Temperature dependence of the rate constants for oxidation of organic compounds by peroxyl radicals in aqueous alcohol solutions

4 AUTHORS, INCLUDING:

Robert Huie
National Institute of Standards and Technology

192 PUBLICATIONS **7,950** CITATIONS

and 882 nm is observed. On the basis of similarity to the C_{70} phosphorescence spectrum, this new band is tentatively assigned to the triplet, distorted by the charge-transfer interaction. The energy of the triplet, ~35 kcal/mol, is consistent with the previously obtained values based on the energy-transfer method.[11] The singlet–triplet splitting is estimated to be 5.5 ± 1 kcal/mol. Due to the very low intensity of the C_{60} triplet exciplex luminescence, a good excitation spectrum has not been obtained.

In summary, well-resolved fluorescence spectra of C_{60} and C_{70} and the phosphorescence spectrum of C_{70} have been obtained, and singlet–triplet splittings have been determined. The fluorescence quantum yield depends on the excitation wavelength, which indicates the existence of upper excited-state photoprocesses. In *N,N*-diethylaniline, charge-transfer complexes with fullerenes are formed. In the excited state, luminescences from both the singlet and triplet exciplex of C_{70} are observed. The existence of charge-transfer complexes of fullerenes and their enhanced absorption in the visible and IR region suggest potential utilities as photosensitizers and photoinitiators.

Note Added in Proof. The photophysical properties of C_{70} have been studied recently by Arbogast et al.[19] Some of the results

reported here, such as the fluorescence spectrum and triplet energy, are reproduced in that study. The paper also show that both C_{60} and C_{70} are reasonably stable with respect to light irradiation, in contrast to the results of ref 14. In another study by Sension et al.[20] on the charge-transfer complex of $C_{60}/N,N$-dimethylaniline (DMA), the formation time of the C_{60}^-DMA$^+$ ion pair was determined to be 1–2 ps and the charge recombination time occurs on a time scale in the range 20–55 ps.

(19) Arbogast, J. W.; Foote, C. S. Unpublished results (private communication).
(20) Sension, R. J.; Szarka, A. Z.; Smith, G. R.; Hochstrasser, R. M. Unpublished results (private communication).

Temperature Dependence of the Rate Constants for Oxidation of Organic Compounds by Peroxyl Radicals in Aqueous Alcohol Solutions

Z. B. Alfassi,[1] R. E. Huie,* M. Kumar,[2] and P. Neta*

Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899 (Received: August 14, 1991; In Final Form: September 27, 1991)

Rate constants for reactions of chlorinated methylperoxyl radicals with chlorpromazine (2-chloro-10-[3-(dimethylamino)-propyl]phenothiazine), trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), and ascorbate in aqueous alcohol solutions have been measured by pulse radiolysis as a function of temperature, generally between 5 and 75 °C. The rate constants varied between 10^6 and 10^9 M^{-1} s^{-1}, the calculated Arrhenius activation energies ranged from 1 to 30 kJ mol^{-1}, and the preexponential factors also varied considerably, with log A ranging from 7 to 14. In general, room temperature rate constants increase with an increase in the number of chlorine atoms on the radical (increasing its electron affinity and thus the driving force for the reaction) and with an increase in the solvent polarity. The Arrhenius preexponential factor and the activation energy both increased as the proportion of water in the solvent mixture increased; i.e., the increase in rate constant with solvent polarity is a result of two compensating effects. Electron transfer from the organic reductants to the chlorinated methylperoxyl radicals is suggested to take place via an inner-sphere mechanism involving a transient adduct of the peroxyl radical to the reductant.

