of simple phenols (k_{-9}) and the decomposition of their quinol ether products (k_{-10}) were previously reported.[13] In the same study, the values of the overall equilibrium constants ($K_{-9}K_{10}$) and overall enthalpy $(\Delta H_{-9} + \Delta H_{10}))$ for the reaction



were determined and found to be independent of the nature of the substituent Y on the phenol moiety.

In a concurrent study, the absolute values of the rate constants for the hydrogen atom transfer reactions in both directions in the tetralin hydroperoxide-2,4,6-tri-*tert*-butylphenoxy radical system ($k_{5'}$ and $k_{-5'}$) were determined as a function of temperature. That study yielded a value of $K_{5'}$ equal to 3×10^4 at 60° and a value for the enthalpy of the reaction ($\Delta H_{5'}$) equal to −7.0 ± 1.7 kcal/mol.[14] Griva and Denisov[15] have recently extended such measurements to the cumene hydroperoxide system and obtained a value of $\Delta H_{5'}$ equal to −6.9 ± 2.0 kcal/mol. Since we had previously determined by direct calorimetric measurement the difference in the enthalpies of formation of the 2,4,6-tri-*tert*-butylphenoxy radical and its hydrogenated precursor, the absolute value of the difference in enthalpies of formation of the organic peroxy radical and hydroperoxide was therefore determined.[16]

The results from all of these measurements may be combined to obtain the absolute rate constants and equilibrium constants in the various reactions of phenols and phenoxy radicals occurring in the 2,4,6-tri-*tert*-butylphenoxy system. The values of K_9 and k_{-9} are derived from the simple relationships in eq IIIa and IIIb. The values of K_{10} and k_{10} are similarily obtained from eq IVa and IVb.

Table I. Summary of Rate Constants for Reactions in Phenol Inhibited Oxidation of 9,10-Dihydroanthracene in Chlorobenzene at 60°[a]

	From direct measurement			From computer fit to eq I			From direct measurement plus computer fit				Direct measurement by other methods	
Phenol	$k_7 \times 10^{-7}$, $(M\ \mathrm{sec})^{-1}$[b]	$k_8/(2k_7)^{1/2} \times 10^3$, $(M\ \mathrm{sec})^{1/2}$	k_8, $(M\ \mathrm{sec})^{-1}$	k_{-5}/k_8	k_5/k_3	$2k_6/k_3k_8 \times 10^{-4}$, M sec	$k_6 \times 10^{-7}$, $(M\ \mathrm{sec})^{-1}$	$k_{-5} \times 10^{-3}$, $(M\ \mathrm{sec})^{-1}$	$k_5 \times 10^{-3}$, $(M\ \mathrm{sec})^{-1}$	K_5	$k_5 \times 10^{-3}$, $(M\ \mathrm{sec})^{-1}$	$qk_5 \times 10^{-3}$, $(M\ \mathrm{sec})^{-1}$
4-OMe·	0.17	19.8	37	17.5	284	4.96	78	0.65	242	384		230[b]
2,6-Di-Me-	6.0	7.1	78	27.5	200	0.30	10	2.14	170	79.5		
4-Phenyl-	0.08	9.5	12	59.5	78	0.76	39	0.71	66	93		
4-Me-	8.0	7.8	99	52.8	55	0.58	24	5.2	47	9.0		
4-*t*-Bu-	3.0	11.2	87	44.7	47	0.30	11	4.1	40	9.8		
2,3-Benzo-	35.0	2.3	62	53.0	39	2.31	61	3.3	33	10.0	25[c]	
3,5-Di-*t*-Bu-	1.0	40.0	176	14.3	14.9	0.21	15	2.5	12.7	5.1		16.8
4-H	3.5	13.0	110	110	9.7	0.34	16	12.1	8.2	0.68	4.5[c]	
3-COOEt-	18.0	86.0	1640	30.7	3.5	0.047	33	50.3	3.0	0.06		

[a] Utilizing absolute value of k_3 equal to 850 $(M\ \mathrm{sec})^{-1}$ for 9,10-dihydroanthracene at 60° (J. A. Howard, communication to authors). [b] Reference 10. [c] Reference 8.

Table II. Summary of Rate and Equilibrium Constants for Reactions of Phenols and 2,4,6-Tri-*tert*-butylphenoxy Radical in Chlorobenzene at 60°

	From direct measurements[a]				Derived from $K_9 = 3 \times 10^4/K_5$			
Phenol	k_{-9}, $(M\ \mathrm{sec})^{-1}$	$k_{-10} \times 10^5$, sec^{-1}	k_9/k_{10} (40°)	$K_{-9}K_{10} \times 10^{-7}$, M^{-1}	$K_9 \times 10^{-3}$	$k_9 \times 10^{-5}$, $(M\ \mathrm{sec})^{-1}$	$K_{10} \times 10^{-10}$, M^{-1}	$k_{10} \times 10^{-7}$, $(M\ \mathrm{sec})^{-1}$
4-OMe-	6000 ± 600[b]	2700 ± 200		(1.3)	0.079	4.75	0.10	2.7
4-*t*-Bu-	108 ± 5	52 ± 1.5	127 ± 8	1.3 ± 0.4[c]	3.1	3.3	4.3	2.3
4-H	8.0 ± 0.05			(1.3)	44.0	3.5	57.0	
3-COOEt-	1.28 ± 0.03	0.34 ± 0.01		(1.3)	500.0	6.4	650.0	2.2

[a] L. R. Mahoney and M. A. DaRooge, *J. Am. Chem. Soc.*, 92, 890 (1970). [b] Extrapolated from data at 25°[cf. M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.*. 32, 1 (1967). [c] The directly measured values of $\Delta H_{-9} + \Delta H_{10}$ at 25° was found to be equal to 20.22 ± 0.15 kcal/mol for a number of 3- and 4-substituted phenols and the value of $K_{-9}K_{10}$ at 40° was found to be equal to 2.2 ± 0.4 × $10^8\ M^{-1}$ at 40° for 4-*tert*-butyl-, 3,5-dimethyl-, and 4-bromophenol.

$$K_9 = K_{5\cdot}/K_5 = 3 \times 10^4/K_5 \qquad \text{(IIIa)}$$

$$k_9 = k_{-9}(3 \times 10^4)/K_5 \qquad \text{(IIIb)}$$

$$K_{10} = K_9K_{10}K_9 = 1.3 \times 10^7K_9 \qquad \text{(IVa)}$$

$$k_{10} = k_{-10}K_{10} \qquad \text{(IVb)}$$

In the present work, we first of all summarize the values of the absolute rate and equilibrium constants obtained from the results of the work described above. We then examine the existence of the classical Brφnsted relationships between these kinetic and thermodynamic quantities and derive values of the Bond Dissociation Energies [BDE (O-H)] for a number of phenols and hydroquinones. Finally based upon these data, detailed analyses of the mechanisms of the hydrogen atom transfer reactions between oxy radicals and the cross termination reactions between oxy radicals are carried out.

