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Solvent Effects on the Rate of Reaction of $\text{Cl}_2^{\cdot-}$ and $\text{SO}_4^{\cdot-}$ Radicals with Unsaturated Alcohols

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Abstract

Rate constants have been measured in several aqueous/organic solvent mixtures for the addition reaction of $\text{Cl}_2^{\cdot-}$ radicals with 2-propen-1-ol and 2-buten-1-ol as a function of temperature and with 2, 3-dimethyl-2-butene at room temperature. The rate constants were in the range of 10^6 – 10^9 L mol⁻¹ s⁻¹, the activation energies were relatively low (1–10 kJ mol⁻¹), and the pre-exponential factors varied over the range $\log A = 7.9$ to 9.4. The rate constants (k) decreased (by up to a factor of 30) upon increasing the fraction of organic solvent and $\log k$ correlated linearly with the dielectric constant for a given water/organic solvent system, but the lines for the different solvent systems had different slopes. A better correlation of $\log k$ was found with a combination of the solvatochromic factor, $E_T(30)$, and the hydrogen-bond donor acidity factor, α . This suggests that the rate of reaction is influenced by the solvent polarity and also by specific solvation of the ionic reactant and product. Solvent effect on the reaction of $\text{SO}_4^{\cdot-}$ with 2-propen-1-ol was studied for comparison. © 1993 John Wiley & Sons, Inc.

Introduction

Studies of the temperature dependence of the electron transfer reactions of inorganic radicals with organic [1] and inorganic [2] reactants have shown that variations in rate constants for various reactants are due mainly to differences in the pre-exponential factor (A) while the activation energy (E_a) varies less strongly. For example, the dominant factor in the reactivity of the $\text{SO}_4^{\cdot-}$ radical in electron transfer reactions is the A factor [3] whereas for hydrogen abstraction reactions the reactivity is determined mainly by E_a [4].

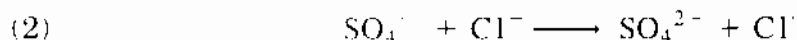
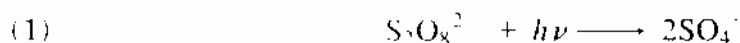
In a recent article [5], we reported the temperature dependence of the rate constants for the addition of $\text{Cl}_2^{\cdot-}$ radicals to the double bonds of unsaturated alcohols and hydrocarbons in water-acetonitrile mixtures. Acetonitrile was found to reduce the rate constant considerably, an effect which was observed previously for electron transfer reactions of peroxy radicals [6]. An even stronger effect of solvent composition on the temperature dependence was found. With two-solvent mixtures, however, it is not possible to determine whether the effect of solvent is due to changes in dielectric constant [7] only or whether additional solvent parameters play a role as well [6]. Therefore, we have extended this work on the addition reactions of $\text{Cl}_2^{\cdot-}$ radical to include mixtures of other solvents with water.

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Experimental

The rate constants were determined by laser-flash photolysis with spectrophotometric detection of $\text{Cl}_2^{\cdot -}$ at 340 nm as described previously [5]. The $\text{Cl}_2^{\cdot -}$ radicals were generated by the reaction of $\text{Cl}^{\cdot -}$ with $\text{SO}_4^{\cdot -}$ radicals produced by 248 nm laser-flash photolysis of $1 \times 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_8$ solutions:



To maximize the fraction of $\text{SO}_4^{\cdot -}$ radicals that reacts with Cl^- rather than with the organic solvent, the concentration of KCl was generally in the range of 0.1–0.5 mol L⁻¹. The results from multiple runs were averaged before undergoing linear least-squares analysis to extract the first-order rate constant. First-order rate constants were determined at three or four different substrate concentrations, varying by a factor of 3–5. Second-order rate constants were derived from a weighted least-squares fit to a plot of the first-order rate constant against the substrate concentration and are generally accurate to $\pm 15\%$. Rate constants were typically measured at four temperatures. Other details of the experiments and the materials used were as described previously [5].

The second-order rate constants for the reactions of $\text{Cl}_2^{\cdot -}$ with the various unsaturated compounds were fit to the Arrhenius expression $k = Ae^{-E/RT}$ by a weighted least-squares routine (weighted by the reciprocal of the squares of the standard errors from the second-order fits). The error limits reported with the Arrhenius parameters are the standard errors from the least-squares fit.

