

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231410021>

# Solvent effects in the reactions of peroxy radicals with organic reductants. Evidence for proton-transfer-mediated electron transfer

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY · NOVEMBER 1989

Impact Factor: 2.78 · DOI: 10.1021/j100359a025

---

CITATIONS

81

---

READS

25

4 AUTHORS, INCLUDING:



Robert Huie

National Institute of Standards and Technology

192 PUBLICATIONS 7,768 CITATIONS

SEE PROFILE



Pichairadhakrishna Maruthamuthu

University of Madras

87 PUBLICATIONS 1,400 CITATIONS

SEE PROFILE

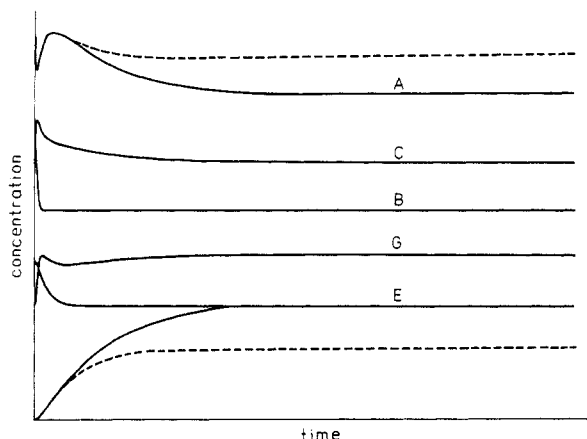
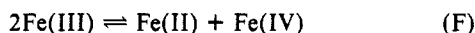


Figure 4. Computed  $c = f(t)$  curves of A-C, G, and E, a qualitative simulation of a nonmonotonous temporal dependence of ferroin (A) as a reactant.<sup>11</sup>

where (E) is the sum of successive steps of anation. The reaction step C or its simpler analogue



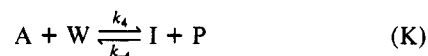
might play a key role in this mechanism. This assumption is supported on one hand by the fact that  $\text{Fe}_2(\text{SO}_4)_3$  in a solution of 0.25 M  $\text{H}_2\text{SO}_4$  in the presence of added phenanthroline leads to the formation of ferroin and on the other hand by the fact that the formation rate of ferroin is inversely proportional to the sulfuric acid concentration (Table I). The reaction step E can be verified by experiments of  $\text{FeSO}_4$  anation by phenanthroline molecules

(Table II). As a parallel step to step D, the oxidation of water molecules by ferroin may proceed as follows:



Oxygen molecules may have the role of a radical scavenger, and still other reaction steps may be taken into account.

We formulated various alternative reaction schemes, based on the proposed mechanism, and were trying to find a solution of their corresponding rate equations. Finally, we selected the following scheme



where A = ferroin, B = Ce(IV), C = ferroin, D = Ce(III), G = Fe(IV), E =  $\text{H}_2\text{O}$  ( $\text{OH}^-$ ), W = water as ligand, I = inactive products of aquation, P = phenanthroline, and F = oxidation products. As we can see in Figure 4, the solution of the corresponding kinetic equations by an analogue computation<sup>11</sup> yields the temporal dependence of the ferroin concentration (of A) that is qualitatively in accordance with our experimental curves (Figures 3 and 4). Any other alternative reaction scheme does not lead to such an accordance. Unfortunately, for the existence of Fe(IV) species as intermediates, we have only such kinetic evidence.

Registry No.  $\text{Ce}^{4+}$ , 16065-90-0; ferroin, 14708-99-7.

## Solvent Effects in the Reactions of Peroxyl Radicals with Organic Reductants. Evidence for Proton-Transfer-Mediated Electron Transfer

P. Neta,<sup>\*1</sup> R. E. Huie,<sup>1</sup> P. Maruthamuthu,<sup>2,3</sup> and S. Steenken<sup>\*2</sup>

Chemical Kinetics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, and Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim, West Germany (Received: February 6, 1989; In Final Form: May 31, 1989)

Absolute rate constants for the reactions of substituted methylperoxyl radicals with ascorbate, urate, trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), and TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) have been determined by pulse radiolysis in different solvents. In water-alcohol or water-dioxane solutions, the rate constants for trihalomethylperoxyl radicals generally increase with increasing water content. The rate constant for reaction of  $\text{CCl}_3\text{O}_2^*$  radicals with trolox was measured in water, MeOH, *i*-PrOH, *t*-BuOH, ethylene glycol, diethyl ether, dioxane, acetone, acetonitrile, formamide, dimethylformamide, pyridine, and  $\text{CCl}_4$ . The rate constants were found to correlate well with a two-parameter equation that includes the dielectric constant of the solvent and the coordinate covalency parameter, a measure of the proton-transfer basicity of the solvent. Kinetic isotope effects in  $\text{H}_2\text{O}/\text{D}_2\text{O}$  of about 2 and activation entropies of about -10 eu for reduction of  $\text{RO}_2^*$  by the organic reductants indicate that electron transfer to the peroxyl radical is concerted with the transfer of proton from the solvent to the incipient hydroperoxide anion.

### Introduction

Rate constants for reactions of peroxyl radicals with organic substrates have been determined for a wide variety of systems.<sup>4</sup> Because of the involvement of the  $\text{CCl}_3\text{O}_2^*$  radical in the toxicity of  $\text{CCl}_4$ ,<sup>5</sup> rate constants have been measured for reaction of

$\text{CCl}_3\text{O}_2^*$  with several molecules of biological importance such as fatty acids, iron porphyrins, and natural antioxidants.<sup>4</sup> Although many of the rate constants refer to the reactions in aqueous solutions, the medium usually contained varying amounts of alcohols to help in the dissolution of  $\text{CCl}_4$  and of the organic substrate. Recently, it has been shown that the rate of oxidation of

(1) National Institute of Standards and Technology.

(2) Max-Planck-Institut für Strahlenchemie.

(3) Visiting scientist from the University of Madras.

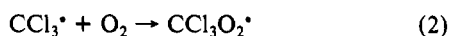
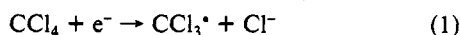
(4) For a compilation see: Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data*, submitted for publication.

(5) Slater, T. F. In: *Biochemical Mechanisms of Liver Injury*; Slater, T. F., Ed.; Academic Press: London, 1978; p 1. Recknagel, R. O.; Glende, E. A., Jr. *CRC Crit. Rev. Toxicol.* 1973, 2, 263. Brault, D. *EHP, Environ. Health Perspect.* 1985, 64, 53.