Results and Discussion

Absolute Rate and Equilibrium Constants. In Table I are summarized the values of the ratios of rate constants obtained for four phenols reported in the earlier work[3] and for five phenols subsequently studied and reported in the present work. The various quantities are grouped according to their source; the values of k_7, $k_8/(2k_7)^{1/2}$, and k_8 were determined by direct experimental measurements, while values of k_5/k_3, k_{-5}/k_8, and $2k_6/k_3k_8$ were obtained from the computer fit of the oxygen absorption rates. The absolute values of k_6, k_5, k_{-5}, and K_5 (k_5/k_{-5}) were then obtained by combining the directly measured and computer fitted results. Since the uncertainties in the absolute values of k_7 are at most 50%,[4] the resulting uncertainties in the absolute values of k_8 are on the order of 30%. The good agreement between the absolute values of k_5 determined by other workers, the values of qk_5 determined in the mixed system, and the computer derived values of k_5 lead us to be confident that the computer derived values of k_5, k_{-5}, and k_6 are reliable to within a factor of 2.

In Table II are summarized the absolute values of the rate constants k_9, k_{-9}, k_{10}, and k_{-10} and the equilibrium constants K_9 and K_{10} at 60° for four phenolic systems. While the directly measured values of k_{-9}, k_{-10}, and k_9/k_{10} are reliable to 5%, the absolute values of k_9 and k_{10} are derived from K_5 and thus are reliable to only a factor of 2.

Brφnsted Relationships. There exists a moderately good linear relationship between the values of logarithm k_5 and logarithm K_5, i.e.

$$\log k_5 = 4.0 + 0.51 \log K_5 \qquad \text{(V)}$$

with a root mean square value of log k_5 equal to 4.56 and a standard deviation from the mean equal to 0.17 units. In contrast, the values of k_9 for the hydrogen atom abstraction by substituted phenoxy radicals from 2,4,6-tri-*tert*-butylphenol are independent of the value of K_9 and within experimental error are given by the relationship in eq VI.

$$\log k_9 = 5.65 \pm 0.15\ (M\ \mathrm{sec})^{-1} \qquad \text{(VI)}$$

For purpose of later discussion, it is of interest to examine the relationships between the values of the absolute rate constants for hydrogen atom abstraction by peroxy and phenoxy radical from hydrocarbons and the equilibrium constants for the abstraction reactions. The values of the logarithms of the equilibrium constants for hydrogen atom abstraction from hydrocarbons by phenoxy radicals are given by the expression in eq VII. Values of log K_3 have not

$$\log K_8 = \log K_3 - \log K_5 \qquad \text{(VII)}$$

been determined by direct experimental measurements for the hydrocarbons of interest here. However, fairly reliable values (±1.0 log units) may be estimated from the experimental measurements of BDE (R–H) for a number of other hydrocarbons and the application of the additivity rules of Benson. From a recent compilation of such data,[17] we calculate values of log K_3 at 60° equal to −2.6 for isobutane, 2.0 for toluene, 4.0 for tetralin, and 11.3 for 9,10-dihydroanthracene. Values of log k_8 for 9,10-dihydroanthracene as substratum were taken from Table I. With tetralin as substratum, the values of k_8 are 0.6 and 0.2 $(M\ \mathrm{sec})^{-1}$ for the unsubstituted phenoxy and 4-methoxyphenoxy radicals, respectively, based upon values of $k_8/(2k_7)^{1/2}$ reported in earlier work.[3] Combining the values of log k_8 and log K_8 with the reported values of log k_3 and log K_3 for the analogous reactions of peroxy radicals with hydrocarbons yields the linear relationship eq VIII, with a root mean square

$$\log [k_{3(8)}/H] = -1.1 + 0.24 \log K_{3(8)} \ (M\ \mathrm{sec})^{-1} \qquad \text{(VIII)}$$

value of log $[k_{3(8)}/H]$ equal to 1.37 and standard deviation from the mean equal to 0.46 units. This relationship compares favorably with that obtained from the extensive correlation of values of log (k_3/H) vs. log K_3 for secondary peroxy radicals at 30° reported earlier,[17] namely

$$\log [k_3/H] = -1.2 + 0.2 \log K_3 \ (M\ \mathrm{sec})^{-1} \qquad \text{(IX)}$$

Bond Dissociation Energies of Phenols and Hydroquinones. Based upon the reasonable assumption that the entropy change for the hydrogen atom transfer reactions between peroxy radicals and phenols (ΔS_5) is zero, the observed values of $-2.3RT$ log K_5 at 60° may be equated to the enthalpy (ΔH_5) of the reaction. Since the absolute value of the bond energy of organic hydroperoxides has been found to be equal to 88.0 ± 1.7 kcal/mol,[14,15] the bond dissociation energies of the -O—H bonds of a number of phenols may be calculated. The values of these fundamentally important quantities are summarized in Table IIIA.

For a number of other phenols and hydroquinones, the values of k_5 have been measured, but values of k_{-5} and thus K_5 are not available. However, utilizing the empirical Brφnsted relationship, values of log K_5 may be estimated. The values of the bond dissociation energies derived in this manner are presented in Table IIIB.

Although the absolute values of the bond energies determined by this method are known to only ±2.0 kcal/mol, few bond dissociation energies of polyatomic molecules are known to much greater precision. Moreover their relative values are much more reliable, i.e., ±0.5 kcal/mol, and thus they should find considerable use not only in theoretical studies of chemical bonding but also in mechanistic studies of chemical reactions in which phenoxy radicals are generated as reactive intermediates.

Hydrogen Atom Transfer Reactions. In Figure 1 are presented plots of the logarithms of the absolute rate constants for the hydrogen atom transfer reactions of peroxy and phenoxy radicals with hydrocarbons, hydroperoxides, and phenols (k_i) vs. the logarithms of the equilibrium constants for the reactions (K_i) in chlorobenzene solution at 60° obtained from the data in Tables I and II. From examination of the figure, we conclude that, when K_3 and K_8 are equal, the values of k_3 and k_8 are approximately equal. The similar response of k_3 and k_8 to the thermochemistry of the transfer reactions from hydrocarbon is what would be predicted from the linear free energy relationships commonly encountered in chemical kinetic studies.[18] However, hydroperoxide is somewhat less reactive, i.e., smaller value of k_i, than phenol at the same value of K_i in hydrogen atom transfer reactions with peroxy and phenoxy radicals, and hydrogen transfer from -OH is much more rapid than that from C–H at the same values of log K_i.

