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Free Energy of Formation of Sulfur Trioxide in Aqueous Solution. Methods for Determining the Energy Level of an Unobservable Intermediate

J. Peter Guthrie[1]

Contribution from the Chemistry Department, University of Western Ontario, London, Ontario, Canada N6A 5B7. *Received January 21, 1980*

Abstract: The acid-catalyzed hydrolysis of monoaryl and monoalkyl sulfate monoanions and the uncatalyzed hydrolysis of monoaryl sulfate monoanions are generally believed to proceed via sulfur trioxide as a short-lived intermediate. SO_3 is very reactive toward water, and its free energy of formation in aqueous solution has not been known. The rate of disappearance of aryl sulfate monoanions is accelerated by amines, but the rate constants for amine catalysis are known to be essentially independent of amine pK_a. This suggests a model for the reaction in which the rate-determining step for hydrolysis is trapping by water of SO_3 in an "encounter complex" formed by S–O bond cleavage, and the rate-determining step for aminolysis is formation of a ternary "encounter complex" containing aryl oxide, amine, and SO_3 either by diffusion of amine into contact with a binary "encounter complex" or by solvolysis of a preassociation complex. Equilibrium constants for sulfate ester formation can be estimated starting from the linear free energy relationship for transesterification of a sultone reported by William et al. An analysis based upon this model leads to a value of $\log K_d = -17.1 \pm 2.2$ for the dehydration of undissociated sulfuric acid. For the acid-catalyzed hydrolysis of monoaryl and monoalkyl sulfate monoanions, we apply the simplest version of Marcus theory to a plot of $\log k$ vs. $\log K$ for the reaction involving neutral sulfate monoester giving neutral products, using pK_a values estimated as previously described. This treatment leads to a value of $\log K_d = -17.7 \pm 3.8$. The two sets of data lead to a consistent value for $\log K_d = -17 \pm 2$.

Introduction

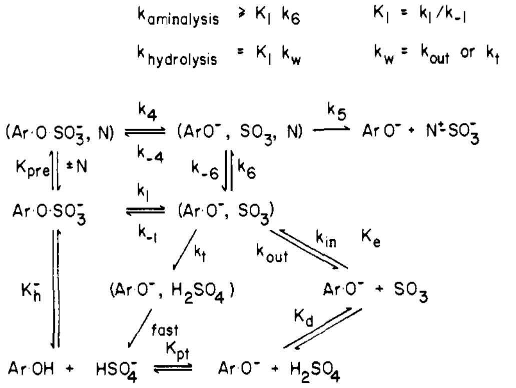
A recurring problem in physical organic chemistry is that of determining the free-energy level of a metastable intermediate which is formed in amounts which are too small to be detectable. We have been interested in several aspects of this problem for some time[2,3] and have recently presented a solution for a particular type of solvolytic intermediate, namely, monomeric metaphosphate ion.[4] We wish now to report that an analysis of the published kinetics, along with a new method based on an application of Marcus theory,[5,6] may be applied to those solvolysis reactions of sulfate monoesters which proceed by way of a transient SO_3 intermediate,[7] and leads to an evaluation of the equilibrium constant for the dehydration of sulfuric acid to give SO_3.

It has been shown in several studies[8,9] that the aminolysis of sulfate monoesters with very good leaving groups leads to the formation (at least in part) of sulfamates and results in substantial increases in the rate of disappearance of starting material, relative to the rate in the absence of amine, but that the rate constants for this nucleophilic catalysis are very insensitive to the nature of the amine.

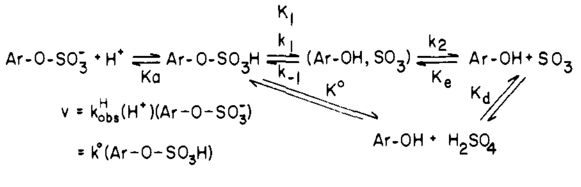
Results and Discussion

The present kinetic analysis is based upon the data found in Table I. The analysis is carried out in terms of Schemes I and II. Figure 1 shows a reaction coordinate diagram for sulfate monoester aminolysis. We use the convention that (A, B) are species within an encounter complex, whereas A + B are species which are separate and free in solution. The ternary complex (ArO^-, SO_3, R_2NH) could reasonably be expected to undergo very rapid reaction in either of two senses, to re-form starting material or form product. Either of these reactions is likely to be faster than the diffusion of the amine away from the complex. Although the amine will probably interact more strongly with SO_3 than will water, it seems unlikely that this will be a much stronger interaction. It necessarily follows, as is shown by Figure 1, that the path of lowest free energy of activation leading to the ternary complex must involve preassociation of amine and ester. This argument was first presented by Jencks in another context.[10]

