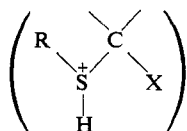


experiments, very little heat evolution is expected upon the second addition of formaldehyde and this is in accord with the observations of Fernandez and Butler. This is *not* due to the fact that morpholine is almost entirely as the methylenediamine, the concentration of which does not significantly change upon addition of an additional equivalent of formaldehyde as concluded by Fernandez and Butler,<sup>33</sup> but the  $\Delta T$  differences are due to large alterations in the composition of the solution with mutually compensating enthalpic changes. Thus, the method of heat evolution<sup>33</sup> is not applicable for the determination of the composition of solutions of amines and formaldehyde in the absence of knowledge of the heats of the several reactions which may occur in such solutions.<sup>3a</sup>

Measured or estimated  $pK_a'$  values from this work and other reports for major methylene derivatives of oxygen, nitrogen, and sulfur are contained in Table IV. Sulfonium ion derivatives



are not included since protonation of methylene derivatives containing a single sulfur atom occurs first on oxygen and nitrogen as a result of their greater basicity.<sup>34</sup>

**Acknowledgment.** Appreciation is due to Miss Ruth Ann Miele and Mrs. Joan Braun for early experiments upon which this work is based.

(34) The  $pK_a'$  values for  $\text{CH}_3\text{CH}_2\text{SH}_2^+$ ,  $\text{CH}_3(\text{CH}_2)_2\text{OH}_2^+$ , and  $\text{CH}_3\text{CH}_2\text{NH}_3^+$  are  $-6.72$ ,<sup>35</sup>  $-2.3$  (see Arnett and Anderson, Table IV, footnote *d*), and  $10.63$ ,<sup>36</sup> respectively.

(35) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(36) D. H. Everett and B. R. W. Pinsent, *Proc. Roy. Soc., Ser. A*, **215**, 426 (1952).

## Appendix

At equilibrium, solutions containing morpholine buffers and formaldehyde may be described by the following equations,<sup>2</sup> where *i* = initial and *f* = final.

$$K_I = [\text{N}_H]/[\text{N}_{BF}][\text{F}_F] \quad (1a)$$

$$K_M = [\text{N}_D]/[\text{N}_H][\text{N}_{BF}] \quad (2a)$$

$$K_{a_1} = [\text{N}_{BF}]a_H/[\text{N}_{AF}] \quad (3a)$$

$$K_{a_2} = [\text{N}_H]a_H/[\text{N}_{HH}] \quad (4a)$$

$$\begin{aligned} [\text{N}_{AT}] &= [\text{N}_{AF}]_i + a_{H_i} + [\text{OH}^-]_f - a_{H_f} - [\text{OH}^-]_i \\ &= [\text{N}_{AF}]_f + [\text{N}_{HH}] + [\text{N}_{DH}] \end{aligned} \quad (5a)$$

$$[\text{N}_{BT}] = [\text{N}_{BF}]_f + [\text{N}_H] + [\text{N}_{DH}] + 2[\text{N}_D] \quad (6a)$$

$$[\text{N}_T] = [\text{N}_{AT}] + [\text{N}_{BT}] \quad (7a)$$

$$[\text{F}_T] = [\text{F}_F] + [\text{N}_H] + [\text{N}_{HH}] + [\text{N}_D] + [\text{N}_{DH}] \quad (8a)$$

These equations can be combined to yield the cubic polynomial in eq 9a, where  $P = [\text{N}_{BF}]_f = [\text{N}_{AF}]_f K_{a_1}/a_{H_f}$ . Equation 9a and equations used to derive it will determine all of the final equilibrium concentrations and unknown equilibrium constants.

$$\begin{aligned} P^3(K_{a_1} + a_{H_i})K_I K_M/K_{a_1} + \\ P^2\{(2[\text{F}_T] - [\text{N}_T])K_M + 1 - a_{H_f}^2/K_{a_1}K_{a_2}\}K_I + \\ P\{1 + ([\text{F}_T] - [\text{N}_{BT}])K_I + \\ ([\text{N}_{AT}] - [\text{F}_T])a_{H_f}K_I/K_{a_2} - a_{H_f}/K_{a_1}\} + \\ ([\text{N}_{AT}] - [\text{N}_{BT}]) = 0 \quad (9a) \end{aligned}$$

## A Steady State Technique for Measuring Phenoxy Radical Termination Constants

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**Abstract:** A new, steady state technique for measuring radical termination rate constants is described. This technique involves photolysis of an  $\alpha$ -diketone together with a hydrogen atom donor in the cavity of an esr spectrometer to produce steady state concentrations of two different radicals, one from the diketone and the other from the donor. The technique is applied to phenoxy radicals in benzene and chlorobenzene solution. Analysis of the results leads to values of the termination constants in benzene ranging from  $1.7 \times 10^7 M^{-1} \text{sec}^{-1}$  for 4-methoxyphenoxy to  $4.5 \times 10^9 M^{-1} \text{sec}^{-1}$  for 2-naphthoxy. In general, the termination constants in chlorobenzene are an order of magnitude lower than in benzene.