Introduction

Absolute rate constants have been measured for a large number of reactions of peroxyl radicals in aqueous and organic solvents,[3] with most of the measurements carried out only at room temperature and only in one solvent. Measurements at varying temperatures were limited mostly to the reactions of *tert*-alkylperoxyl radicals in organic solvents.[4] These reactions are relatively slow, with very low A factors and low to moderate activation

energies. For example, the reactions of *tert*-butylperoxyl radicals with phenols and anilines take place with rate constants generally much less than 10^4 M^{-1} s^{-1} at room temperature with log A = 3–7 and E_a between 1 and 20 kJ mol^{-1}. The reaction of methylperoxyl radical with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) in water is much faster ($k = 4.3 \times 10^7$ M^{-1} s^{-1} at room temperature) and has a much higher preexponential factor (log A = 12.1).[5] The effect of this higher preexponential factor is partly offset by a higher activation energy (27 kJ mol^{-1}). The mechanisms of the two types of reactions have been suggested to be different; whereas *tert*-butylperoxyl was suggested to react with phenols and anilines in organic solvents via hydrogen abstraction

$$\text{ROO}^\bullet + \text{ArOH} \rightarrow \text{ROOH} + \text{ArO}^\bullet \qquad (1)$$

the reaction of methylperoxyl with TMPD in water was suggested to involve electron transfer.

$$\text{ROO}^\bullet + \text{TMPD} \rightarrow \text{ROO}^- + \text{TMPD}^{\bullet+} \qquad (2)$$

It appears, however, from solvent and temperature effects, that both reactions take place via an intermediate complex of the

(1) Visiting Professor from Ben-Gurion University of the Negev, Beer Sheva, Israel.
(2) Visiting scientist from Bhabha Atomic Research Centre, Bombay, India.
(3) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1990**, *19*, 413.
(4) (a) Howard, J. A.; Furimsky, E. *J. Organomet. Chem.* **1972**, *46*, C45. (b) Furimsky, E.; Howard, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 369. (c) Howard, J. A.; Furimsky, E. *Can. J. Chem.* **1973**, *51*, 3738. (d) Howard, J. A.; Ohkatsu, Y.; Chenier, J. H. B.; Ingold, K. U. *Can. J. Chem.* **1973**, *51*, 1543. (e) Chenier, J. H. B.; Furimsky, E.; Howard, J. A. *Can. J. Chem.* **1974**, *52*, 3682. (f) Chenier, J. H. B.; Howard, J. A. *Can. J. Chem.* **1975**, *53*, 623. (g) Howard, J. A.; Tong, S. B. *Can. J. Chem.* **1980**, *58*, 1962. (h) Howard, J. A.; Tait, J. C.; Yamada, T.; Chenier, J. H. B. *Can. J. Chem.* **1981**, *59*, 2184. (i) Tavadyan, L. A.; Mardoyan, V. A.; Nalbandyan, A. B. *Dokl. Akad. Nauk SSSR* **1981**, *259*, 1143 (translated *Dokl. Phys. Chem.* **1981**, *259*, 737). (j) Bennett, J. E.; Brunton, G.; Forrester, A. R.; Fullerton, J. D. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1477.

(5) Neta, P.; Huie, R. E.; Maruthamuthu, P.; Steenken, S. *J. Phys. Chem.* **1989**, *93*, 7654.

TABLE I: Rate Constants for Reaction of Peroxyl Radicals at Different Temperatures