Scheme I



Scheme II



Equilibrium Constants for Hydrolysis. Our analysis will require equilibrium constants for the sulfate monoester hydrolysis reactions. These equilibrium constants are not experimentally measurable at present, but we have found an indirect way to estimate them which seems reliable enough for the present task. Initially we will determine values for K_h^- (see Scheme I). The

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[1] Alfred P. Sloan Fellow, 1975–1979.
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[8] Benkovic, S. J.; Benkovic, P. A. *J. Am. Chem. Soc.* **1966**, *88*, 5504.
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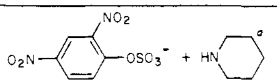
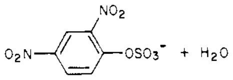
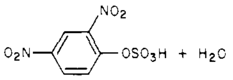
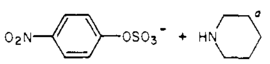
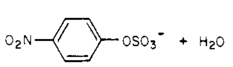
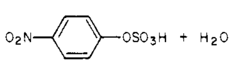
Table I. Rate Constants Used in This Paper. All in Aqueous Solution at 25 °C

reaction	log *k*
	-2.63^{b-d}
	-4.42^{e-g}
	$1.63^{e,g,h}$
	$-5.91^{b,i,j}$
	$-9.21^{b,j,k}$
	$0.25^{b,h,l}$
$C_6H_5OSO_3H + H_2O$	$-1.65^{b,h,l,m}$
$CH_3OSO_3H + H_2O$	$-4.66^{b,h,n,o}$

[a] Other amines have similar rate constants. [b] *k* in $M^{-1}\ s^{-1}$. [c] Rate constant measured at 39 °C and corrected to 25 °C assuming that $\Delta S^{\ddagger}$ is the same as for *p*-nitrophenyl sulfate plus piperidine, ref 8. [d] Reference 9. [e] *k* in s^{-1}. [f] Rate constant at 45 °C, corrected to 25 °C using the measured E_a. [g] Reference 22. [h] Calculated from the second-order rate constant for acid-catalyzed hydrolysis, using a pK_a value for the ester from Table III. [i] Rate constant for piperidine, measured at 35 °C and corrected to 25 °C using the measured $\Delta H^{\ddagger}$. [j] Reference 8. [k] Rate constant at 35 °C corrected to 25 °C using the measured $\Delta H^{\ddagger}$. [l] Reference 3. [m] Rate constant at 49 °C corrected to 25 °C using the measured E_a. [n] Rate constant at 65 °C, corrected to 25 °C using the measured E_a. [o] Reference 4.

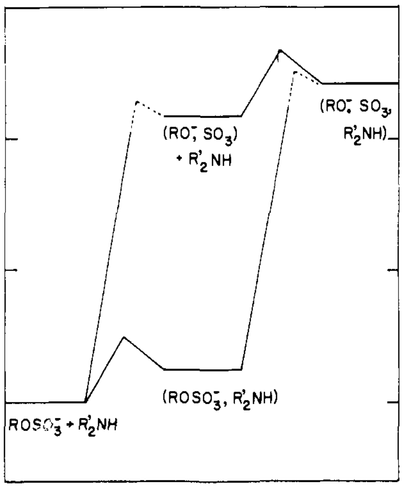


Figure 1. Reaction coordinate diagrams for the two possible paths leading to the ternary encounter complex (RO^-, SO_3, R'NH): solvolysis of $ROSO_3^-$ to a binary encounter complex followed by diffusion of the amine into contact with this binary complex, or preassociation of $ROSO_3^-$ and R'_2NH and solvolysis of this preassociation complex. If collapse of the ternary complex to the preassociation complex is faster than diffusion of the amine out of the ternary complex (as shown in the figure, although this is merely probable and not required a priori), then the lowest energy path to the ternary complex must be by the preassociation route (see ref 10).

