A Mechanistic Study of the Dimerization of Phenoxyl Radicals

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Abstract: The activation energies for the dimerization of 14 substituted phenoxyl radicals have been determined in benzene and chlorobenzene solution. Comparison of these results with the results of an independent thermochemical analysis of the intermediates formed in the dimerization reactions reveals that the radical systems fall into two classes. Those radicals which yield initial keto dimers whose heats of formation from the monomeric phenoxyl radicals exceed 20 kcal/mol manifest absolute rate constants and activation energies for dimerization which are consistent with diffusion theory. In contrast for radicals such as 4 phenyl- and 4 methoxyphenoxyl which yield initial dimers whose heats of formation are considerably less than 20 kcal/mole, the values of the absolute rate constants and activation energies are not consistent with diffusion theory. It is proposed that for the latter systems the formation of the initial keto dimers is reversible and the rate-controlling step is the enolization of the keto dimer. On the basis that acid catalyzes the enolization, the effect of acid on the rate constants and activation energies for the dimerization reactions, the formation of products, and the phenol-inhibited oxidation of hydrocarbons has been determined. The results of these studies are in quantitative agreement with the proposed mechanism.

From an analysis of the results of a number of kinetic studies of the antioxidant behavior of nonhindered phenols it was concluded that the rate constants for the steady state bimolecular termination of phenoxyl radicals varied over several orders of magnitude with changes in the remote substituion on the phenolic moiety.[1] These rate changes have now been observed by means of a new esr technique, described in the preceding paper,[2] by which the absolute values of the steady state rate constants are determined. However, the large variation of the termination constants with substituent was unexplained. The goal of the present work is the elucidation of a unified mechanism for these termination reactions.

Based upon the results of a temperature study utilizing the new esr technique and a thermochemical analysis of the intermediates and products formed in the reactions of phenoxyl radicals, a mechanism is proposed which accounts for the variations in the observed rate constants. Predictions based upon the proposed mechanism are quantitatively verified in studies of the effect of acid on the rates of hydrocarbon oxidation inhibited by phenol, on the rate of product formation under preparative photochemical conditions, and on the steady state termination constants.

Experimental Section

Temperature Studies. Steady State Rate Constants for Phenoxyl Radicals. Samples were prepared and irradiated as previously described.[2] The temperature was controlled by means of the Varian Temperature Controller. The controller was calibrated by means of a thermocouple inside an esr tube containing chlorobenzene. The accuracy and reproducibility of the temperature are estimated to be ±1.0°.

When the sample upon photolysis yields both the semidione radicals from the α-diketones and the phenoxyl radidals only the relative radical concentrations at a given temperature must be determined; thus it is not necessary to correct for the temperature-dependent sensitivity of the esr spectrometer.

In samples which were saturated with *p*-toluenesulfonic acid, the concentration of the acid, determined by titration, was equal to 6×10^{-3} *M* in benzene and 1×10^{-3} *M* in chlorobenzene.

Standard Radicals. In determining the activation energies for the semidione radicals from biacetyl and camphorquinone, a standard pitch sample was utilized to yield a calibration curve for the change in the sensitivity of the spectrometer with temperature.

The activation energies for the termination of these standard semidione radicals were determined by two techniques. In the steady state technique[2] the α-diketone (1.0 *M*) and dihydro compound or isopropyl alcohol (0.1 *M*) are irradiated in the esr spectrometer and one takes advantage of the fact that the rate of production of the radicals is dependent only on the total light intensity and not upon the temperature. Thus under steady state conditions the rates of formation and termination of radicals at two different temperatures may be equated. A plot of the log of the relative radical concentrations *vs.* $1/T$ therefore has a slope proportional to the value of the activation energy for termination.

In the second method, the rotating sector technique,[3] the termination rate constants were determined at several temperatures and the activation energy was obtained from a standard log k *vs.* $1/T$ plot. The plots consisted of from 4 to 10 individual points. Both methods gave the same values of the activation energy within the quoted error limits (Table I).

Photolysis of Biacetyl in Benzene Containing 2,6-Di-*tert*-butylphenol. Two 10-ml solutions of 1.37 *M* biacetyl, 0.219 *M* 2,6-*tert*-butylphenol, and 2.5×10^{-3} *M* *n*-pentacosane in benzene were prepared. One sample was saturated with *p*-toluenesulfonic acid. The samples were then pipetted into Pyrex tubes, outgassed with argon, and then irradiated in parallel in a Rayonet RPR-100 photochemical reactor using the Model MGR-100 Merry-Go-Round and the RPR-3000 Å lamps. Aliquots were taken at various irradiation times and were injected into a Beckman G. C. 4 chromatograph with a logarithmic scale recorder and an Infotronics digital readout system, Model CRC-114 SB/42. The column utilized for the chromatographic separation was 1.5% OV 17 on Gas Chrom Q. The reaction was monitored by following the appearance of 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl. Standard solutions of the latter compound, prepared by the method of Kharasch and Joshi[4] (mp 187°, lit. 185°), and *n*-pentacosane were utilized for the calibration.

