

Picosecond Kinetics of the Reaction $\text{H}_3\text{O}^+ + \text{SO}_4^{2-} \rightarrow \text{HSO}_4^- + \text{H}_2\text{O}$

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The kinetics of the reaction $\text{H}_3\text{O}^+ + \text{SO}_4^{2-} \rightarrow \text{HSO}_4^- + \text{H}_2\text{O}$ in aqueous solution have been studied over the temperature range 10–60 °C by IR line broadening. Rate constants and activation energy have been determined. A large change of ionic strength, brought about by addition of 4 M NaCl, had no noticeable effect on the rate constant. The significance of this is discussed. Deuteration was found to lower the rate constants and to somewhat increase the activation energy.

Introduction

The kinetics of the reaction $\text{H}_3\text{O}^+ + \text{SO}_4^{2-} \rightarrow \text{HSO}_4^- + \text{H}_2\text{O}$ with rate constant k_f have been studied quite extensively by Chen and Irish¹ and also by Ikawa et al.² through the broadening of the Raman lines of SO_4^{2-} . Their work, however, still left some questions open. The one which interested us most was whether the sulfate must find a proton in its immediate vicinity to combine with or whether a proton could be transported from further away over hydrogen-bonded water molecules. We tried to answer this question by perturbing the solvent: adding a large amount of NaCl to break the ordered structure of the water.

Chen and Irish found that the reaction $\text{D}_3\text{O}^+ + \text{SO}_4^{2-} \rightarrow \text{DSO}_4^- + \text{D}_2\text{O}$ was considerably faster than the corresponding reaction with H, and while they advanced explanations for this finding, we still thought it surprising enough to warrant further experimental investigation.

Finally, the kinetic work published covered room temperature only. A temperature study yields activation energies capable of providing further insight into the kinetics.

Our experiments utilized infrared lines of the species involved. The broadening of these lines yields information similar to that provided by the broadening of Raman lines.³

Experimental Section

Spectra were taken with a Nicolet DX-20 interferometer. Line fitting was done directly on the instrument's monitor by appropriately programming its computer. Solutions were contained in a Barnes "Circle" ATR cell having a ZnSe crystal and providing an effective path length of $\sim 15 \mu\text{m}$.

Results

Aqueous solutions of H_2SO_4 exhibit three peaks in the 1000–1250- cm^{-1} region of the IR spectrum, with maxima at 1050, 1100, and 1195 cm^{-1} with a few cm^{-1} variations between different solutions. The corresponding peaks for D_2SO_4 are at 1054, 1100, and 1186 cm^{-1} . Solutions of Na_2SO_4 exhibit, in this region, a single peak at 1100 cm^{-1} and so this peak must be assigned to SO_4^{2-} . The insensitivity of this peak to D substitution is, of course, in keeping with this assignment. The remaining two peaks would then belong to HSO_4^- (or DSO_4^-), as H_2SO_4 is completely dissociated at our concentrations.¹ Indeed, these two peaks exhibit a rather constant ratio of intensities. Apart from those visible peaks, one must also consider the very broad peak at about 1170 cm^{-1} observed in solutions of HCl and due to H_3O^+ . This peak gives rise to a broad background underlying the former, rather

TABLE I: Q_c and $\Delta\nu_{1/2}$ Values for Several H_2SO_4 Solutions^a

$[\text{H}_2\text{SO}_4]^b$, M	Q_c^c , M	$\Delta\nu_{1/2}^d$, cm^{-1}	4 M NaCl present
0.29	0.06	36	no
0.29	0.10	40	no
0.59	0.10	40	no
0.59	0.14	42	no
0.88	0.25	48	no
1.17	0.34	50	no
0.29	0.15	37	yes
0.59	0.20	40	yes
0.60	0.13	38	yes
0.88	0.27	46	yes
1.17	0.35	50	yes
Na_2SO_4 (1 M)		35	no
Na_2SO_4 (0.6 M)		35	yes

^aSolutions mentioned in this table except for the last two entries are without HCl or Na_2SO_4 added. ^bNominal concentration. ^c $Q_c = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-]$. ^d1100- cm^{-1} band.

