Kinetic and Thermochemical Study of the Reaction of 2,4,6-Tri-*t*-butylphenoxy Radical with Substituted Phenols[1]

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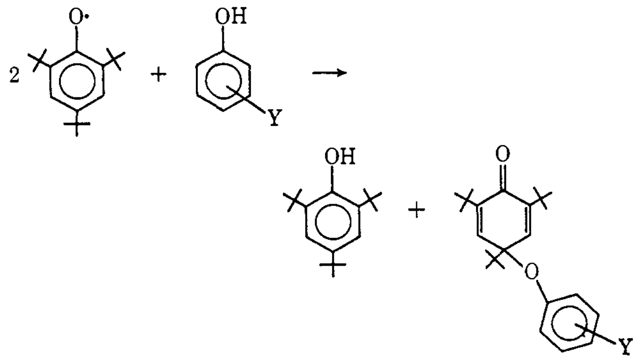
Abstract: Estimates of the differences in the heats of formation of a series of substituted phenols, BH, and their phenoxy radicals, B·, in chlorobenzene solution are obtained by means of a systematic kinetic and thermochemical study of the system shown in eq 1 and 2, where A· and AH represent the 2,4,6-tri-*t*-butylphenoxy radical and 2,4,6-tri-*t*-butylphenol and AB represents the corresponding quinol ether product. The absolute values of k_1 at a series of temperatures and the ratio of k_2/k_{-1} at 40° are determined by means of stop-flow techniques. A novel procedure whereby hydroquinones are utilized as phenoxy radical scavengers allows the determination of the values of k_{-2}. The absolute values of both k_1 and k_{-2} increase by a factor of *ca.* 10^4 when the substituent is changed from the 3-carboethoxy to 4-methoxy group on BH and AB, respectively. In contrast the ratios of rate constants k_2/k_{-1} are relatively insensitive to the nature of the substituent for *meta*- and *para*-substituted phenoxy radicals, varying by a factor of only 2 in the series. The values of the equilibrium constants, $k_1k_2/k_{-1}k_2$, at 40° ($2.2 \pm 0.4 \times 10^8\ M^{-1}$), and the over-all heats at the reaction at 25° (-20.3 ± 0.5 kcal/mole) are also independent of substitution for *m*- and *p*-phenols. However, the observed heat of reaction for several phenols disubstituted at the *ortho* position with chloro and methyl groups are found to be equal to -15.5 ± 0.5 kcal/mole. It is then shown that the 5 kcal/mole difference is due to the presence of strain energy in the quinol ether compounds derived from the di-*ortho*-substituted phenols. As a result of this strain energy the values of k_{-2} for such quinol ethers are extremely large. Utilizing the previously determined value of $(\Delta H_f)^{\mathrm{C_6H_5Cl}}{}_{\mathrm{A\cdot}} - (\Delta H_f)^{\mathrm{C_6H_5Cl}}{}_{\mathrm{AH}}$, the values of $(\Delta H_f)^{\mathrm{C_6H_5Cl}}{}_{\mathrm{B\cdot}} - (\Delta H_f)^{\mathrm{C_6H_5Cl}}{}_{\mathrm{BH}} + \Delta E_2^{\ddagger}$ for 4-methoxy-, 4-*t*-butyl-, 3,5-dimethyl-, 4-bromo-, 3-carboethoxy, and 2,4,6-trichlorophenol are then calculated. On the assumption that $\Delta E_2^{\ddagger}$ is relatively constant in the series the values of $(\Delta H_f)^{\mathrm{C_6H_5Cl}}{}_{\mathrm{BH}} - (\Delta H_f)^{\mathrm{C_6H_5Cl}}{}_{\mathrm{B\cdot}}$ are found to increase by 8 kcal/mole from BH equal to 4-methoxyphenol to BH equal to 3-carboethoxyphenol. The relationship of these thermodynamic properties to the previously reported empirical correlations of the rates of hydrogen atom abstraction from phenols by various oxy radicals with substituent parameters is then discussed. Finally, the chemical behavior of two complex systems in which phenoxy radicals are generated as reactive intermediates are successfully analyzed by means of the results derived from the present study.

A direct calorimetric determination of the difference in the heats of formation of solution of the 2,4,6-tri-*t*-butylphenoxy radical and 2,4,6-tri-*t*-butylphenol has recently been carried out in our laboratory.[2] The results of that study together with the results of earlier equilibrium studies then allowed the heats of formation of a variety of other "stable" free radicals to be calculated.

In the present work we turn our attention to a determination of the heats of formation of simply substituted phenoxy radicals. Systematic studies of systems in which simple phenoxy radicals are generated as reactive intermediates have revealed that the chemical dynamics manifested by such systems may be satisfactorily described only by means of rate expressions derived from multistep reaction schemes.[3,4] The reactions which are involved in the schemes include reversible hydrogen atom transfer reactions of phenoxy radicals with hydroperoxides[5-7] with hydrocarbons[3,7] and with hindered phenols.[4] In addition to these transfer reactions there is strong evidence that the formation of products from the bimolecular reactions of certain phenoxy radicals may be highly reversible processes.[8] Thus a knowledge of the thermochemical properties of simply substituted phenoxy radicals is of primary importance for the analysis of many systems in which they occur as reactive intermediates.

The objective of the present work was to obtain estimates of the heats of formation of substituted phenoxy radicals for the first time by means of a detailed kinetic and thermochemical study of the quantitative reaction of the 2,4,6-tri-*t*-butylphenoxy radical with substituted phenols, *i.e.*[4,9]



That objective has been realized and in the course of the work considerable information concerning the kinetic behavior of phenoxy radicals and the thermal stability of dimers derived from phenoxy radicals has been obtained.

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[1] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, PETR-1.

[2] L. R. Mahoney, F. C. Ferris, and M. A. DaRooge, *J. Amer. Chem. Soc.*, **91**, 3883 (1969).

[3] L. R. Mahoney, *ibid.*, **89**, 1895 (1967).

[4] L. R. Mahoney and M. A. DaRooge, *ibid.*, **89**, 5619 (1967).

[5] J. R. Thomas, *ibid.*, **85**, 2166 (1963): **86**, 4807 (1964).

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

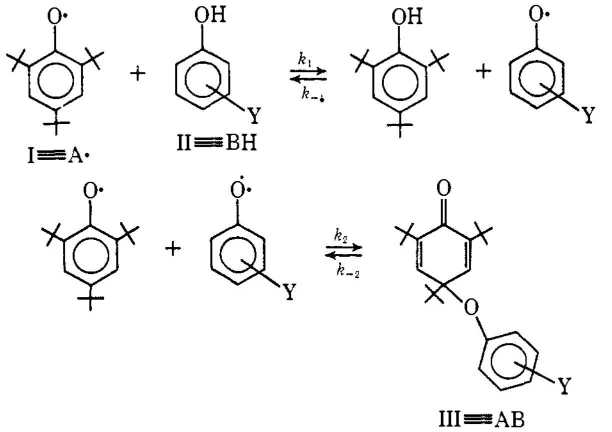
[7] L. R. Mahoney and F. C. Ferris, *J. Amer. Chem. Soc.*, **85**, 2345 (1963).

[8] C. D. Cooper, H. S. Blanchard, and G. F. Finkbeiner, *ibid.*, **87**, 3996 (1965).

[9] M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.*, **32**, 1 (1967).

Results

I. Kinetic Studies of the Individual Reactions. The overall reaction of the 2,4,6-tri-*t*-butylphenoxy radical with phenols IIa–f may be divided into the two reactions



II, IIIa, Y = 4-methoxy
b, Y = 4-*t*-butyl
c, Y = 3,5-dimethyl
d, Y = 4-bromo
e, Y = 3-carboethoxy
f, Y = 2,4,6-trichloro
g. Y = 2,6-dimethyl
h, 2,4,6-trimethyl

In the present section the absolute values of k_1 for IIb–f and k_2 for IIIa–f as functions of temperature and the values of the ratio k_2/k_{-1} for IIb–d at a single temperature in chlorobenzene solution have been determined.