radical	reactant[a]	solvents[b]	ratios	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹	T, °C	k, M⁻¹ s⁻¹
$CCl_3OO^\bullet$	CPZ	$H_2O/2\text{-PrOH}/CCl_4$	95/5/0.05	4	5.6×10^8	24	1.1×10^9	55	3.2×10^9		
$CCl_3OO^\bullet$		$H_2O/2\text{-PrOH}/CCl_4$	90/10/0.06	2	5.2×10^8	18	9.9×10^8	40	2.3×10^9	67	4.0×10^9
						19	1.1×10^9	63	3.4×10^9	82	3.4×10^9
$CCl_3OO^\bullet$		$H_2O/2\text{-PrOH}/CCl_4$	80/20/0.1	4	5.6×10^8	24	1.1×10^9	55	3.2×10^9		
$CCl_3OO^\bullet$		$H_2O/2\text{-PrOH}/CCl_4$	69/29/2	5	5.1×10^8	24	6.6×10^8	35	1.3×10^9	54	1.9×10^9
								44	1.5×10^9	64	1.3×10^9
$CCl_3OO^\bullet$		$H_2O/2\text{-PrOH}/CCl_4$	49/49/2	9	2.2×10^8	17	2.7×10^8	32	3.7×10^8	50	3.8×10^8
										69	4.7×10^8
$CCl_3OO^\bullet$		$H_2O/2\text{-PrOH}/CCl_4$	9/89/2	7	5.8×10^7	16	5.9×10^7	30	7.1×10^7	48	9.5×10^7
										67	1.1×10^8
$CCl_3OO^\bullet$		$2\text{-PrOH}/CCl_4$	50/50	5	1.5×10^7	21	2.0×10^7	41	2.4×10^7	63	2.4×10^7
$CCl_3OO^\bullet$		$\text{dioxane}/2\text{-PrOH}/CCl_4$	40/20/40	4	1.1×10^7	20	1.1×10^7	40	1.2×10^7	62	1.1×10^7
$CHCl_2OO^\bullet$		$H_2O/2\text{-PrOH}/CHCl_3$	90/10/0.1	8	3.7×10^8	21	5.5×10^8	42	$\sim 7 \times 10^8$	71	1.2×10^9
$CHCl_2OO^\bullet$		$H_2O/2\text{-PrOH}/CHCl_3$	10/88/2	10	1.8×10^6	39	3.9×10^6				
$CHCl_2OO^\bullet$		$H_2O/2\text{-PrOH}/CHCl_3$	9/81/10	4	2.4×10^6	20	3.1×10^6	35	3.8×10^6	52	5.5×10^6
$CH_2ClOO^\bullet$		$H_2O/2\text{-PrOH}/CH_2Cl_2$	90/10/0.5	3	2.8×10^7	20	3.7×10^7	39	3.9×10^7	56	4.7×10^7
$CH_2ClOO^\bullet$		$H_2O/2\text{-PrOH}/CH_2Cl_2$	66/33/1	4	1.7×10^6	17	2.1×10^6	37	2.6×10^6	56	3.1×10^6
$CCl_3OO^\bullet$	trolox	$H_2O/2\text{-PrOH}/CCl_4$	90/10/0.1	4	4.2×10^8	22	4.5×10^8	44	1.3×10^9	70	1.7×10^9
$CCl_3OO^\bullet$		$H_2O/2\text{-PrOH}/CCl_4$	49/49/2	5	1.0×10^8	24	1.1×10^8	57	1.5×10^8	69	1.7×10^8
$CCl_3OO^\bullet$		$2\text{-PrOH}/CCl_4$	96/4	6	1.4×10^7	27	1.9×10^7	48	3.0×10^7	71	3.5×10^7
$CHCl_2OO^\bullet$		$H_2O/2\text{-PrOH}/CHCl_3$	90/10/0.1	9	1.6×10^8	20	2.6×10^8	37	3.6×10^8	59	5.0×10^8
$CH_2ClOO^\bullet$		$H_2O/2\text{-PrOH}/CH_2Cl_2$	90/10/0.5	6	7.0×10^7	21	1.2×10^8	42	$\sim 9 \times 10^7$	59	1.5×10^8
$CCl_3OO^\bullet$	Asc[c]	$H_2O/2\text{-PrOH}/CCl_4$	90/10/0.1	5	2.5×10^8	21	3.7×10^8	44	5.0×10^8	71	5.4×10^8
$CH_3OO^\bullet$		$H_2O/DMSO$	90/10	1	9.8×10^5	16	1.6×10^6	39	2.4×10^6	58	3.6×10^6
$CH_3OO^\bullet$	urate[d]	$H_2O/DMSO$	90/10	2	5.3×10^6	18	6.7×10^6	40	8.3×10^6	70	1.2×10^7

[a] CPZ = chlorpromazine, Asc = ascorbate. [b] Solutions were under air, except for $CH_3OO^\bullet$ where the $H_2O/DMSO$ mixture was bubbled with N_2O/O_2 (4:1). [c] pH 7. [d] pH 13.

peroxyl radical with the substrate, possibly involving a solvent molecule as well.