Table II. Equilibrium Constants for Sulfate Ester Hydrolysis[a] in Aqueous Solution at 25 °C

ester	log $K^{\circ\ a,b}$	log $K^{-\ b,c}$
DNPOSO$_3$H[d]	13.86 (3.12)	11.00 (3.21)
pNPOSO$_3$H[e]	11.30 (2.51)	9.24 (2.60)
PhOSO$_3$H	8.92 (2.01)	
CH$_3$OSO$_3$H	4.19 (1.50)	

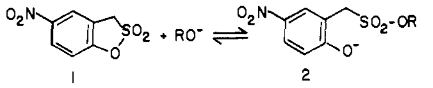
[a] $K^\circ = [ROH][H_2SO_4]/[ROSO_3H]$. [b] Values in parentheses are uncertainties, estimated by error analysis. [c] $K^- = [ROH] \times [HSO_4^-]/[ROSO_3^-]$. [d] DNP is 2,4-dinitrophenyl. [e] pNP is *p*-nitrophenyl.

Table III. pK_a Values for Sulfate Monoesters

	pK_a[a]		pK_a[a]
H$_2$SO$_4$	-2.96^b	pNPOSO$_3$H	-4.86^c
CH$_3$OSO$_3$H	-3.54^b	DNPOSO$_3$H	-5.66^c
PhOSO$_3$H	-3.88^c		

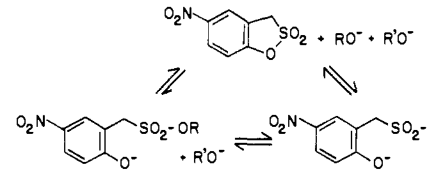
[a] For dilute aqueous solutions at 25 °C. [b] Reference 12. [c] Calculated assuming that ΔpK_a relative to H_2SO_4 will be the same as ΔpK_a for $ROPO_3H^-$ relative to $H_2PO_4^-$, with suitable symmetry corrections, using the pK_a values collected in ref 4.

most closely analogous set of equilibrium constants which have been measured is for the reaction of sultone **1** with phenoxides.

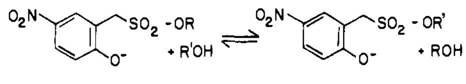


1 2

This system has been thoroughly studied by Williams et al.[11] Since the correlation which they found for k_f for a series of phenols (log k_f linear in pK_a^{phenol}) also fitted the point for CF_3CH_2OH, it seems reasonable to assume that it will hold for other alcohols, as will their correlation for log K_{eq}. From the latter we may derive an equation for the equilibrium constants for transesterification.



If William's equation, log $K_{eq} = -12.92 \pm 2.16 + (1.85 \pm 0.24)pK_a^{ROH}$, holds for both RO^- and $R'O^-$, then clearly the equilibrium constant for transesterification, K_{te}^-, is given by log $K_{te}^- = 1.85 \pm 0.24(\text{p}K_a^{R'OH^-} - \text{p}K_a^{ROH})$. It is then straightforward to derive the expression for the equilibrium constant, K_{tc}°, for the neutral transesterification, as log $K_{tc}^\circ = 0.85 \pm 0.24(\text{p}K_a^{R'OH} - \text{p}K_a^{ROH})$. If one ester hydrolysis equilibrium constant is known,



then any other hydrolysis equilibrium constant may be calculated by a simple thermodynamic cycle.

$$\begin{tikzcd}
 & X\text{-}SO_2\text{-}OH + ROH + R'OH \arrow[dl, shift left, harpoon] \arrow[dr, shift left, harpoon] & \\
X\text{-}SO_2\text{-}OR + R'OH \arrow[ur, shift left, harpoon] \arrow[rr, shift left, harpoon] & & X\text{-}SO_2\text{-}OR' + ROH \arrow[ll, shift left, harpoon] \arrow[ul, shift left, harpoon]
\end{tikzcd}$$