Results and Discussion

Acetonitrile (ACN) was chosen as the organic solvent in the previous study [5] because its reactions with $\text{SO}_4^{\cdot -}$ and with $\text{Cl}_2^{\cdot -}$ are slow and its optical absorption at 248 nm is negligible. Indeed, reactions of these radicals were monitored in the presence of up to ca. 80% ACN (20% water) with little loss in sensitivity. (Experiments could not be carried out in 100% ACN since the $\text{Na}_2\text{S}_2\text{O}_8$ is not soluble). The suitability of other solvents for studies of $\text{Cl}_2^{\cdot -}$ reactions also depends on the relative rate of reaction of $\text{SO}_4^{\cdot -}$ with Cl^- and the organic solvent and on its optical absorption at 248 nm. Based on these criteria, we attempted to use methanol as a solvent for these reactions. From the rate constants reported for aqueous solutions [8], we estimated that in the presence of 50% methanol and 0.5 mol L⁻¹ Cl^- the yield of $\text{Cl}_2^{\cdot -}$ radicals should be 24% of that found in aqueous solutions in the absence of methanol. In fact, the yield of $\text{Cl}_2^{\cdot -}$ was found to be too small to monitor clearly in this system, probably because the addition of methanol reduces k_2 (reaction between two negatively charged ions) more than it reduces the rate of reaction of $\text{SO}_4^{\cdot -}$ with the alcohol. Acetone and dimethyl sulfoxide are ruled out as solvents for these studies because of their high optical

absorbance at 248 nm, the laser wavelength used for production of $\text{SO}_4^{\cdot-}$. Only *tert*-butyl alcohol (*t*-BuOH) (up to 50%), *p*-dioxane (up to 30%), and acetic acid (AcOH) (up to 70%) were found to be suitable co-solvents with water for these studies.

Table I summarizes the rate constants for the unsaturated alcohols which were measured at various temperatures and in several solvent mixtures, Figure 1 shows Arrhenius plots for one alcohol, and Table II lists the Arrhenius parameters calculated from the results of Table I. All activation energies are found to be very small, less than 11 kJ mol⁻¹. The pre-exponential factors vary between log *A* = 7.9 and 9.4. These results are similar to those found previously [5] for unsaturated alcohols in water/ACN

TABLE I. Rate constants for reactions of $\text{Cl}_2^{\cdot-}$ radicals at different temperatures.

Substrate	Solvent ^a	T, °C	<i>k</i> ^b	T, °C	<i>k</i> ^b	T, °C	<i>k</i> ^b	T, °C	<i>k</i> ^b
2-propen-1-ol	water	4	3.9×10^7	23	5.2×10^7	43	6.8×10^7	67	8.2×10^7
	29% V dioxane	5	1.4×10^7	23	1.9×10^7	44	2.5×10^7	61	3.0×10^7
	25% W <i>t</i> -BuOH	5	2.2×10^7	23	2.5×10^7	43	2.9×10^7	62	3.0×10^7
	36% W <i>t</i> -BuOH	5	1.4×10^7	22	1.5×10^7	43	1.7×10^7	63	2.2×10^7
	53% W <i>t</i> -BuOH	5	8.1×10^6	23	1.0×10^7	41	1.3×10^7	64	1.4×10^7
2-buten-1-ol	water	11	1.6×10^8	23	1.9×10^8	35	2.0×10^8	45	2.1×10^8
	70% V ACN	4	1.3×10^7	29	7.2×10^6	47	7.6×10^6	69	9.3×10^6
	15% W <i>t</i> -BuOH	5	1.1×10^8	23	1.1×10^8	45	1.2×10^8	64	1.2×10^8
	32% W <i>t</i> -BuOH	5	5.1×10^7	26	5.4×10^7	47	5.7×10^7	69	5.6×10^7
	50% W <i>t</i> -BuOH	6	2.4×10^7	26	2.5×10^7	49	3.0×10^7	69	3.5×10^7

^aThe solvent was water with a fraction of an organic solvent given by volume (%V) or by weight (%W).