A. Values of k_1 and k_2/k_{-1}. Under conditions such that $k_{-2}(\mathrm{AB}) \ll k_2(\mathrm{A\cdot})(\mathrm{B\cdot})$,[10] the reactions

$$\mathrm{A\cdot} + \mathrm{BH} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{AH} + \mathrm{B\cdot} \tag{1}$$

$$\mathrm{A\cdot} + \mathrm{B\cdot} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{AB} \tag{2}$$

are sufficient to describe the rate of the overall reaction. Assuming a steady state for the concentration of B·, *i.e.*, $\mathrm{d(B\cdot)/d}t = 0$, the rate of disappearance of A· is given by the expression

$$\frac{-\mathrm{d(A\cdot)}}{\mathrm{d}t} = \frac{2k_1k_2(\mathrm{A\cdot})(\mathrm{BH})}{k_2 + k_{-1}\left[\dfrac{(\mathrm{AH})}{(\mathrm{A\cdot})}\right]} \tag{3}$$

In the case where $k_2 \gg k_{-1}[(\mathrm{AH})/(\mathrm{A\cdot})]$ the rate expression reduces to

$$\frac{-\mathrm{d(A\cdot)}}{\mathrm{d}t} = 2k_1(\mathrm{A\cdot})(\mathrm{BH}) \tag{4}$$

Earlier studies of the reaction of phenols with A· in benzene solution at room temperature revealed that eq 4 accurately described the rate of decay of A· at ratios of (AH)/(A·) less than or equal to 20.[9] A systematic kinetic study of the reaction in chlorobenzene has led to the same results; *i.e.*, the rate of disappearance of A· is directly proportional to the first powers of the concentrations of A· and BH. Typical results observed for the values of the first-order decay constant of A as a function of the concentration of BH are shown in Figure 1 and the values of k_1 at various temperatures for the substituted phenols are summarized in Table I. The value of k_1 for IIa in chlorobenzene was not determined in the present work. In earlier work a value of k_1 for IIa in benzene at room temperature was found to be equal to 3000 ± 300 M^{-1} sec^{-1}.[9] The special experimental arrangement utilized for that study is not at present available to us.

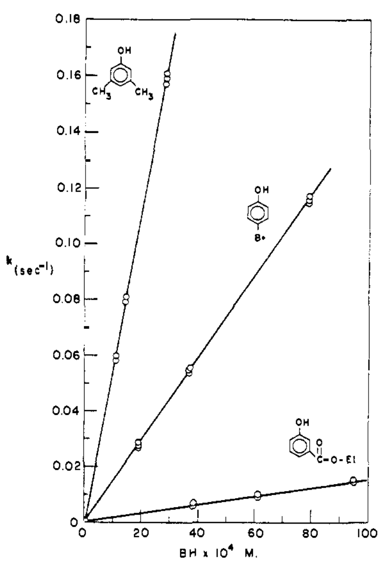


Figure 1. The dependence of the first-order decay constant for the 2,4,6-tri-*t*-butylphenoxy radical on the concentration of the substituted phenols in chlorobenzene at 40°.

Table I. Summary of Values of k_1 in Chlorobenzene

Phenol	Temp, °C	k_1, M^{-1} sec^{-1}
Ib	30.0	51.3 ± 1.25
	40.0	67.1 ± 1.0
	60.0	108.0 ± 5.0
Ic	30.0	16.3 ± 0.35
	40.0	29.0 ± 1.0
	60.0	47.3 ± 1.9
Id	30.0	5.35 ± 0.3
	40.0	7.5 ± 0.3
	60.0	16.3 ± 0.7
Ie	30.0	0.43 ± 0.02
	40.0	0.76 ± 0.03
	60.0	1.28 ± 0.03
If	30.0	2.68 ± 0.14
	40.0	3.97 ± 0.15
	60.0	6.40 ± 0.18

Values of the ratio k_2/k_{-1} were obtained by means of the following procedure. Under conditions such that $k_2 \ll k_{-1}[(\mathrm{AH})/(\mathrm{A\cdot})]$ eq 3 reduces to the expression

$$\frac{-\mathrm{d(A\cdot)}}{\mathrm{d}t} = \frac{2k_1k_2}{k_{-1}}\frac{(\mathrm{A\cdot})^2(\mathrm{BH})}{(\mathrm{AH})} \tag{5}$$

By the initial addition of high concentrations (greater than 0.1 M) of AH and by employing low concentrations of A· (less than 5 × 10^{-4} M) in the stop-flow experiments the rate of decay of A· becomes second order in A· and inversely proportional to the concentration of

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[10] The inequality is satisfied during the rate measurements since the half-life for the decomposition of IIIb is equal to 12 × 10³ sec (*vide infra*) at 40° while the duration of the stop-flow experiments for 90% decay of A· is in the range 2–20 sec.

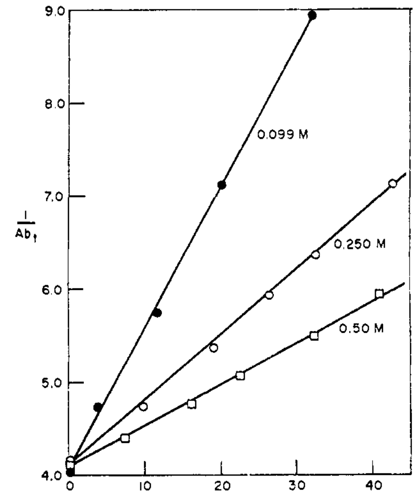


Figure 2. Determination of the ratio k_2/k_{-1} for IId at 40°; plots of 1/absorbance *vs.* time as a function of added 2,4,6-tri-*t*-butylphenol.

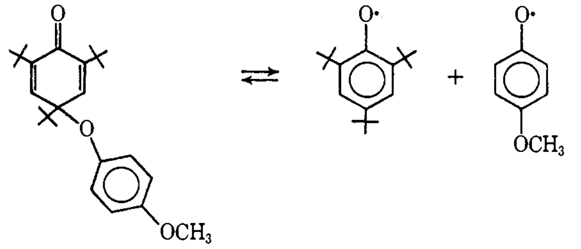
AH at constant BH in agreement with eq 5. Typical plots of $1/(\mathrm{A}\cdot)\epsilon$ *vs.* time are presented in Figure 2 for IId and the values of k_2/k_{-1} derived from eq 5 and the previously determined values of $2k_1$ are summarized in Table II. This technique did not prove to be successful for the 2,4,6-trichlorophenol system since the value of k_2/k_{-1} apparently exceeds 10^3; $1/A\epsilon$ *vs.* time plots are not linear at 40°, and thus sufficiently high ratios of $(\mathrm{AH})/(\mathrm{A}\cdot)$ could not be obtained in the stop flow apparatus.

Table II. Summary of Values of k_2/k_{-1} at 40° in Chlorobenzene

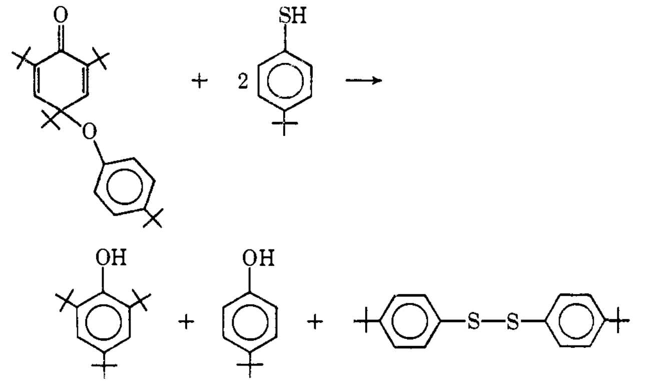
Phenol	Concn of phenol, $\times 10^4$ *M*	Concn of 2,4,6-tri-*t*-butylphenol, *M*	Slope,[a] $\sec^{-1}$	k_2/k_{-1}[b]
IIb	40.1	0.25	0.774 ± 0.040	128 ± 7
		0.50	0.385 ± 0.020	127 ± 8
IIc	49.3	0.099	0.381 ± 0.040	72 ± 6
		0.250	0.196 ± 0.020	55 ± 4
IId	46.5	0.099	0.185 ± 0.010	110 ± 7
		0.250	0.077 ± 0.004	115 ± 5
		0.500	0.042 ± 0.002	109 ± 5

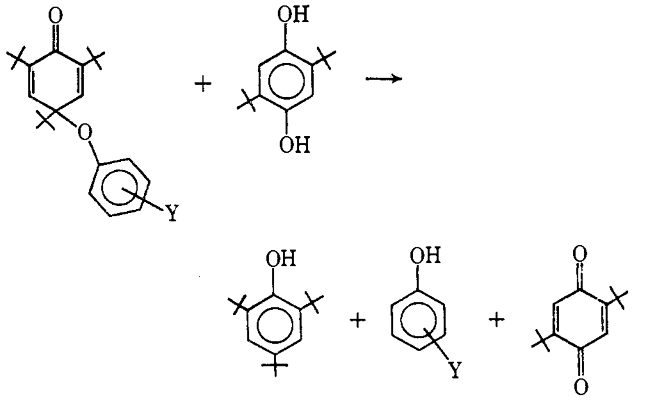
[a] Obtained from plots of 1/absorbance *vs.* time at concentrations of I less than or equal to 5×10^{-4} *M*. [b] Calculated from eq 5 utilizing ϵ for (I) equal to 410 M^{-1} cm^{-1} [C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **81,** 1175 (1959)].