In order to complete the analysis and calculate equilibrium constants for sulfate ester hydrolysis it is necessary to make two assumptions: (1) that the linear free energy relations discussed above hold for methanol as well; (2) that the equilibrium constant for an esterification involving sulfuric acid will be equal to the equilibrium constant for the analogous esterification involving the sulfonic acid **2** (R = H). The first assumption appears reasonable in view of the considerable range of phenols studied and the fact that trifluoroethanol fitted the same equation. The second assumption is justified by the recent findings[12] that equilibrium constants for hydrolysis of esters of inorganic acids such as sulfuric acid are only slightly sensitive to the pK_a of the acid. Since the sulfonic acid and sulfuric acid should have rather similar pK_a values, this assumption seems satisfactory.

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(11) Deacon, T.; Farrar, C. R.; Sikkel, B. J.; Williams, A. *J. Am. Chem. Soc.* **1978**, *100*, 2525.

(12) Guthrie, J. P. *Can. J. Chem.* **1978**, *56*, 2342.

Since the equilibrium constant for the hydrolysis of monomethyl sulfate is known,[12] the equilibrium constants for hydrolysis of the other esters may now be calculated. The values so derived are given in Table II.

From the equilibrium constants for neutral ester formation and pK_a values for sulfuric acid and the aryl sulfate monoesters from Table III it is straightforward to derive the equilibrium constants for formation of the anionic esters from the phenols and bisulfate ion.

Kinetics of Monoester Monoanion Hydrolysis and Aminolysis. The observation that rate constants for aminolysis of aryl sulfates are very insensitive to amine pK_a[8,9] implies that N–S bond formation is not important in the rate-determining step for aminolysis. On the other hand, aminolysis leads to significant rate enhancements; therefore, there must be a change in the rate-determining step, so that the rate-determining step for the aminolysis is the capture of the SO_3 formed by unimolecular breakdown of the ester monoanion, while the rate-determining step in the hydrolysis of the ester monoanion would then be the diffusion step in which SO_3 escapes from the phenoxide leaving group.

Since SO_3 is expected to be very reactive toward even weak nucleophiles such as solvent water, it is virtually certain that free SO_3 would be trapped by solvent before it had time to encounter a nonsolvent nucleophile, and certainly before it had time to encounter the leaving group and re-form starting material. If the amine is to produce a rate enhancement, it must capture the SO_3 while it is still in the initially formed "encounter complex" with the phenoxide. Since a reaction of a strong nucleophile with a strong electrophile is expected to be very fast, it is reasonable to ascribe the very low sensitivity of the rates of nucleophile trapping to the essentially diffusion-controlled nature of this trapping.

The rate-determining step for aminolysis is then either the actual trapping step, involving N–S bond formation, or diffusion together of the amine and the encounter complex of SO_3 and the phenoxide leaving group, or O–S bond cleavage in a preassociation complex of the monoester monoanion and the amine. As was argued above the first possibility seems unlikely. If trapping of SO_3 by aryl oxide is fast relative to diffusion away of amine from the ternary encounter complex, then the second possibility is ruled out: this appears probable but not certain. Diffusion of amine away from the ternary complex is likely to be close to the limiting rate for separation of species with no favorable interaction, since the amine is unlikely to interact strongly with SO_3 unless it forms a full covalent bond. If this is so, then there is only a small range of values available for the trapping of SO_3 by aryl oxide, if in fact this is faster than diffusion away of amine, since the rate constant for diffusional separation is 10^{11} s^{-1}, and the upper limit for a rate constant is 10^{13} s^{-1}. Thus, even if the preassociation mechanism obtains, the rate of aminolysis cannot be much faster than the rate of diffusion together of amine and the binary encounter complex of SO_3 and aryl oxide. The rate constant for the diffusion step may be estimated as $10^{9\pm1}$ M^{-1} s^{-1} (vide infra). This allows us to estimate an absolute lower limit on K_1, the equilibrium constant for the initial bond-cleavage step.