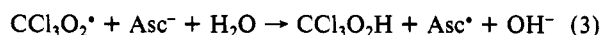
chlorpromazine by several peroxyl radicals is strongly dependent on solvent polarity and that variations in the fraction of alcohol in the aqueous medium can change the rate constant by 1 order of magnitude or more.<sup>6</sup> This finding suggests that in order to assess the biological importance of a peroxyl radical reaction it is necessary to know the composition of the medium in which the reaction takes place and the exact medium effects on such a reaction. To quantitate solvent effects, we studied the reduction of  $\text{CCl}_3\text{O}_2^\bullet$  by the natural antioxidants ascorbate and urate (2,6,8-trihydroxypurine) and by the water soluble analogue of vitamin E, trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), in a variety of solvents. To obtain an impression of the importance of proton-transfer steps in the transition state of the redox reaction between the peroxyl radical and the electron donors, the solvent kinetic isotope effect ( $\text{H}_2\text{O}/\text{D}_2\text{O}$ ) also was studied for several other peroxyl radical reactions.

In addition, we carried out comparative studies with  $\text{CBr}_3\text{O}_2^\bullet$  and  $\text{CF}_3\text{O}_2^\bullet$  in a limited number of solvent mixtures. The latter comparison was undertaken because of the unexpected behavior of the three halogenated methylperoxyl radicals in various oxidation reactions, where the order of reactivities was found<sup>7</sup> to be  $\text{CF}_3\text{O}_2^\bullet > \text{CBr}_3\text{O}_2^\bullet > \text{CCl}_3\text{O}_2^\bullet$ .

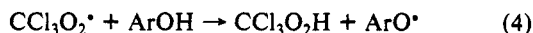
The three halogenated peroxyl radicals studied are prepared by dissociative one-electron reduction of  $\text{CCl}_4$ ,  $\text{CBr}_4$ , or  $\text{CF}_3\text{Br}$  and subsequent rapid reaction with oxygen, as described before,<sup>7-10</sup> e.g.



These peroxyl radicals have been suggested to react with reductants such as ascorbate, urate, phenothiazines, or TMPD by one-electron oxidation.<sup>7-10</sup>



The reaction of phenol derivatives such as  $\alpha$ -tocopherol (vitamin E) in neutral solutions is also likely to take place by electron transfer although in this case hydrogen abstraction is also possible.



However, as shown below, solvent effects on the rates of reaction 3, 4, and analogous ones for other organic reductants support the electron-transfer mechanism.

### Experimental Section<sup>11</sup>

The materials used were of the highest grade commercially available and were used as received. Methanol, 2-propanol, ethylene glycol, diethyl ether, acetone, *N,N*-dimethylformamide (DMF), pyridine,  $\text{CCl}_4$ , and KOH were obtained from Mallinckrodt. Formamide, dimethyl sulfoxide (DMSO),  $\text{CBr}_4$ , 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (trolox), uric acid, and sodium ascorbate were obtained from Aldrich; *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) was from Fluka; 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) was from Boehringer; acetonitrile and dioxane were from Kodak; *tert*-butyl alcohol was from Fisher; and  $\text{CF}_3\text{Br}$  was from Du Pont. Water was purified by a Millipore Super-Q system. Fresh solutions were prepared before each experiment under equilibrium with air, except for the study of  $\text{CF}_3\text{O}_2^\bullet$  radicals where the solutions were purged with a mixture of  $\text{CF}_3\text{Br}$  and  $\text{O}_2$  (4:1). Samples were transferred to the irradiation cell and were irradiated with 50-ns pulses of 2-MeV electrons from a Febetron Model 705<sup>9</sup>

TABLE I: Rate Constants for Reactions of Peroxyl Radicals with Ascorbic Acid and Ascorbate Ions

radical	solvent	pH	v:v	mole fraction of alcohol	$k/\text{M}^{-1} \text{s}^{-1}$
$\text{CCl}_3\text{O}_2^\bullet$	<i>i</i> -PrOH-H <sub>2</sub> O	1	1:8	0.028	$1.4 \times 10^7$
			3:7	0.092	$9.9 \times 10^6$
			1:1	0.19	$3.1 \times 10^5$
		7	2:1 <sup>a</sup>	0.32	$1.8 \times 10^6$
			1:8	0.028	$5.8 \times 10^8$
			1:1	0.19	$1.3 \times 10^8$
$\text{CF}_3\text{O}_2^\bullet$	<i>i</i> -PrOH-H <sub>2</sub> O	7	2:1 <sup>a</sup>	0.32	$1.1 \times 10^8$
		7	1:1	0.19	$1.9 \times 10^8$
$\text{CBr}_3\text{O}_2^\bullet$	<i>i</i> -PrOH-H <sub>2</sub> O	7	1:9	0.05	$6.8 \times 10^8$
		7	1:4	0.06	$5 \times 10^8$
		7	2:3	0.14	$2.1 \times 10^8$
			7:3	0.36	$1.7 \times 10^8$

<sup>a</sup> Solution contained also 10%  $\text{CCl}_4$  in the other cases the amount of  $\text{CCl}_4$  was 1% or less.

TABLE II: Rate Constants for Reactions of Peroxyl Radicals with Urate Ions

radical	solvent <sup>a</sup>	v:v	mole fraction of alcohol	$k/\text{M}^{-1} \text{s}^{-1}$
$\text{CCl}_3\text{O}_2^\bullet$	MeOH-H <sub>2</sub> O	1:9	0.05	$1.4 \times 10^9$
		1:3	0.13	$1.3 \times 10^9$
		1:1	0.31	$1.2 \times 10^9$
		4:1	0.64	$1.2 \times 10^9$
		1:9	0.003	$1.5 \times 10^9$
		7:18	0.084	$7.0 \times 10^8$
$\text{CF}_3\text{O}_2^\bullet$	<i>i</i> -PrOH-H <sub>2</sub> O	1:1	0.19	$1.9 \times 10^8$
		2:1 <sup>b</sup>	0.32	$1.2 \times 10^8$
		1:1	0.31	$1.3 \times 10^9$
		1:9	0.003	$1.0 \times 10^9$
		1:1	0.31	$2.9 \times 10^8$
		7:3	0.36	$1.4 \times 10^8$
$\text{CBr}_3\text{O}_2^\bullet$	<i>i</i> -PrOH-H <sub>2</sub> O	1:1	0.19	$2.5 \times 10^8$
		7:3	0.36	$1.8 \times 10^8$