TABLE II: $A = \Delta\nu_{1/2}/\Delta[\text{H}^+]$ for the 1100- cm^{-1} Line at Different Temperatures

	T , °C	A , cm^{-1}/M	k_f , $10^{12} \text{M}^{-1} \text{s}^{-1}$
H_2SO_4	10	9.7 ± 2.5	1.8 ± 0.5
	23	9.2 ± 0.8	1.7 ± 0.15
	40	11.5 ± 2.5	2.2 ± 0.5
	60	15.1 ± 2.5	2.8 ± 0.5
$\text{H}_2\text{SO}_4 + 4 \text{ M NaCl}$	23	10.0 ± 1.5	1.9 ± 0.3
	5	3.3 ± 2.5	0.6 ± 0.5
D_2SO_4	25	4.4 ± 2.5	0.8 ± 0.5

sharper lines. The lines at 1050, 1100, and 1195 cm^{-1} (and the corresponding ones for D_2SO_4) are Lorentzian in their low-frequency wings and Gaussian in the high-frequency wings. The broad H_3O^+ line is Lorentzian throughout. The various lines are sufficiently well separated as not to require use of the full expression for exchange-broadened lines.

The molar extinction coefficients for SO_4^{2-} can be determined accurately from measurement of Na_2SO_4 solutions, and so the concentration of SO_4^{2-} can be obtained from the intensity of the 1100- cm^{-1} line. The rest of the concentrations then follow from the stoichiometric relations.

Each spectrum was analyzed by fitting to it, by computer, a synthetic spectrum consisting of the four lines mentioned. In this way both the intensities and the line widths could be determined. Some representative results are collected in Table I.

Concentrations of H_2SO_4 (D_2SO_4) up to 1.5 M, HCl up to 1.3 M, and Na_2SO_4 up to 1.2 M were used. A series of measurements in the presence of 4 M NaCl were also carried out. The bulk of the measurements were at 23 °C; however, measurements at 5, 10, 40, and 60 °C were also performed. D_2SO_4 experiments were, of course, performed in D_2O solutions.

As a check on reliability values of $Q_c = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-]$ are plotted in Figure 1 vs. nominal H_2SO_4 concentrations along with similar results obtained by Chen and Irish¹ using Raman spectroscopy. It is evident that the results from both sources agree well with one another.

(1) Chen, H.; Irish, D. E. *J. Phys. Chem.* 1971, 75, 2672.(2) Ikawa, S.; Yamada, M.; Kimura, M. *J. Raman Spectrosc.* 1977, 6, 89.

(3) Picosecond kinetics provide a mechanism which is responsible for line broadening as explained in some detail by MacPhail and Strauss (MacPhail, R. A.; Strauss, H. L. *J. Chem. Phys.* 1985, 82, 1156), who also summarize much of the relevant literature. Since other line-broadening mechanisms are also operative, care must be exercised in interpretation. Despite such difficulties, it has proved possible, in quite a number of instances, to derive useful kinetic information from line broadening (see, e.g.: Cohen, B.; Weiss, S. *J. Phys. Chem.* 1983, 87, 3606; 1984, 88, 3974). In the present case where relatively small changes in H^+ concentration cause noticeable broadening (whereas other species do not) and considering the overall consistency of the interpretation, invoking kinetic broadening appears to be justified.

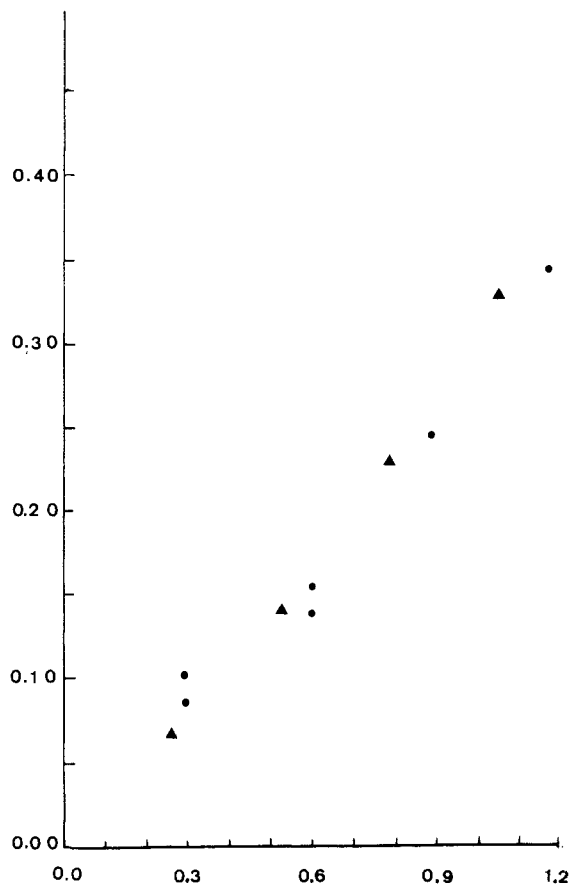


Figure 1. $Q_c = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-]$ vs. nominal H_2SO_4 concentration for H_2SO_4 solutions at 23 °C: ●, our results; ▲, Chen and Irish.