Gas Absorption Study. The rate measurements reported in this work were determined on the automatic constant-pressure apparatus described in earlier work from this laboratory.[5]

Results and Discussion

Temperature Dependence of Steady State Termination Constants. In the preceding paper[2] it was demonstrated that the system obtained upon the photolysis of an α-diketone, K, in the presence of a phenolic hydrogen donor molecule, ArOH, in benzene or

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[1] *Cf.* L. R. Mahoney, *Angew. Chem., Int. Ed. Engl.*, 8, 547 (1969).

[2] S. A. Weiner, *J. Amer. Chem. Soc.*, **94**, 581 (1972).

[3] S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969).

[4] M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, 22, 1439 (1957).

[5] L. R. Mahoney, R. W. Bayma, A. Warnick, and C. H. Ruof, *Anal. Chem.*, 36, 3516 (1964).

Table I. Summary of Kinetic and Thermochemical Quantities

Radical	C_6H_6 log $k_{30°}$	C_6H_6 $\Delta E_{4(5)}^{\ddagger}$ kcal/mole	C_6H_5Cl log $k_{30°}$	C_6H_5Cl $\Delta E_{4(5)}^{\ddagger}$ kcal/mole	$-\Delta H_8$ kcal/mole	$-(\Delta H_8 + \Delta H_9)$ kcal/mole
CQH·[a]	8.3	4.2 ± 0.2	7.9	3.9 ± 0.4		
Ac_2H·[b]	9.3	4.2 ± 0.4	8.7	3.2 ± 0.4		
3,5-Di-COOEt[c]	9.3	4.2 ± 0.8	8.3	3.2 ± 0.8	<25.2	<71.2
3-COOEt[c]	9.0	1.5 ± 1.3	8.0	4.8 ± 1.2	25.2	71.2
3,5-Di-Me[c]	9.5	4.2 ± 0.8	8.4	3.2 ± 0.8	21.8	67.8
4,5 Benzo-[c]	9.6	−1.3 ± 0.8	8.7		19.0	65.0
4-Me[c]	9.2	0.2 ± 1.1	7.9	0.4 ± 0.6	19.2	65.2
4-*tert*-Bu[c]	8.9	−2.9 ± 1.5	7.7	−3.0 ± 0.8	19.0	65.0
4-H[c]	8.7	−1.4 ± 1.6	7.7	−7.0 ± 4.0	21.0	67.0
2,6-Di-Me[c]	8.6	5.9 ± 1.5	7.4		16.2	62.2
3,5-Di-*tert*-Bu[c]	8.1	1.2 ± 1.5	6.9		17.6	63.6
4-Phenyl[c]	7.5	−3.8 ± 0.8	6.3	−5.4 ± 1.2	16.0	62.0
4-*O*-Me[c]	7.2	1.6 ± 0.8	6.1	1.4 ± 0.8	14.2	60.2
2,6-Di-*tert*-Bu[c]	7.5	6.8 ± 1.0	6.1		14.0	60.0

[a] Radical is semidione from camphorquinone. [b] Radical is semidione from biacetyl. [c] Substituent on phenolic moiety.

chlorobenzene solution could be described by the following reaction scheme

$$K \xrightarrow{h\nu} K^* \tag{1}$$

$$K^* + ArOH \xrightarrow{k_2} \cdot KH + ArO\cdot \tag{2}$$

$$ArO\cdot + \cdot KH \xrightarrow{k_3} K + ArOH \tag{3}$$

$$2ArO\cdot \xrightarrow{k_4} \text{nonradical products} \tag{4}$$

$$2\cdot KH \xrightarrow{k_5} \text{nonradical products} \tag{5}$$

Further it was shown that under steady state conditions

$$\frac{k_4}{k_5} = \frac{(\cdot KH)_{ss}^2}{(ArO\cdot)_{ss}^2} \tag{6}$$

where $(\cdot KH)_{ss}/(ArO\cdot)_{ss}$ represents the ratio of the steady state concentrations of the semidione radical derived from the diketone to the steady state concentration of the phenoxyl radical.

Combining the Arrhenius equation and eq 6

$$(\Delta E_4^{\ddagger} - \Delta E_5^{\ddagger})/2.3RT = 2 \log \frac{(\cdot KH)_{ss}}{(ArO\cdot)_{ss}} - \log \frac{A_4}{A_5} \tag{7}$$

A systematic study of the ratio of concentrations of the radicals as a function of temperature for a large number of phenols in benzene and chlorobenzene as solvent revealed that, in agreement with eq 7, the log of the ratios were linear functions of $1/T$. Typical results are shown in Figure 1.