If the rate-determining step for aminolysis were diffusion of amine into contact with the binary encounter complex, then K_1 could be calculated from $k_{\text{aminolysis}} = k_{\text{diff}}K_1$, and from this k_w could be calculated using $k_{\text{hydrolysis}} = k_wK_1$. If in addition k_w represented diffusional escape of SO_3 from the encounter complex, then a complete solution to the problem would be possible. Unfortunately there is no way to tell whether k_w represents diffusional escape or trapping of SO_3 in the encounter complex by surrounding water.

It is, however, possible to impose a limit on the equilibrium constant for dehydration of H_2SO_4, as follows. Whatever the actual mechanism for the k_w step, the observed rate of uncatalyzed hydrolysis represents a lower limit on the free energy of activation for the diffusional escape path. The rate constant for diffusion together would be expected to be the normal value except that only part of the surface of the SO_3 is important. We will use a value based upon a suggestion by Hine[13] that the equilibrium constant for formation of an encounter complex where there is neither attraction or repulsion is 0.017 M^{-1}; this corresponds to having the nucleophile in either of two spherical regions of radius 1.5 Å on either side of the electrophile. (This distance is the van der Waals radius of oxgyen; sulfur is normally considered to be larger, but for S^{VI} this may not be correct; in the absence of better information we will use the same value.) For this contact distance the rate constant for diffusion apart is 10^{11} s^{-1} by the Eigen equation,[14] and the rate constant for diffusion together is then $10^{9.2}$ M^{-1} s^{-1}.

If we know k_e and $K_h^-K_{pt}$, and can place a limit on K_1k_{out}, we can place a limit on K_d. Values for K_{pt} can be calculated from the pK_as for the phenol and sulfuric acid.[12] Provided that the mechanism does indeed involve an SO_3 intermediate, this analysis enables us to place an absolute upper limit on the equilibrium constant K_d. Since $K_d = K_1/K_{pt}K_h^-K_e$ and $K_e = k_{in}/k_{out}$, if $k_{\text{hydrolysis}} \geq K_1k_{out}$, and k_{in} is the normal value for diffusion, $k_{\text{diffusion}}$, then $K_d \leq k_{\text{hydrolysis}}/K_{pt}K_h^-k_{\text{diffusion}}$. The value so obtained is log $K_d \leq -17.7$ for either the *p*-nitrophenyl or the 2,4-dinitrophenyl ester. However, it must be borne in mind that there are substantial uncertainties in K_h^-. Analysis of the propagation of errors[15] through the calculation of K_h^- leads to an estimated uncertainty of 2.7 log units in log K_h^- for the *p*-nitrophenyl ester and 3.3 log units for the dinitrophenyl ester. This means that the absolute upper limit on K_d is log $K_d < -14.9$.

The exchange of ^{18}O into H_2SO_4 in water has been studied;[16] the mechanism is believed to involve formation of neutral H_2SO_4 which then loses water to give SO_3. The rate of reaction depends upon the concentrations of H^+ and HSO_4^-. Following ref 16 we plot log (rate of exchange) vs. log $[HSO_4^-] - H_0$ and obtain a straight line, which can be extrapolated to log $[HSO_4^-] - H_0 = 0.0$, i.e., $[HSO_4^-] = [H^+] = 1.0$ M in ideal aqueous solution, and so determine the apparent second-order rate constant for the exchange in water; the value so obtained is log $k_2 = -9.43$. From the pK_a of H_2SO_4 (Table III) we can calculate the rate constant for loss of water from neutral sulfuric acid. Since SO_3, if it is an intermediate, must be more stable than the transition state for the exchange, this allows us to calculate an absolute lower limit for K_d, which must be greater than $10^{-19.26}$.

Combining the two limits gives a value for the equilibrium constant of $-19.3 \leq \log K_d \leq -14.9$ or $\log K_d = -17.1 \pm 2.2$. The uncertainty is in considerable measure due to the uncertainties in the estimates of K_h. Interestingly enough, if one were to assume that the rate-determining step in the aminolysis was diffusion of the amine into contact with the encounter complex, and that the rate-determining step in the hydrolysis was diffusional escape of SO_3 from the encounter complex, almost the same value of K_d would be obtained. Clearly the major limitation on our knowledge of the energetics of SO_3 comes from the imperfect knowledge of the hydrolysis equilibria.