It has been reported that phenol quenches both the fluorescence and phosphorescence of biacetyl.<sup>1,2</sup> The mechanism suggested was one of reversible hydrogen atom transfer.<sup>1</sup> Thus it was felt that this

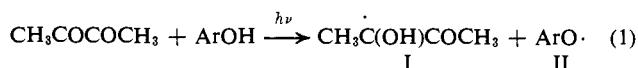
system might provide a convenient photolytic source of phenoxy radicals. Previously a technique for obtaining absolute termination constants by direct photolysis in an electron spin resonance (esr) spectrometer cavity has been reported.<sup>3</sup>

(1) N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **91**, 7113 (1969).

(2) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **12**, 1823 (1958).

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

We observed both the diacetylsemidione (I) and the phenoxy (II) radical according to reaction 1 when a



benzene solution of biacetyl containing a phenol was photolyzed in an esr spectrometer cavity. It was further noted that both radicals were at steady state. This phenomenon was observed for 14 phenols in combination with any of 3  $\alpha$ -diketones in both benzene and chlorobenzene solution. The ratio of semidione to phenoxy radical varies as a function of solvent, phenol, and  $\alpha$ -diketone employed. In this paper we shall show how this ratio of steady state radical concentrations provides a direct measure of the rate constants for phenoxy radical terminations. These values in conjunction with the results of other experimental measurements<sup>4,5</sup> lead to a complete set of absolute rate and equilibrium constants for the chemistry of phenoxy radicals.<sup>6,7</sup>

### Experimental Section

**Materials.** Benzene, isopropyl alcohol, biacetyl, and *p*-cresol were distilled prior to use. Chlorobenzene was purified by column chromatography on alumina. Camphorquinone, benzil, benzoin, dihydrocamphorquinone, and the substituted phenols were recrystallized from hexane prior to use. All compounds had melting points in agreement with those in the literature.

**Steady State Irradiations.** All samples were prepared in 3-mm i.d. Suprasil tubes and were outgassed with argon. Samples were approximately 1 *M* in diketone and 0.1 *M* in phenol. The irradiations were carried out directly in a Varian E-3 esr spectrometer which had been modified as previously described.<sup>3</sup> The cavity also contained a crystal of magnesium oxide which had been doped with manganese. All radical concentrations were measured relative to this external standard. The light source was a 2500-W Hanovia mercury-xenon lamp. A 20-cm Pyrex filter containing an aqueous solution of copper sulfate was used to eliminate all light of wavelength shorter than 330 nm. The sample tube was cooled by a stream of prepurified nitrogen. The temperature in the sample tube was  $30 \pm 1^\circ$ . The tubes were irradiated for no more than 30 min. This time limit was chosen as it corresponds to less than 1% reaction as followed by vapor phase chromatography and/or uv spectroscopy while still allowing ample time for several esr spectra to be obtained.<sup>8</sup> Over this time period, all the lines observed were assignable to either the phenoxy radical or the semidione ( $\text{RCO}\dot{\text{C}}(\text{OH})\text{R}'$ ) radical. In some instances, when the irradiation was continued for periods of greater than 60 min, new lines appeared. It is assumed that these were due to abstraction of hydrogen atoms from the product(s) of the initial phenoxy radical decay, giving rise to new (and different) phenoxy radicals. This phenomenon has been previously observed.<sup>9</sup>

To test the dependence of the radical concentrations on the light intensity, the light beam was focussed onto a series of neutral density filters, previously calibrated, and then allowed to pass into the cavity.

**Measurement of Decay Constants by Rotating Sector.** The measurement of absolute termination constants using a rotating sector in conjunction with an esr spectrometer has been previously described.<sup>3</sup> The only changes made were that a Varian CAT C-1024 was used and that a pinhole device 3 mm in diameter was placed in front of the lamp at a distance of 0.125 in. from the sector

(4) L. R. Mahoney, *Angew. Chem., Int. Ed. Engl.*, **8**, 547 (1969), and references cited therein.