There have been a number of studies of the reactions of halogenated methylperoxyl radicals in this[6,7] and other[8] laboratories. Most of these studies have involved organic reactants which are known to be one-electron reductants, and the reaction was typically monitored by following the buildup of the resulting organic radical. The reactivity of the methylperoxyl radicals was found to increase as the degree of halogen substitution on the central carbon increased, with a linear correlation between log k and the Taft substitution constant, σ^*. Several reactions of halogenated methylperoxyl radicals with organic reductants have also been investigated in various solvents.[5,6] In mixed water–alcohol solvents, the rate constant was found to increase as the mole fraction of water increased, often reaching a maximum value and then decreasing as pure water is approached. Studies of the reaction of $CCl_3OO^\bullet$ with trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) in numerous solvents showed that the rate constant increased with the dielectric constant of the solvent but that it also correlated with the coordinate covalency parameter, a measure of the proton-transfer basicity of the solvent. This result was interpreted to suggest that electron transfer from the substrate (S) to the peroxyl radical is concerted with the proton transfer to the incipient hydroperoxide anion.

$$ROO^\bullet + S + H_2O \rightarrow ROOH + S^{\bullet+} + OH^- \qquad (3)$$

More recently, we have been carrying out studies of the temperature dependence of the rate constants of a number of inorganic free radical reactions, particularly those involving electron transfer.[9] Whereas the rate constants were found to increase with the exothermicity of the reaction, this was found to be due to an increase in the preexponential factor. The expected relation between the exothermicity and the activation energy was not observed for the oxidation of organic reductants or simple anions. We suggested that this behavior was due to the formation of

intermediate adducts in the reactions, with subsequent electron transfer taking place by an inner-sphere mechanism. For the reactions of substitution-inert transition-metal complexes Fe$(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $W(CN)_8^{4-}$, the activation energy was found to decrease with increasing exothermicity of the reaction, suggesting that these reactions proceeded by a simple outer-sphere electron transfer.

In the present work, we have extended our investigations of the temperature dependence of free radical reactions in the liquid phase to include a series of halogenated peroxyl radicals. We chose to study the reactions of the three radicals $ClCH_2OO^\bullet$, $Cl_2CHOO^\bullet$, and $Cl_3COO^\bullet$ with chlorpromazine (2-chloro-10-[3-(dimethylamino)propyl]phenothiazine), which reacts by electron transfer, and with trolox, a representative phenol which can react by either electron transfer or hydrogen abstraction. The reactions of the CCl_3O_2 were studied over a range of 2-propanol/water mixtures; the reactions of the other radicals were studied with 10% 2-propanol in water mixtures.

Experimental Section

The rate constants were determined by kinetic spectrophotometric pulse radiolysis as described before.[5-7] The chlorinated peroxyl radicals were produced by reduction of the corresponding chloro compound in aerated solutions. Methylperoxyl was produced in aqueous DMSO solutions saturated with a 4:1 mixture of N_2O/O_2. The rate of reaction of the peroxyl radical with the organic reductant was determined by following the buildup of the optical absorption due to the radicals produced from chlorpromazine (at 525 nm), trolox (at 420 nm), ascorbate (360 nm), or urate (360 nm). The second-order rate constants were determined from plots of k_{obs} vs concentration employing three substrate concentrations that differed by a factor of 4. The experiment was repeated at four or five temperatures, generally between 5 and 75 °C. The temperature was achieved in a flow system by passing the solution through a thin coiled quartz tubing immersed in a thermostated fluid immediately before entering the irradiation cell, and the temperature was read by a thermocouple immersed in the solution at the point of its exit from the cell. Other details of the materials used and the experimental procedures were as described before.[5-7] Except where noted, the rate constants were measured in the solvent mixtures at their natural pH without the addition of buffers.

Results and Discussion

The second-order rate constants determined for the various reactions at the different temperatures are summarized in Table

(6) Neta, P.; Huie, R. E.; Mosseri, S.; Shastri, L. V.; Mittal, J. P.; Maruthamuthu, P.; Steenken, S. *J. Phys. Chem.* **1989**, *93*, 4099.

(7) Alfassi, Z. B.; Mosseri, S.; Neta, P. *J. Phys. Chem.* **1987**, *91*, 3383.

