The concordance, with the exception of H_2 ion, is rather good, considering the determinations were made on three different mass spectrometers, manufactured by different companies. The wide differences in hydrogen mass 2 peak heights are undoubtedly due mainly to thermal decomposition in the source region, where there existed different structures, temperatures and differential pumping rates out of the source region, in the case of the three different types of mass spectrometer.

The use of the monoisotopic material enables the origin of the small peak at mass 11.5 to be identified unambiguously. This peak was noted by both Hipple[1] and Dibeler and Mohler.[2] The constitution of peak 23 is presented in the following Table VI. The figures are relative to the dominant peak = 100 in each spectrum.

TABLE VI

CONSTITUTION OF PEAK 23

Ion	Normal B_2H_6	96% $B_2^{10}H_6$
$B_2{}^{11}H$	4.8	0
$B^{11}B^{10}H_2$	31.4	4.7
$B_2^{10}H_3$	1.4	23.9
Peak 23 height	37.6	28.6
Peak 11.5 height	0.66	0.075
Ratio 11.5 peak to $B^{11}B^{10}H_2$ ion contribution	0.021	0.017

It will be seen that peak 11.5 is proportional to the $B^{11}B^{10}H_2$ ion only. Hence, doubly ionized $B^{11}B^{10}H_2$ ion of mass 23 is responsible for this peak. The appearance potential of peak 11.5 was measured as approximately 23 volts (argon calibration), whereas the appearance potential for the singly ionized peaks was about 15 volts. Very small peaks of double ionization also were found at masses 12.5 and 13.5.

Summary

The mass spectrum of the monoisotopic molecule $B_2^{10}H_6$ was determined. This was compared with the calculated monoisotopic spectrum from measurements on B_2H_6 of normal isotopic boron ratio.

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The Kinetics of the Acid-Catalyzed Hydrolysis of Amine Disulfonate Ion; The Third Ionization Constant of Amine Disulfonic Acid[1]

BY GEORGE J. DOYLE[2] AND NORMAN DAVIDSON

Amine disulfonate ion (imidodisulfonate ion) is known to hydrolyze irreversibly and quantitatively in dilute acid at a measurable rate according to the equation[3,4,5]

$$HN(SO_3)_2^- + H_2O \xrightarrow{H^+} HSO_4^- + H_2NSO_3^- \quad (1)$$

Wagner[6] in the course of his study of the kinetics of the hydrolytic decomposition of the sulfur–nitrogen acids did one experiment on the hydrolysis of amine disulfonate in dilute hydrochloric acid solution. On the basis of this meager evidence he concluded that the rate of hydrolysis is proportional to the product of the concentrations of hydrogen ion and amine disulfonate ion, and is therefore autocatalytic. Sisler and Audrieth[4] have presented valuable data on the hydrolysis of amine disulfonate and on the two-step hydrolysis of amine trisulfonate ion (nitrilo-sulfonate ion) to amine disulfonate and thence to amine monosulfonate ion (sulfamate ion) at several temperatures. This data is not, however, extensive enough for a kinetic analysis. Because of the lack of quantitative data, we have investigated more thoroughly the kinetics of reaction (1).

Materials.—The distilled water, standard base (0.02 *N* sodium hydroxide) and standard acid (0.02 *N* hydrochloric acid) were prepared and stored so as to be free of carbonate or carbon dioxide. A solution of sodium chloride used to adjust ionic strength was prepared from the C. P. salt which was dried four hours at 200°.[7] A solution of sodium sulfate used as a source of sulfate ion was prepared from the C. P. anhydrous salt which was ignited one and one-half hours at 700–800°.[8]

Potassium amine disulfonate was prepared by hydrolysis of potassium amine trisulfonate

$$N(SO_3)_3^{=} + H_2O \xrightarrow{H^+} HN(SO_3)_2^- + HSO_4^- \quad (2)$$

This in turn was prepared by reaction of a large excess of potassium bisulfite with potassium nitrite in hot aqueous solution (Sisler and Audrieth's modification[4,9] of Claus and Koch's[10] method)

$$NO_2^- + 3HSO_3^- \longrightarrow N(SO_3)_3^{=} + H_2O + OH^- \quad (3)$$

A preparation on a scale of about ten times greater than that used by Sisler and Audrieth gave a yield of potassium amine disulfonate, washed free of sulfate, of 64% based on potassium nitrite; Sisler and Audrieth report 51%. The

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(1) A more detailed account of this research is contained in the thesis by George J. Doyle, submitted in partial fulfillment of the requirements for the degree of Master of Science at the California Institute of Technology.