Table III. Bond Energies [BDE (OH)] of Phenols and Hydroquinones

A. Derived from Values of $-2.3RT$ log K_5 at 60° in Chlorobenzene

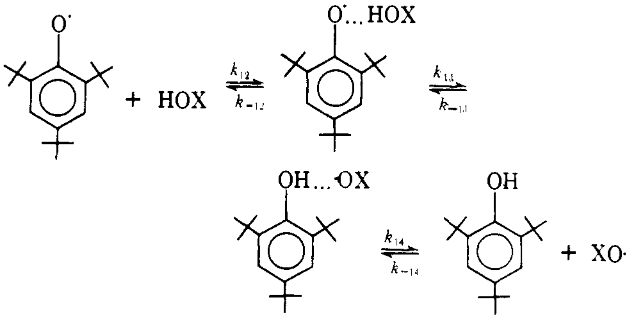
Compd	ΔH_5, kcal/mol	BDE (OH), kcal/mol
3-COOEt-phenol	+1.87	89.9
Phenol	+0.26	88.3
3,5-Di-*tert*-butylphenol	−1.08	86.9
2-Hydroxynaphthalene	−1.52	86.5
4-*tert*-Butylphenol	−1.53	86.5
4-Methylphenol	−1.47	86.5
4-Phenylphenol	−3.0	85.0
2,6-Dimethylphenol	−2.91	85.1
4-Methoxyphenol	−3.97	84.0

B. Derived from Brφnsted Relationship (Equation V) and Values of k_5

Compd	$k_5 \times 10^{-4}$, $(M\ \mathrm{sec})^{-1}$	BDE (OH), kcal/mol
3-Hydroxyphenol	0.117	90.9
4,4′-Dihydroxybiphenyl	8.25	85.2
1,4-Dihydroxybenzene	12.5	84.6
1-Hydroxynaphthalene	13.8	84.5
1,5-Dihydroxynaphthalene	55.0	83.6
3-Hydroxyfluorene	92.0	82.0
3-Hydroxypyrene	370.0	80.2
3,10-Dihydroxypyrene	680.0	79.2
3,8-Dihydroxypyrene	850.0	79.0

To account for the second and third phenomena, we shall now present a detailed analysis of the mechanism of hydrogen atom transfer reactions between oxy radicals.

Hydrogen Transfer from ROOH vs. Phenol. The experimentally observed values of the rate constants for hydrogen atom transfer between oxy radicals are likely to be complex quantities and not rate constants representing simple bimolecular hydrogen atom transfers. Results from a number of studies[9,19,20] are consistent with the view that the mechanism of these reactions involves a prior equilibrium formation of a hydrogen-bonded complex of the oxy radical with the -OH substrate followed by a rate-controlling atom transfer within the complex. Thus for reactions −5 and −9



and under conditions such that $k_{-12} \gg k_{13}$[21]

$$k_{\mathrm{obsd}} = K_{12}k_{13}$$

Very accurate values of the absolute rate constants for transfer of hydrogen from phenols and hydroperoxides by the 2,4,6-tri-*tert*-butylphenoxy radical have been determined by the direct stopped-flow technique.[13,14] At 30° (60°) in CCl_4 solution, the value of $k_{-5'}$ is equal to 1.35 ±

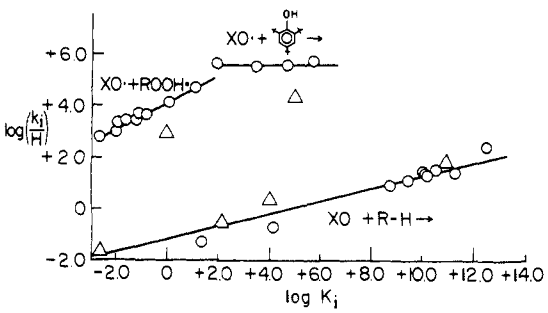


Figure 1. Brønsted plots of logarithms of the absolute rate constants [log (k_i/H)], vs. logarithms of the equilibrium constants (log K_i) for hydrogen atom transfer reactions at 60° in chlorobenzene solution. The circles (○) represent phenoxy radicals, and the triangles (△) represent peroxy radicals.

0.07 $(M\ \mathrm{sec})^{-1}$ [2.5 ± 0.1 $(M\ \mathrm{sec})^{-1}$] for *tert*-butyl hydroperoxide and, for phenol, k_{-9} is equal to 7.9 ± 0.4 $(M\ \mathrm{sec})^{-1}$ [15.7 ± 0.9 $(M\ \mathrm{sec})^{-1}$], while the equilibrium constants for the overall reactions are nearly identical in chlorobenzene at 60°, i.e., 3.3×10^{-5} for organic hydroperoxide and 2.3×10^{-5} for phenol. The values of K_{12} will, of course, depend upon the structure of the oxy radical and the solvent and temperature of the reaction in question. If one invokes the occurrence of the prior equilibrium mechanism for these transfer reactions, then this rate difference of a factor of 6 may be due to a difference in the values of K_{12} for phenol and hydroperoxide. We shall now present evidence, albeit indirect, that the rate difference is primarily due to this effect.

Taft et al.[22] have demonstrated the existence of linear free energy relationships for a number of O-H reference acids in hydrogen bond formation with a wide variety of proton acceptors. The relationships are of the form shown in eq X, where log K_f is the logarithm of the formation con-

$$\log K_f = m(\log K_f)_0 + c \qquad \text{(X)}$$

stant of the hydrogen bonded complex of the acid in question and $(\log K_f)_0$ is the logarithm of the formation constant of the hydrogen bonded complex of 4-fluorophenol with the same proton acceptor, and m and c are constants characteristic of the reference acid, solvent, and temperature but *independent* of the proton acceptor. For phenol at 25° in CCl_4 solution, they report the relationship in eq XI. In a se-

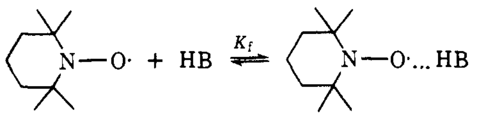
$$\log K_{f,\mathrm{phenol}} = 0.97\ (\log K_{f,\mathrm{4F\text{-}phenol}}) - 0.13 \qquad \text{(XI)}$$

ries of ancillary experiments, we have determined the values of K_f for the hydrogen bonding of *tert*-butyl hydroperoxide with dimethylformamide, pyridine, tetrahydrofuran, and dioxane in CCl_4 at 25°. A plot of the values of log $K_{f,\mathrm{ROOH}}$ vs. log $K_{f,\mathrm{4F\text{-}phenol}}$ for these four proton acceptors yields the linear relationship in eq XII, with the standard deviation

$$\log K_{f,\mathrm{ROOH}} = 0.73\ (\log K_{f,\mathrm{4F\text{-}phenol}}) - 0.37 \qquad \text{(XII)}$$

equal to 0.01, and the root mean square value of log $K_{f,\mathrm{ROOH}}$ equal to 0.89 units.

Lim and Drago[23] have recently measured the values of K_f in CCl_4 solution at 25° for a number of phenols and fluorinated alcohols with the stable nitroxide radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl:



These workers report a value of $K_{f,\mathrm{phenol}}$ equal to 27 ± 1 M^{-1} from which we calculate a value of log $K_{f,\mathrm{4\text{-}F\text{-}phenol}}$ equal to 1.61 units for the nitroxide radical. Relationship VIII appears to be valid for the nitroxide radical since the values of K_f we calculate from eq X for 2,2,2-trifluoroethanol and hexafluoroisopropyl alcohol, utilizing the values of m and c of Taft et al.,[22] are 20 and 155 M^{-1} compared with the experimental values of 19 ± 1 and 127 ± 38 M^{-1}, reported by Lim and Drago.