^bRate constant in L mol⁻¹ s⁻¹.

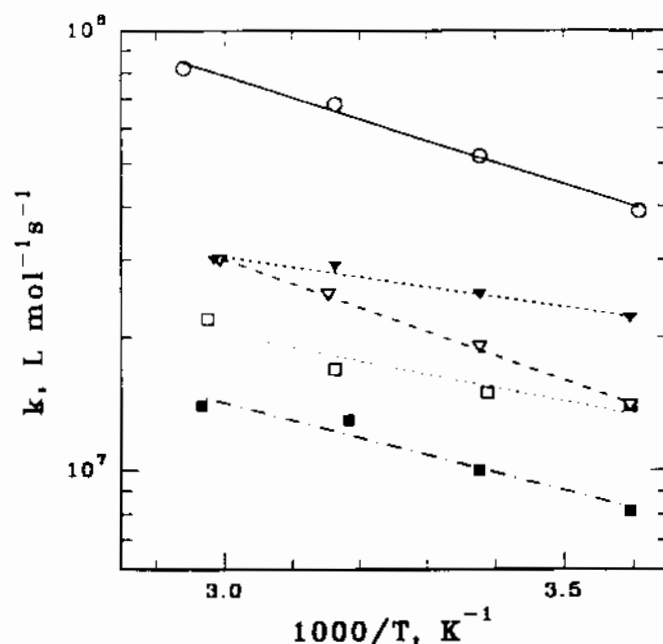


Figure 1. Rate constants for the reaction of $\text{Cl}_2^{\cdot-}$ with 2-propen-1-ol as a function of temperature in various solvents. ○ — 100% water; ▽ — 29% dioxane; ▼ — 25% *t*-BuOH; □ — 36% *t*-BuOH; and ■ — 53% *t*-BuOH.

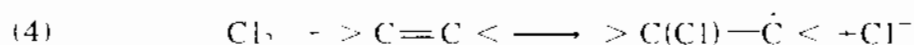
TABLE II. Arrhenius parameters and k_{298} value for reactions of $\text{Cl}_2^{\cdot-}$ radicals.

Substrate	Solvent ^a	mole fraction (organic)	E_{298}	E_a (kJ mol ⁻¹)	log A	k_{298} (L mol ⁻¹ s ⁻¹)
2-propen-1-ol	water	0	78.4	9.9 ± 2.2	9.4	5.2 × 10 ⁷
	29% V dioxane	0.08	53.5	10.7 ± 0.5	9.1	1.9 × 10 ⁷
	25% W <i>t</i> -BuOH	0.08	57.0	4.6 ± 0.6	9.2	2.5 × 10 ⁷
	36% W <i>t</i> -BuOH	0.12	46.8	6.3 ± 0.8	9.3	1.5 × 10 ⁷
	53% W <i>t</i> -BuOH	0.21	34.1	7.6 ± 1.3	9.4	1.0 × 10 ⁷
2-buten-1-ol	water	0	78.4	4.8 ± 0.8	9.1	1.9 × 10 ⁸
	70% V ACN	0.43	49.2	ca. 0		7.2 × 10 ⁶
	15% W <i>t</i> -BuOH	0.04	67.0	2.1 ± 0.6	8.4	1.1 × 10 ⁸
	32% W <i>t</i> -BuOH	0.10	50.0	1.1 ± 0.6	7.9	5.4 × 10 ⁷
	50% W <i>t</i> -BuOH	0.20	35.2	6.2 ± 0.7	8.6	2.5 × 10 ⁷

^aThe solvent was water with a fraction of an organic solvent given by volume (%V) or by weight (%W).

mixtures. But in the previous work, a correlation between log A and E_a (an isokinetic effect) was observed for the reaction of $\text{Cl}_2^{\cdot-}$ and 2,3-dimethyl-2-butene, for which there was a large variation in these parameters with the change in the water/ACN ratio. In the present study, there is no clear correlation between the Arrhenius parameters and the solvent composition, possible due to the smaller range of values measured. The value of k_{298} , however, showed a strong correlation with ACN mol fraction in water/ACN mixtures [5] and is found here to behave similarly in water/*t*-BuOH.