B. Values of k_{-2}. In earlier work from our laboratory evidence derived from a variety of kinetic and product studies was consistent with the decomposition at 60° in chlorobenzene of quinol ether IIIa to form its precursor phenoxy radicals



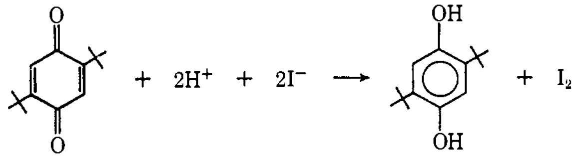
With the purpose of developing a technique for the measurement of the rates of quinol ether decompositions a number of potential scavengers for these phenoxy radicals were investigated. Thiophenols are efficient scavengers of phenoxy radicals; 4-*t*-butylthiophenol reacts quantitatively with IIIb at 50° to yield the corresponding diphenyl disulfide and the phenolic compounds. However, the most satisfactory scavengers for the kinetic investigation were found to be 2,5-di-*t*-butyl- and 2,5-di-*t*-pentylhydroquinone. A complete product analysis revealed that these compounds quantitatively react with quinol ethers IIIb and IIIc according to the equation





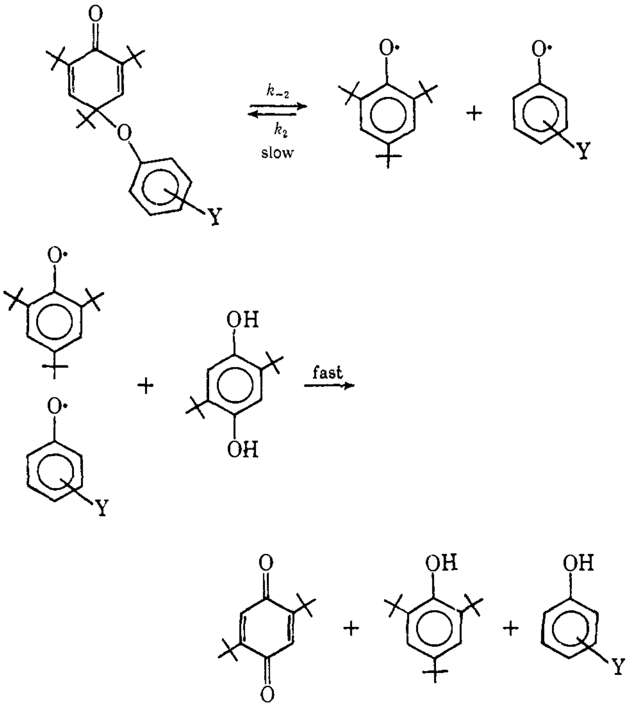
Moreover, the amount of quinone produced in the reaction agreed within ±3% with the amount of quinol ether reacted in the case of all compounds reported in the present work.

The concentration of the quinone formed during the course of the reaction may be conveniently followed by several techniques. For the reactions of the quinol ethers IIIb–e an iodometric technique was found to be satisfactory since those quinol ethers are inert toward the iodide ion at room temperature in glacial acetic acid while the quinones react rapidly and quantitatively to form the corresponding hydroquinone and molecular iodine, *i.e.*



The liberated iodine was then determined by thiosulfate titration. However, the quinol ethers IIIa and IIIf liberate iodine from solutions of sodium iodide in glacial acetic acid at room temperature and a spectrophotometric analysis at 4500 Å of the quinone formed during the reaction was utilized for the analysis for these systems.

A systematic kinetic study of the reaction revealed that the rate of formation of the quinone was independent of the concentration of the hydroquinone and was accurately first order with respect to the concentration of the quinol ether. In Figure 3 is shown a typical first-order plot of the quinone formation *vs.* time for IIIb at two concentrations of hydroquinone scavenger. These results are consistent with the scheme



Under these conditions the slow step in the formation of quinone will be reaction 2 and the reaction will be *independent* of the concentration of hydroquinone and first order with respect to the concentration of quinol ether as is experimentally observed. The values of the first-order rate constant, k_{-2}, at various temperatures in chlorobenzene determined for the quinol ethers IIIa–f by means of this scavenging technique are summarized in Table III.

II. Calorimetric Determination of the Overall Heat of Reaction. The overall heat of the reaction at 25° was directly determined utilizing the calorimetric technique previously reported for 4-*t*-butylphenol.[2] A solid sample of the phenolic compound, BH, is dissolved in the calorimeter containing an excess of the 2,4,6-tri-*t*-butylphenoxy radical under argon. Under these conditions the heat of the reaction (ΔH_{reactn}) is given by the relationship

$$(\Delta H_{\text{reactn}}) = (\Delta H_{\text{obsd}}) - (\Delta H_{\text{soln}})_{\text{BH}}$$

where (ΔH_{obsd}) is equal to the heat evolved per mole of BH dissolved in the calorimeter and $(\Delta H_{\text{soln}})_{\text{BH}}$ is equal to the partial molal enthalpy of solution at infinite dilution of BH in chlorobenzene. In Table IV are summarized the values of these quantities determined for the phenolic compounds IIa–h reported in the present work. The low value of $(\Delta H_{\text{reactn}})_{\text{IIf}}$ led us to determine the same quantity for two other 2,6-disubstituted phenols. In those cases the heats of the reaction were also less exothermic by approximately 5 kcal/mol than the heats of reaction for the *meta*- and *para*-substituted phenols.

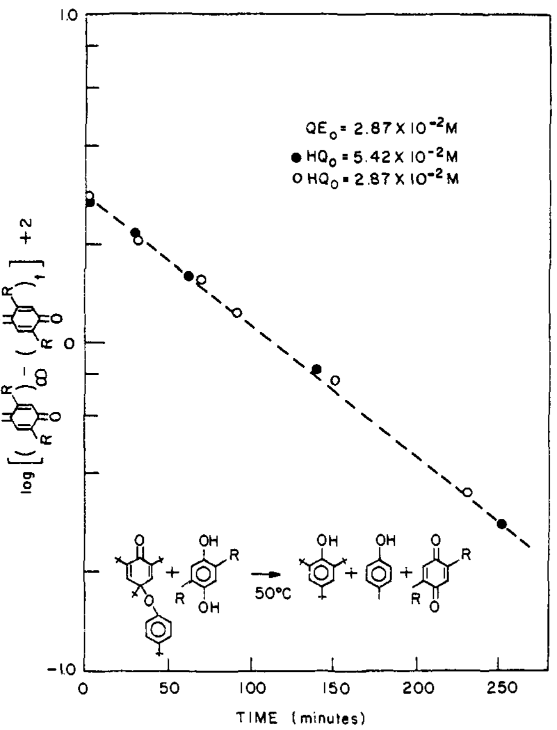


Figure 3. Typical first-order plots for the formation of 2,5-di-*t*-pentylquinone from the reaction of quinol ether IIIb in the presence of two different initial concentrations of 2,5-di-*t*-pentylhydroquinone.

Discussion

I. Equilibrium Constants and Heats of Reaction. The overall equilibrium constants for the reaction of the 2,4,6-tri-*t*-butylphenoxy radical with IIb–d at 40° in chlorobenzene to form 2,4,6-tri-*t*-butylphenol and the corresponding quinol ethers are equal to the product of the values of the constants k_1, k_2/k_{-1}, and $1/k_{-2}$ determined at that temperature for the respective compounds by means of the kinetic studies. The calculated values of these overall equilibrium constants are insensitive to the substitution of the *meta*- and *para*-substituted phenols, being equal to $2.2 \pm 0.4 \times 10^8\ M^{-1}$ at 40° in chlorobenzene.