(5) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **92**, 890, 4063 (1970).

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

(7) L. R. Mahoney and S. A. Weiner, *J. Amer. Chem. Soc.*, **94**, 585 (1972).

(8) As noted in reference 1, there is little or no formation of new products in these systems.

(9) W. G. B. Huysmans and W. A. Waters, *J. Chem. Soc. B*, 1047 (1966).

in order to decrease the width of the light beam at the sector. The results are plotted according to eq 2 which is the integrated form

$$(\text{R})_0/(\text{R})_t = 1 + 2k(\text{R})_0 t \quad (2)$$

of the simple second-order decay where  $(\text{R})_0$  is the steady state radical concentration. The values cited in the text are for  $k$ , not for  $2k$ . The values of  $k$  for the standard semidione radicals in benzene and chlorobenzene solutions were obtained by two slightly different methods.

In the simplest method, method A, the value of  $2k(\text{R})_0$  in the aromatic solvents was divided by that in isopropyl alcohol for each radical where  $k$  is known<sup>10</sup> and the relative radical concentrations were obtained by comparison with the external standard.

In the second method, method B, the decay of the camphorsemidione radical in isopropyl alcohol was measured and the known value of  $k$  was used to determine the steady state radical concentration. This value in turn was used to calibrate the external standard in terms of moles per liter of free radical. The calibrated standard was then used to determine the values of  $(\text{R})_0$  which together with the values of  $2k(\text{R})_0$  yield absolute values of  $k$ . The values of  $k$  for the three semidione radicals used as standards and for *p*-benzosemiquinone are given in Table I.

Table I. Termination Constants<sup>a</sup> of Standard Radicals as a Function of Solvent

Radical <sup>b</sup>	Method <sup>c</sup>	Solvent		
		Isopropyl alcohol <sup>d</sup>	Benzene	Chlorobenzene
Camphorquinone	A	0.42	1.8	0.63
	B	0.42 <sup>e</sup>	1.7	0.57
Biacetyl	A	3.9	18	5.5
	B	3.5	26	5.4
Benzil	A	3.3	15	4.6
	B	3.6	18	5.5
<i>p</i> -Benzoquinone	A	0.57	1.9	0.63
	B	0.59	2.0	0.70

<sup>a</sup> The numbers cited are for  $k \times 10^{-8}$  in units of  $M^{-1} \text{sec}^{-1}$  at a temperature of  $30 \pm 1^\circ$ . <sup>b</sup> The radical is formed by addition of a hydrogen atom to the compound at the carbonyl oxygen. <sup>c</sup> The methods are described in the text. <sup>d</sup> The values given for  $k$  in isopropyl alcohol by method A are taken from reference 10 except for *p*-benzosemiquinone which comes from unpublished data of G. S. Hammond and S. A. Weiner. <sup>e</sup> This value is by definition of method B.

### Results and Discussion

#### Dependence of Radical Concentration on Light Intensity and Concentration of Phenol and $\alpha$ -Diketone.

In all cases studied, both radicals, a phenoxy and a semidione, were observed. There were no lines in the esr spectra which were not assignable to one or the other radical. The hyperfine coupling constants for the phenoxy radicals as obtained from these spectra are given in Table II. The constants were identical within experimental error, 0.05 G, in benzene and chlorobenzene solution and are in good agreement with literature values.<sup>9,11,12</sup> In all cases, both radicals were at steady state as determined by the fact that the peak heights and linewidths were constant over several scans. The ratio of phenoxy to semidione radical concentration varied as a function of substituent on the parent phenol and also as a function of which diketone was used. For a given phenol, the ratio of semidione to phenoxy radical was higher when camphorquinone was used than when either biacetyl or benzil was used.

(10) S. A. Weiner, E. J. Hamilton, Jr., and B. M. Monroe, *J. Amer. Chem. Soc.*, **91**, 6350 (1969).

(11) J. Pannell, *Chem. Ind. (London)*, 1797 (1962).

(12) T. J. Stone and W. A. Waters, *Proc. Chem. Soc. London*, 253 (1962); *J. Chem. Soc.*, 213 (1964).