The values of the activation energies for the semidione radicals derived from camphorquinone and from biacetyl, $\Delta E_5^{\ddagger}$, were determined by means of the rotating sector technique. These values were then combined with the values of $\Delta E_4^{\ddagger} - \Delta E_5^{\ddagger}$ obtained from the results of the temperature study and eq 7 to yield values of $\Delta E_4^{\ddagger}$ for the phenoxyl radicals. The values of $\Delta E_4^{\ddagger}$ derived by this procedure are summarized in Table I.

Examination of Table I reveals that for the semidione radical and for the phenoxyl radicals derived from 3,5-dimethyl-, 3,5-dicarboethoxyl-, and 3-carboethoxyphenol the activation energies are in the range of 3.0–4.0 kcal/mole in both benzene and chlorobenzene solution. These values are in reasonable agreement with values of *ca.* 3.0 kcal/mole predicted for these solvents on the basis of diffusion theory for radical termination in solution. For the other phenoxyl radicals the observed values of $\Delta E_4^{\ddagger}$ are not consistent with the simple diffusion model. Not only are the activation energies complex functions of remote substituent, there are a number of cases in both benzene and chlorobenzene in which they are actually negative. A negative activation energy cannot be associated with a simple bimolecular reaction in solution. Their occurrence is suggestive of a complex mechanism involving an equilibrium formation of a metastable intermediate followed by a slow, rate-controlling reaction of the intermediate to form a stable product. On this basis it is of interest to consider the thermochemical stabilities of the intermediates and the products derived from the bimolecular reaction of phenoxyl radicals.

Thermochemistry of Intermediates and Products. For many of the phenoxyl radicals in Table II, no product studies have been reported. However for simple phenoxyl,[6] 2,6-di-*tert*-butyl-,[7] 2,6-dimethyl-,[7] and 2,4-di-*tert*-butylphenoxyl[8] radicals, in nonpolar solvents, the product studies indicate that isomeric dihydroxybiphenyls are the major final products. These

Table II. Summary of the Effect of Acid on Kinetic Quantities

A. Effect of Acid on Steady State Rate Constants

Radical	log $k_{30°}$ C_6H_6	log $k_{30°}$ C_6H_6 (H^+)	log $k_{30°}$ C_6H_5Cl	log $k_{30°}$ C_6H_5Cl (H^+)
Ac_2H·	9.3	9.2	8.7	8.7
3,5-Di-COOEt	9.3	9.2		
4-Phenyl	7.5	9.3	6.3	8.9
3,5-Di-*tert*-butyl	8.1	9.4		
2,6-Di-*tert*-butyl	7.5	8.5		
4-H	8.7		7.7	8.3

B. Effect of Acid on Activation Energies

Radical	$\Delta E_{4(5)}^{\ddagger}$ C_6H_6	$\Delta E_{4(5)}^{\ddagger}$ C_6H_6(H^+)	$\Delta E_{4(5)}^{\ddagger}$ C_6H_5Cl	$\Delta E_{4(5)}^{\ddagger}$ C_6H_5Cl(H^+)
Ac_2H·	4.2 ± 0.4	3.6 ± 1.5	3.2 ± 0.4	
4-Phenyl	−3.8 ± 0.8	3.6 ± 1.8		
4-H	−1.4 ± 1.6		−7.0 ± 4.0	4.6 ± 0.7

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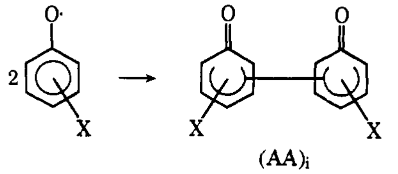
[6] H. I. Joschek and S. I. Miller, *J. Amer. Chem. Soc.*, **88**, 3273 (1966).

[7] E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 263 (1966).

[8] E. C. Horswill and K. U. Ingold, *ibid.*, **44**, 269 (1966).

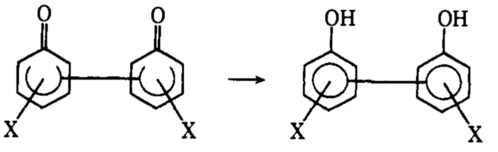
final products are formed *via* an initial dimerization of the phenoxyl radicals to produce the isomeric diketo intermediates, $(AA)_i$,



(8)

$(AA)_i$

where X is a substituent on the phenolic moiety. The compounds, $(AA)_i$, then enolize to form the final products, $(AA)_p$,



(9)

$(AA)_p$

Utilizing the values of the differences in the heats of formation of phenoxyl radicals and their parent phenols obtained from the results of other studies from our laboratory,[9,10] it is possible to calculate fairly reliable values for the heats of reactions ΔH_8 and $\Delta H_8 + \Delta H_9$ as functions of the substituent, X. In the final columns of Table I are summarized the values of ΔH_8 and $\Delta H_8 + \Delta H_9$ obtained from such an analysis, the details of which are presented in the Appendix.