On the assumption that the differences in the heat capacities of the products and the reactants, $\Sigma\Delta C_p$ products $- \Sigma\Delta C_p$ reactants, are constant in the temperature interval 25–40° in chlorobenzene the enthalpy changes associated with the reaction (ΔH reaction) are equal to those values measured in the calorimeter at 25°. The value of the entropy change for the reaction at 40° is then calculated to be *ca.* −32 eu. These entropy changes are, of course, equal to the sum of the entropy changes associated with the hydrogen atom transfer reaction and the radical–radical coupling reaction. Although it seems likely that the large negative entropy change associated with the radical–radical coupling reaction makes the overwhelming contribution to the negative entropy change, the assumption that the

Table III. Summary of Values of k_{-2} for Quinol Ethers in Chlorobenzene

Quinol ether	Temp, °C	HQ_0/QE_0[a]	$k_{-2} \times 10^5$ sec^{-1}
IIIa	15[b]	2.0:1.0	26.0
	15	1.0:1.0	25.7
	25[b]	2.0:1.0	87.5
	25	2.0:1.0	87.5
	25	1.0:1.0	88.2
	35[b]	1.0:1.0	251
	35	1.0:1.0	257
	35	2.0:1.0	257
	35	2.0:1.0	269
	45[b]	2.0:1.0	745
	45	2.0:1.0	762
IIIb	30	1.8:1.0	1.13
	40	1.8:1.0	3.89
	40	1.0:1.0	3.99
	50	1.0:1.0	13.55
	50	1.0:1.0	14.75
	50	1.8:1.0	14.80
	60	3.0:1.0	52.5
	60	1.5:1.0	53.6
	60	2.0:1.0	51.2
	60	3.0:1.0	53.6
IIIc	40	2.3:1.0	0.94
	50	1.85:1.0	3.91
	50	3.54:1.0	3.79
	60	1.84:1.0	13.95
	60	3.3:1.0	14.1
IIId	40	1.46:1.0	0.381
	50	1.87:1.0	1.58
	60	1.64:1.0	5.50
IIIe	60	1.0:1.0	0.343
	80[b]	2.0:1.0	4.44
	100[b]	1.2:1.0	40.2
	100	2.0:1.0	40.7
IIIf	15[b]	2.0:1.0	42.0
	15	1.0:1.0	45.3
	15	1.0:1.0	47.1
	25[b]	1.0:1.0	165
	25	2.0:1.0	170
	25	1.0:1.0	160
	35[b]	1.0:1.0	537
	35	2.0:1.0	577

[a] Ratio of initial concentration of hydroquinone to quinol ether. [b] Temperature control was equal to ±0.05° in these experiments. In all other experiments temperature control was equal to ±0.02°.

Table IV. Summary of Heats of the Overall Reaction Determined by Solution Calorimetry

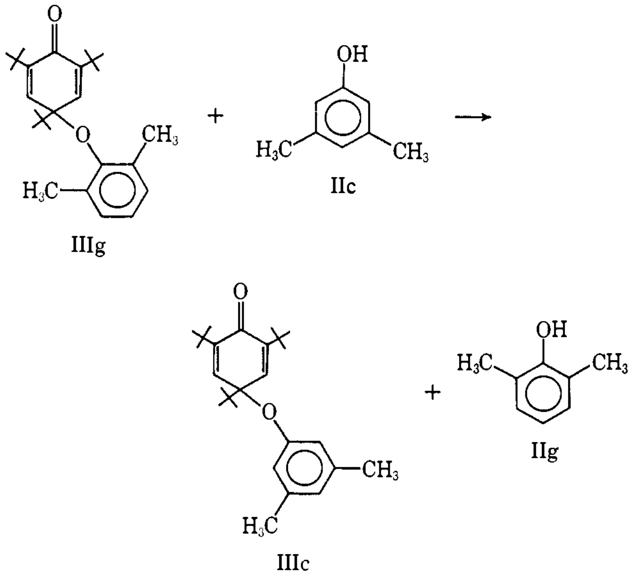
Phenol	$\Delta\bar{H}_{soln}$, kcal/mole	$-(\Delta\bar{H}_{obsd})$, kcal/mole	$-(\Delta\bar{H}_{reactn})$, kcal/mole
IIa	6.95 ± 0.06	13.28 ± 0.20	20.23 ± 0.26
IIb	5.72 ± 0.10	14.22 ± 0.16	19.94 ± 0.24
IIc	6.31 ± 0.02	13.81 ± 0.07	20.12 ± 0.09
IId	5.52 ± 0.03	14.83 ± 0.06	20.35 ± 0.09
IIe	8.37 ± 0.06	12.12 ± 0.13	20.49 ± 0.19
IIf	5.10 ± 0.02	10.75 ± 0.01	15.85 ± 0.03
IIg	5.15 ± 0.02	10.24 ± 0.30	15.35 ± 0.32
IIh	5.68 ± 0.10	9.69 ± 0.10	15.37 ± 0.20

entropy change associated with the hydrogen atom transfer reaction is negligible is premature.[11]

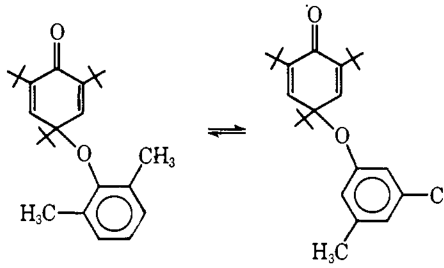
The overall heats of reaction of *o*-dichloro- and *o*-dimethylphenols are approximately equal and 5 kcal/mole less exothermic than the *meta-* and *para*-substituted phenols. This difference is due to the presence of steric strain in the quinol ethers derived from di-*ortho*-substituted phenols. From Table IV the heat of the reaction

$$\Delta H = -4.73 \pm 0.41 \text{ kcal/mole}$$
$$= (\Delta H_f)^{C_6H_5Cl}{}_{IIg} - (\Delta H_f)^{C_6H_5Cl}{}_{IIc} + (\Delta H_f)^{C_6H_5Cl}{}_{IIIc} - (\Delta H_f)^{C_6H_5Cl}{}_{IIIg}$$

Utilizing the known heats of formation of IIg and IIc



in their standard states as solids at 25°[12] and their partial molal heats of solution at infinite dilution in chlorobenzene (Table IV) a value of $(\Delta H_f)^{C_6H_5Cl}{}_{IIIc} - (\Delta H_f)^{C_6HCl_5}{}_{IIIg}$ equal to −5.25 ± 0.50 kcal/mole is calculated. This quantity is equal to the enthalpy change for the hypothetical reaction



and therefore corresponds to the strain energy introduced in a quinol ether upon substitution of dimethyl and dichloro groups at the *ortho* position of the phenolic portion of the molecule. The presence of this strain energy has a profound effect on the rates of decomposition of quinol ethers derived from di-*ortho*-substituted phenols (*cf.* sections II and V).

II. Individual Rate Constants. In Table V are summarized the values of the activation energies, $\Delta E^{\ddagger}$, and log A factors for the various rate constants calculated from plots of log k *vs.* $1/T$ and the Arrhenius equation

$$\log k = \log A - \frac{\Delta E^{\ddagger}}{2.3RT}$$

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(11) D. J. Williams and R. Krelick [*J. Amer. Chem. Soc.*, 90, 2775 (1968)] reported that the entropy changes for disassociation of dimers of 2,6-di-*t*-butyl-4-substituted phenoxy radicals varied by up to 8 eu units. These large effects may be associated with changes in the order of solvent molecules.

(12) R. J. L. Andon of D. P. Biddiscombe, J. D. Cox, R. Handley, D. Harrop, E. F. G. Herrington, and J. F. Martin, *J. Chem. Soc.*, 5246 (1960). The corresponding information for dichlorophenols is not available.

Table V. Summary of Activation Parameters for Reactions 1 and 2[a]

Compd	Log A_1	$\Delta E^{\ddagger}_1$, kcal/mole	Log A_{-2}	$\Delta E^{\ddagger}_{-2}$, kcal/mole
IIa			12.2 ± 0.3	21.0 ± 0.5
IIb	5.5 ± 0.3	4.8 ± 0.5	13.8 ± 0.4	26.1 ± 0.6
IIc	6.4 ± 0.2	6.8 ± 0.3	14.5 ± 0.4	28.0 ± 0.6
IId	6.5 ± 0.2	7.5 ± 0.3	13.9 ± 0.5	27.8 ± 0.8
IIe	5.9 ± 0.2	8.2 ± 0.3	13.9 ± 0.7	29.5 ± 1.0
IIf	4.6 ± 0.2	5.5 ± 0.3	13.5 ± 0.3	22.3 ± 0.5

[a] The uncertainties in the values of $\Delta E^{\ddagger}_i$ and log A_i calculated according to the procedure of Benson [*cf.* S. W. Benson, "Foundations of Chemical Kinetics," Mc-Graw Hill Book Co., Inc., New York, N. Y., 1960, p 91].

The values of the log A factors for reaction 1 for the *meta-* and *para*-substituted phenols are relatively constant, *i.e.*, 6.0 ± 0.5 units. This value is small compared to those reported for most bimolecular transfer reactions in solution. However, it is consistent with the formation of an activated complex involving a hydrogen atom transfer to the highly hindered 2,4,6-tri-*t*-butylphenoxy radical.[13] The absolute values of k_1, which vary by a factor of over 10^2 at 30° for the substituted phenols, are controlled primarily by the values of the activation energies which decrease by 3.5 kcal/mole in the series 3-carboethoxyphenol to 4-*t*-butylphenol and may be correlated by σ^+-substituent parameters with a ρ value equal to -2.8 ($r = 0.91$).