For the "acid-catalyzed" reactions of sulfate monoester monoanions a different analysis is needed since there is no convenient indicator to tell us what the rate-determining step is; clearly the use of amine catalysis is precluded! We therefore examined the application of Marcus theory.[5,6] In its simplest form, this theory predicts a relationship between rate constants and equilibrium constants for a single microscopic chemical step; for such a step the Marcus equation may be written[17] as

$$\log k = \log (k_BT/h) - b(1 - \log K/4b)^2 \tag{1}$$

$$XSO_3H \rightleftharpoons XH + H_2SO_4 \tag{2}$$

The equilibrium constants for reaction 2 can be calculated from known quantities, but this process actually involves several steps: solvolysis of the neutral ester to give SO_3 in an encounter complex, followed by either diffusional escape of SO_3 or trapping by a water

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(13) Hine, J. *J. Am. Chem. Soc.* **1971**, *93*, 3701.

(14) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(15) Bevington, P. R. "Data Reduction and Error Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969.

(16) Hoering, T. C.; Kennedy, J. W. *J. Am. Chem. Soc.* **1957**, *79*, 56.

(17) This equation is equivalent to eq 1 in ref 6, but has been transformed[13] from $\Delta G^{\ddagger}$ and ΔG° to log k and log K using transition-state theory.

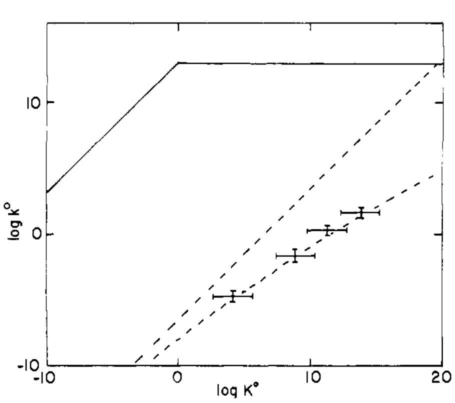

Figure 2. Marcus plot for the "acid-catalyzed" reaction of sulfate monoester monoanion. k^0 and K^0 are calculated for the reaction of the neutral ester using the pK_a values from Table III. The curve was determined by fitting the data to eq 3 by the method of least squares, with b and log (K_dK_e) as adjustable parameters.

molecule of the solvent cage. Diffusional escape or trapping by solvent water should be insensitive to the nature of the leaving group, particularly when this is a neutral phenol, which should interact rather weakly with SO_3. Thus we expect that, if reaction of SO_3 formed in a preequilibrium were rate limiting, we would have $k_{obsd} = k_wK_1$, with k_w essentially constant. Since $K^\circ = K_1/K_eK_d$, and both K_e and K_d should be the same for all esters, the only variation in either k_{obsd} or K° is in K_1, and therefore a plot of log k_{obsd} vs. log K° would be linear with slope = 1.0. On the other hand, if the formation of SO_3 were rate determining, then the rate constant for this process should be sensitive to the nature of the leaving group, and there will be a relationship between log k_{obsd} and log K° which will not have unit slope, and would show curvature (in accordance with the Marcus equation) if the data covered a wide enough range of K°. In fact (see Figure 2), the data follow the second pattern, and we conclude that S–O bond breaking is rate determining. If we apply the steady-state approximation to the process shown in Scheme II, we obtain the equation

$$k^\circ = k_1k_2/(k_{-1} + k_2)$$

$$\log k_1 = \log (k_BT/h) - b(1 - \log K_1/4b)^2 \qquad (3)$$

$$\log K_1 = \log K^\circ + \log (K_dK_e)$$

which relates the observed rate constant for the "acid-catalyzed" reaction corrected to be in terms of the neutral ester to the equilibrium constant for the formation of leaving group and free SO_3 from the ester. This differs from the equilibrium constant which can be calculated as described above by the product of the equilibrium constants for dissociation of the encounter complex and hydration of SO_3 to give H_2SO_4. k_2 in eq 3 may be assumed to be the usual value for diffusion apart of species from an encounter complex, with no important stabilization or destabilization, i.e., 10^{11} s^{-1}. This is equivalent to assuming that solvation of SO_3 by water and a phenol or alcohol is equivalent. Although this will not be exactly correct, particularly for the more acidic phenols, the solvation will always be less favorable than or equivalent to solvation by water. This is in marked contrast to the situation with a phenoxide leaving group, where solvation is expected to be much better than by water. The data, in the form of paired values of log k°, and log K° can now be fitted to eq 3 with two adjustable parameters, namely, b and log (K_dK_e).