(8) Packer, J. E.; Willson, R. L.; Bahnemann, 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) Huie, R. E.; Clifton, C. L. *J. Phys. Chem.* **1990**, *94*, 8561. Alfassi, Z. B.; Huie, R. E.; Neta, P.; Shoute, L. C. T. *J. Phys. Chem.* **1990**, *94*, 8800. Shoute, L. C. T.; Alfassi, Z. B.; Neta, P.; Huie, R. E. *J. Phys. Chem.* **1991**, *95*, 3238. Huie, R. E.; Shoute, L. C. T.; Neta, P. *Int. J. Chem. Kinet.* **1991**, *23*, 541.

TABLE II: Arrhenius Parameters and Room Temperature Rate Constants for Reactions of $CCl_3OO\cdot$ Radicals

reactant	solvents	ratios	E_a, kJ mol^{-1}	log A	k_{298}, M^{-1} s^{-1}
chlorpromazine	H_2O/2-PrOH/CCl_4	95/5/0.05	~28	14.1	1.4 × 10^9
	H_2O/2-PrOH/CCl_4	90/10/0.06	23.7 ± 1.0	13.2	1.2 × 10^9
	H_2O/2-PrOH/CCl_4	80/20/0.1	27.1 ± 0.8	13.8	1.2 × 10^9
	H_2O/2-PrOH/CCl_4	69/29/2	11.1 ± 5.0	11.0	1.1 × 10^9
	H_2O/2-PrOH/CCl_4	49/49/2	9.4 ± 1.0	10.1	2.9 × 10^8
	H_2O/2-PrOH/CCl_4	9/89/2	8.7 ± 1.0	9.4	6.9 × 10^7
	2-PrOH/CCl_4	50/50	5.6 ± 2.1	8.3	2.0 × 10^7
	dioxane/2-PrOH/CCl_4	40/20/40	1.1 ± 1.0	7.2	1.1 × 10^7
trolox	H_2O/2-PrOH/CCl_4	90/10/0.1	16.6 ± 1.0	11.7	6.9 × 10^8
	H_2O/2-PrOH/CCl_4	49/49/2	5.8 ± 1.3	9.1	1.2 × 10^8
	2-PrOH/CCl_4	96/4	11.7 ± 1.3	9.3	1.9 × 10^7
ascorbate	H_2O/2-PrOH/CCl_4	90/10/0.1	10.5 ± 1.4	10.4	3.9 × 10^8

TABLE III: Arrhenius Parameters and Room Temperature Rate Constants for Reactions of Peroxyl Radicals

reactant	radical	solvents	ratios	E_a, kJ mol^{-1}	log A	k_{298}, M^{-1} s^{-1}
chlorpromazine	$CCl_3OO\cdot$	H_2O/2-PrOH/CCl_4	90/10/0.06	23.7 ± 1.0	13.2	1.2 × 10^9
	$CHCl_2OO\cdot$	H_2O/2-PrOH/$CHCl_3$	90/10/0.1	14.0 ± 1.1	11.2	5.6 × 10^8
	$CHCl_2OO\cdot$	H_2O/2-PrOH/$CHCl_3$	9/81/10	11.5 ± 1.1	8.6	3.4 × 10^6
	$CH_2ClOO\cdot$	H_2O/2-PrOH/CH_2Cl_2	90/10/0.5	6.1 ± 1.2	8.6	3.6 × 10^7
	$CH_2ClOO\cdot$	H_2O/2-PrOH/CH_2Cl_2	66/33/1	8.8 ± 0.2	7.9	2.3 × 10^6
trolox	$CCl_3OO\cdot$	H_2O/2-PrOH/CCl_4	90/10/0.1	16.6 ± 1.0	11.7	6.9 × 10^8
	$CHCl_3OO\cdot$	H_2O/2-PrOH/$CHCl_3$	90/10/0.1	17.2 ± 2.8	11.5	2.7 × 10^8
	$CH_2ClOO\cdot$	H_2O/2-PrOH/CH_2Cl_2	90/10/0.5	6.4 ± 5.8	9.1	9.5 × 10^7
ascorbate	$CCl_3OO\cdot$	H_2O/2-PrOH/CCl_4	90/10/0.1	10.5 ± 1.4	10.4	3.9 × 10^8
	$CH_3OO\cdot$	H_2O/DMSO	90/10	15.2 ± 0.7	8.9	1.9 × 10^6
urate	$CH_3OO\cdot$	H_2O/DMSO	90/10	9.4 ± 0.9	8.5	7.0 × 10^6