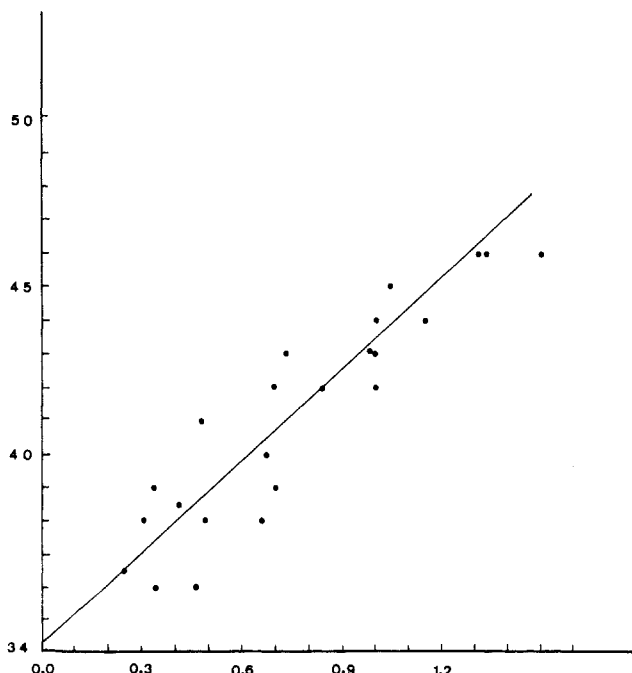


Figure 2. $\Delta\nu_{1/2}$ of SO_4^{2-} line at 1100 cm^{-1} vs. $[\text{H}^+]$ at 23 °C.

As observed by Chen and Irish and by Ikawa et al. in the Raman (in their case the line at 981 cm^{-1}), the 1100-cm^{-1} line attributed to SO_4^{2-} increases in width with $[\text{H}^+]$. This is shown in Figure 2 where $\Delta\nu_{1/2}$ ⁴ (half-width at half-height) is plotted vs. $[\text{H}^+]$ at 23 °C. We find that $\Delta\nu_{1/2}$ for the 1100-cm^{-1} line can

(4) Half-width at half-height is defined as $\frac{1}{2}[\nu_{1/2}(2) - \nu_{1/2}(1)]$, where $\nu_{1/2}(2)$ and $\nu_{1/2}(1)$ are the frequencies at half the peak maximum to both sides of the maximum. For a symmetrical peak, the half-width at half-height would be $\nu_0 - \nu_{1/2}$ where ν_0 is the frequency at the peak maximum.

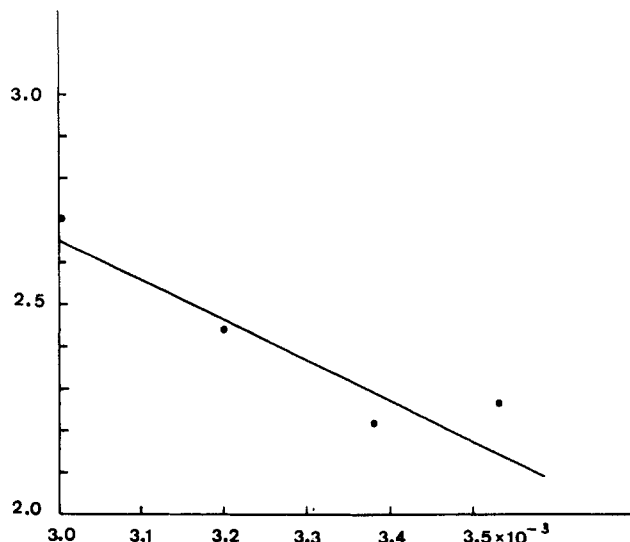


Figure 3. $\ln A$ ($A = \Delta\nu_{1/2}/\Delta[\text{H}^+]$ where $\Delta\nu_{1/2}$ pertains to the SO_4^{2-} line at 1100 cm^{-1}) vs. $1/T$.