The rate constants for the decomposition of quinol ethers, k_{-2}, are affected by the substitution of the phenol in the same manner as are the values of k_1, increasing four orders of magnitude from 3-carboethoxyphenol to 4-methoxyphenol. A plot of log k_{-2} at 60° *vs.* σ^+ values, Figure 4, yields a ρ value equal to -3.3 ($r = 0.97$). In section IV (*vide infra*) we shall discuss these σ^+ correlations with respect to the thermodynamic properties of phenoxy radicals as a function of their remote substitution.

The absolute values of k_1 for 2,4,6-trichlorophenol are relatively low as would be predicted for the compound due to (1) the electron-withdrawing chloride groups and (2) the steric hindrance due to the presence of *ortho* substituents. In contrast the value of k_2 for IIIf, the quinol ether derived from the trichlorophenol is extremely high. We have shown in the previous section that such quinol ethers derived from di-*ortho*-substituted phenols possess 5 kcal of excess energy due to steric strain. This strain weakens the quinol ether bond, the activation energy for reaction 2 is correspondingly lowered and the rate of decomposition for this compound is greatly increased. This phenomenon appears to be a rather general one for quinol ethers. For example, the quinol ethers derived from dimers of 2,6-di-*t*-butylphenoxy radicals have extremely low heats of formation, 5–10 kcal/mole,[11] due presumably to even larger strain energies in those molecules.

In contrast to the very large effects of substituents on the rates of reactions (1) and (−2) the ratios of the rate constants k_2/k_{-1} appear to be essentially independent of *meta* or *para* substitution varying by a factor of 2 (60–130) for the three systems examined at 40°. A value for the same ratio for the 4-methoxyphenoxy-2,4,6-tri-*t*-butylphenol system has previously been estimated from the results of oxygen adsorption studies[4] to be in the range of 36–72 at 60° in chlorobenzene solution. Moreover the activation energies for the two reactions are also quite similar since within the experimental uncertainties for all of the substituted phenols examined

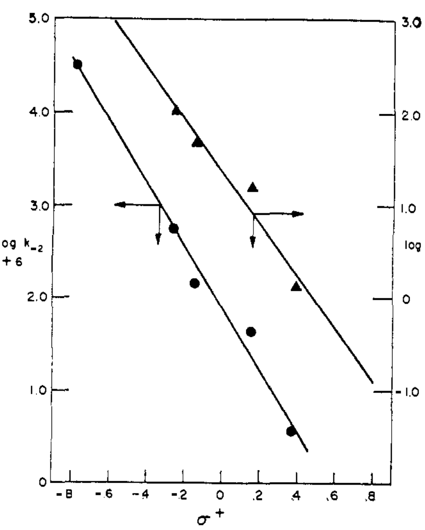

Figure 4. Correlation of values of log k_1 (▲) and log k_{-2} (●) at 60° in chlorobenzene *vs.* the σ^+ substituent parameters of Brown.

$$\Delta E^{\ddagger}_2 - \Delta E^{\ddagger}_{-1} = (\Delta H\,\text{reaction}) + \Delta E^{\ddagger}_1 - \Delta E^{\ddagger}_{-2} \cong 0$$

in the present work. The absence of substituent effects on the value of these ratios is consistent with the other results of the present work since the value of the equilibrium constant for the overall reaction is independent of substituent while the ρ values for reactions 1 and 2 are approximately equal. The relatively small values of these ratios suggest that values of k_{-1} are extremely large, *i.e.*, 10^4–10^6 M sec^{-1} since in analogy with the values of k_2 for the dimerization of 2,6-di-*t*-butyl-4-substituted phenoxy radicals[11] k_2 should be in the range of 10^6–10^8 M^{-1} sec^{-1}. As a result the values of the equilibrium constants for the hydrogen atom transfer, k_1/k_{-1}, will be very small. In the next section we shall see that the transfer reactions are indeed endothermic.

III. Estimates of the Heats of Formation of Phenoxy Radicals. Estimates of the differences in the heats of formation of substituted phenoxy radicals and their parent phenols in chlorobenzene solution $(\Delta H_f)^{C_6H_5Cl}{}_{B} - (\Delta H_f)^{C_6H_5Cl}{}_{BH}$, may be made by means of the following analysis. The enthalpy change for the overall reaction of the 2,4,6-tri-*t*-butylphenoxy radical with substituted phenols may be partitioned into the enthalpy change for the hydrogen atom transfer reaction

$$A\cdot + BH \rightleftharpoons AH + B\cdot$$

where $(\Delta H_{\text{transfer}}) = (\Delta H_f)^{C_6H_5Cl}{}_{AH} - (\Delta H_f)^{C_6H_5Cl}{}_{A\cdot} + (\Delta H_f)^{C_6H_5Cl}{}_{B} - (\Delta H_f)^{C_6H_5Cl}{}_{BH}$ and the enthalpy change for the radical–radical coupling reaction

$$A\cdot + B\cdot \rightleftharpoons AB$$

where

$$(\Delta H_{\text{coupling}}) = \Delta E^{\ddagger}_2 - \Delta E^{\ddagger}_{-2}$$

Therefore we may write

$$(\Delta H_f)^{C_6H_5Cl}{}_{B\cdot} - (\Delta H_f)^{C_6H_5Cl}{}_{BH} + \Delta E^{\ddagger}_2 = (\Delta H_{\text{reactn}})^{C_6H_5Cl} + (\Delta H_f)^{C_6H_5Cl}{}_{A\cdot} - (\Delta H_f)^{C_6H_5Cl}{}_{AH} - \Delta E^{\ddagger}_{-2} \quad (6)$$

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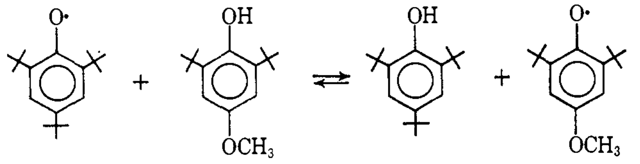
(13) R. W. Krelick and S. L. Weissman, *J. Amer. Chem. Soc.*, **84**, 306 (1962).

The value of $(\Delta H_f)^{C_6H_5Cl}{}_{A\cdot} - (\Delta H_f)^{C_6H_5Cl}{}_{AH}$ in chlorobenzene has been directly determined in our laboratory and is equal to +28.25 ± 0.08 kcal/mole.[2] The other terms on the right side of eq 6 have been determined in the present work. The value of $\Delta E^{\ddagger}{}_2$, the activation energy for the radical–radical coupling reaction, should be quite small, on the order of 2 kcal/mole.[14]

Table VI. Summary of Values of $\Delta H_{\text{transfer}} + \Delta E^{\ddagger}{}_2$ and $(\Delta H_f)^{C_6H_5Cl}{}_{B} - (\Delta H_f)^{C_6H_5Cl}{}_{BH} + \Delta E^{\ddagger}{}_2$ for Substituted Phenols

Phenol	$\Delta H_{\text{transfer}} + \Delta E^{\ddagger}{}_2$, kcal/mole	$(\Delta H_f)^{C6H5Cl}{}_{B\cdot} - (\Delta H_f)^{C_6H_5Cl}{}_{BH} + \Delta E^{\ddagger}{}_2$, kcal/mole
IIa	0.8 ± 0.8	29.0 ± 0.9
IIb	6.1 ± 0.8	34.3 ± 0.9
IIc	7.9 ± 0.7	36.1 ± 0.8
IId	7.5 ± 0.9	35.7 ± 1.0
IIe	9.0 ± 1.2	37.2 ± 1.3
IIf	6.5 ± 0.8	34.7 ± 0.9

In Table VI are summarized the values of $(\Delta H_f)^{C_6H_5Cl}{}_{B\cdot} - (\Delta H_f)^{C_6H_5Cl}{}_{BH} + \Delta E^{\ddagger}{}_2$ for the phenols examined in the present work. Assuming that $\Delta E^{\ddagger}{}_2$ is relatively constant in the series, the values of these quantities are remarkably dependent upon the substitution of the phenol; the OH bond energies decreasing 8 kcal/mole in proceeding from 3-carboethoxyphenol to 4-methoxyphenol. There are a number of reports in the literature that indicate that the position of equilibria involving phenols and their phenoxy radicals in oxidation–reduction systems are influenced in the same manner by remote substitution. For example, with phenol as a standard, the changes in the value of Fieser's "critical oxidation potentials" [15] may be correlated with σ^+ values; a plot of $-(\Delta\text{voltage})(23.0)/2.303RT$[16] vs. σ^+ ($\sigma^+ < +0.2$) yields a straight line with a ρ value equal to -5.0 ($r = 0.96$). The difference in the "critical oxidation potentials" of 4-methoxyphenol and 4-alkylphenols corresponds to −4.0 to −5.0 kcal/mole compared to a value of −5 kcal/mole from Table VI. An identical value for the difference in 4-*t*-butyl and 4-methoxy substitution is derived from the enthalpy change estimated for the reaction



in benzene at 25°.[17]