The calculated value of K_f for *tert*-butyl hydroperoxide at 25° in CCl_4 with the nitroxide radical is then 6.3 M^{-1} or a factor of 4.3 lower than the value observed for phenol as the hydrogen donor. This difference compares favorably with the observed rate difference of 6.0 in the same solvent at 30 and 60° with the 2,4,6-tri-*tert*-butylphenoxy radical. The pK_{BH} value we calculated for the nitroxide radical is 1.61 units. If the proton acceptor strength of the 2,4,6-tri-*tert*-butylphenoxy radical is somewhat higher, i.e., equal to 2.22 units, the values of K_f for phenol and hydroperoxide would then differ by a factor of 6. Unfortunately one is very limited as to the choice of oxy radicals for direct study of their proton acceptor properties. The nitroxide radical with very low BDE (OH)[24] and thus low reactivity in hydrogen atom transfer reactions appears to be the only species with which such direct studies may be carried out.

The consequences of the extension of this prior equilibrium hydrogen bonding mechanism to other hydrogen atom transfer reactions will now be considered. From Figure 1 we see that hydrogen atom transfer from hydroperoxide is 5-10 times more rapid by phenoxy radical than by peroxy radical and that transfer from 2,4,6-tri-*tert*-butylphenol is also 10 times more rapid by phenoxy than by peroxy radicals in chlorobenzene at 60°. Taken together, these results could be accounted for if the proton acceptor strengths of the simple phenoxy radical exceeds that of the peroxy radical. Since thiophenols[25] are extremely weak acids, we would anticipate that the prior hydrogen bonding of these molecules with oxy radicals would not be important in their hydrogen atom transfer reactions. The recent work of Howard and coworkers[9] is consistent with this prediction.

Hydrogen Transfer from -O—H vs. C—H. We now turn our attention to the large rate differences (10^4 to 10^5) which exist between -O—H and C—H bonds in hydrogen atom abstraction reactions by peroxy and phenoxy radicals. The preceding discussion would indicate a rate enhancement of only 10-50 would be anticipated because of the more favorable hydrogen bonding interactions of oxy radicals with -O—H compared with C—H substrates. There must therefore exist larger effects which manifest themselves in the formation of the activated complexes for these transfer reactions.

Johnston and coworkers[26] have developed a highly successful and computationally simple procedure, the Bond-Energy-Bond-Order method (BEBO), for the calculation of the potential energies of activation ($\Delta V^{\ddagger}$) for hydrogen atom transfer reactions of the type

$$\mathrm{Y\cdot} + \mathrm{XH} \longrightarrow (\mathrm{Y}\ldots\mathrm{H}\ldots\mathrm{X}) \longrightarrow \mathrm{YH} + \mathrm{X\cdot}$$

in the gas phase. The method is empirical, but the empiricism lies *outside* the field of chemical kinetics.

The potential energy of the complex (Y . . H . . X) is resolved into two terms, $\Delta V_{\mathrm{bonding}}$ and $\Delta V_{\mathrm{triplet}}$. The term $\Delta V_{\mathrm{bonding}}$ represents the potential energy change in the system due to the breaking of the X-H bond, and formation of the Y-H bond and is given by the expression XIII, where

$$\Delta V_{\mathrm{bonding}} = D_{\mathrm{XH}}(1 - n^{p}) - D_{\mathrm{YH}}(1 - n)^{q} \qquad \text{(XIII)}$$

Table IV. Calculation of Potential Energies of Activation (BEBO) for Hydrogen Atom Transfer Reactions

XH	D_{XH}, kcal/mol	Y	D_{YH}, kcal/mol	D_{XY}, kcal/mol	β, A°$^{-1}$	ΔR_s, A°	n_{XH}	$\Delta V^\ddagger_{bonding}$, kcal/mol	$\Delta V^\ddagger_{triplet}$, kcal/mol	$\Delta V^\ddagger$, kcal/mol
A. Peroxy Radicals										
R–H	88	ROO·	88	55.4[a]	2.05	0.62	0.45	3.5	3.9	7.4
ROO–H	88	ROO·	88	8.0[b]	3.9[c]	0.45	0.50	1.7	0.17	1.87
				8.0[b]	6.5[d]	0.45	0.50	1.7	0.02	1.72
B. Alkoxy Radicals										
RO–H	104	RO·	104	38	2.38	0.45	0.50	2.0	2.9	4.9
H–CH_2OH	94	RO·	104	87	1.74	0.62	0.65	−0.2	7.5	7.3
H–$C(CH_3)_2OH$	90	RO·	104	87	1.74	0.62	0.75	−1.2	7.2	6.0
C. HBR Catalysis of Isobutane Oxidation										
H–$C(CH_3)_3$	91	Br·	87.5	66.2	1.845	0.58	0.25	3.1	5.4	8.5
H–$C(CH_3)_3$	91	ROO·	88	70	1.825	0.62	0.40	5.3	6.2	11.5

[a] Calculated from group additivity values of Benson ($\Delta H_{f,ROOR} = 2\Delta H_{f,ROOH} - \Delta H_{f,H_2O_2}$; and $\Delta H_{ROOH} = \Delta H_{f,ROH} + 19$) for R · equal to the allyl group. [b] K. Adamic, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, 47, 3803 (1969). [c] Value of W_{XY}· equal to 600 cm^{-1}. [d] Value of W_{XY}· equal to 1000 cm^{-1}.

D_{XH} and D_{YH} are the bond dissociation energies of X-H and Y-H molecules, n is a progress variable (order of X-H bond), and p and q are bond indices calculable for any pair of atoms for which single bond energies and distances are known. For the C-H bond, $p(q)$ is equal to 1.087 and for the -O—H bond, 1.028, and for HBr, 0.892.

The quantity $\Delta V_{triplet}$ represents the repulsive energy of the complex due to the necessary occurrence of parallel electron spins on X and Y during the course of the transfer reaction. It is given by the expression XIV, where D_{XY} is

$$\Delta V_{triplet} = 0.25\, D_{XY}e^{-\Delta R_s}[(n - n^2)^{0.26\beta}] \times [2 + e^{-\beta\Delta R_s}(n - n^2)^{0.26\beta}] \quad (XIV)$$

the bond dissociation energy of the X-Y molecule, β is the Morse parameter obtained from the spectroscopic data on XY, and ΔR_s is equal to the sums of the X-H and Y-H bond distance minus the bond distance in the X-Y molecule.

The potential energy of formation of the complex is then equal to the sum of the bonding and repulsive or triplet energies both of which are functions of the bond order n. in the XH bond. The value of n is varied from 1.0 to 0, and the maximum value of the potential energy of the complex corresponds to the potential energy of activation for the reaction ($\Delta V^\ddagger$).