When the data for the acid-catalyzed reactions are fitted to eq 3, the results are $b = 8.4 \pm 3.2$ and log $(K_dK_e) = -19.3 \pm 3.8$; see Figure 2. The observation of a slope of intermediate value, neither zero nor one, strongly supports the assumption that bond breaking is rate limiting. For the aryl sulfate monoanions a similar plot (involving only two points) has unit slope, consistent with the assumption that bond breaking is far advanced in the transition state.

As was discussed above we will assume that the phenol or alcohol leaving group and water are equivalent in solvating power, and use the value which Hine proposed[13] for K_e for the case where there is neither attraction nor repulsion, i.e., $K_e = 0.017$ M^{-1}. This assumption leads to a value of log $K_d = -17.7 \pm 3.8$.

It has been suggested[18] that the reaction of the neutral monoester (the "acid-catalyzed" reaction) might involve decomposition of the zwitterion, rather than reaction of the neutral species itself. The latter implies some form of concerted proton transfer accompanying the S–O bond cleavage. The zwitterion mechanism looks improbable if one estimates the pK_a for loss of a proton from the zwitterion, which can be done as follows. The starting point is protonated phenol, for which a pK_a of −6.7 has been proposed;[19] if the effect of two nitro groups is similar to that for phenol or anilinium ion (in either case about 3 log units per nitro group in the ortho or para position[25]), then the pK_a of protonated dinitrophenol would be about −12.7; the effect of replacing one of the hydrogens on the positive oxygen by SO_3^- can be estimated from the pK_a difference between sulfamic acid (pK_a = 1.0[25]) and ammonium ion (pK_a = 9.6[25]) as ΔpK_a of 8.6; this leads to a pK_a for the zwitterion from dinitrophenol sulfate of −20.9, and a rate constant for the decomposition of the zwitterion, $k_{zwitt} = k^\circ K_a^{zwitt}/K_a^{ester} = 10^{1.63} \times 10^{20.9}/10^{5.66} = 10^{16.9}$. Even allowing for the gross uncertainties inherent in this sort of pK_a estimation, this rate constant seems impossibly high, and so we reject the zwitterion mechanism.

The different analyses of the available kinetics data for the reactions of sulfate monoesters lead to the conclusion that log $K_d = -17 \pm 2$. The errors are deplorably large, but in the absence of some new method for determining equilibrium constants for sulfate ester formation, or a massive program to determine heats of combustion, it is hard to see how the limits can be made smaller in the near future. The value which we report is at least much more precise than the qualitative judgment that the equilibrium was very unfavorable, which was all that was possible before the present investigation. Although both of the methods which we have employed have weaknesses and theoretical deficiencies, the fact that two independent methods lead to answers in good agreement lends some confidence to the result.

Thermodynamics of Aqueous Sulfur Trioxide. From the equilibrium constant for dehydration of sulfuric acid and the known free energies of formation of aqueous, undissociated H_2SO_4 (−176.1 kcal/mol[12]) and H_2O (−56.69 kcal/mol[20]) one can calculate the free energy of formation of aqueous SO_3 as −96 ± 3 kcal/mol (standard state, 1 M aqueous solution). From the free energy of formation of gaseous SO_3 (−88.52 kcal/mol[20]) (standard state, gas at 1 atm) we can calculate the free energy of transfer from gas to aqueous solution as −8 kcal/mol. This is a very favorable value when compared to SO_2 (+0.14 kcal/mol[21]) or CO_2 (+1.95 kcal/mol, calculated from data in ref 20). A plausible explanation derives from the large formal charge (2+) on the central sulfur in SO_3; this should interact strongly with the dipole in H_2O in a way which is less important for SO_2 (formal charge on sulfur of 1+) and unimportant for CO_2.

Calculations

Calculations for this paper were carried out on a XITAN microcomputer using programs written in BASIC.

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