It is of interest to compare the values of $(\Delta H_f)^{C_6H_5Cl}{}_{B\cdot} - (\Delta H_f)^{C_6H_5Cl}{}_{BH}$ with the values of $(\Delta H_f)^{gas}{}_{B\cdot} - (\Delta H_f)^{gas}{}_{BH}$ calculated by Hush.[18] The results of his calculations yielded a value of $(\Delta H_{HB})^{gas} - (\Delta H_{B\cdot})^{gas}$ for simple phenol equal to 30–32 kcal/mole. The calculation was based upon the values of Fiesers "critical oxidation potentials" determined in water–alcohol mixtures and included a 3 kcal/mole correction for the differences in the enthalpy of solution of phenol and its phenoxy radical due to specific hydrogen bonding interaction of phenol with water. Although Hush assumed that bonding interaction would be removed upon the loss of the hydrogen atom to form the phenoxy radical, recent results suggest that oxy radicals *also* form strong hydrogen bonds with hydroxylic solvents.[19] Removing that correction yields a value of $(\Delta H_f)^{gas}{}_{B\cdot} - (\Delta H_f)^{gas}{}_{BH}$ equal to 33–35 kcal/mole for simple phenol. Examination of Table VI reveals that this value is in the range expected for the unsubstituted phenol–phenoxy radical system in chlorobenzene, *i.e.*, similar to the 4-bromophenol–4-bromophenoxy radical system.

IV. Correlations of the Rates of Reactions of Phenols and the Equilibrium Properties of Phenoxy Radicals. The establishment of quantitative relationships between the rate constants and the value of the equilibrium constants manifested by chemical systems has been a subject of intensive investigation for many years.[20,21] Since little if any data are available concerning the thermodynamic properties of free radicals in solution, various empirical correlations of the rates of free-radical reactions of *meta*- and *para*-substituted benzene derivatives have been attempted with substituent parameters derived from the analysis of ionic systems. Among the most successful of these correlations have been those which involved the correlation of the rate constants, k_X, for hydrogen abstraction by various oxy radicals, X·, form substituted phenols, with the σ^+ values of

$$X\cdot + BH \underset{k_{-X}}{\overset{k_X}{\rightleftharpoons}} XH + B\cdot$$

Brown.[22,23] The success of these correlations has been attributed to the presence of polar contribution to the structure of the activated complex,[22,23] *i.e.*

$$X\cdot\ H\text{–}B \rightleftharpoons X^{\delta-}H^{\delta+}B\cdot$$

The results of the present study demonstrate that the *thermodynamic* quantities $(\Delta H_f)_{B\cdot} - (\Delta H_f)_{BH}$ are strongly influenced by remote substituents and thus the σ^+-substituent parameters actually reflect (perhaps fortuitously[24]) the position of transfer *equilibrium* systems,

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(14) D. J. Williams and R. Krelick [*J. Amer. Chem. Soc.*, 90, 2775 (1968)] reported values of $\Delta H^{\ddagger}{}_2$ in the range of +2.0 to −3.0 kcal/mole for the coupling reaction of 2,6-di-*t*-butyl-4-substituted phenoxy radicals. If $\Delta E^{\ddagger}{}_2$ is equal to 2 kcal/mole then $\Delta E^{\ddagger}{}_{-1}$ would be of comparable magnitude, *i.e.*. 1–2 kcal/mole. Such abnormally low values of the activation energy for hydrogen atom transfer from hindered phenols have been reported by Krelick and Weissman.[13] Moreover, the absolute rate constants for hydrogen atom abstraction by peroxy radicals from 2,4.6-tri-*t*-butylphenol also appear to be nearly independent of temperature in the range 30–60°.[1]

(15) L. Fieser, *J. Amer. Chem. Soc.*, 52, 5204 (1930).

(16) Calculated on the assumption that the oxidations correspond to a reversible one electron hydrogen atom transfer. These systems are not reversible in an electrochemical sense: however, such linear free energy relationships have been shown to be successful for many irreversible systems; *cf.*, P. Zeeman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967.

(17) C. D. Cook, C. B. Depatic, and E. S. English, *J. Org. Chem.*, 24, 1356 (1959).

(18) N. S. Hush, *J. Chem. Soc.*, 2375 (1953).

(19) L. M. Andronov, G. E. Zarkov, and Z. K. Mainyes [*Russ. J. Phys. Chem.*, 41, 590 (1967)] report data consistent with the view that peroxy radicals form a hydrogen-bonded complex with water whose heat of formation from reactants is equal to −4.8 kcal/mole. This value is approximately equal to the hydrogen bond of water with phenol and assuming that the phenoxy radical and peroxy radical will be similar the 3 kcal/mole correction should not be included.

(20) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapters 3, 4, and 7.

(21) R. A. Marcus, *J. Phys. Chem.*, 72, 891 (1968).

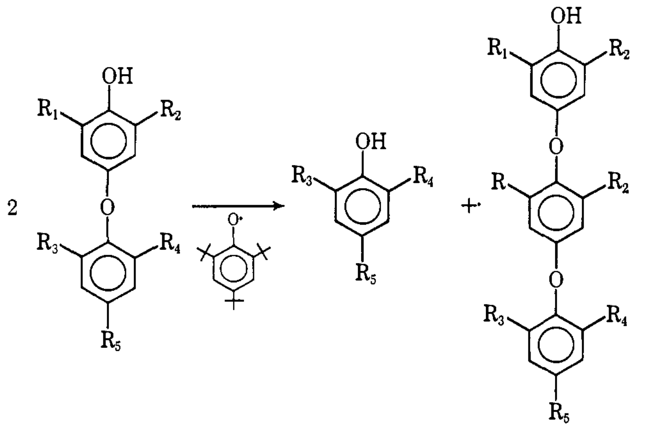
(22) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 41, 1744 (1963).

(23) G. A. Russell and R. C. Williamson Jr., *J. Amer. Chem. Soc.*, 86, 2357 (1964).

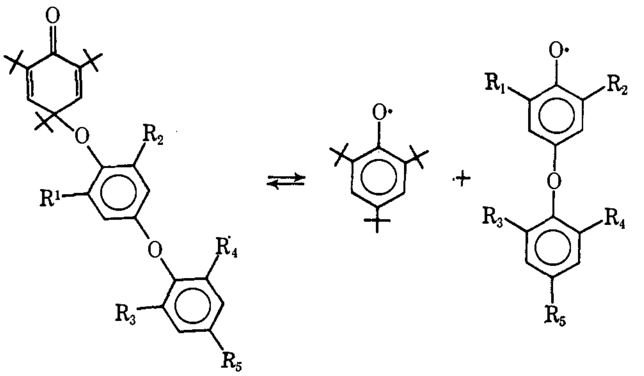
(24) Polar contributions to the structure of the 2,4,6-tri-*t*-butylphenoxy radical have been invoked to account for its esr spectrum [*cf.* E. Muller, A. Rieker, and K. Scheffler, *Ann.*, 64, 36 (1961)]. However, we have recently shown that the solution properties of that free-radical

k_x/k_{-x}, involving phenoxy radicals. The ρ values obtained from the σ^+ correlations for the reactions of oxy radicals with substituted phenols are extremely large and decrease with increasing exothermicity of the transfer reaction. In the present work a value of ρ equal to *ca.* -2.8 units was observed with X equal to the 2,4,6-tri-*t*-butylphenoxy radical. Earlier work yielded values of ρ equal to -1.0 and -0.74 for X equal to the polystyrenylperoxy radical in styrene[25] and the *t*-butoxy radical in chlorobenzene,[26] respectively. The order is that predicted from an application of the Hammond postulate;[27] the activated complex will resemble reactants in the case of very exothermic reactions (*i.e.*, where X is *t*-butoxy, $(\Delta H_f)_{XH} - (\Delta H_T)_{H\cdot}$ is equal to *ca.* -50 kcal/mole) and products in the case of endothermic reactions (*i.e.*, 2,4,6-*t*-butylphenoxy where $(\Delta H_f)_{XH} - (\Delta H_f)_{X\cdot}$ is equal to -28.0 kcal/mole).