<sup>a</sup> Solution contained 0.1 M KOH. <sup>b</sup> Solution contained 10%  $\text{CCl}_4$ , in the other cases the amount of  $\text{CCl}_4$  was 1% or less.

or with 400-ns pulses from a 3-MeV van de Graaff accelerator.<sup>12</sup>

The reactions leading to the formation of the peroxyl radicals in the various solvent systems have been discussed before.<sup>7-10</sup> The peroxyl radicals are produced very rapidly, generally within 1  $\mu\text{s}$  after the pulse. The rates of their reaction with ascorbate (pH 7), urate (pH 13), trolox (pH 4 or neutral organic solvent), and TMPD (pH 8) were determined by following the buildup of absorption of the product radicals at 360, 360, 420, and 565 nm, respectively. Each experiment was carried out with at least three different concentrations of the substrate, varying by at least a factor of 4. Second-order rate constants were derived from plots of the first-order rates vs concentration. When the first-order rates are very high, the formation of the peroxyl radical (reaction 2) may limit the rate of the subsequent oxidation (reactions 3 and 4). In such cases, the plot of first-order rate vs concentration tends to curve and to approach a plateau. It is important to ascertain in each case that the second-order rate constant derived from the plot is not affected by the above limitation. The rate constants reported in the tables are generally accurate to  $\pm 15\%$  unless indicated otherwise. Measurement were carried out at room temperature,  $21 \pm 1^\circ\text{C}$ , except for the studies of temperature effects, which were done between 0 and  $40^\circ\text{C}$ .

### Results and Discussion

**Reactivity of Peroxyl Radicals in Aqueous Solvents.** The rate constants determined for oxidation of ascorbate ion are summarized in Table I. They were measured in alcohol-water mixtures since ascorbate is insoluble in anhydrous organic media. Even with these restrictions, it is clear that the rate constant for reaction of ascorbate with  $\text{CCl}_3\text{O}_2^\bullet$  is strongly dependent on the proportion of alcohol in the solvent; the rate constant decreases by a factor

(6) Alfassi, Z. B.; Mosseri, S.; Neta, P. *J. Phys. Chem.* **1987**, *91*, 3383.  
 (7) Huie, R. E.; Brault, D.; Neta, P. *Chem.-Biol. Interact.* **1987**, *62*, 227.  
 (8) Packer, J. E.; Willson, R. L.; Bahnmann, D.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 296; Mönig, J.; Asmus, K.-D.; Schaeffer, M.; Slater, T. F.; Willson, R. L. *Ibid.* **1983**, 1133.  
 (9) Brault, D.; Neta, P. *J. Phys. Chem.* **1984**, *88*, 2857.  
 (10) Neta, P.; Huie, R. E.; Mosseri, S.; Shastri, L. V.; Mittal, J. P.; Maruthamuthu, P.; Steenken, S. *J. Phys. Chem.* **1989**, *93*, 4099.  
 (11) The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology nor does it imply that the equipment or material identified are necessarily the best available for the purpose.  
 (12) Jagannadham, V.; Steenken, S. *J. Am. Chem. Soc.* **1984**, *106*, 6542.

TABLE III: Rate Constants for Reactions of Peroxyl Radicals with Trolox

radical	solvents	v:v	mole fraction of organic	$k^a/M^{-1}s^{-1}$
$CCl_3O_2^*$	MeOH-H <sub>2</sub> O	1:9	0.05	$3.2 \times 10^8$
		1:3	0.13	$4.5 \times 10^8$
		1:1	0.31	$3.6 \times 10^8$
		3:1	0.57	$1.3 \times 10^8$
		1:0	1.00	$3.1 \times 10^7$
	<i>i</i> -PrOH-H <sub>2</sub> O	1:4	0.06	$3.2 \times 10^8$
		1:1	0.19	$1.6 \times 10^8$
		4:1	0.48	$4.8 \times 10^7$
	dioxane-H <sub>2</sub> O	1:0 <sup>b</sup>	1.00	$2.1 \times 10^7$
		1:9	0.023	$6.2 \times 10^8$
$CF_3O_2^*$	MeOH-H <sub>2</sub> O	3:7	0.083	$4.0 \times 10^8$
		1:1	0.175	$2.6 \times 10^8$
		9:1	0.66	$7 \times 10^7$
		1:0 <sup>b</sup>	1.00	$1.5 \times 10^7$
	<i>i</i> -PrOH-H <sub>2</sub> O	1:9	0.05	$5.4 \times 10^8$
		1:3	0.13	$7.0 \times 10^8$
		1:1	0.31	$7.4 \times 10^8$
		3:1	0.57	$4.2 \times 10^8$
		1:0	1.00	$1.5 \times 10^8$
$CBr_3O_2^*$	MeOH-H <sub>2</sub> O	1:9	0.003	$4.7 \times 10^8$
		1:3	0.13	$7.1 \times 10^8$
		1:1	0.31	$4.6 \times 10^8$
		3:1	0.57	$1.4 \times 10^8$
		1:0	1.00	$3.7 \times 10^7$
$NCCH_2O_2^*$	<i>i</i> -PrOH-H <sub>2</sub> O	1:1	0.19	$2.6 \times 10^8$
		CH <sub>3</sub> CN		$\sim 2 \times 10^6$
$CH_3O_2^*$	DMSO-H <sub>2</sub> O	1:9		$< 1 \times 10^5$

<sup>a</sup>Rate constants were measured in the solvent mixtures without addition of acid or base; with predominantly aqueous solutions, the pH was  $\sim 4.1$ . The phenolic OH group of trolox ( $pK = 11.9$ ; ref 14) is thus not ionized. <sup>b</sup>Solution contains also 10% CCl<sub>4</sub>, result reported again in Table IV.

of 5 when the *i*-PrOH content is increased from 12% to 60%. Qualitatively, the same trend holds for  $CF_3O_2^*$  and  $CBr_3O_2^*$ . The reaction of ascorbic acid (which is a much less powerful reductant than ascorbate anion<sup>14</sup>) with  $CCl_3O_2^*$  also exhibits a very pronounced solvent effect. Higher rate constants in more polar media are expected for the oxidation of ascorbate by the peroxyl radicals if the mechanism involves electron transfer.