As would be anticipated, the heats of the overall reactions, $\Delta H_8 + \Delta H_9$, are exothermic by more than 60 kcal/mole and the overall reactions are not reversible. However the exothermicities of the reactions to form the diketo intermediates, ΔH_8, are in *all* cases sufficiently small that these intermediates may be classified as metastable and the strong possibility exists that reaction 8 is reversible.[11]

Proposed Mechanism. If reaction 8 is reversible the steady state rate constants for the bimolecular disappearance of phenoxyl radicals are complex quantities given by the expression,

$$k_4 = k_8\left(\frac{k_9}{k_{-8} + k_9}\right) \tag{10}$$

Although the degree of reversibility is governed by the relative values of k_{-8} and k_9 for each system, the values of k_{-8} will decrease with increasing exothermicity of reaction 8. Examination of the variation of k_4 and $\Delta E_4^{\ddagger}$ with ΔH_8 in Table I are in general agreement with eq 10. Under conditions such that $k_9 \gg k_{-8}$,

$$k_4 = k_8 \tag{11}$$

and the observed values of k_4 and $\Delta E_4^{\ddagger}$ will be consistent with a diffusion model for termination. This situation applies to the semidione radicals and to the phenoxyl radicals derived from 3,5-dicarboethoxyl-3,5-dimethyl-, and 3-carboethoxyphenol, systems in which the heats of formation of the diketo intermediates exceed 20 kcal/mole. Conversely for the systems in which the heats of formation of the diketo dimers are significantly smaller than 20 kcal/mole, *i.e.*, the 4-phenyl-, 4-methyl-, and 3,5-di-*tert*-butylphenoxyl radicals, the values of k_4 are several orders of magnitude smaller than k_8.[12]

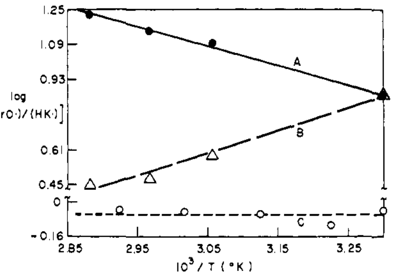
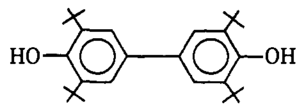


Figure 1. Plots of the log of the ratios of the steady state concentrations of phenoxyl radical and the semidione from biacetyl *vs.* $1/T$. Curve A represents 4-phenylphenoxyl in benzene. Curve B represents 2,6-di-*tert*-butylphenoxyl in benzene. Curve C represents 4-phenylphenoxyl in benzene in the presence of 6×10^{-3} *M* *p*-toluenesulfonic acid.

The proposed mechanism is susceptible to a direct test. On the basis that the enolization reaction, eq 9, is catalyzed by acid, the addition of sufficient acid should increase the values of k_9 to the point such that $k_9 \gg k_{-8}$ for all the phenoxyl radical systems. Under these conditions all the phenoxyl radical systems will manifest values of k_4 and $\Delta E_4^{\ddagger}$ consistent with the diffusion controlled model.

Effect of Acid on Steady Rate Constants. The esr experiments for a number of key systems were repeated with added *p*-toluenesulfonic acid. The results of these experiments are summarized in Table II. We see that the acid has no effect on the values of k_4 for the biacetylsemidione and 3,5-dicarboethoxyphenoxyl radicals, systems which manifest values of k_4 and $\Delta E_4^{\ddagger}$ consistent with the diffusion model. In contrast for the phenoxyl radicals derived from simple phenol, 3,5-di-*tert*-butyl-, 2,6-di-*tert*-butyl-, and 4-phenylphenol, the values of k_4 increased dramatically upon the addition of acid. Moreover, a systematic temperature study for the simple phenoxyl and 4-phenylphenoxyl radicals revealed that the values of $\Delta E_4^{\ddagger}$ in the presence of acid become equal to that of the semidione of biacetyl, *i.e.*, *ca.* 4.0 kcal/mole (*cf.*, curve C, Figure 1). We therefore conclude that in the presence of acid the diffusion controlled model satisfactorily describes the termination of the simple phenoxyl and 4-phenylphenoxyl radicals.[13] These findings are in quantitative agreement with those predicted by the proposed mechanism.

Effect of Acid on the Yield of Dimer of 2,6-Di-*tert*-butylphenoxyl. A study of the initial yields of the enolized dimer of the 2,6-di-*tert*-butylphenoxyl radical,



produced by the photolysis of biacetyl in a benzene solu-

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(9) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **92**, 890 (1970).

(10) L. R. Mahoney and M. A. DaRooge, manuscript in preparation.

(11) With a value of log A_{-8} equal to 14.0,[9] the half-lives for a diketo dimer at 30° are equal to 7×10^{-1} sec and 7×10^{-6} sec with $\Delta E_{-8}^{\ddagger}$ equal to 20 and 14 kcal/mole.

(12) The values of k_8 will of course vary with the diffusion coefficient of the free radical and with the magnitude of the cage effect for each system. However, these effects should be small in comparison with the effects with which we are now concerned.

(13) We note that in the presence of acid k_4 in benzene is equal to three times k_4 in chlorobenzene. This difference is exactly the change in the diffusion coefficient due to change in solvent viscosity calculated from the modified Debye equation.