Table II. Hyperfine Coupling Constants of Phenoxy Radicals

X	Position <sup>a</sup>		
	2,6	3,5	4
4,5-Benzo <sup>b</sup>		Not assigned	
3,5-CH <sub>3</sub>	6.24	1.69	10.0
3,5-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	6.98		9.38
4-CH <sub>3</sub> <sup>c</sup>	5.93 (6.0)	1.47 (1.45)	11.86 (11.95)
3,4,5-CH <sub>3</sub>	5.91	1.69	11.79
3-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> <sup>d</sup>	6.95, 7.80 (6.65, 7.5)	1.91 (2.0)	11.33 (10.15)
4- <i>tert</i> -C <sub>4</sub> H <sub>9</sub>	6.25 (6.0)	1.65 (≤ 1.4)	0.42
H <sup>e</sup>	6.60 (6.65)	1.88 (1.8)	10.10 (10.1)
2,6-CH <sub>3</sub>	7.22 (6.5)	1.99 (1.65)	10.13 (9.5)
3,5- <i>tert</i> -C <sub>4</sub> H <sub>9</sub>	6.60		10.00
4-C <sub>6</sub> H <sub>5</sub>		Not assigned	
2,6- <i>tert</i> -Bu <sup>f</sup>		1.95 (2.0)	9.62 (9.65)
4-CH <sub>3</sub> O <sup>g</sup>	5.38 (5.75)	0.57 (0.8)	1.83 (1.7)
4-HO <sup>h</sup>	5.2 (5.13)	0.35 (0.31)	1.8 (1.79)

<sup>a</sup> If there is a substituent at a position for which a number is given, this refers to the hydrogen atoms of the substituent. <sup>b</sup> The radical is 2-naphthoxy. While the spectrum was not analyzed it resembles that for the same radical published in reference 12. <sup>c</sup> Values in parentheses taken from reference 12. <sup>d</sup> Values in parentheses taken from reference 12 for 3-CO<sub>2</sub>H. <sup>e</sup> Values in parentheses taken from reference 11. <sup>f</sup> Values in parentheses taken from reference 9. <sup>g</sup> Values in parentheses taken from T. E. Gough, *Trans. Faraday Soc.*, **62**, 2321 (1966).

The latter two compounds gave very similar ratios. For any given phenol-diketone system, the ratio of semidione to phenoxy radical was 3–6 times higher in benzene than in chlorobenzene solution.

The dependence of this ratio on the concentration of initial reactants was examined only for the system 4-phenylphenol–biacetyl in benzene. The concentration of biacetyl was varied from 0.5 *M* to 2 *M*. In all instances, each individual radical concentration as well as the ratio of semidione to phenoxy radical was constant (Table III). This same system was used to

Table III. Dependence of Steady-State Radical-Concentrations in Benzene Solution at 30° on 4-Phenylphenol and Biacetyl Concentrations

Biacetyl ( <i>M</i> )	4-Phenylphenol ( <i>M</i> )	HK· <sup>a,b</sup>	ArO· <sup>a,c</sup>	HK·/ArO·
1.00	0.040	55	66	0.71
1.00	0.020	58	78	0.74
1.00	0.008	60	78	0.77
1.00	0.004	54	73	0.74
2.00	0.040	57	80	0.71
0.50	0.040	55	73	0.75

<sup>a</sup> The radical concentrations are given in units of the derivative peak height. <sup>b</sup> The radical is biacetylsemidione. <sup>c</sup> The radical is 4-phenylphenoxy.

measure the effect of light intensity. Plots of the logarithm to the base 10 of the concentration of both 4-phenylphenoxy and biacetylsemidione radicals relative to the external standard *vs.* the intensity are shown in Figure 1. The slopes of the plots are approximately 0.5 demonstrating that the radical concentration varies as the square root of the light intensity. Furthermore, while the individual radical concentrations vary with the light intensity, the ratio of biacetylsemidione to 4-phenylphenoxy radical is independent of the intensity. As a check, results for the system camphorquinone–

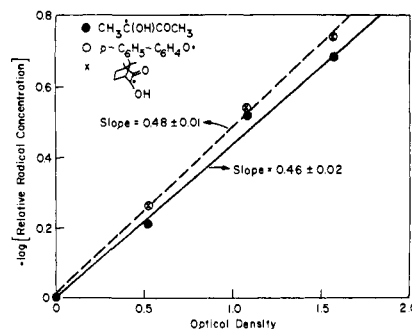
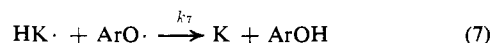
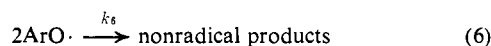
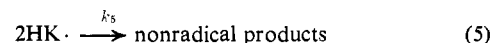
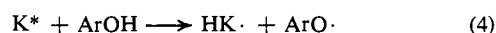


Figure 1. Plots of  $-\log$  of the relative radical concentrations for biacetylsemidione (O), 4-phenylphenoxy (●), and camphorsemidione (X) *vs.* the value of the neutral density filters. The slopes were determined by a least-squares procedure and the error limits represent one standard deviation.

dihydrocamphorquinone in benzene solution also are given in Figure 1. In this system only one radical is produced on irradiation and, as expected, the value of the slope is 0.5.