Uric acid was studied in its dianion form at pH 13 because the reactivity of the monoanion at pH 7 is very low. The results for urate ions in *i*-PrOH-H<sub>2</sub>O solutions (Table II) follow the same general trends as found for ascorbate. In both cases, the order of reactivity in the same solvents is found to be  $CF_3O_2^* > CBr_3O_2^* > CCl_3O_2^*$ . The same order is found also for trolox (see discussion of Table III below). These results support those of the previous study,<sup>7</sup> where the rate constants were determined in somewhat different solvent mixtures. It is still unclear what causes the tribromo radical to react more rapidly than the trichloro.

The rate constants for oxidation of urate by  $CCl_3O_2^*$  radicals in aqueous MeOH solutions were found to be practically unaffected by solvent composition, unlike the case of aqueous *i*-PrOH solutions. This implies that correlation of the rate constant with only the dielectric constant of the solvent mixture, as used in a previous study,<sup>6</sup> is an oversimplification. Therefore, we decided to carry out measurements with additional solvent mixtures. In order to be able to span a wide variety of solvents, we chose the neutral molecule trolox, which is sufficiently soluble in aqueous as well as in organic solvents. Furthermore, this compound is an excellent model of the natural antioxidant tocopherol (vitamin E), and thus, the results are likely to have implications for biological systems. The results obtained for trolox are summarized in Tables III and IV.

The results for  $CCl_3O_2^*$  with trolox in mixtures of water with MeOH, *i*-PrOH, and dioxane are summarized in Table III. Quantitative correlations between  $\log k$  and the dielectric constant  $\epsilon$  of the solvent mixture were attempted, as was done before.<sup>6</sup> The results for *i*-PrOH-H<sub>2</sub>O solutions gave a straight line in agreement with the previous findings.<sup>6</sup> However, in MeOH-H<sub>2</sub>O solutions

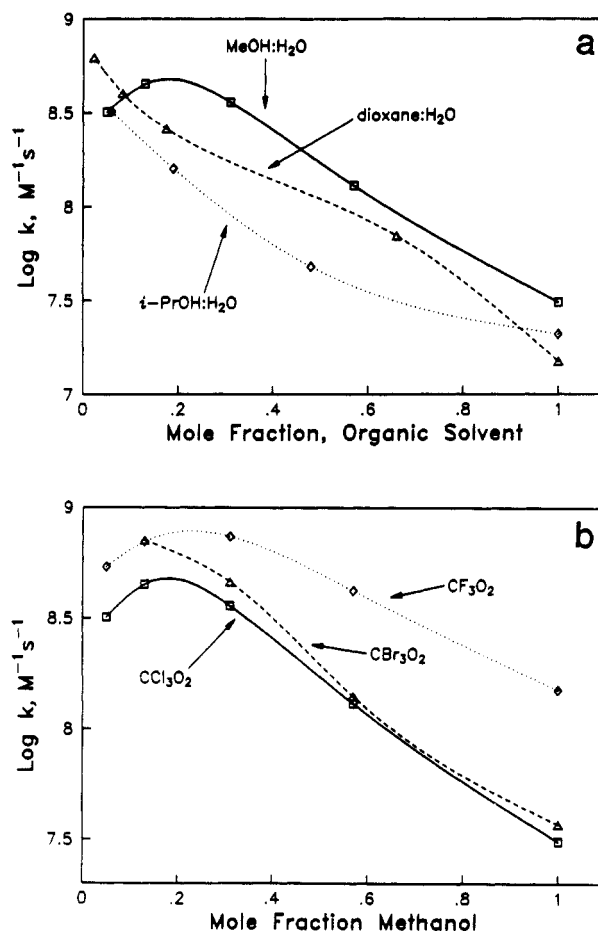


Figure 1. Solvent effects on the rate constants for oxidation of trolox by  $CCl_3O_2^*$  (a) and other trihalomethylperoxyl radicals (b).

there was considerable curvature at high MeOH content and a maximum in the  $k$  value at low MeOH content. The  $\log k$  vs  $\epsilon$  plot for dioxane-H<sub>2</sub>O solutions also showed considerable curvature. Since the dielectric constants of the mixture may not be directly related to the volume ratios of the solvents, it was decided to plot the results in terms of mole fractions.

Figure 1a shows that the rate constant for  $CCl_3O_2^*$  with trolox in aqueous *i*-PrOH or dioxane changes smoothly from  $\sim 6 \times 10^8 M^{-1} s^{-1}$  in nearly pure water to  $\sim 2 \times 10^7 M^{-1} s^{-1}$  in the neat organic solvent. On the other hand, the curve for aqueous MeOH is more complex and shows a clear maximum at 0.16 mole fraction of MeOH. This maximum may be the result of "structure-making" properties of MeOH in water.<sup>13</sup> The reactivity of  $CF_3O_2^*$  with trolox (Figure 1b) in aqueous MeOH exhibits a similar behavior but with a smaller slope and with the maximum shifted to 0.24 mole fraction of MeOH. The reactivity of  $CBr_3O_2^*$  again is intermediate between the reactivities of the other two radicals, but it was not possible to establish a peak in the curve due to the low solubility of  $CBr_4$  in water.

**Reactivity of  $CCl_3O_2^*$  in Nonaqueous Solvents.** It is clear that there is a strong solvent effect in the reaction of  $CCl_3O_2^*$  with trolox, but the underlying cause of this effect is not apparent from the results on the alcohol-water systems. We have probed the effect of solvent on this reaction further by determining its rate constant in 13 different solvents, all of which contain CCl<sub>4</sub> as a radical source. The results of these measurements and the reaction conditions are presented in Table IV. Correlation of the rate constants with the driving force of the reaction in the various solvents based on the Marcus theory cannot be done since the one-electron redox potentials of trolox<sup>14</sup> and of  $CCl_3O_2^*$ <sup>15</sup> are not

(13) See, e.g., Franks, F.; Ives, D. J. G. *Q. Rev., Chem. Soc.* **1966**, *20*, 1. Arnett, E. M. In *Physico-Chemical Processes in Mixed Aqueous Solvents*; Franks, F., Ed.; Elsevier: New York, 1967; p 105. Maham, Y.; Freeman, G. R. *Can. J. Chem.* **1988**, *66*, 1706.

known in the various solvents, and thus, the driving force of the reaction is not known.<sup>16</sup> We would expect the rate constant for the reaction to increase with increasing solvent polarity and hydrogen-bonding capacity since the electron-transfer reaction between trolox and  $\text{CCl}_3\text{O}_2^\bullet$  should involve a polar transition state. Therefore, we have attempted to correlate our experimentally determined rate constants with a number of parameters that may represent these solvent properties.