In Table IV are summarized the values of the parameters utilized and the results of the calculation of the potential energies of activation by the BEBO method for the thermoneutral hydrogen transfer reactions of peroxy radical with hydroperoxide and with a hydrocarbon with D_{RH} equal to 88.0 kcal/mol. We see that the value of $\Delta V^\ddagger$ for the transfer from hydrocarbon is 5.6 kcal/mol higher than for transfer from hydroperoxide. Neglecting for the moment differences in the values of the preexponential factor for the two reactions (vide infra), this energy difference corresponds to a rate factor of ca. 10^4 at laboratory temperatures, in strikingly good agreement with the experimental results. The main source of this calculated difference is due to the very low value of $\Delta V_{triplet}$ for the hydrogen atom transfer between the oxy radicals which is in turn due to the values of D_{XY} for the respective reactions:

$$ROOR \longrightarrow R\cdot + \cdot OOR, \quad \Delta H = +55.4 \text{ kcal/mol}$$

$$ROOOOR \longrightarrow 2ROO\cdot, \quad \Delta H = +8.0 \text{ kcal/mol}$$

Low values of $\Delta V_{triplet}$ will be a rather general rule for XY molecules of low bond dissociation energies. The dialkyl peroxide molecule which serves as the X-Y molecule for the identity hydrogen atom transfer between alkoxy radical possesses a relatively low BDE, i.e.

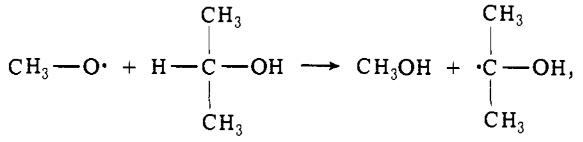
$$ROOR \longrightarrow 2RO\cdot, \quad \Delta H = +38.0 \text{ kcal/mol}$$

Accordingly we have carried out the BEBO calculations for the thermoneutral reaction

$$CH_3—O\cdot + CH_3OH \longrightarrow CH_3OH + CH_3O\cdot, \quad \Delta H = 0$$

and for the exothermic reactions

$$CH_3—O\cdot + CH_3—OH \longrightarrow CH_3OH + \cdot CH_2—OH, \quad \Delta H = -10 \text{ kcal/mol}$$



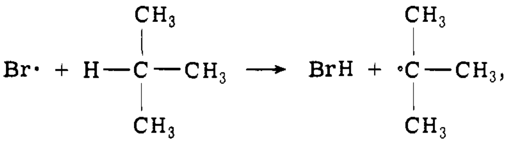
$$CH_3—O\cdot + H—\underset{CH_3}{\overset{CH_3}{C}}—OH \longrightarrow CH_3OH + \cdot\underset{CH_3}{\overset{CH_3}{C}}—OH,$$

$$\Delta H = -14 \text{ kcal/mol}$$

From the results of the calculations presented in Table IV, we see that, because of the lower values of $\Delta V_{triplet}$, the calculated values of the activation for the thermoneutral reaction are actually lower than those for the very exothermic carbon-hydrogen bond breaking reactions. The results of a recent ESR study[27] substantiate this BEBO prediction. These workers found that the rates of the thermoneutral hydrogen atom transfer reaction between *tert*-butyloxy radicals were fully competitive with the highly exothermic hydrogen atom abstraction from primary alkyl hydrogens.

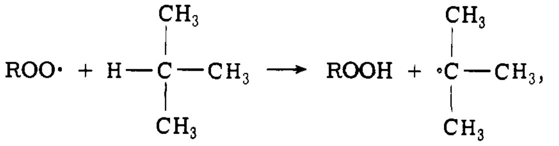
From the value of n_{XH} corresponding to the value of $\Delta V^\ddagger$ and the bond length-bond order relationship of Pauling,[24] it is possible to calculate the distance between the X and Y moieties in the transition state for the hydrogen atom transfer reaction. For the thermoneutral hydrogen atom transfer between peroxy radicals, the oxygen moieties are separated by 2.28 Å while, for the thermoneutral transfer between peroxy radicals and hydrocarbon, the oxygen-carbon separation is 2.42 Å. It seems likely that the relative tightness of the activated complex in the oxygen-oxygen system would result in lower values of the preexponential term of the Arrhenius equation for such a system compared with those observed in the oxygen-carbon system. The data presently available[9,19] are consistent with this prediction. In addition to this effect, a contribution due to the prior equilibrium hydrogen-bonding step in the oxygen-oxygen system must also be contributing to the low values of the observed preexponential terms and activation energies.[19]

Differences in the values of q, the bond index for the abstracting atom or free radical, may also result in relative values of $\Delta V^{\ddagger}$ which would not be predicted from purely thermochemical considerations. An excellent example of this effect is afforded by the correct prediction of catalysis of hydrocarbon oxidation by HBr[28] from the relative values of $\Delta V^{\ddagger}$ calculated for abstraction of hydrogen from isobutane by bromine atoms and peroxy radicals:



$$\mathrm{Br\cdot + H{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3 \longrightarrow BrH + \cdot\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3,}$$

$\Delta H = +3.5$ kcal/mol



$$\mathrm{ROO\cdot + H{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3 \longrightarrow ROOH + \cdot\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3,}$$

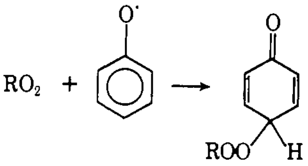
$\Delta H = +3.0$ kcal/mol

From the results given in Table IV, we see that the value of $\Delta V^{\ddagger}$ is ca. 3.0 kcal/mol lower for the bromine atom abstraction because of its lower value of $\Delta V_{\mathrm{bonding}}$ for the reaction. The $\Delta V_{\mathrm{triplet}}$ vs. n_{XH} are virtually identical for the bromine atom and peroxy radicals for this reaction.[29]

Before leaving the reader with the false impression that all workers presently engaged in kinetic studies of hydrogen atom transfer reactions should instead devote themselves to spectroscopic and structural studies on X-Y molecules, an apparent shortcoming of the method will now be considered. The values of $\Delta V^{\ddagger}$ calculated by the BEBO method of Johnston are significantly lower than the values of $\Delta E^{\ddagger}$ reported from the experimental studies of the autoxidation of hydrocarbons in the liquid state. Thus $\Delta V^{\ddagger}$ calculated for the hydrogen atom abstraction by peroxy radical from isobutane and toluene (*p*-xylene) are 11.5 and 5.7 kcal/mol compared with experimental values of $\Delta E^{\ddagger}$ equal to ca. 15.5 and 10-11.5[16] kcal/mol for abstraction by *tert*-butylperoxy radical. Zavitsas[30] has recently reported an alternative method for the calculation of the potential energies of activation for hydrogen atom transfer reactions. In contrast to Johnston's, his bonding term is calculated from the Morse curves of the reactant and product molecules, but his triplet repulsion term is also calculated from equation XIII with a value of 0.45 vs. 0.25 utilized by Johnston for the value of the arbitrary constant in the equation. This change of constants results in a corresponding increase in $\Delta V_{\mathrm{triplet}}$ by a factor of 1.8. If we introduce this factor in the results of Table IV, it has little effect on $\Delta V^{\ddagger}$ for transfer between oxy radicals, nor has it any effect on the correct prediction of HBr catalysts. However, the values of $\Delta V^{\ddagger}$ calculated are now in better agreement with the experimental values of $\Delta V^{\ddagger}$ 16.4 and 8.8 kcal/mol for isobutane and toluene, respectively.[17] Unfortunately if such a procedure were extended to gas phase systems, the good agreement between experiment and calculated values reported by Johnston and Parr[31] would disappear. Even with this limitation, the BEBO technique and/or the method of Zavitsas should prove to be extremely valuable predictive and analytical tools in the study of free radical hydrogen atom transfer reactions.