Table III summarizes the rate constants measured at 298 K for the alkene in various solvent mixtures and for 2-propen-1-ol in water/acetic acid mixtures. In all solvents studied, the reactivity of $\text{Cl}_2^{\cdot-}$ increases in the order 2-propen-1-ol, 2-buten-1-ol, and 2,3-dimethyl-2-butene, i.e., with increased substitution at the double bond, indicating that the reaction is via addition.

TABLE III. Rate constants for reaction of $\text{Cl}_2^{\cdot-}$ in different solvent mixtures.

Substrate	Solvent ^a	mole fraction (organic)	E_{298}	k_{298} (L mol ⁻¹ s ⁻¹)
2,3-dimethyl-2-butene	10% V dioxane	0.02	71.0	5.2 × 10 ⁸
	20% V dioxane	0.05	62.3	3.1 × 10 ⁸
	7.4% W <i>t</i> -BuOH	0.02	73.0	5.7 × 10 ⁸
	22% W <i>t</i> -BuOH	0.06	60.6	3.5 × 10 ⁸
	39% W <i>t</i> -BuOH	0.14	44.5	1.2 × 10 ⁸
2-propen-1-ol	10% V AcOH	0.03	71.6	3.6 × 10 ⁷
	30% V AcOH	0.12	64.0	2.7 × 10 ⁷
	50% V AcOH	0.23	60.8	2.1 × 10 ⁷
	70% V AcOH	0.42	38.8	1.9 × 10 ⁷

^aThe solvent was water with a fraction of an organic solvent given by volume (%V) or by weight (%W).

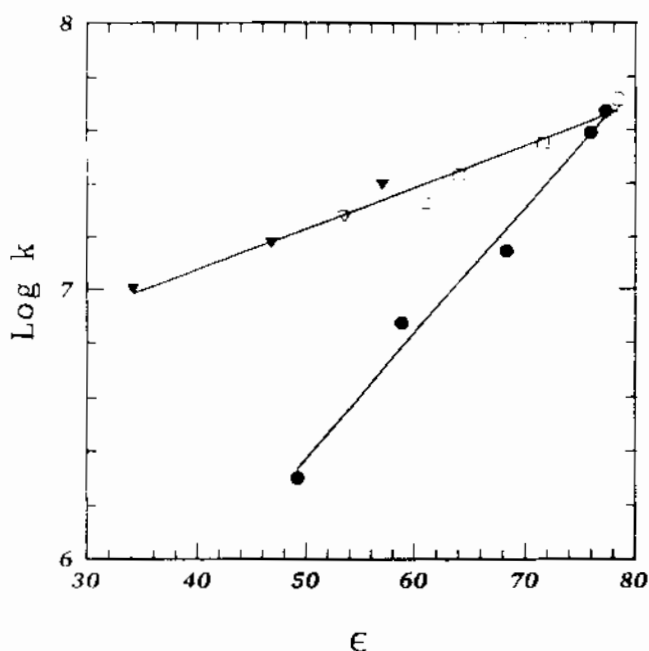


Figure 2. Correlation of $\log k$ for the reaction of Cl_2^- with 2-propen-1-ol in various solvents with the dielectric constant of the medium, ϵ . \circ — water; \bullet — ACN; \blacktriangledown — t -BuOH; ∇ — dioxane; and \square — acetic acid.

To test whether the effect of solvent on rate constant is due predominantly to solvent polarity, we attempted to correlate $\log k_{298}$ (from this work and from ref. [5]) and the dielectric constant ϵ (from refs. [9] and [10] for water/organic mixtures) for the reaction of Cl_2^- with 2-propen-1-ol (Fig. 2). There appear to be two lines, with water/ACN on a steep line and the other solvent mixtures on another, more gradual, line. The reaction of Cl_2^- with 2,3-dimethyl-2-butene also shows a strong solvent dependence, with the correlation between $\log k$ and ϵ showing a steeper line for acetonitrile than for the other two solvents, dioxane, and t -BuOH. These findings indicate that the dielectric constant of the medium is not sufficient to determine the rate of reaction and that other solvent parameters play a role. The similarity of the three O -containing solvents and their difference from the N -containing solvent may point to the importance of the nature of the solvent in affecting the reaction rate through specific solvation.