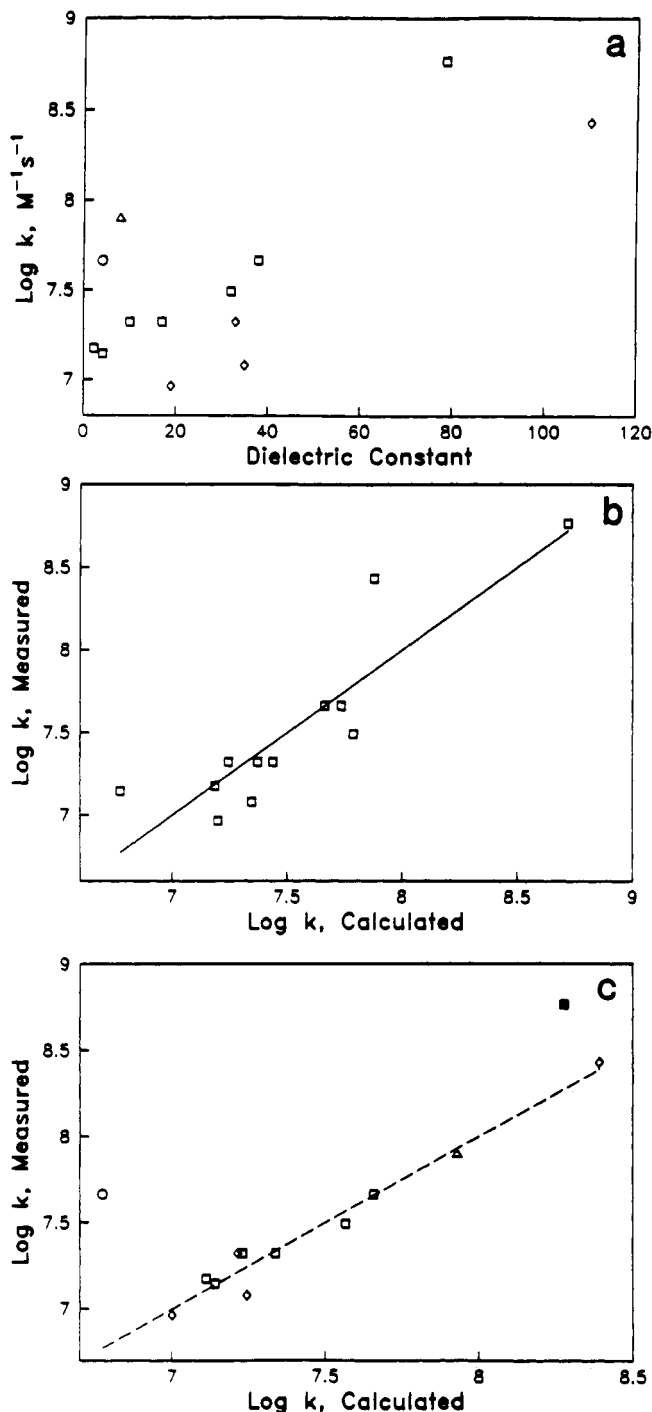
The most obvious solvent property is the dielectric constant, also included in Table IV. Indeed, correlation of  $\log k$  with the solvent dielectric constant does show the proper qualitative trend, with water and formamide promoting a higher rate constant and the other solvents of lower dielectric constant giving lower rates (Figure 2a), but the fit is very unsatisfactory. Therefore, we have attempted to correlate  $\log k$  with other solvent parameters. Of these, only the acceptor number,  $\text{AN}$ ,<sup>17</sup> and the solvent polarity parameter,  $E_T$ ,<sup>18</sup> show a somewhat better correlation than the dielectric constant. Even a five-parameter correlation<sup>19</sup> (Figure 2b) did not yield a satisfactory fit. Inclusion of the solvent viscosity did not improve the fit. Since the dielectric constant showed some correlation with  $\log k$ , as did those parameters that relate to the polarity or the proton-donating ability of the solvent, we attempted to fit the data to each of these parameters paired with the dielectric constant. This procedure produced much better fits than obtained above ( $R^2 \approx 0.8$ ). The best fit ( $R^2 = 0.95$ ) was obtained by pairing the dielectric constant with  $\xi$ , the coordinate covalency parameter, and excluding  $\text{CCl}_4$  for which there is no value for  $\xi$ . For the solvents we initially used, this parameter only takes the values 0.0 and 0.2. We therefore determined the rate constant for the reaction of  $\text{CCl}_3\text{O}_2^\bullet$  with trolox in pyridine, for which  $\xi = 0.6$  and for which the dielectric constant otherwise suggests a low rate constant. The measured rate constant was found to be in very good agreement with the predicted value (Figure 2c).

Finally, one outlier from this correlation became apparent: the datum for water ( $\text{CCl}_4$ , which is a much worse outlier, having been eliminated previously). Unlike the other solvents, water can provide a proton easily to the transition state. As discussed below, this may have an additional enhancing effect on the reaction. With water removed, the fit was improved ( $R^2 = 0.97$ ), resulting in the equation

$$\log k = 6.711 \pm 0.088 + (0.0152 \pm 0.0010)\epsilon + (1.83 \pm 0.18)\xi \quad (5)$$

The experimental data are plotted against this equation in Figure 2c.

Unlike most of the other empirical parameters we have considered, the values for  $\xi$  were not derived from properties of the compounds as solvents but as solutes interacting with other solutes. For example, the free energies of proton transfer from aqueous  $\text{NH}_4^+$  to various bases were correlated with  $\beta$  and  $\xi$ . It was concluded from these studies that  $\xi$  refers to proton-transfer basicities, whereas  $\beta$  refers to hydrogen-bonding basicities. Therefore, the importance of  $\xi$  suggests the involvement of proton transfer to the solvent in the course of the reaction. The mechanism by which the solvent may enhance the rate of reaction through accepting a proton is by removing the proton from neutral trolox,  $\text{ArOH}$ , to form the more reactive anion,  $\text{ArO}^-$ , in the transition state. Such an effect of solvent basicity may be also expressed by a more accurate parameter than  $\xi$ , i.e., the actual  $\text{p}K_b$  of the solvent.<sup>20</sup> Such values, however, are not known for