be expressed as $34.2 + A[\text{H}^+]$ with A , as obtained from a least-squares fit, being $9.2 \pm 0.8\text{ cm}^{-1}/\text{M}$. The value of A in the presence of 4 M NaCl was $10.0 \pm 1.5\text{ cm}^{-1}/\text{M}$, which is not significantly different from the value in the absence of NaCl. A values at different temperatures are collected in Table II for both H_2SO_4 and D_2SO_4 . A plot of $\ln A$ vs. $1/T$ for H_2SO_4 is reproduced in Figure 3. It conforms reasonably well (considering experimental uncertainties) to a straight line. From the slope we obtain an activation energy of $1800 \pm 500\text{ cal/mol}$. The value obtained for D_2SO_4 , based on measurements at only two temperatures, is 2400 cal/mol , the uncertainty probably being similar to that found for H_2SO_4 . The difficulty in the D_2SO_4 case, limiting measurements to two temperatures only, was that DSO_4^- dissociates less than HSO_4^- (as evidenced by lower Q_c values) and dissociation, in both cases, decreases with temperature.⁵ Above room temperature D_2SO_4 solutions had either too little $[\text{D}^+]$ to provide sufficient broadening or too little $[\text{SO}_4^{2-}]$ for its line to be resolved.

As noted by Chen and Irish, the HSO_4^- lines also broaden somewhat with $[\text{H}^+]$. The effect, however, being rather small, it was not pursued.

Discussion

Addition of 4 M NaCl must affect the water structure. The fact that this has no effect, to within experimental error, on the rate of the $\text{H}_3\text{O}^+ + \text{SO}_4^{2-} \rightarrow \text{HSO}_4^- + \text{H}_2\text{O}$ reaction must be interpreted as implying that the proton is coming from near by and not from further away over hydrogen-bond bridges. On the other hand, it is known that addition of various salts does affect the $Q_c = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-]$ values.⁶ Thermodynamically

$$Q_c = K \frac{\gamma_{\text{HSO}_4^-}}{\gamma_{\text{H}^+} \gamma_{\text{SO}_4^{2-}}} a_{\text{H}_2\text{O}}$$

where K is the equilibrium constant, the γ 's are activity coefficients, and $a_{\text{H}_2\text{O}}$ is the activity of water. It would seem, in the light of the finding just mentioned, that the effect of salt addition on Q_c is through modification of the reverse reaction $\text{HSO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$ probably by changing $a_{\text{H}_2\text{O}}$.

In contrast to Chen and Irish, we find k_f for H to be larger than that for D by a factor of ~ 2 , a result more in keeping with what might be intuitively expected.

The activation energy of the reaction is somewhat higher for the D-substituted species, but the difference is of the order of the experimental uncertainty and so does not allow conclusions to be

(5) For recent results, see: Dawson, B. S. W.; Irish, D. E.; Toogood, G. *J. Phys. Chem.* **1986**, *90*, 334.

(6) Chen, H.; Irish, D. E. *J. Phys. Chem.* **1971**, *75*, 2681.

drawn. Both activation energies are of the order to be expected for ultrafast reactions.

From the measured broadening, rate constants can be calculated through the relation

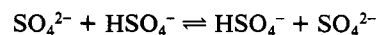
$$k_f = 2\pi cA$$

The rate constants are collected in Table I. It is seen that their magnitudes considerably exceed the diffusion-controlled limit. Such high rate constants are consistently found in picosecond kinetics⁷ and are explained by noting that the reactions dealt with do not involve diffusion but rather repeated dissociation and association of nearby species.

Our rate constant for H₂SO₄, $17 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ at 23 °C, is rather larger than the room-temperature rate constants obtained by Chen and Irish, $6.4 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, and by Ikawa et al., $4.5 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. This discrepancy does not seem to result from a systematic difference between Raman and IR results since the D₂SO₄ rate constant of Chen and Irish, $10.4 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, agrees with our 25 °C rate constant of $8 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ (being, if anything, larger than our value). We cannot, at present, offer an explanation of the disagreement beyond noting that in many cases our solutions differ in composition from those used by the previous

workers (containing, e.g., no K⁺ or NH₄⁺) and that intuition would favor $k_{\text{H}^+} > k_{\text{D}^+}$, as we do find. Further work on the influence of added ions is clearly indicated and we plan to carry it out.