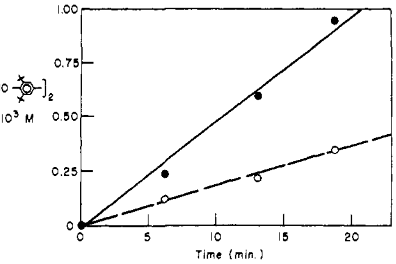


Figure 2. Yield of the dimer of 2,6-di-*tert*-butylphenoxyl radical as a function of time from the photolysis of 1.37 *M* biacetyl in the presence of 0.2 *M* 2,6-di-*tert*-butylphenol in benzene solution. The solid points, ●, represent the yield in the presence of 6 × 10^{-3} *M* *p*-toluenesulfonic acid and the open points, ○, in the absence of acid.

tion containing the parent phenol with and without *p*-toluenesulfonic acid, was carried out. From the results presented in Figure 2 we see that the rate of formation of the dimer is increased by a factor of *ca.* 2.5 by the addition of acid.

This value compares favorably with a value derived from the following calculation. Since the total light which both samples absorb is equal, the rate of formation of free radicals is equal for the noncatalyzed and acid-catalyzed systems. Therefore at steady state we may write.

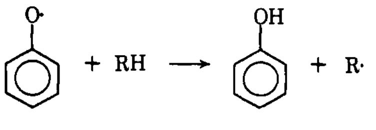
$$k_5(\mathrm{KH}\cdot)_{\mathrm{H}^+}{}^2 + k_{3\mathrm{H}^+}(\mathrm{KH}\cdot)_{\mathrm{H}^+}(\mathrm{ArO}\cdot)_{\mathrm{H}^+} + k_{4\mathrm{H}^+}(\mathrm{ArO}\cdot)_{\mathrm{H}^+}{}^2 = k_5(\mathrm{KH}\cdot)^2 + k_3(\mathrm{KH}\cdot)(\mathrm{ArO}\cdot) + k_4(\mathrm{ArO}\cdot)^2 \quad (12)$$

where the subscripts, H+, refer to acid-catalyzed sample. Utilizing eq 6 and rearranging,

$$\frac{\left(\dfrac{\mathrm{d\ Dimer}}{\mathrm{d}t}\right)_{\mathrm{H}^+}}{\left(\dfrac{\mathrm{d\ Dimer}}{\mathrm{d}t}\right)} = \frac{k_{4\mathrm{H}^+}(\mathrm{ArO}\cdot)_{\mathrm{H}^+}{}^2}{k_4(\mathrm{ArO}\cdot)^2} = \left\{\frac{2(k_4)^{1/2}(k_5)^{1/2} + k_3}{2(k_4)_{\mathrm{H}^+}{}^{1/2}(k_5)^{1/2} + k_{3\mathrm{H}^+}}\right\}\left(\frac{k_{4\mathrm{H}^+}}{k_4}\right) \quad (13)$$

Substituting values of k_4 and $k_{4\mathrm{H}^+}$ (Table II), and assuming that k_3 and $k_{3\mathrm{H}^+}$ are equal to k_5, the diffusion controlled rate constant, a value of 2.2 is calculated for the ratio of rates of formation of the dimer in the presence and in the absence of acid.

Effect of Acid on the Phenol-Inhibited Oxidation of Hydrocarbons. In contrast to hindered phenols and hydroquinones[14] high concentrations of nonhindered phenols[15] do not completely surpress the free radical initiated oxygen absorption of solutions of hydrocarbons. The results of kinetic studies are consistent with the view that at high concentrations of phenol, the main chain carrier is the phenoxyl radical, and chains



(14)

terminate *via* reaction 4. Under these conditions the rate of oxygen absorption is given by the expression

$$\frac{-\mathrm{dO_2}}{\mathrm{d}t} = R_\mathrm{i} + \frac{k_{14}}{(2k_4)^{1/2}}(R_\mathrm{i})^{1/2}(\mathrm{RH}) \quad (15)$$

where R_i is equal to the known rate of radical production from the initiator and RH is the concentration of the hydrocarbon.

We have measured the rates of oxygen absorption of a chlorobenzene solution containing 0.099 *M* dihydroanthracene, 3.1 × 10^{-4} *M* tetraphenylbutane, and 0.0473 *M* phenol at 60° in the absence of and in the presence of 6.5 × 10^{-4} *M* *p*-toluenesulfonic acid. The uncatalyzed rate was found to be equal to 8.3 × 10^{-7} *M* sec^{-1} while the acid-catalyzed sample yields a rate equal to 2.5 × 10^{-7} *M* sec^{-1}. The value of $[(k_{4\mathrm{H}^+})^{1/2}/(k_4)^{1/2}][k_{14}/k_{14\mathrm{H}^+}]$ calculated from eq 15 and the known value of R_i is equal to 5.7. This value may be compared to a value of $[(k_{4\mathrm{H}^+})/(k_4)]^{1/2}$ equal to 5.0, calculated from the esr values of $k_{4\mathrm{H}^+}$ and k_4 which at 60° are equal to 5.0 × 10^8 M^{-1} sec^{-1} and 0.2 × 10^8 M^{-1} sec^{-1}, respectively. This agreement is quite important since it demonstrates that the values of the absolute rate constants for the steady state bimolecular disappearance of phenoxyl radicals obtained by the esr technique are applicable to data obtained in systems in which the phenoxyl radicals are generated *via* a thermal source of free radicals.