**Figure 2.** Correlation of the rate constant for oxidation of trolox by  $\text{CCl}_3\text{O}_2^\bullet$  with various solvent parameters. (a) Dielectric constant:  $\diamond$ , for solvents with a  $\xi$  value of 0.0;  $\square$ , for solvents with a  $\xi$  value of 0.2;  $\triangle$ , for  $\text{CCl}_4$ ; and  $\Delta$ , for pyridine. (b) Five parameter correlation according to the following equation:  $\log k = \log k_0 + s\pi^* + a\alpha + b\beta + e\xi + d\delta$ , where  $\pi^*$  represents the solvent polarity,  $\alpha$  represents the solvent hydrogen-bond-donor acidity,  $\beta$  represents the hydrogen-bond-acceptor basicity,  $\xi$  is a coordinate covalency parameter, and  $\delta$  is a polarizability correction term, which is zero for all solvents except  $\text{CCl}_4$ , for which the value is 0.5. The values of these parameters are given in Table IV.  $\log k$  predicted by the above equation is plotted against the experimental  $\log k$ . (c) Correlation with dielectric constant and  $\xi$ :  $\diamond$ , for solvents with a  $\xi$  value of 0.0;  $\square$ , for solvents with a  $\xi$  value of 0.2;  $\Delta$ , for pyridine with a  $\xi$  value of 0.6;  $\blacksquare$ , for water;  $\circ$ , for  $\text{CCl}_4$  for which the value of  $\xi$  is unknown.

all the solvents studied, and even those that are known have been determined often on the basis of correlations not too different from those discussed above. As a result, our attempts to correlate  $\log k$  with  $\epsilon$  and  $\text{p}K_b$  were less comprehensive and not more accurate than the above correlation with  $\epsilon$  and  $\xi$ .

(14) Steenken, S.; Neta, P. *J. Phys. Chem.* **1982**, *86*, 3661.

(15) Huie, R. E.; Neta, P. *Int. J. Chem. Kinet.* **1986**, *18*, 1185.

(16) However, the one-electron oxidation potential for trolox in water has been determined to be 0.48 V vs NHE at pH 7,<sup>14</sup> and the value for  $\text{CCl}_3\text{O}_2^\bullet$  has been estimated from kinetics to be  $>1$  V.<sup>15</sup> The driving force in  $\text{H}_2\text{O}$  at pH 7 is therefore  $>0.5$  V = 12 kcal mol<sup>-1</sup>.

(17) Gutmann, V. *Electrochim. Acta.* **1976**, *21*, 661.

(18) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Justus Liebig's Ann. Chem.* **1963**, *661*, 1.

(19) Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.



(20) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965.

TABLE IV: Solvent Effects on Rate Constants of Reaction of  $\text{CCl}_3\text{O}_2^*$  with Trolox

solvent <sup>a</sup>	$k/\text{M}^{-1} \text{s}^{-1}$	$\log k$	$\epsilon^b$	$\pi^*$	$\alpha$	$\beta$	$\xi$
$\text{H}_2\text{O}$ ( $\text{CCl}_4$ satd)	$5.8 \times 10^8$	8.76	78.5	1.09	1.17	0.18	0.2
$\text{HCONH}_2\text{-CCl}_4$ (99:1)	$2.7 \times 10^8$	8.43	110	0.97	0.71	0.55	0.0
pyridine- $\text{CCl}_4$ (9:1)	$8.0 \times 10^7$	7.90	11.3	0.87	0.0	0.64	0.6
$(\text{CH}_3\text{OH})_2\text{-CCl}_4$ (30:1)	$4.6 \times 10^7$	7.66	37.5	0.92	0.9	0.52	0.2
$\text{CCl}_4\text{-acetone}^c$ (20:1)	$4.6 \times 10^7$	7.66	3.0	0.28	0.0	0.0	
$\text{MeOH-CCl}_4$ (99:1)	$3.1 \times 10^7$	7.49	32.3	0.6	0.93	0.62	0.2
<i>i</i> -PrOH- $\text{CCl}_4$ (9:1)	$2.1 \times 10^7$	7.32	16.7	0.48	0.76	0.95	0.2
<i>t</i> -BuOH- $\text{CCl}_4$ (9:1)	$2.1 \times 10^7$	7.32	10.0	0.41	0.68	1.01	0.2
DMF- $\text{CCl}_4$ (9:1)	$2.1 \times 10^7$	7.32	33.3	0.88	0.0	0.69	0.0
dioxane- $\text{CCl}_4$ (9:1)	$1.5 \times 10^7$	7.18	2.2	0.55	0.0	0.37	0.2
ether- $\text{CCl}_4$ (9:1)	$1.4 \times 10^7$	7.15	4.1	0.27	0.0	0.47	0.2
$\text{CH}_3\text{CN-CCl}_4$ (9:1)	$1.2 \times 10^7$	7.08	34.4	0.75	0.19	0.31	0.0
acetone- $\text{CCl}_4$ (9:1)	$9.2 \times 10^6$	6.96	18.9	0.71	0.08	0.48	0.0

<sup>a</sup> The ratio between solvents is given in v/v. All solutions were air equilibrated. In the absence of  $\text{O}_2$  or  $\text{CCl}_4$ , the oxidation of trolox was much slower or unobservable. <sup>b</sup> Dielectric constant for the solvent mixture calculated by weighted combination of the values for the two solvents as was done in ref 6 (based on: Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van-Nostrand-Reinhold: Princeton, NJ, 1970). <sup>c</sup> Acetone was added to  $\text{CCl}_4$  to help solubilize the trolox.

TABLE V: Rate Constants and Activation Parameters for Reduction of  $\text{RO}_2^*$  in  $\text{H}_2\text{O}$  and Solvent Kinetic Isotope Effect in  $\text{H}_2\text{O}/\text{D}_2\text{O}$ 

reaction	$k(\text{H}_2\text{O})$ (20 °C)/ $\text{M}^{-1} \text{s}^{-1}$	$k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$	$E_a^a/\text{kcal/mol}$	$\Delta S^{*b}/\text{cal}/(\text{mol K})$	$\log A$
$\text{CH}_3\text{O}_2^* + \text{TMPD}^c$	$4.3 \times 10^7$	2.6	6.5	-5	12.1
 + $\text{TMPD}^d$	$1.6 \times 10^8$	1.7	4.1	-9	11.3
 + $\text{ABTS}^e$	$5.0 \times 10^6$	1.8	3.4	-18	9.2
$\text{C}_6\text{H}_5\text{O}_2^* + \text{ABTS}$	$3.8 \times 10^9$				
$\text{CCl}_3\text{O}_2^* + \text{promethazine}^{f,g}$	$1.4 \times 10^8$	1.8			
$\text{CCl}_3\text{O}_2^* + \text{phenolate}^{g,h}$	$9.6 \times 10^6$				
$\text{CCl}_3\text{O}_2^* + p\text{-methylphenolate}^{g,h}$	$2.2 \times 10^8$	2.0			
$\text{CCl}_3\text{O}_2^* + p\text{-methoxyphenolate}^{g,h}$	$8.2 \times 10^8$				
$\text{CCl}_3\text{O}_2^* + p\text{-methoxyphenol}^i$	$3.4 \times 10^6$				
$\text{CCl}_3\text{O}_2^* + \text{trolox}^j$	$1.6 \times 10^8$				