**A Mechanistic Interpretation of the Results.** The results are explained in terms of reactions 3–7 which



constitute the simplest set of equations consistent with the experimental observations. The symbol  $K^*$  stands for an excited state of the  $\alpha$ -diketone and  $I$  for the rate at which that state(s) is produced. As mentioned earlier,  $I$  is independent of  $\alpha$ -diketone concentration under the experimental conditions. Turro and Engel have shown that both the lowest excited singlet and triplet states of biacetyl abstract the OH hydrogen atom from phenol.<sup>1</sup> This scheme is consistent with the observation that little or no net chemical reaction occurs in these systems<sup>1</sup> provided that termination proceeds predominantly *via* reaction 7.

The kinetic analysis of this reaction scheme is straightforward. Experimentally both radicals are seen to be at steady state and thus we can equate their respective rates of initiation and termination. However, both radicals are formed in the same step and thus their rates of initiation are equal. Accordingly, we may equate their rates of termination. When this is done, the cross termination step drops out. The results are tabulated according to eq 9 (Table IV).

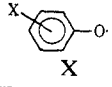
$$2k_5(\text{HK}\cdot)^2 + k_7(\text{ArO}\cdot)(\text{HK}\cdot) = I =$$

$$2k_6(\text{ArO}\cdot)^2 + k_7(\text{ArO}\cdot)(K\cdot) \quad (8)$$

$$k_6 = k_5[(\text{HK}\cdot)/(\text{ArO}\cdot)]^2 \quad (9)$$

In using the relative radical concentrations to determine values of  $k_6$  it is necessary to include the statistical factors which contribute to the intensities of the individual lines. These factors were assigned on the basis of complete analyses of the spectra based on the values of the hyperfine splitting constants. The error

**Table IV.** Termination Constants<sup>a</sup> for Phenoxy Radicals in Benzene and Chlorobenzene Solutions

 X	C <sub>6</sub> H <sub>6</sub>			C <sub>6</sub> H <sub>5</sub> Cl		
	CQ <sup>b</sup>	Bz <sub>2</sub> <sup>c</sup>	Ac <sub>2</sub> <sup>d</sup>	CQ <sup>b</sup>	Bz <sub>2</sub> <sup>c</sup>	Ac <sub>2</sub> <sup>d</sup>
4,5-Benzo <sup>e</sup>			45			5.0
3,5-CH <sub>3</sub>		35	31	2.7		2.4
3,5-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	23	19	18	1.8	1.7	2.1
4-CH <sub>3</sub>			15			0.76
3,4,5-CH <sub>3</sub>						0.71
3-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	10	12	9.2	0.82	1.0	0.80
4- <i>tert</i> -C <sub>4</sub> H <sub>9</sub>	7.7		8.1	0.50		0.44
H			6.3			0.55
2,6-CH <sub>3</sub>			4.5			0.26
3,5- <i>tert</i> -C <sub>4</sub> H <sub>9</sub>	1.0		1.2	0.082		
4-C <sub>6</sub> H <sub>5</sub>			0.34			0.019
2,6- <i>tert</i> -C <sub>4</sub> H <sub>9</sub>		0.28	0.32		0.013	
4-CH <sub>3</sub> O			0.17			0.014

<sup>a</sup> The values cited are for  $k_6 \times 10^{-8}$  in units of  $M^{-1} \text{sec}^{-1}$  rather than  $2k_6$ . The error limits are  $\pm 40\%$ . <sup>b</sup> The standard was camphorsemidione. <sup>c</sup> The standard was benzilsemidione. <sup>d</sup> The standard was biacetylsemidione. <sup>e</sup> The radical is 2-naphthoxyl.