Although a large number of solvent parameters, which reflect other solvent characteristics in addition to polarity (e.g., basicity, hydrogen bonding), have been reported in the literature for pure solvents [11], these parameters are not known for solvent mixtures. They may be calculated for a binary solvent mixture from the values for the pure solvents (P_{org} , P_{w}) and the mole fraction f by assuming simple additivity, $P_{\text{mix}} = fP_{\text{org}} + (1 - f)P_{\text{w}}$. For the dielectric constant, where the values have been measured for solvent mixtures [9, 10], the dependence is not always linear. Therefore, such calculations should be taken only as approximations, as a method to weigh in the solvent parameter. Of several parameters examined (including E_{T} (30), AN, DN, δ , β , and α , from ref. [11], we found a reasonable linear

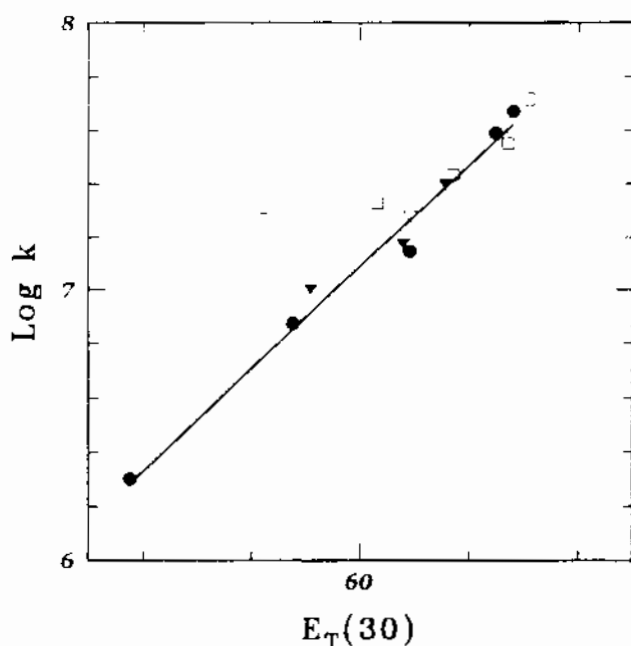
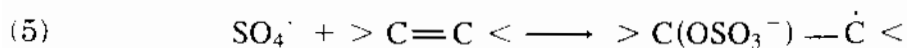


Figure 3. Correlation of $\log k$ for the reaction of Cl_2^- with 2-propen-1-ol in various solvents with $E_T(30)$. ○ — water; ● — ACN; ▼ — *t*-BuOH; ▽ — dioxane; and □ — acetic acid.

relation between $\log k$ and the solvatochromic factor $E_T(30)$ ¹ (Fig. 3), but found that acetic acid deviated considerably from the line, with the measured rate constants higher than predicted. The likely reason for this deviation is the ability of acetic acid to form strong hydrogen bonds. To test this assumption, we have correlated the measured values of $\log k$ with $E_T(30)$ and α , a hydrogen-bond donor acidity factor [11]. Figure 4 shows that there is a good linear correlation for all of the solvent mixtures [according to $\log k_{\text{calc}} = -0.02 + (0.09 + 0.02)E_T + (1.62 \pm 0.34)\alpha$]. These correlations suggest that the rate constant is influenced by the extent of solvation of the Cl^- ion produced in reaction 4. This ion will be poorly solvated by ACN but better solvated by hydroxylic solvents, particularly water. Cl_2^- also will be better solvated by water, but because of its larger size and the distribution of its charge on both atoms, the differences among the solvents will be smaller.

To compare these results with those for an addition reaction in which no small anion is released, we examined the solvent effect on the rate of reaction of SO_4^- with 2-propen-1-ol (Table IV). This reaction has been shown to proceed via addition [12].



The correlation of $\log k$ with ϵ (Fig. 5) shows a better agreement between the results for water/ACN (solid circles and line) and water/acetic acid (squares) in the case of SO_4^- than was seen above for Cl_2^- . We also correlated the results with E_T and α (not shown), obtaining a better fit than that observed

¹ $E_T(30)$ values are based on the transition energy for the longest wavelength absorption band of a solution of a pyridinium-*N*-phenoxide betaine dye, number 30 in the list of Dimroth et al., which provided the most sensitive measure of the solvation of electrolytes by the solvent. See ref. [11] for more details.