I. These values were fit to the Arrhenius expression $k = Ae^{-E_a/RT}$ by a weighted least-squares routine; the weights were taken as the reciprocal of the squares of the standard errors derived from the second-order fits. Representative plots are shown in Figure 1. The Arrhenius parameters are presented in Tables II and III, along with the calculated value of the rate constant at 298 K. The error limits reported for the activation energy are the standard errors from the least-squares fit. Due to the long extrapolation involved, we have chosen not to report the calculated statistical error limits for the preexponential factors. We estimate that, over the temperature range of these studies, the errors in the rate constants calculated from the Arrhenius expressions are ±20%.

The calculated Arrhenius activation energies range from 1 to 30 kJ mol^{-1}. In many cases, the activation energy is very low, much below the activation energy for diffusion ($\sim$17.5 kJ mol^{-1}).[9] For these reactions, however, the rate constants which were measured are well below the diffusion limit, and thus the temperature dependence of the rate constant is not expected to be affected by the temperature dependence of the diffusion rate.

The rate constants for the reactions of both chlorpromazine and trolox with substituted methylperoxyl radicals increase with increasing number of chlorine atoms on the radical, as has been observed previously for the reactions of a number of these radicals with ascorbate and TMPD.[6-8] This increase in the rate constant is due to an increase in the preexponential factor for the reaction with increasing chlorine substitution on the peroxyl radical.

The rate constant for oxidation of chlorpromazine by $Cl_3COO\cdot$ was determined as a function of temperature in various mixtures of water, 2-PrOH, dioxane, and CCl_4. The rate constants were found to increase as the dielectric constant of the solvent mixture increases, similar to what we have observed before. Again, the observed increase in rate constant is found to be due to an increase in the preexponential factor which overcomes the effect of an increase in the activation energy.

The results we have obtained clearly show that the variation in the rate constant with the degree of halogen substitution on the peroxyl radical or with the dielectric constant of the solvent is due to a change both in the preexponential factor for the reaction and in the activation energy. These parameters vary in such a manner as to result in opposite effects on the measured rate constants. That is, as the activation energy increases, leading to a lower rate constant, the preexponential factor also increases to
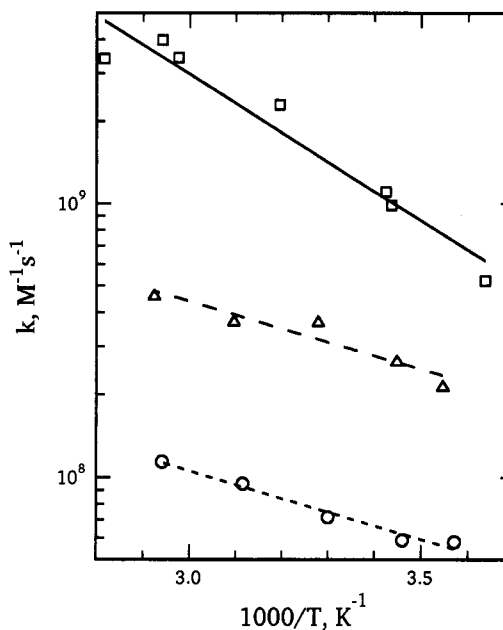

Figure 1. Arrhenius plots for the reaction of $CCl_3OO\cdot$ with chlorpromazine in water/2-PrOH/CCl_4 mixtures (□, 90/10/0.06; △, 49/49/2; ○, 9/89/2).

a greater degree, leading to a higher rate constant. The net result is a smaller change in rate constant than would be expected on the basis of the change in A or E_a alone. In this study, the change in the preexponential factor has predominated. This greater importance of the preexponential factor in determining the reactivity of many radical reactions in solution has been noted in our previous work.[9]