Two other points which require comment are the following: The possibility of an alternative mechanism



for proton transfer must be considered. Our experimental reason for preferring proton exchange between sulfate ion and hydronium as the cause for line broadening, rather than exchange with bisulfate, is the lack of broadening of the lines of the latter.

Still another mechanism for apparent line broadening would be the partial lifting of degeneracy of the ν_3 triply degenerate band (which is the 1100-cm⁻¹ line) through interaction with neighbors. We consider this possibility unlikely in view of the fact that only H⁺ (or D⁺) is found to cause broadening and the overall consistency of the interpretation in terms of kinetic broadening.

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Registry No. H₃O⁺, 13968-08-6; D₃O⁺, 24847-51-6; SO₄²⁻, 14808-79-8.

(7) Cohen, B.; Weiss, S. *J. Phys. Chem.* 1984, 88, 3974.

Correlation of Alkyl and Polar Groups in the Gas-Phase Pyrolysis Kinetics of α -Substituted Ethyl Chlorides

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The kinetics of the gas-phase pyrolysis of several secondary chlorides were determined in a static system over the temperature range of 369.9–490.1 °C and the pressure range of 28–298 Torr. The reactions in seasoned vessels, with the free radical suppressor propene and/or toluene always present, are homogeneous and unimolecular and obey a first-order rate law. The observed rate coefficients are represented by the following Arrhenius equations: for 2-chloropropionitrile, $\log k_1 (\text{s}^{-1}) = (13.45 \pm 0.57) - (236.1 \pm 8.2) \text{ kJ mol}^{-1}$; for methyl 2-chloropropionate, $\log k_1 (\text{s}^{-1}) = (12.22 \pm 0.54) - (217.0 \pm 7.4) \text{ kJ mol}^{-1} (2.303RT)^{-1}$; for methyl 3-chlorobutyrate, $\log k_1 (\text{s}^{-1}) = (13.65 \pm 0.39) - (214.9 \pm 5.0) \text{ kJ mol}^{-1} (2.303RT)^{-1}$. The data of this work together with those reported in the literature confirm previous correlations that α -alkyl substituents of ethyl chloride give a good straight line, when $\log k/k_0$ vs. σ^* values ($\rho^* = -3.58 \pm 0.24$, correlation coefficient = 0.996, and intercept = -0.0066 at 360 °C) are plotted, while α -polar substituents give rise to an inflection point at $\sigma^*(\text{CH}_3) = 0.00$ into another straight line ($\rho^* = -0.46 \pm 0.06$, correlation coefficient = 0.972, and intercept = 0.017 at 360 °C). Several other polar α -substituents have been found to enhance the dehydrochlorination process by means of their electron delocalization or resonance effect. Revising a work reported on the pyrolysis kinetics of pinacolyl chloride, a Wagner–Meerwein rearrangement appears to be a reasonable explanation for the formation of about 12% of the 2,3-dimethylbutene products.

Introduction

The Taft correlation for the gas-phase pyrolysis of aliphatic primary² and tertiary³ chlorides were considered as additional evidence of Maccoll's theory⁴ on the polar nature of the transition state for alkyl halide pyrolyses in the gas phase. This conclusion was derived from the fact that if the transition state for the pyrolysis of these halides is represented by the elongation of the C–Cl bond and a subsequent polarization in the sense $\text{C}^{\delta+} \cdots \text{Cl}^{\delta-}$,

then the +I inductive electron release of alkyl substituents will tend to stabilize the partially charged carbon reaction center; thus enhancement of the reaction rates follows. In the case of substituents of –I, electron-withdrawing effect must reduce the elongation and the degree of polarization of the C–Cl bond, which is the rate-determining step of these reactions. Therefore, the elimination rates will be slower and the sequence very much in accord with their electronegative differences.

Prior to these investigations, a linear Taft correlation of alkyl groups and a very small population of polar substituent at the α -carbon of ethyl chloride pyrolyses were also described.⁵ The Taft plot for alkyl substituents gave a straight line of $\rho^* = -3.55$ at 360 °C and another slope at $\sigma^*(\text{CH}_3) = 0.00$ and for very few

(1) Taken from the thesis of Rosa M. Domínguez, submitted to the Faculty of IVIC, February 1986, in partial fulfillment of the requirements for the Degree of Magister Scientiarum.

(2) Chuchani, G.; Martín, I.; Rotinov, A.; Hernández A., J. A.; Reikonen, N. *J. Phys. Chem.* 1984, 88, 1563.

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