(2) Present address: Department of Chemistry, University of Indiana, Bloomington, Indiana.

(3) Raschig, *Ann.*, **241**, 161 (1887).

(4) Sisler and Audrieth, THIS JOURNAL, **60**, 1947 (1938).

(5) Audrieth, Sveda, Sisler and Butler, *Chem. Rev.*, **26**, 49 (1940).

(6) Wagner, *Z. physik. Chem.*, **19**, 678 (1896).

(7) Sorensen, *Z. anal. Chem.*, **44**, 149 (1905).

(8) Remy and Siegmund, *ibid.*, **93**, 321 (1933).

(9) "Inorganic Syntheses," McGraw-Hill Book Co., New York N. Y., 1946, Vol. II, p. 182.

(10) Claus and Koch, *Ann.*, **152**, 336 (1869).

improvement in the yield is presumably due to the larger scale of operations. A slight modification of the procedure of these authors that was introduced was to wash the trisulfonate prior to hydrolysis with chilled, dilute ammonia (1:100) instead of water.

The salt was analyzed for sulfur, nitrogen and material not volatile on ignition with sulfuric acid (taken as potassium sulfate[8]). The analysis for nitrogen was done by a semi-micro Kjeldahl procedure according to E. C. Wagner,[11] using an apparatus of the type devised by Redemann.[12] Sulfur was determined as barium sulfate after hydrolysis and oxidation of the disulfonate with nitric acid containing a little hydrochloric acid as a catalyst.[13] To avoid coprecipitation of nitrate by barium sulfate, excess nitric acid was removed by repeated evaporation with hydrochloric acid. The results of the analysis, shown in Table I, indicate a purity of 97.6–98.5%.

Table I

Analysis of Potassium Amine Disulfonate

K		N		S	
Found	Calcd.	Found	Calcd.	Found	Calcd.
30.43	30.87	5.55	5.53	24.74	25.31
30.38		5.50		24.75	
		5.44			

Another method of analysis was used to check the extent of deterioration, if any, with time. A weighed sample of the salt was dissolved in dilute base in order to neutralize any possible acid impurity and thus prevent premature hydrolysis. The solution was then adjusted to the equivalence point by adding acid. A known excess of acid was added and the disulfonate hydrolyzed completely by heating to 85–95° for an hour, and then titrated with standard base. The hydrolysis of sulfamic acid if it occurs to any extent during the heating will not affect the titer of the solutions. This analytical method indicated a purity of greater than 99% and showed no decomposition of the disulfonate, stored in a vacuum desiccator over anhydrous calcium sulfate, in a period of five months.

The Third Ionization Constant of Amine Disulfonic Acid.—A determination of the equilibrium constant for the reaction

$$HN(SO_3)_2^- \rightleftarrows H^+ + N(SO_3)_2^= \qquad (4)$$

is in itself desirable and was necessary in order to select a suitable indicator for the acid titrations in the rate measurements. That the equilibrium constant for the reaction is not negligibly small is suggested by the fact that salts like $K_3N(SO_3)_2$ have been prepared.[5]

The value of the ionization function (classical ionization constant)

$$k_a = [H^+][N(SO_3)_2^=]/[HN(SO_3)_2^-] \qquad (a)$$

with concentrations expressed in volume molal units, was determined at an ionic strength of 1.00 and 25° by measuring with an electronic (Beckman) pH meter and a glass electrode the pH's of dilute buffer solutions made by partially neutralizing the imide hydrogen of the disulfonate ion with sodium hydroxide and adjusting the ionic strength to 1.00 with sodium chloride. The pH's of dilute hydrochloric acid solutions adjusted to an ionic strength of 1.00 were also measured. In the latter solutions, the hydrogen ion concentration was taken equal to the stoichiometric concentration of hydrochloric acid, and the activity coefficient of hydrogen ion was taken to be the same as in the buffer solutions. The concentrations of hydrogen ion in the buffer solutions are then readily calculated and from this the value of the function (a).

In order to obtain some check on the method, the value of the ionization function $[H^+][HPO_4^=]/[H_2PO_4^-]$ was determined by the same method at ionic strengths of 1.00 and 0.15. The results of these measurements are contained in Table II. An average value of the ionization function for the disulfonate ion is about 3.2×10^{-9} at $\mu = 1$.