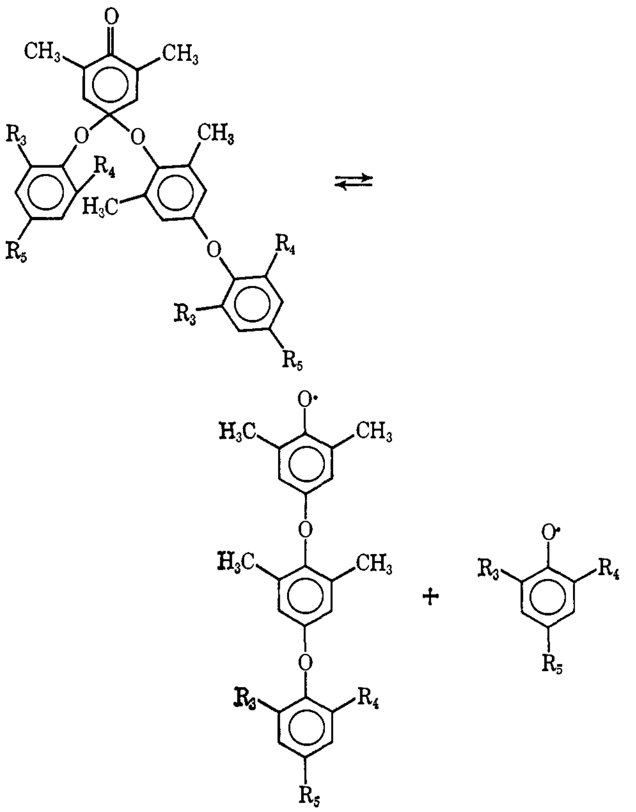
V. **Analysis of Complex Systems.** An important use of the results of the present study is for the analysis of complex systems which involve hydrogen atom transfer equilibrium of phenoxy radicals followed by reversible and/or irreversible formation of products. Bolon[28] has recently described the results of a study of the free-radical redistribution of phenol dimers catalyzed by the 2,4,6-tri-*t*-butylphenoxy radical



The very rapid redistribution at room temperature of the dimers were $R_1 = R_2 = CH_3$ in contrast to the slow redistribution in systems where $R_1 = R_2 = H$ is due to rapid reversible decomposition of the sterically strained intermediate quinol ether

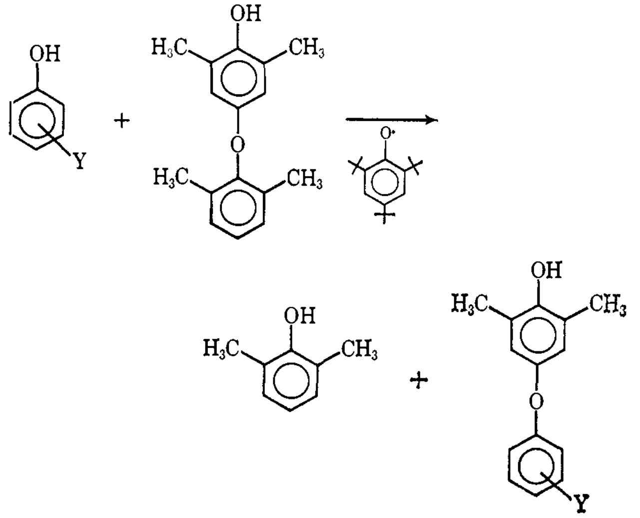


Within the class $R_1 = R_2 = CH_3$ the relative rates of redistribution depend upon the relative stabilities of the monomeric radical substituted with R_3, R_4, and R_5 groups *via* the second equilibrium

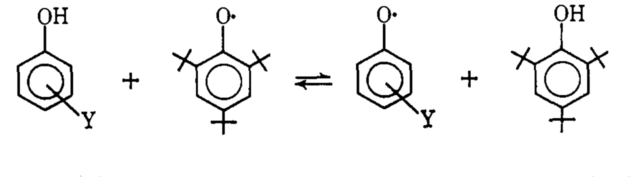


The observed rates of redistribution are fully in accord with the results of the present work, *i.e.*, increasing by a factor of 10^4 in the series $R_3 = R_4 = R_5 = H$ to $R_3 = R_4 = R_5 = CH_3$.

A second type of reaction studied by Bolon was the redistribution



When Y was an electron-withdrawing substituent no redistribution was observed. This result is no doubt due to the very unfavorable rate and equilibrium for the transfer



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parallel those of 1,3,5-tri-*t*-butylbenzene in a series of solvents;[2] a result not consistent with the view that the radical possesses strong dipolar character.

(25) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744, 2800 (1963).

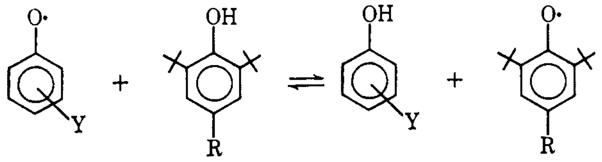
(26) K. U. Ingold, *ibid.*, **41**, 2816 (1963).

(27) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(28) D. A. Bolon, *J. Org. Chem.*, **32**, 1584 (1967).

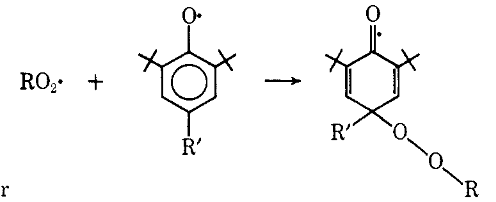
Moreover all the redistributions were inhibited by compounds such as hydroquinones and thiophenols; compounds of the type which we have shown quantitatively scavenge phenoxy radicals.

The mechanism of the synergistic behavior of mixtures of hindered and unhindered phenols as antioxidants recently proposed from our laboratory[4] is based upon the rapid transfer and favorable equilibrium for the systems

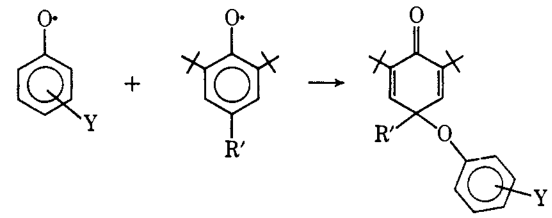


As we have seen the values of $(\Delta H_f)_{B\cdot} - (\Delta H_f)_{BH}$ for the *meta-* or *para-*substituted phenoxy radicals compared with the corresponding value for the 2,4,6-tri-*t*-butylphenol phenoxy radical are in full accord with the proposed mechanism, *i.e.*, the transfer equilibria as written are exothermic or, in the case of 4-methoxyphenoxy, thermoneutral.

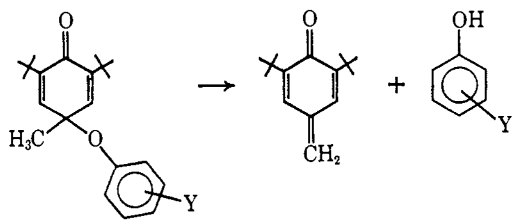
The second step in that proposed mechanism involves the terminations of chains *via* the reactions



and/or



In practical systems at high temperature (*i.e.*, 160°) both of these reactions with R′ equal to *t*-butyl should be reversible while with R′ equal to methyl irreversible decompositions such as



are possible.[29] Thus the 4-methyl compound should be a much more efficient member of the synergistic mixture than the 4-*t*-butyl compound. The results of Ingold[30] at these high temperatures are consistent with this prediction.

Experimental Section

Materials. The phenols utilized in the present study were obtained from commercial sources and purified by recrystallization to yield materials which had melting points which agreed with literature values.

The quinol ethers were prepared according to the procedure of Becker.[31] The nmr spectra of the quinol ethers were recorded in carbon tetrachloride and in all cases the spectra were consistent with the paraquinol ether structure.[32]

Calorimetric Study. The calorimeter and experimental techniques were the same as previously reported from our laboratory.[2]

Determination of k_1 and k_2/k_{-1}. The stop-flow spectrophotometric apparatus and technique of measurement have been described in earlier reports from this laboratory.[4,9]

Vapor Phase Chromatographic Analysis of Products from the Reaction of IIIb and IIIc with 2,5-Di-*t*-pentylhydroquinone. A solution containing 4 mmoles of IIIb and 4 mmoles of 2,5-di-*t*-pentylhydroquinone in 100 ml of chlorobenzene was placed in a 60° constant-temperature bath for 16 hr. After removal from the bath the yellow solution was subjected to vpc analysis utilizing a Hewlett-Packard Model 5750 chromatograph with a 1-m column packed with 7.5% O.V.-17 phenylsilicone on 100–120 mesh gas chrom Q, programmed from 80 to 250° at 20°/min. After the solvent peak, three component peaks with retention times of 4.9, 6.6, 7.2 min were observed. These retention times were found to be identical with those manifested by chlorobenzene solutions of 4-*t*-butylphenol, 2,4,6-tri-*t*-butylphenol, and 2,5-di-*t*-pentylquinone, respectively. Moreover, vpc of mixtures of the reaction solution with solutions of those three components failed to reveal any new components in the chromatogram.