<sup>a</sup> The error limits are  $\pm 1$  kcal/mol. <sup>b</sup> Error limits  $\pm 2$  cal/(mol K). <sup>c</sup> Measured at pH 8;  $[\text{DMSO}] = 1 \text{ M}$ ;  $[\text{TMPD}] = 0.4\text{--}1.0 \text{ mM}$ . <sup>d</sup> [Dioxane] =  $0.1 \text{ M}$ ;  $[\text{TMPD}] = 0.1\text{--}0.4 \text{ mM}$ . <sup>e</sup> pH 7. <sup>f</sup> pH 4. <sup>g</sup> Solution contained 5% acetone and 5% 2-propanol and is saturated with  $\text{CCl}_4$ . <sup>h</sup> pH 11–12. <sup>i</sup> From ref 15, in *i*-PrOH- $\text{H}_2\text{O}$ , 2:3. <sup>j</sup> From Table III, in *i*-PrOH- $\text{H}_2\text{O}$ , 1:1.

In conclusion, the rate constant for reaction of  $\text{CCl}_3\text{O}_2^*$  with trolox and with other reductants of the  $\text{ArOH}$  type is increased upon an increase in solvent polarity and solvent basicity. Furthermore, since the product  $\text{CCl}_3\text{O}_2^-$  is basic and tends to protonate to give the hydroperoxide, the reaction is also accelerated by hydrogen bond donation from the solvent, an effect that is particularly important in water. A possibility that cannot be excluded a priori is a change of mechanism from electron transfer to hydrogen transfer in going from polar to nonpolar solvents. An H atom transfer is difficult to distinguish from a proton-transfer-assisted electron transfer. It is not likely, however, that H atom transfer would be very sensitive to solvent polarity and is, therefore, considered to be unimportant in the systems described.

**Kinetic Isotope Effects in  $\text{H}_2\text{O}/\text{D}_2\text{O}$ .** To further characterize the redox mechanism leading to the reduction of the peroxy radical and the oxidation of the reductant, experiments were performed in  $\text{D}_2\text{O}$  in addition to those in  $\text{H}_2\text{O}$ , using essentially no cosolvents other than those necessary to improve the solubility of  $\text{CCl}_4$  (see Table V). Reductants were used that do not contain transferable hydrogen atoms, so the mechanism necessarily consists of electron transfer. The strong reductant TMPD ( $E_7(\text{TMPD}^{*+}/\text{TMPD}) = 0.26 \text{ V}$  vs  $\text{NHE}^{14}$ ) was used as the electron-donor vis-à-vis  $\text{CH}_3\text{O}_2^*$  (produced<sup>10</sup> by OH reaction with DMSO in the presence of  $\text{O}_2$ ). The rate constant for reaction in  $\text{D}_2\text{O}$  was found to be smaller than that in  $\text{H}_2\text{O}$  by the factor 2.6. From the temperature dependence (0–40 °C; correlation coefficient,  $>0.99$ ) of the rate constant  $k(\text{CH}_3\text{O}_2^* + \text{TMPD})$  in  $\text{H}_2\text{O}$ , the activation parameters for the electron transfer were found to be  $E_a = 6.5 \text{ kcal mol}^{-1}$  and  $\Delta S^* = -5 \text{ cal mol}^{-1} \text{ K}^{-1}$ . The kinetic isotope effect in the reaction with TMPD of the more electron-deficient peroxy radical derived from dioxane,  $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CHO}_2^*$ , was found to be similar to that for

$\text{CH}_3\text{O}_2^*$ ,  $k(\text{H}_2\text{O})/k(\text{D}_2\text{O}) = 1.7$  ( $k(\text{H}_2\text{O})$  at 20 °C =  $1.6 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ ). The same value ( $k(\text{H}_2\text{O})/k(\text{D}_2\text{O}) = 1.8$ ) was measured for the reaction of the dioxanylperoxy radical with ABTS, a less powerful reductant than TMPD, as reflected by the considerably smaller rate constant for oxidation of ABTS by the peroxy radical ( $k = 5 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ ; see Table V). It is interesting to compare this rate constant with that for reaction of the phenoxyl radical,  $\text{PhO}^*$ , with ABTS,  $k = 3.8 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ . This high value indicates that  $\text{PhO}^*$  is a much stronger oxidant than is  $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CHO}_2^*$ .

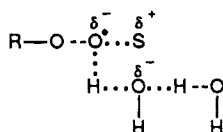
The radical  $\text{CCl}_3\text{O}_2^*$  was reacted with promethazine (observing the production of its radical cation at 510 nm) and with phenolate and *p*-methyl- and *p*-methoxyphenolate ions at pH 11–12 (monitoring the formation of the corresponding phenoxyl radicals at 390–430 nm). In the case of promethazine and *p*-methylphenolate,  $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$  is again 1.8–2.0, evidence that the mechanism is similar to that with the reductants ABTS and TMPD. For reaction with the phenolates, a Hammett plot can be constructed. With the  $\sigma_p$  values for H,  $\text{CH}_3$ , and  $\text{OCH}_3$ , a  $\rho$  of  $-7.2$  is obtained ( $r = 0.997$ ). This value, which reflects the enormous acceleration of the electron donation from the phenolate to the peroxy radical by electron-releasing para substituents on the phenyl ring, may be compared with  $\rho = -7.9$ , found<sup>21</sup> for reaction of  $\text{CH}_2\text{CHO}^*$  with phenolates. The similar values indicate that the oxidizing powers of  $\text{CCl}_3\text{O}_2^*$  and  $\text{CH}_2\text{CHO}^*$  are of similar magnitude. This is also reflected in the absolute rate constants, e.g., the oxidation of phenolate, for which  $k(\text{CCl}_3\text{O}_2^*) = 9.6 \times 10^6$  (Table V) and  $k(\text{CH}_2\text{CHO}^*) = 4.3 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ ,<sup>21</sup> or the oxidation of TMPD, for which  $k(\text{CCl}_3\text{O}_2^*) = 1.7 \times 10^9$  and

$$k(\text{CH}_2\text{CHO}^*) = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1,10,21}$$

The previous finding<sup>10</sup> that the effect of substituents on the peroxy radical is described by *positive*  $\rho^*$  values shows that the rates of electron transfer are also determined by the electron deficiency of the electron acceptor, the peroxy radical.