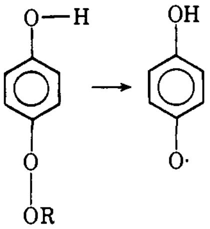
Radical-Radical Reactions. The complex mechanisms of the bimolecular termination reactions of nonhindered and trialkyl-substituted phenoxy radicals have been the subject of a recent series of studies from our laboratory.[6,32] A key to the unraveling of the mechanism of these reactions has been the simultaneous application of kinetic and thermochemical information. In the present section, we shall apply the same tools for the analysis of the termination reactions involving peroxy with phenoxy radicals and 2,4,6-tri-*tert*-butylphenoxy radicals with peroxy and phenoxy radicals.

For the reaction of peroxy radical with simple phenoxy radical (eq XV), the heat of reaction is exothermic by 40 kcal/mol.[33] Thus in contrast to the self reactions of a number of phenoxy radicals where $-\Delta H_7$ is less than 20 kcal/mol,[5] the initially formed, nonenolized, product (eq X) will be thermally stable at 60° with respect to decomposition to its precursors. From the results in Table I, we see that the values of the absolute rate constants (k_6) for these reactions vary from 1.0 to 7.8 × 10^8 (M sec)$^{-1}$. These values are in the range one would anticipate for a diffusion-controlled reaction in chlorobenzene solution; the values for the bimolecular reactions of the semidiones from camphorquinone and biacetyl are 1.2 × 10^8 and 7.5 × 10^8 (M sec)$^{-1}$, and the value for the *acid*-catalyzed and thus *irreversible* dimerization of simple phenoxy is 4 × 10^8 (M sec)$^{-1}$ in chlorobenzene at 60°.[5]



(XV)

Upon enolization of XV, a metastable peroxy substituted phenol (eq XVI) would be obtained. This compound would rapidly decompose to semiquinone and alkoxyl radicals (eq XVI). The semiquinone radical is an extremely efficient hydrogen donor with a BDE (OH) equal to 58 kcal/mol and would scavenge RO· in either a simultaneous cage or a subsequent fast reaction. Thus the overall stoichiometric factor for reaction of phenol with peroxy radicals would be equal to 2.0 as has been frequently reported.[2]



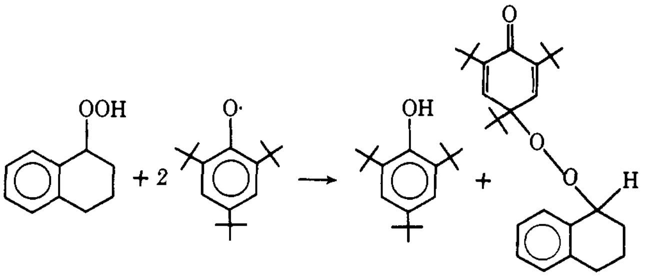
+ RO· $\Delta H = 8.0$ kcal/mol (XVI)

From the results summarized in Table II, we see that the values of the absolute rate constants (k_{10}) for the bimolecular reactions of 3- and 4-substituted phenoxy radicals with the 2,4,6-tri-*tert*-butylphenoxy radical are independent of the substitution of the phenoxy radical and are equal to 2.5 ± 0.3 × 10^7 (M sec)$^{-1}$ at 60°. These values may be compared with a value of 2 × 10^8 (M sec)$^{-1}$ recently reported by Griva and Denisov for the analogous reaction of cumylperoxy radical and 2,4,6-tri-*tert*-butylphenoxy in cumene at 40°.[15] The difference in these rate constants is presumably due to the steric interactions of the phenoxy moiety vs. the peroxy moiety in the formation of the 4-substituted quinol ether-phenoxy and peroxy compounds. A quantitative estimate of this effect may be obtained by the following analysis.

The enthalpy of the radical-radical reaction (ΔH_{10}) is derived from the relationship in eq XVII. The values of

$$\Delta H_{10} = [\Delta H_{-9} - \Delta H_{10}] + [\Delta H_{\mathrm{B}} - \Delta H_{\mathrm{BH}}] + [\Delta H_{\mathrm{AH}} - \Delta H_{\mathrm{A\cdot}}] \quad \mathrm{(XVII)}$$

$[\Delta H_{-9} + \Delta H_{10}]$[13] and $[\Delta H_{\mathrm{B}\cdot} - \Delta H_{\mathrm{BH}}]$[16] have been determined in earlier work by direct calorimetric measurements, while the values of $[\Delta H_{\mathrm{AH}} - \Delta H_{\mathrm{A}\cdot}]$ are those reported in the present work for the individual phenols. The values of ΔH_{10} obtained by this procedure are summarized in Table V. Utilizing the heat of the reaction



determined in the present work (cf. Experimental Section), which is equal to $\Delta H_{-5} + \Delta H_{11}$, and the value of $\Delta H_{-5'}$ reported earlier,[14,15] we obtain a value for ΔH_{11} equal to −32.3 ± 2.0 kcal/mol. If the steric interactions of the peroxy and phenoxy moieties with the 4-*tert*-butyl group of the quinol ether like products were the same, a value of −27 kcal/mol would have been observed. Accordingly we attribute an unfavorable steric interaction of the phenoxy moiety equal to ca. 5 kcal/mol compared with peroxy moiety in the final product.

In Table V are included the experimentally determined activation energies (ΔE_{-10}^{+}) for the decomposition of the quinol ethers.[13] Comparison of the values of $\Delta E_{-10}^{\pm}$ and $-\Delta H_{10}$ reveals that the activation energies for the combination reaction (ΔE_{10}) must be abnormally small, i.e., between 0 and 3.0 kcal/mol, compared with $\Delta E^{\ddagger}$ diffusion which in chlorobenzene is equal to 4.6 ± 0.7 kcal/mol for simple phenoxy radicals.[5] The occurrence of abnormally small apparent activation energies for radical combination reactions involving 2,6-di-*tert*-butyl phenoxy radicals is not restricted to the present system. Williams and Krelick[35] reported *apparent negative* activation energies for the diffusion into the solvent cage of pairs of 2,6-di-*tert*-butyl-4-substituted phenoxy radicals.