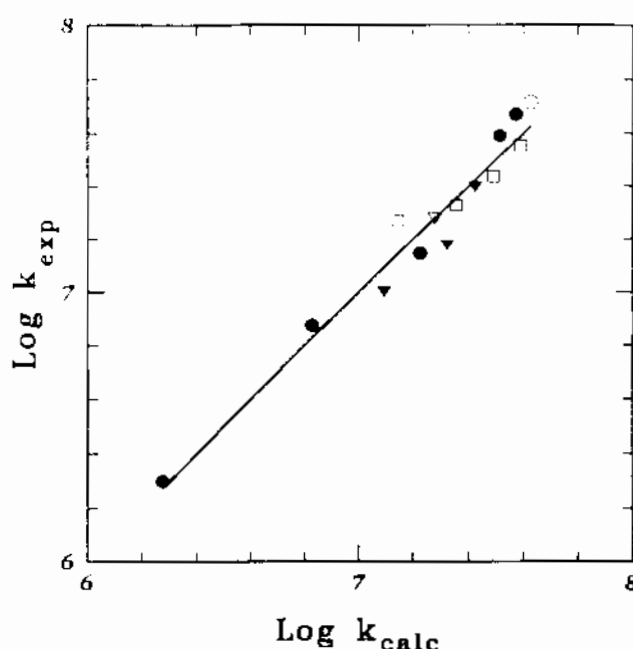


Figure 4. Correlation of $\log k_{\text{exp}}$ for the reaction of Cl_2 with 2-propen-1-ol in various solvents with $\log k_{\text{calc}}$ (according to the best fit relation $\log k_{\text{calc}} = -0.02 + (0.09 \pm 0.02) E_T + (1.62 \pm 0.34)\alpha$). \circ — water; \bullet — ACN; \blacktriangledown — *t*-BuOH; ∇ — dioxane; and \square — acetic acid.

TABLE IV. Rate constants for reaction of $\text{SO}_4^{\cdot -}$ with 2-propen-1-ol in different solvent mixtures.

Solvent ^a	mole fraction (organic)	ϵ_{298}	k_{298} ($\text{L mol}^{-1} \text{s}^{-1}$)
Water	0	78.4	3.0×10^9
10% V ACN	0.04	75.9	1.1×10^9
30% V ACN	0.13	68.3	6.0×10^8
50% V ACN	0.26	58.5	2.8×10^8
70% V ACN	0.45	49.2	1.1×10^8
95% V ACN	0.87	38.1	2.6×10^7
5% V AcOH	0.02	73.5	1.1×10^9
15% V AcOH	0.05	69.6	8.9×10^8
25% V AcOH	0.09	65.7	7.2×10^8
45% V AcOH	0.20	61.1	5.1×10^8

^aThe solvent was water with a fraction of an organic solvent given by volume (%V) or by weight (%W).

for ϵ . The coefficient for α , however, was statistically not very significant (the uncertainty was as large as the coefficient). On the other hand, a very good fit was found between $\log k$ and E_T alone, with the exception of the point for pure water (Fig. 6). This supports the above conclusion that increased hydrogen bond donor acidity increases the rate of reaction by promoting the release of Cl^- from the initial adduct of $\text{Cl}_2^{\cdot -}$ with the alkene.