These results suggest that the activation energy and the preexponential factor are correlated by the isokinetic relationship[10]

$$E_a = R\beta \ln A + e_0$$

where R is the gas constant, β is the isokinetic temperature, and

(10) Exner, E. *Prog. Phys. Org. Chem.* **1973**, *10*, 411. Linert, W.; Jameson, R. F. *Chem. Soc. Rev.* **1989**, *18*, 477.
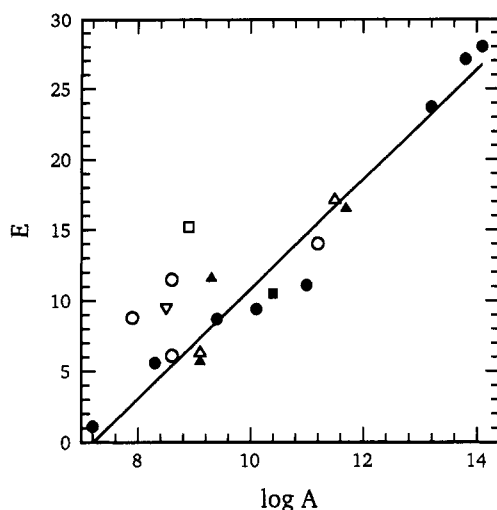
Figure 2. Isokinetic relationship between the activation energy (E, in kJ mol^{-1}) and the preexponential factor (log A, where A is in M^{-1} s^{-1}) for the reactions of the peroxyl radicals with the organic compounds. The line was fit to the data for CCl$_3$OO$^{\bullet}$ only ($\bullet$, chlorpromazine; $\blacktriangle$, trolox; $\blacksquare$, ascorbate). The data for the other radicals, CHCl$_2$OO$^{\bullet}$, CH$_2$ClOO$^{\bullet}$, and CH$_3$OO$^{\bullet}$, are also shown for comparison (O, chlorpromazine; $\triangle$, trolox; $\square$, ascorbate; ∇, urate).

e_0 is an intercept. In Figure 2, we have plotted the activation energy against the logarithm of the preexponential factor; the line in the figure is a fit to the CCl$_3$OO$^{\bullet}$ data only ($R^2 = 0.97$) and corresponds to $\beta = 202$ K.

There have been a number of reaction series for which an isokinetic relationship has been reported.[10] In light of our observations, we have analyzed some previous results on the temperature dependence of free radical reactions to see whether they also show an isokinetic relationship.[11] Howard and co-workers have reported on the temperature dependence for several *tert*-butylperoxyl radical reactions in isopentane.[4] For the reactions of some trivalent phosphorus compounds, nonhindered phenols, aromatic amines, and thiophenols with $E_a > 4$ kJ mol^{-1}, we have found that these data fit a reasonable isokinetic relation.[11] For some reactions of hindered phenols and aromatic amines where $E_a = 4 \pm 2$ kJ mol^{-1} there appears to be no apparent isokinetic relation, but the line from the other data sets did intersect these points. Freeman and co-workers[12] have carried out extensive investigations of the effect of mixed alcohol–water solvents on the reactivity of the solvated electron. Their results show a pronounced isokinetic relationship for reactions which are not diffusion limited, for example, the reaction of e$_s^-$ with nitrobenzene. For the reactions e$_s^-$ + CrO$_4^{2-}$ and e$_s^-$ + NO$_3^-$, slightly different fits are obtained for the two solvent mixtures 1-propanol–water and 2-propanol–water.[11] There has also been a study of an excited-state electron-transfer reaction for which an isokinetic effect was observed, the quenching of *RuL$_3^{2+}$ emission by Cu(II) in aqueous solution.[13] A similar effect was not observed for quenching by Eu(III).

We have also applied the isokinetic concept to our earlier work on the temperature dependence of the electron-transfer reactions of small inorganic free radicals in aqueous solutions.[9] Nearly 50 reactions were studied, involving eight different radicals and a variety of organic and inorganic reductants. Even for this mixed group of reactions an isokinetic relation is apparent, but with a large amount of scatter. On the other hand, if we examine our

results on hydrogen abstraction reactions,[14] we find no such relationship. For these reactions, the preexponential factors are essentially constant (on a C–H basis) and the rate constant is controlled by the activation energy. In turn, the activation energy is related to the C–H bond strength.