Within the framework of classic structural chemistry, it is difficult to invoke the occurrence of the prior equilibrium formation of metastable intermediates in such combination reaction as we have in reactions of a number of nonhindered phenoxy radicals[30] to account for these anomalous activation energies. However, the results of recent theoretical calculations[36] of the interaction energy for two benzyl radicals approaching in two parallel planes as a function of the interplanar separation suggest the existence of a sandwich configuration i.e.

which at a separation of 2.9 Å is stabilized to an extent of approximately *22 kcal/mol* compared with the radicals at infinite separation! At distances less than 2.9 Å, the energetically favored interaction is the head-to-head configuration i.e.

which then collapses to the final stable product, bibenzyl, at still shorter distances.[37] A similar calculation for the phenoxy radicals has not been reported, but the results of such a calculation may be of considerable use in the understanding of detailed mechanisms of phenoxy radical combination reactions.

Table V. Thermodynamic and Kinetic Quantities for Reactions of Oxy Radicals with 2,4,6-Tri-*tert*-butylphenoxy Radicals

Radical	$\Delta H_{-9} + \Delta H_{10(11)}$, kcal/mol	ΔH_{10}, kcal/mol	$\Delta E_{-10}^{\ddagger}$, kcal/mol
4-OMe-phenoxy	−20.23 ± 0.26	−19.8	21.0 ± 0.5
4-*tert*-Butylphenoxy	−19.94 + 0.24	−26.1	26.1 ± 0.5
3-COOEt-phenoxy	−20.49 + 0.19	−30.0	29.5 ± 1.0
Tetralylperoxy	−25.28 ± 0.23	−32.3	

Experimental Section

Materials. All phenols were obtained from commercial sources and were purified by recrystallization to yield materials whose melting points agreed with literature values.

Tetralin hydroperoxide was prepared and purified according to the procedure of Knight and Swern.[38]

tert-Butyl hydroperoxide (Lucidol) was purified by the azeotopic and fractional distillation method of Hiatt et al.[39]

Spectral grade carbon tetrachloride was stored over Linde 4A molecular sieves for several days prior to use.

Spectral grade dioxane was refluxed over the distilled from sodium metal under nitrogen. Reagent grade tetrahydrofuran was refluxed over and distilled from calcium hydride.

Pyridine was refluxed over and distilled from sodium hydroxide.

Rates of Oxygen Absorption. The rates of oxygen absorption were determined by means of the automatic recording constant pressure gas apparatus previously described.[40] The computer fitting of the oxygen data was carried out as previously reported.[3] In all cases, the average percentage deviations of the experimental rates of oxidation and the calculated rates were less than or equal to 5%. In Table VI are presented the results obtained from the computer fit for 2,6-dimethylphenol as the inhibitor.

Calorimetric Study. The calorimetric measurements of the heat of reaction of excess 2,4,6-tri-*tert*-butylphenoxy radical (A·) in 0.335 mol % tetralin-chlorobenzene solution with solid tetralin hydroperoxide (ROOH) were carried out with the same calorimeter and by the procedures we previously described.[33] From the plot of calories evolved vs. moles of solid tetralin hydroperoxide reacted (Figure 2), a value of −18.87 ± 0.20 kcal/mol was obtained for the reaction

$$\underset{\text{(solid)}}{\mathrm{ROOH}} + 2\mathrm{A}\cdot \longrightarrow \mathrm{AH} + \mathrm{AOOR}$$

An independent determination of the heat of solution of tetralin hydroperoxide in the same solvent gave a value for the dissolution equal to +6.81 ± 0.03 kcal/mol.

Infrared Studies. The infrared spectra of *tert*-butyl hydroperoxide in carbon tetrachloride and in mixtures of carbon tetrachloride and the donor molecules were recorded at 25° in a 0.1-cm cell by means of a Perkin-Elmer Model 521 grading spectrophotometer with a Barnes variable temperature chamber Model 104. The baseline absorptions were determined by recording the spectra in the solvent mixtures without added hydroperoxide. The concentrations of hydroperoxide were sufficiently dilute, less than or equal to $2.0 \times 10^{-2}\ M$ so only the absorption of the monomer hydroperoxide at 3555 cm^{-1} was observed in carbon tetrachloride solution. Upon addition of the donor solvents, additional broad absorption bands in the range of 3500 ± 10 cm^{-1} were observed. The ratio of the absorbance at 3555 cm^{-1} in the presence of the added donor to that in pure carbon tetrachloride times the total concentration of the hydroperoxide was equated to the concentration of free hydroperoxide, and the values of the equilibrium constants (K_{f}) were calculated from the relation

$$K_{\mathrm{f}} = \frac{1 - \dfrac{(\mathrm{ROOH})_{\mathrm{free}}}{(\mathrm{ROOH})_0}}{\dfrac{(\mathrm{ROOH})_{\mathrm{free}}}{(\mathrm{ROOH})_0}\{(\mathrm{Donor})_0 - [(\mathrm{ROOH})_0 - (\mathrm{ROOH})_{\mathrm{free}}]\}}$$

Table VI. Rates of Initiated Oxidation of 9,10-Dihydroanthracene in Chlorobenzene at 60° Containing 2,6-Dimethylphenol

AH × 10^3, mol $l.^{-1}$	TPB × 10^3, mol $l.^{-1}$	RH, mol $l.^{-1}$	RO_2H × 10^4, mol $l.^{-1}$	Rate × 10^7, mol $l.^{-1}$ sec^{-1} (Calcd)	Rate × 10^7, mol $l.^{-1}$ sec^{-1} (Obsd)
0.0987	0.3	0.099	2.75	13.4	15.5
0.4935	0.3	0.099	1.1	6.6	7.2
0.987	0.3	0.099	1.1	5.4	5.6
0.05	0.3	0.099	41.1	23.3	23.2
0.0987	0.3	0.099	41.1	18.4	20.2
0.1	0.3	0.099	41.1	18.2	16.9
0.2	0.3	0.099	41.1	13.3	13.1
0.50	0.3	0.099	41.1	8.7	8.2
1.0	0.3	0.099	41.1	6.6	6.4
1.0	1.21	0.196	1.1	25.8	25.6
2.0	1.21	0.196	1.1	21.3	21.2
0.1	0.3	0.196	2.2	34.1	32.5
0.1	0.3	0.196	1.1	32.5	33.6
0.2	0.3	0.196	1.1	24.4	25.0
0.2	0.3	0.196	1.1	24.4	24.8
0.5	0.3	0.196	1.1	15.6	15.7
1.0	0.3	0.196	1.1	11.6	12.1
1.0	0.3	0.196	1.1	11.6	11.0
2.0	0.3	0.196	1.1	9.4	8.9
2.0	0.3	0.196	1.1	9.4	9.3
16.0	0.3	0.196	1.1	7.3	7.2
39.48	0.3	0.196	2.2	7.1	7.3
2.0	0.075	0.196	1.1	4.6	4.5
0.05	0.3	0.242	2.75	58.0	58.7
0.1	0.3	0.242	1.1	45.2	44.5
0.5	0.3	0.242	1.1	21.0	18.6
1.0	0.3	0.242	1.1	15.3	14.3
100.0	0.3	0.242	1.1	8.4	8.8