limit of  $k_6$  is  $\pm 40\%$  based on error limits of  $\pm 20\%$  for  $k_5$  and  $\pm 10\%$  for the relative radical concentrations. The values of  $k_6$  obtained are independent of which particular  $\alpha$ -diketone was used. This is especially pleasing as not only is the rate constant for camphorsemidione termination an order of magnitude less than those for benzil- and biacetylsemidione radicals but camphorsemidione terminates by disproportionation whereas the latter two terminate by recombination. The results show that there is a pronounced substituent effect for phenoxy radical termination as well as a surprisingly constant effect of about an order of magnitude on changing the solvent from chlorobenzene to benzene. This solvent effect cannot be explained solely on the basis of diffusion theory as this predicts only a threefold increase on going from chlorobenzene to benzene solution. This increase is observed for the three semidione radicals used as standards as well as for *p*-benzosemiquinone which can be regarded as 4-hydroxyphenoxy radical. An explanation is proposed for the variation of the termination constants of phenoxy radicals as a function of substituent in a companion paper.<sup>7</sup>

**Comparison with Literature Values for Phenoxy Radical Terminations.** Huysmans and Waters conclude that in benzene solution the phenoxy radicals derived from phenol, *p*-cresol, and 2,6-dimethylphenol must be shorter lived than those from 4-methoxyphenol and 2,6-di-*tert*-butylphenol.<sup>9</sup> This conclusion was based on their inability to detect the phenoxy radicals from the former phenols. The data in Table III show that for these phenoxy radicals the termination constants are at least 15-fold higher than for the phenoxy radicals derived from 4-methoxyphenol and 2,6-di-*tert*-butylphenol. The fact that the hyperfine coupling constants for 2,6-alkylphenoxy radicals are

essentially identical indicate that there is no correlation between spin density and the rate of radical termination. This was noted earlier in a study on substituted cumyl radicals.<sup>3</sup>

The rate constant for termination of phenoxy radical in aqueous solution has been measured by flash photolysis.<sup>13,14</sup> Land and Porter<sup>13</sup> report a value of  $k_6 = 5.4 \times 10^8 M^{-1} \text{sec}^{-1}$  while Dobson and Grossweiner<sup>14</sup> report  $k_6 = 6.4 \times 10^9 M^{-1} \text{sec}^{-1}$ . However, the former value is based on the assumption that the extinction coefficient for phenoxy radical is equal to that of the 2,4,6-tri-*tert*-butylphenoxy radical while the latter is based on a measured value of the extinction coefficient. Applying this value to Land and Porter's value of  $k/\epsilon$  and then averaging lead to  $k_6 = (4.8 \pm 2.3) \times 10^9 M^{-1} \text{sec}^{-1}$  for phenoxy radical in aqueous solution. Dobson and Grossweiner also report that  $k_6 = (6.5 \pm 0.3) \times 10^9 M^{-1} \text{sec}^{-1}$  for 4-methylphenoxy radical in aqueous solution.<sup>14</sup> These values correspond to diffusion control in water (calcd  $6.4 \times 10^9 M^{-1} \text{sec}^{-1}$ ).<sup>13</sup> The values in Table IV for the same two radicals in benzene solution are approximately one order of magnitude lower than the calculated diffusion controlled rate constant. An explanation for these discrepancies is proposed in a companion paper.<sup>7</sup>

## Conclusions

In this paper, we have reported a new technique for measuring radical termination rate constants in solution. This technique is relatively simple to use as it only requires measurements of relative radical concentrations. In order for the technique to be applicable, there must be no cross radical reaction other than termination, no reaction of the radicals with either starting materials or products, and the absolute termination constant of one of the radicals must be known. The only apparent limitation on the value of the termination constant to be measured is that it be greater than  $10^5 M^{-1} \text{sec}^{-1}$ .

This method has been applied to a series of phenoxy radicals in benzene and chlorobenzene solutions using three different semidione radicals as standards. The rate constants obtained varied from  $10^6$  to  $10^9 M^{-1} \text{sec}^{-1}$ . These results are utilized in subsequent papers to completely unravel the steps in the inhibition of oxidation by phenols.<sup>6,7</sup> We have attempted to extend our studies to other series of compounds using  $\alpha$ -diketones as hydrogen atom abstracting reagents but have so far met with little success.

**Acknowledgment.** I should like to thank Dr. L. R. Mahoney for suggesting this problem and both he and Dr. K. U. Ingold for many helpful and stimulating conversations. I also thank Dr. B. M. Monroe for a generous gift of dihydrocamphorquinone.

- (13) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2013 (1963).  
 (14) G. Dobson and L. I. Grossweiner, *ibid.*, **61**, 708 (1965).