Nature of the Solvent and Reaction (9). A key step in the proposed mechanism is reaction 9, the enolization of the metastable diketo intermediates to dihydroxybiphenyls. In the presence of hydroxylic solvents, *i.e.*, water, there is sufficient catalyst present such that the rate of reaction 9 should be very high and the rate of dimerization of phenoxyl radicals will approach the diffusion-controlled value. Consistent with this view, Land and Porter[16] and Dobson and Grossweiner[17] reported values of the absolute rates of dimerization of phenoxyl and 4-methylphenoxyl radicals in water equal to the rate constant for the diffusion-controlled reaction *i.e.*, *ca.* 6 × 10^9 M^{-1} sec^{-1}.

The interesting question now arises as to the nature of the mechanism and the identity of potential catalysts for reaction 9 with benzene and chlorobenzene as solvents. The rates of the nonhindered phenol inhibited oxidation of hydrocarbons in chlorobenzene solution have been routinely measured in our laboratory and over a period of 6 years have been found to be highly reproducible. A similar reproducibility has been observed in the esr experiments which have been carried out for a period of over 1 year.

An explanation for the high degree of reproducibility would involve the idea that the added phenol is functioning as a catalyst for the enolization. This mechanism is not supported by the findings in the preceding paper.[2] In that work a systematic variation of the concentration of 4-phenylphenol over a moderately wide concentration range (0.004–0.04 *M*) failed to reveal any effect on the value of k_4. Thus if the added phenol is acting as a catalyst it must manifest a peculiar concentration dependence. A second possibility is that reaction 9 is surface catalyzed. However the values of $k_4/k_{4\mathrm{H}^+}$ obtained from the esr method and those obtained from the oxygen absorption study are in excellent agreement, *vide supra*, although the surface

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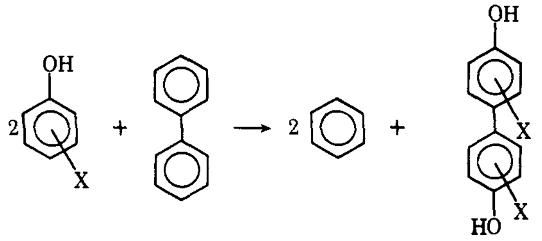
[14] L. R. Mahoney, *J. Amer. Chem. Soc.*, **88**, 3035 (1966).
[15] L. R. Mahoney, *ibid.*, 1895 (1967).
[16] E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2013 (1963).
[17] G. Dobson and L. I. Grossweiner, *ibid.*, **61**, 708 (1965).

to volume ratio in the esr tube is on the order of 10 times higher than in the gas absorption cell.

Thus at present we have no satisfactory explanation for the nature of the catalyst(s) for reaction 9 in the absence of added catalyst in chlorobenzene. This question along with the associated questions of the relative effectiveness of various catalysts for reaction 9, as functions of concentration and structure, are currently under investigation and will be the subject of future reports from this laboratory.

Appendix. Thermochemistry of Products and Intermediates

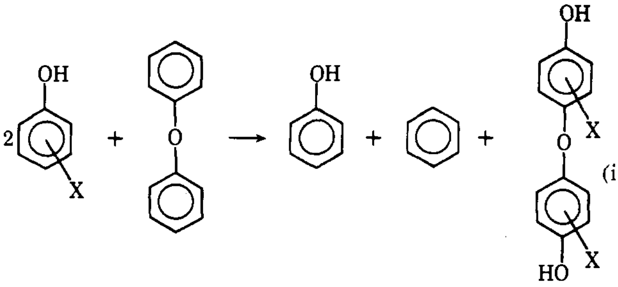
Heat of Formation of Enolized Dimers, $\Delta H_8 + \Delta H_9$. Consider the hypothetical thermoneutral reactions in the gas phase,



(i)

(AA) product

and



(ii)

(AOA) product

where X represents a substituent(s) on the phenolic moiety.[18] Utilizing the known heats of formation of phenol, benzene, and diphenyl in the gas phase[19] and a value of + 13 kcal/mole for the heat of formation of diphenyl ether in the gas phase[20] at 298°K, we find