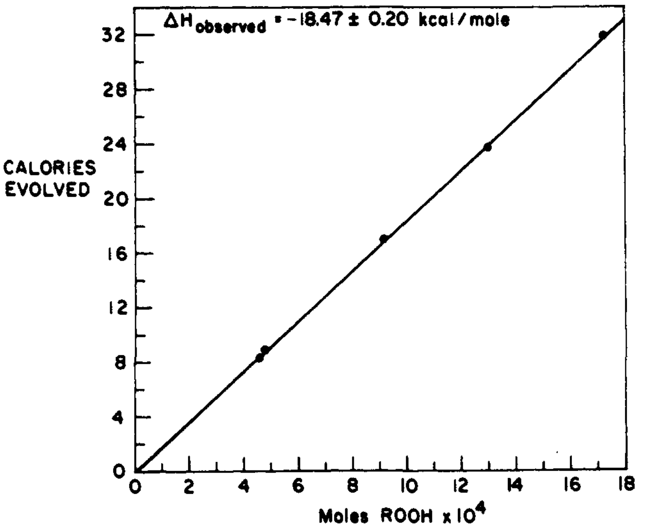


Figure 2. Heat evolved upon reaction of solid tetralin hydroperoxide with 2,4,6-tri-*tert*-butylphenoxyl in tetralin-chlorobenzene solutions at room temperature.

Values of K_f for hydroperoxide with dioxane, tetrahydrofuran, pyridine, and dimethylformamide were equal to 2.8 ± 0.2, 3.5 ± 0.3, 10.5 ± 0.5, and 13.7 ± 0.8 M^{-1}, respectively. Applying a statistical correction of 2 for dioxane and plotting log $K_{f,ROOH}$ vs. log $K_{f,4F\text{-}phenol}$ yielded the linear relationship eq X reported in the text.

BEBO Calculations. The BEBO calculations were performed utilizing a program written in BASIC on the Ford DEC-10 computer. The program included eq XIII and XIV or where the value of β was calculated from the relationship

$$\beta = 0.65\omega_{XY}\left(\frac{M_1M_2}{(M_1 + M_2)E_{XY}}\right)^{1/2}$$

where ω_{XY} is the fundamental stretching frequency of the X-Y molecule in 100 cm^{-1} units, M_1 and M_2 are the atomic weights of the reacting end atoms of the X· and Y· moieties, and E_{XY} is the dissociation energy of the X-Y molecules in kcal/mol.

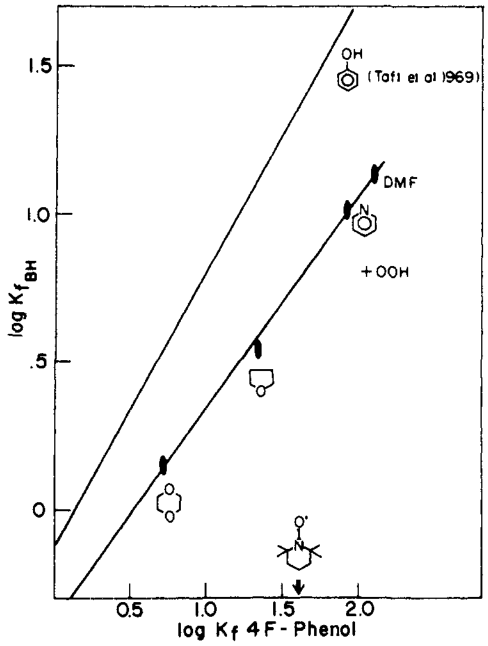


Figure 3. Linear free energy relationships for the formation of the hydrogen bonded complexes of phenol and of *tert*-butyl hydroperoxide and the formation of hydrogen bonded complexes of 4-fluorophenol with the same proton acceptor molecules.

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$$\text{ROO}\cdot + \text{HBr} \longrightarrow \text{ROOH} + \text{Br}\cdot$$

Spectroscopic and structural information are not available for the compound ROOBr for the calculation of $\Delta V_{triplet}$. However, the low bond dissociation energy of HOBr suggests that the value for the peroxy bromide would be very low, and thus the transfer reactions will manifest a very low $\Delta V^{\ddagger}$.
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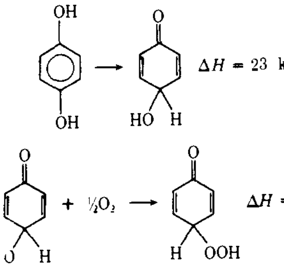

of [$\Delta H_{f,\text{ROO}\cdot} - \Delta H_{f,\text{ROOH}}$] and [$\Delta H_{f,\text{phenoxy}} - \Delta H_{f,\text{phenol}}$] reported in the present and in earlier studies.
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Charge Relay at the Peptide Bond. A Proton Magnetic Resonance Study of Solvation Effects on the Amide Electron Density Distribution[1a]

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Abstract: The proton magnetic resonance (^{1}H NMR) manifestations of amide solvation in polypeptides have been studied using alumichrome and alumichrome C as model compounds. The extreme structural rigidity of the alumichromes allowed the investigation to center on the chemical shifts of the amides as conformational drifts are precluded. The data have been analyzed primarily in terms of two main events: (a) H bonding of the amide nitrogen to basic solvents (Me_2SO, DMF, and pyridine), and (b) protonation of the amide carbonyl by Brønsted acids (chloroform, TFE, and TFA). The two solvent types cause a low-field shift of the amide proton resonance which in case (a) arises from a direct effect, while in case (b), consistent with an earlier suggestion of Schwyzer and Ludescher, the deshielding would result from the extreme electronic lability of the peptide link which permits an electron density flow to the carbonyl. The solvent-induced chemical shift is shown to depend on the extent of exposure of the pertinent hydrogen and oxygen atoms so that the magnitude and direction of the effect reflect conformational features of the molecule at the amide sites. The distinct amide spectra for the two alumichromes, which differ only in a single L-alanyl for glycyl substitution at site 2, can thus be rationalized from their structures. The study proves that the temperature coefficient of the proton resonance frequency affords an excellent criterion to determine the extent of exposure of the NH group, whatever the solvent. The chemical shifts in amphoteric water can be explained by combining the effects observed for the nucleophilic and acidic solvents. However, as judged by the amides' NH ^{1}H NMR, water behaves more like a proton acceptor than as a donor. The extent of the NH resonance frequency shifts indicates synergistic effects between intramolecular H bonding and C=O protonation. On the basis of the amide solvation effects, the apparent pK_a for $DCCl_3$ as a base is estimated to be about −6.

In 1969 Schwyzer and Ludescher[2] tentatively distinguished "internal" from "external" amides in cyclic peptides on the basis of the shifts induced on their proton magnetic resonance (^{1}H NMR)[3] by solvent perturbation. The authors rationalized that carbonyl protonation in an acidic solvent (TFA) and amide-to-solvent H bonding in a basic