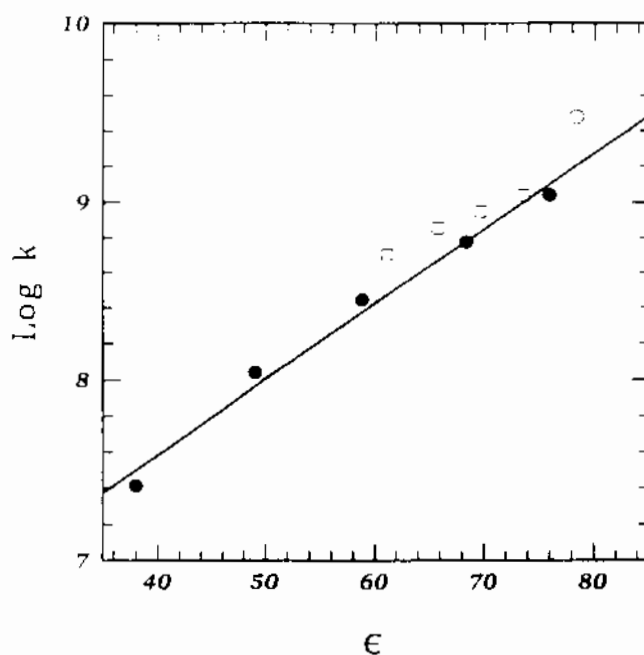


Figure 5. Correlation of $\log k$ for the reaction of $\text{SO}_4^{\cdot -}$ with 2-propen-1-ol in various solvents with the dielectric constant of the medium, ϵ . \circ —water; \bullet —ACN; and \square —acetic acid. Line drawn through the points for ACN.

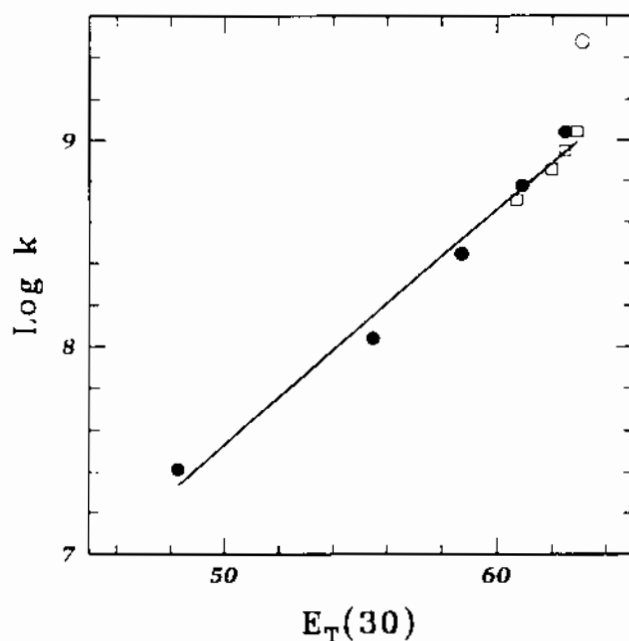


Figure 6. Correlation of $\log k$ for the reaction of $\text{SO}_4^{\cdot -}$ with 2-propen-1-ol in various solvents with $E_T(30)$. \circ —water; \bullet —ACN; and \square —acetic acid.

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Bibliography

- [1] Z. B. Alfassi, R. E. Huie, P. Neta, and L. C. T. Shoute, *J. Phys. Chem.*, **94**, 8800 (1990).
- [2] L. C. T. Shoute, R. E. Huie, P. Neta, and Z. B. Alfassi, *J. Phys. Chem.*, **95**, 3238 (1991).
- [3] R. E. Huie and C. L. Clifton, *J. Phys. Chem.*, **94**, 8561 (1990).
- [4] C. L. Clifton and R. E. Huie, *Int. J. Chem. Kinet.*, **21**, 677 (1989).
- [5] S. Padmaja, P. Neta, and R. E. Huie, *J. Phys. Chem.*, **96**, 3354 (1992).
- [6] P. Neta, R. E. Huie, P. Maruthamuthu, and S. Steenken, *J. Phys. Chem.*, **93**, 7654 (1989).
- [7] Z. B. Alfassi, S. Mosseri, and P. Neta, *J. Phys. Chem.*, **91**, 3383 (1987).
- [8] P. Neta, R. E. Huie, and A. B. Ross, *J. Phys. Chem. Ref. Data*, **17**, 1027 (1988).
- [9] Y. Marcus, *Ion Solvation*, Wiley, New York, 1985, Chap. 7.
- [10] J. Timmermans, *The Physico-Chemical Constants of Binary Systems in Concentrated Solutions*, Interscience, New York, 1960, vol. 4.
- [11] C. Reichardt, *Solvent Effects in Organic Chemistry*, Verlag Chemie, Weinheim, 1979, pp. 225-252.
- [12] M. J. Davies and B. C. Gilbert, *J. Chem. Soc., Perkin Trans. 2*, 1809 (1984).

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