Standard solutions of 0.03–0.06 *M* solutions of 4-*t*-butylphenol, 2,4,6-tri-*t*-butylphenol, and 2,5-di-*t*-pentylquinone yielded chromatograms whose integrated areas were linearly related to the concentrations of the solutions. Utilizing this standardization technique the concentration of the products in the reaction mixture were found to be (analysis in triplicate) 4-*t*-butylphenol, 0.040 ± 0.002 *M*: 2,4,6-tri-*t*-butylphenol, 0.0395 ± 0.001 *M*: and 2,5-di-*t*-pentylquinone, 0.390 ± 0.001 *M*.

The identification and the analysis of the products of IIIc and 2,5-di-*t*-pentylhydroquinone were carried out in an identical manner. The retention time for 3,5-dimethylphenol was equal to 3.8 min. The concentrations of the products in the reaction mixture were found to be 3,5-dimethylphenol, 0.0395 ± 0.0015 *M*: 2,4,6-tri-*t*-butylphenol, 0.0390 ± 0.001 *M*: and 2,5-di-*t*-butylquinone, 0.0390 ± 0.001 *M*.

Infrared Analysis and Product Isolation from the Reaction of IIIb with 2,5-Di-*t*-butylhydroquinone. A solution of 2.0 mmoles of IIIb and 2.0 mmoles of 2,5-di-*t*-butylhydroquinone in 100 ml of argon-flushed chlorobenzene was placed on a constant-temperature bath at 60° for 3 hr. The solution was cooled and then extracted three times with dilute NaOH followed by twice with water. A 50-ml aliquot of the chlorobenzene layer was evaporated to dryness at room temperature, the resultant solid was redissolved in 50 ml of carbon tetrachloride and analyzed by infrared spectroscopy. The spectrum was found to be superimposable in all respects on that obtained from a synthetic mixture of 2.0 mmoles of 2,5-di-*t*-butylquinone and 2.0 mmoles of 2,4,6-tri-*t*-butylphenol in 100 ml of carbon tetrachloride. The remaining portion of the base-extracted chlorobenzene layer was evaporated to dryness at room temperature and the resultant solid was fractionally recrystallized from ethyl alcohol to afford a yellow solid, mp 150–154°; admixture with 2,5-di-*t*-butylquinone, mp 152–154°, and a white solid, mp 128–130°; admixture with 2,4,6-tri-*t*-butylphenol, 132–135°. The infrared spectra of the two solids in carbon tetrachloride were identical with spectra obtained from authentic samples of the two compounds.

The sodium hydroxide extracts and washings were combined, neutralized with dilute hydrochloric acid, and the resulting solution was extracted with benzene. The benzene layer was evaporated to dryness at room temperature. The residual solid was then recrystallized from ethyl alcohol to afford a white solid, mp 95–99°; admixture with 4-*t*-butylphenol 97–100°.

Kinetic Study of the Reaction of IIIa and IIIf with 2,5-Di-*t*-pentylhydroquinone. A solution of 2,5-di-*t*-pentylhydroquinone in chlorobenzene was placed in a Beckman spectrophotometric cell,

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(29) Preliminary calorimetric measurements of the reaction of the 2,4,6-tri-*t*-butylphenoxy radical with 2,6-di-*t*-butyl-4-methylphenol to produce 2,4,6-tri-*t*-butylphenol and the quinol methide of 2,6-di-*t*-butyl-4-methylphenol yield results which suggest that this decomposition of quinol either derived from the 4-methyl compound as written will be exothermic by approximately 8 kcal/mole.

(30) K. U. Ingold, *J. Inst. Petrol.*, **117**, 375 (1961).

(31) H. D. Becker, *J. Org. Chem.*, **29**, 3068 (1964).

(32) T. Matsuura, A. Nishimaga, K. Ogura, and K. Omura, *ibid.*, **34**, 550 (1969).

flushed with purified argon, and the cell was then inserted in a temperature-controlled compartment of a Beckman D.U. spectrophotometer. After temperature equilibration a finely powdered sample, 10–20 mg, of the quinol ether IIIa or IIIf was added to solution *via* a microsalt funnel which had been in thermal contact with the liquid in the cell. Upon addition the quinol ether immediately dissolved and the liquid in cell was stirred with a small capillary which had been previously suspended into the cell. The absorbance of the solution, Ab_t, at 4500 Å was then determined as a function of time. The absorbance of the solution at times corresponding to 8–10$t_{1/2}$, Ab_∞, agreed within ±3% with that calculated from the initial concentrations of IIIa and IIIf. The value of the molar extinction coefficient from 2,5-di-*t*-butylquinone at 4500 Å is equal to 32.5 ± 0.3 M^{-1} cm^{-1}. The first-order rate constant, k_{-2}, was then calculated from plots of log $[Ab_\infty - Ab_t]$ *vs.* time. Such plots were linear for over 4$t_{1/2}$ in all cases.

Kinetic Study of the Reaction (IIIb–IIId) with 2,5-Di-*t*-pentylhydroquinone. Solutions of III and 2,5-di-*t*-pentylhydroquinone or di-*t*-butylhydroquinone in chlorobenzene were placed in 10-ml volumetric flasks, flushed with purified argon, and the stoppers sealed with paraffin wax. The flasks were placed in the constant-temperature bath and allowed to equilibrate. At various intervals of time the flasks were removed and quenched to room temperature. Aliquots were then withdrawn and delivered into solutions of NaI in glacial acetic acid under a CO_2 atmosphere. After standing for 20 min at room temperature the liberated iodine was titrated with standardized thiosulfate solution. Plots of log $[(\text{titer})_\infty - (\text{titer})_t]/(\text{titer})_\infty$ *vs.* time were linear for over 3 half-lives and the value of $(\text{titer})_\infty$, $(\sigma - 10t/2)$, agreed within ±3% with the value calculated from the initial concentration of III. Blank experiments with III and with the hydroquinone yielded negligible titers.

Acknowledgment. The authors wish to acknowledge the excellent technical assistance rendered by Mrs. Jennie Chen and Mr. F. C. Ferris during the course of the study.

Rates and Isotope Effects in the Quinone Oxidation of Leuco Triphenylmethane Dyes[1]

Edward S. Lewis, James M. Perry,[2] and Reuben H. Grinstein[3]

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Abstract: Rates and hydrogen isotope effects in the oxidation of some leuco dyes of the form of 4,4′-bisdimethylamino-*n*-X-triphenylmethane by quinones (mostly halogenated *p*-benzoquinones) have been studied. For the case of the 4′′-dimethylamino substituent (chloranil) the rates were studied as a function of temperature in acetonitrile and in methanol with both hydrogen and deuterium in the tertiary position. In acetonitrile the rate constant of the hydrogen compound is given by $k_H = 1.2 \times 10^5 \exp(-8150/RT)$ and the isotope effect by $k_H/k_D = 0.041 \exp(3360/RT)$. The isotope effects were less precise in methanol, and were somewhat smaller, but the A_H/A_D factor was still less than unit. Rates and isotope effects are presented for several other quinones and leuco dyes and electronic and perhaps small steric effects were observed. The oxidation with 2,3-dichloro-5,6-dicyanoquinone was too fast to measure, but competitive measurements showed that the reaction had about the same ρ as with chloranil but a smaller isotope effect. The results are entirely consistent with tunneling in this hydride-transfer reaction.

The study of hydrogen-transfer reactions has proved interesting in part because they represent the simplest examples of nucleophilic, radical, and electrophilic substitution, and also because extra information is readily available from the hydrogen isotope effect. Of these, the electrophilic substitutions, or hydride transfer, has been subject to the least study.

The rates of several hydride transfers are readily measured, although some are extremely fast;[4] they therefore cover much the same very wide range of rates characteristic of proton-transfer reactions. There is a further uncertainty in hydride-transfer reactions not common to proton-transfer reactions, namely the geometry of the transition state. In proton transfers, the linear transition state appears to be energetically favorable, but arguments have been presented for triangular transition states from some hydride-transfer reactions.[5] These arguments are more plausible than rigorous, and can hardly be taken as convincing.

The subject for the present work is the oxidation of substituted leuco malachite greens by chloranil and other quinones. This reaction has been shown to be quantitative[6] in dimethylformamide, and the kinetics have been studied in methanol solution, in which the oxidation of dye is quantitative, but the chloranil is used to excess by a side reaction.[7] The study of this presumed hydride transfer was made more interesting because large isotope effects have been reported in the oxidation of some triphenylmethanes by carbonium ions.[8]

Results

The reaction studied is the reaction 1. Also shown are the compounds studied, with the exception of a few quinones not derived from *p*-benzoquinone. As noted before,[7] the reaction is first order in each of the reagents, independent of acid concentration, and in acetonitrile is independent of water or oxygen content of the sol-

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