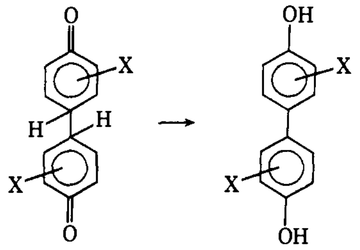
$$\Delta H_{\text{f(AA)product}} = 2\Delta H_{\text{fArOH}} + 4.0$$

and

$$\Delta H_{\text{f(AOA)product}} = 2\Delta H_{\text{fArOH}} + 16.2$$

Thus, the enolized carbon–carbon dimer is the more stable, thermodynamically, than the carbon–oxygen dimer. We note that the carbon–carbon dimer is the product most frequently reported from the oxidation of phenols in nonpolar solvents, *vide supra.*

Heat of Enolization of Diketo Intermediates. We estimate a value for the heats of enolization of the carbon–carbon diketo intermediates, *i.e.*,

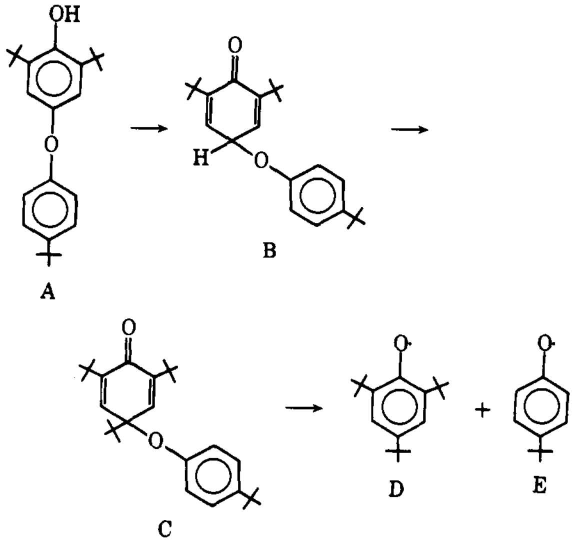


(iii)

equal to approximately −46 kcal/mole. This estimate is derived from two sources.

(1) Benson's Additivity Rules.[21] On the assumption that there is no resonance interaction of the double bonds with the carbonyl groups in the isomeric cyclohexadienones, the heats of formation of cyclohexa-2,4-dien-1-one and cyclohexa-2,5-dien-1-one are calculated to be equal to 0 and +1.0 kcal/mole, respectively, in the gas phase at 298°K. The heat of formation of phenol is equal to −23.2 kcal/mole under the same conditions.

(2) Heats of Disassociation of Quinol Ethers of 2,4,6-Tri-*tert*-butylphenoxyl. From the series of reactions



(iv)

the heat of ketonization is calculated to have a minimum value of +24 ± 3 kcal/mole. The heat of formation of A is estimated to be equal to −100 ± 3 kcal/mole from the known heat of formation of 2,4,6-tri-*tert*-butylphenol in the gas phase at 298°K[18] and reaction i. The heat of formation of B is therefore equal to ΔH_{keto} − 100 ± 3.0 kcal/mole. The heat of formation of C is calculated from Benson's additivity rules to be equal to −107 ± 3.0 kcal/mole + ΔH_{keto} + *nonbonded* interactions corresponding to the H to *tert*-butyl transformation. The values of D and E are calculated to be equal to −63.0 and −13.5, respectively, from the heats of formation of the phenols in the gas phase and the experimentally determined differences in the heats of formation of the phenols and phenoxyl radicals in chlorobenzene solution.[9,10] The

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(18) The heats of these reactions should be independent of X for the alkylated phenols. *Cf.* L. R. Mahoney, F. C. Ferris, and M. A. DaRooge, *J. Amer. Chem. Soc.*, **91**, 3883 (1969).

(19) D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969.

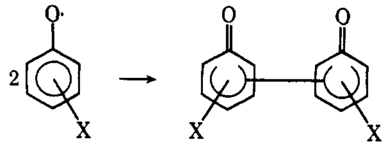
(20) A value of 16 kcal/mole is estimated for the heat of vaporization of diphenyl ether together with a value of −3.48 for the heat of formation of the liquid.[19]

(21) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

$$\mathrm{C \longrightarrow D + E} \qquad \text{(v)}$$

heat of reaction is equal to the activation energy for the disassociation of the quinol ether in chlorobenzene, namely 25 kcal/mole.[9]

Heat of Dimerization of Phenoxyl Radicals, ΔH_8. Combining the results from the preceding section, the heats of the reactions



(vi)

are equal to $-50 + 2[(\Delta H_f)_{\mathrm{ArO}\cdot} - (\Delta H_f)_{\mathrm{ArOH}}]$. The values of $(\Delta H_f)_{\mathrm{ArO}\cdot} - (\Delta H_{f\mathrm{ArOH}})$ are derived from the results of other studies from our laboratory.[9,10]

The Question of an Intermediate in a Simple Nucleophilic Substitution at Sufinyl Sulfur. The Acetate-Catalyzed Exchange of Methanol-d_3 with Methyl *p*-Toluenesulfinate[1a]