The last two entries in Table V show that the rate constant for oxidation of trolox by  $\text{CCl}_3\text{O}_2^*$  is nearly 2 orders of magnitude greater than that for *p*-methoxyphenol. This difference reflects the difference in the redox potentials ( $E(\text{ArO}^*/\text{ArOH})$ ) between trolox ( $E_7 = 0.48 \text{ V}$ ) and *p*-methoxyphenol ( $E_7 = 0.73 \text{ V}$  vs NHE).<sup>22</sup> The excellent electron-donating abilities of vitamin E are due to the favorable stereo-electronic properties of the molecule.<sup>23</sup>

As seen in Table V, the solvent kinetic isotope effect for reduction of the peroxy radicals is about 2, independent of the nature of the electron donor. Since, with the reductants studied, H atom transfer is not possible, the kinetic isotope effect indicates that protons from the solvent are involved in the electron-transfer step. A way that this can happen is by protonation, via hydrogen bonding, of the incipient hydroperoxide anion formed by transfer of the electron from the substrate (S) to the peroxy radical. In other words, in the transition state, electron transfer and proton transfer from the solvent may be concerted, as shown below:



A requirement of this type of mechanism is that the activation

(22) Jovanovic, S. V.; Steenken, S.; Simic, M. G. *J. Phys. Chem.*, in press.

(23) Burton, G. W.; Doba, T.; Gabe, E. J.; Hughes, L.; Lee, F. L.; Prasad, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 7053.

entropy should be negative, since proton transfer from the solvent involves a pronounced reorganization of the solvent shell. Essentially, a water molecule is a third reaction partner and the negative charge resulting from reduction of  $\text{RO}_2^*$  ends up as an  $\text{OH}^-$  ion, which is strongly solvated. Immobilization of water molecules in the transition state of the electron-transfer reaction should be reflected by negative activation entropies, and as seen by the data in Table V, this is in fact the case.

## Conclusion

Substituted methylperoxy radicals have been reduced by various organic reductants, and the rates of these reactions have been determined as a function of solvent and temperature. On the basis of the solvent effects, including solvent kinetic isotope effects, and the activation parameters, it is concluded that the electron transfer from the donor to the peroxy radical is concerted with protonation of the incipient hydroperoxide anion. This explains the very pronounced dependence of the electron-transfer rates on solvent polarity and proton-donor capacity. A consequence of this is that under conditions of low polarity or poor proton donicity (as in e.g., membranes) reaction by electron transfer is likely to be considerably slowed down, giving H atom transfer a chance to dominate.

The observation that the rate constant for the oxidation of trolox is increased with increasing proton-transfer basicity of the solvent suggests a similar involvement of nonaqueous solvents in the transition state. Here, the solvent serves to mediate the transfer of the proton from the OH group of trolox and similar compounds to the peroxy radical. As observed in these studies, water is more efficient than predicted by its proton-acceptor basicity due to its capacity to act as a proton donor.

**Acknowledgment.** This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

## Collision-Induced Electronic Quenching of $\text{BH}(\text{A}^1\Pi)$

C. H. Douglass<sup>†</sup> and Jane K. Rice\*

Chemistry Division/Code 6111, Naval Research Laboratory, Washington, DC 20375-5000

(Received: March 28, 1989; In Final Form: May 31, 1989)

Electronic quenching cross sections of  $\text{BH}(\text{A}^1\Pi)$  in  $v' = 0$  were measured by examining fluorescence decay times in the presence of 16 collision partners at 298 K. The partners exhibit wide variations in mass, electric dipole moment, and higher order moments. Except for the extremely low cross sections measured for He and  $\text{SF}_6$ , values range from 5 to  $150 \text{ \AA}^2$ . Of the 14 remaining partners, 11 are represented moderately well by a multipole attractive force model, OCS and  $\text{CH}_2\text{F}_2$  fall well below the calculated cross section, and  $\text{CHFCl}_2$  has an experimental cross section larger than predicted by this model. A temperature comparison is made for the quenching of  $\text{BH}(\text{A}^1\Pi)$  by  $\text{CO}_2$  at 298 and 473 K. The measured rate constant at 473 K exhibits a 10% decrease compared to the 298 K value with an uncertainty of  $\sim 11\%$ .

## Introduction

Electronic quenching by collision is defined as the deactivation of an electronically excited molecule,  $\text{A}^*$ , following a collision with a second molecule, M, which remains chemically unchanged following the collision. This deactivation is the result of the disposal of electronic energy into other forms of energy such as vibrational, rotational, and translational energy. The kinetics of this process are characterized by the bimolecular rate constant  $k_{\text{Q,M}}$ , or the cross section  $\sigma_{\text{Q,M}}$ . The mechanism for this energy transfer is thought by some to involve the formation of a collision complex through attractive electrostatic forces between the molecule,  $\text{A}^*$ , and the collision partner, M.<sup>1,2</sup> Several diatomic

molecules have been studied extensively to characterize the factors important to the quenching process. Most important are the physical properties of the quencher, i.e., its electrostatic moments, geometry, and mass. These all affect the dynamics of the collision and the likelihood of formation of the collision complex. Other factors which affect the quenching cross section are the rotational excitation of the  $\text{A}^*$  molecule and the temperature of the gases (i.e., their relative velocity).

Many of the observations of quenching behavior when rates are greater than gas kinetic values have been explained by the

(1) Selzle, H. L.; Lin, S. H.; Schlag, E. W. *Chem. Phys. Lett.* **1979**, *62*, 230.

(2) Holtermann, D. L.; Lee, E. K. C.; Nanes, R. J. *Chem. Phys.* **1982**, *77*, 5327.

<sup>†</sup> Applied Research Corp., 8201 Corporate Dr., Landover, MD 20785.