In our previous papers, we have discussed the low A factors and low activation energies for electron-transfer reactions, and the apparently poor correlation of the activation energy with the exothermicity of the reaction, in terms of the reversible formation of a transient intermediate. For peroxyl radicals the equilibrium reaction

$$\text{ROO}^{\bullet} + \text{S} \rightleftarrows \text{ROO–S}^{\bullet} \qquad (4)$$
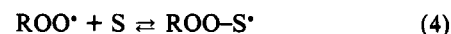
is followed by the electron-transfer reaction, which is probably assisted by proton donation from water:

$$\text{ROO–S}^{\bullet} + \text{H}_2\text{O} \rightarrow \text{ROOH} + \text{S}^+ + \text{OH}^- \qquad (5)$$

If a steady state in ROO–S$^{\bullet}$ is assumed, then the observed rate constant will be given by

$$k_{\text{obs}} = k_4 k_5 / (k_{-4} + k_5)$$

or, as a function of temperature:

$$k_{\text{obs}} = \frac{A_4 A_5 e^{-(E_4+E_5)/RT}}{A_{-4} e^{-E_{-4}/RT} + A_5 e^{-E_5/RT}}$$

If $k_5 \gg k_{-4}$, then a simple Arrhenius expression will result

$$k_{\text{obs}} = A_4 e^{-E_4/RT}$$

If, on the other hand, $k_5 \ll k_{-4}$, then

$$k_{\text{obs}} = \frac{A_4 A_5 e^{-(E_4+E_5)/RT}}{A_{-4} e^{-E_{-4}/RT}} = \frac{A_4 A_5}{A_{-4}} e^{-(E_4+E_5-E_{-4})/RT}$$

Although we can say little about the rate constants for reactions 4 and −4, the rate constant for reaction 5 is probably related to the driving force for the reaction and to the ability of the solvent to promote the electron transfer. In any given solvent, the driving force is expected to increase with the degree of halogen substitution on the peroxyl radical. For a given reaction, our previous work showed that the rate of the reaction was related to both the dielectric constant of the solvent and the proton-donating ability of the solvent. We expect that the electron-transfer step has little temperature dependence, possibly even a negative value due to the negative temperature dependence for the dielectric constant, and the variation in its rate constant is probably due to a variation in the preexponential factor.[15] If this is correct, then the observed activation energy varies from E_4 to $E_4 - E_{-4}$ as k_5 becomes slower relative to k_{-4}. The observed preexponential factor also ranges from A_4 to $A_4 A_5 / A_{-4}$. Under these conditions, where $k_5 \ll k_{-4}$, A_5 is probably much less than A_{-4}. Therefore, the observed preexponential factor also decreases. The proposed mechanism for these electron-transfer reactions, then, leads to a kinetic expression in basic agreement with the results.

Supplementary Material Available: Plots of the activation energy against the logarithm of the preexponential factor (3 pages). Ordering information is given on any current masthead page.

(11) A figure is available in the supplementary material.
(12) (a) Senannayake, P. C.; Freeman, G. R. *J. Phys. Chem.* **1987**, *91*, 2123. (b) Maham, Y.; Freeman, G. R. *Can. J. Chem.* **1988**, *66*, 1706. (c) Lai, C. C.; Freeman, G. R. *J. Phys. Chem.* **1990**, *94*, 302. (d) Sedigallage, A. P.; Freeman, G. R. *Can. J. Chem.* **1990**, *68*, 940.
(13) Baggott, J. E.; Philling, M. J. *J. Phys. Chem.* **1980**, *84*, 3012.

(14) (a) Clifton, C. L.; Huie, R. E. *Int. J. Chem. Kinet.* **1989**, *21*, 677. (b) Huie, R. E.; Clifton, C. L.; Kafafi, S. A. *J. Phys. Chem.*, in press.
(15) In a recent study of the temperature and solvent dependence of intramolecular electron transfer, the activation energies were found to be small and to fall in a narrow range while the preexponential factors increased with the dielectric constant of the medium: Heitele, H.; Pöllinger, F.; Weeren, S.; Michel-Beyerle, M. E. *Chem. Phys. Lett.* **1990**, *168*, 598.