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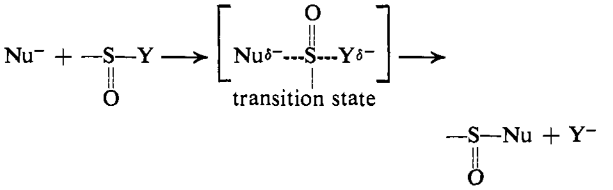
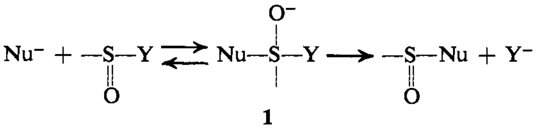
Abstract: The rate of exchange of methoxyl groups between methanol-d_3 and methyl *p*-toluenesulfinate (eq 8) has been studied in a series of acetate–acetic acid buffers in methanol-d_3 as solvent at 62°. Under these conditions the rate constant for the exchange, k_e, is the sum of two terms: $k_e = k'[\mathrm{AcO^-}]/[\mathrm{AcOH}] + k_{\mathrm{OAc}}[\mathrm{AcO^-}]$. The first of these is due to a specific methoxide ion catalyzed exchange involving reaction of $\mathrm{CD_3O^-}$ with the sulfinate ester. Various considerations suggest that the second term represents general base, rather than nucleophilic, catalysis by acetate. More detailed considerations, including the magnitude of the solvent isotope effect associated with k_{OAc}, argue that the general base catalysis is the result of a combination of specific methoxide ion catalysis with general acid catalysis by acetic acid and that the rate-determining step in the process is the reaction of $\mathrm{CD_3O^-}$ with a hydrogen-bonded complex of the sulfinate ester and acetic acid.

One of the most important questions to answer regarding the mechanism of representative nucleophilic substitutions at sulfinyl (>S=O) sulfur is the exact timing of the two covalency changes that occur during such a reaction. On the one hand, one can conceive of a process (eq 1), analogous to S_N2 substitutions at sp³ carbon, in which bond making and bond breaking are truly synchronous. On the other hand, the existence of stable species such as $\mathrm{SF_4}$ makes it equally conceivable that substitution could follow a path (eq 2) in which an actual intermediate **1** is formed.



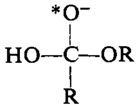
$$\mathrm{Nu^- + {-}\underset{\overset{\|}{O}}{S}{-}Y \longrightarrow \underset{\text{transition state}}{\left[Nu^{\delta-}{\cdots}\overset{\overset{O}{\|}}{\underset{|}{S}}{\cdots}Y^{\delta-}\right]} \longrightarrow {-}\underset{\overset{\|}{O}}{S}{-}Nu + Y^-} \qquad (1)$$



$$\mathrm{Nu^- + {-}\underset{\overset{\|}{O}}{S}{-}Y \rightleftarrows \underset{\mathbf{1}}{Nu{-}\overset{\overset{O^-}{|}}{\underset{|}{S}}{-}Y} \longrightarrow {-}\underset{\overset{\|}{O}}{S}{-}Nu + Y^-} \qquad (2)$$

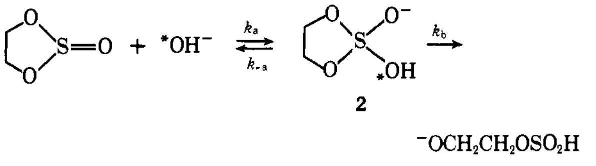
In the hydrolysis of an ester of a carboxylic acid the presence of an intermediate on the reaction path was first demonstrated by Bender[2] *via* the expedient of subjecting a carbonyl ^{18}O-labeled ester to partial hydrolysis and showing that the ester recovered after partial hydrolysis had undergone substantial exchange of oxygen-18. Application of this type of experiment to the hydrolysis of ethylene sulfite by Bunton and coworkers[3] led to no significant exchange of oxygen-18 between the solvent and the recovered ester.

Given the fact that in the alkaline hydrolysis of alkyl carboxylates oxygen equilibration *via* transfer of a proton between labeled and unlabeled oxygens in the tetrahedral intermediate



$$\mathrm{HO{-}\overset{\overset{*O^-}{|}}{\underset{\underset{R}{|}}{C}}{-}OR}$$

is competitive with the breakdown of that intermediate,[2] the results of Bunton, *et al.*, might seem at first glance to indicate that the alkaline hydrolysis of the sulfite must not be occurring by a mechanism (eq 3) involving



(3)

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(1) (a) This research was supported by National Science Foundation Grants GP-10732X and GP-25799; (b) to whom inquiries should be addressed at the University of Vermont; (c) NDEA Fellow, Oregon State University, 1968–1971.

(2) M. L. Bender, *J. Amer. Chem. Soc.*, 73, 1626 (1951).

(3) C. A. Bunton, P. D. B. de la Mare, P. M. Greasley, D. R. Llewellyn, N. H. Pratt, and J. G. Tillett, *J. Chem. Soc.*, 4751 (1958).