Table II

Ionization Functions at 25°

F		*M*				
Anion	NaOH	HCl	NaCl	pH	H^+, *M*	Ionization function $\times 10^{+9}$, moles/liter
Amine Disulfonate Ion: Ionic Strength,[14] 1.00						
0	0	0.01123	0.989	1.82	0.01123	
0	0	0.001123	.999	2.83	0.001123	
0.0200	0.00999		.910	8.39	3.02×10^{-9}	3.0
.0200	$.00499_5$		.925	7.91	$9.11 \times$	3.0
.0200	.01498		.892	8.82	$1.12 \times$	3.4
.0100	$.00499_5$		.955	8.34	$3.38 \times$	3.4
.0100	$.00199_8$		.964	7.78	$12.3 \times$	3.1
.0100	.00699		.949	8.68	$1.55 \times$	3.6
Dihydrogen Phosphate Ion: Ionic Strength,[14] 1.00						
0.0200	0.00999		0.960	6.20	4.67×10^{-7}	467
.0100	$.00499_5$		.980	6.20	$4.67 \times$	467
Dihydrogen Phosphate Ion: Ionic Strength,[14] 0.150						
0	0	0.001123	0.149	2.98	0.001123	
.0200	0.00999		.110	6.71	2.09×10^{-7}	210
.0100	$.00499_5$		.130	6.68	$2.24 \times$	220

In order to compare the observed values of the ionization function for the $H_2PO_4^-$ ion with the thermodynamic ionization constant we have used the approximate equation

$$\log f_i = -\frac{A z_i^2 \mu^{1/2}}{1 + \mu^{1/2}} + \beta_i \mu \qquad (b)$$

In this relation: f_i = activity coefficient of i^{th} ion; A = Debye–Hückel coefficient; z_i = electronic charge of i^{th} ion; μ = "ionic strength" = $1/2 \, \Sigma c_i z_i^2$ where c_i's are in volume molal units[14]; β_i = a constant characteristic of the i^{th} ion and of the medium.

Application of equation (b) to the results for the ionization functions of the $H_2PO_4^-$ ion leads to a value of 6.1×10^{-8} for the ionization constant of the $H_2PO_4^-$ ion, in excellent agreement with the value of 6.226×10^{-8} determined by Nims.[15] Probably equation (b) is not very accurate for ionic strengths as high as 1.0. Therefore, this excellent agreement suggests merely that the method of measurement can be used to obtain values of ionization functions that can be extrapolated to an

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(11) Wagner, *Ind. Eng. Chem., Anal. Ed.*, **12**, 771 (1940).

(12) Redemann, *ibid.*, **11**, 635 (1939).

(13) Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938).

(14) In this article, all concentrations are expressed in volume molal units. The "ionic strength," μ, is therefore not strictly that originally defined by Lewis and Randall (This Journal, **43**, 1140 (1911)) using concentrations in weight-molalities, but is one-half the "ional concentration," Γ, used by Harned and Owen (Ref. 19, p. 33)

(15) Nims, This Journal, **55**, 1946 (1933)

ionic strength of zero with some accuracy but it does not prove that the measured ionization functions at ionic strength 1.0 are reliable.

Rate Determination Procedure.—The reaction (1) was followed by titrating samples of the reaction mixture for total strong acid. It may be calculated from the value of the ionization function for the disulfonate ion that an indicator changing in the *p*H range of 5.0–6.0 is desirable for the titration of bisulfate ion in the presence of disulfonate ion. Brom cresol green-methyl red mixed indicator (end-point 5.1) was used.

A reaction mixture was prepared by rapidly dissolving a known quantity of solid disulfonate in a thermostated solution of the other components in a 250-ml. volumetric flask, adding a small amount of water to adjust the volume and agitating again. The solution was then emptied into a 500-ml. glass-stoppered Erlenmeyer flask immersed in the thermostat. Two 10-ml. samples were taken with calibrated pipets and analyzed to determine the initial hydrogen ion concentration. In some runs, two final samples were hydrolyzed completely by heating to 80–90° for one hour, as a check on the disulfonate concentration. For the rate measurements at 25°, the samples were rapidly titrated with 0.02 *N* base. For the reactions at higher temperature, where the rate of hydrolysis was greater, the samples were run into excess base and back titrated with acid.

Initial Rate Studies at 25.00° at an Ionic Strength of 1.00.—To establish the kinetics of the reaction, a series of experiments was done with the ionic strength[14] fixed at 1.00. An ionic strength of about this magnitude is recommended to minimize the variations due to the salt effect on the rate of an ionic reaction.[16,17]

To establish tentatively the rate law, the average initial rates over the first 10% of hydrolysis for several series of experiments were obtained from graphically smoothed values of the reaction variable (amount of acid produced by the hydrolysis at time $t = x$) and the dependence of initial rates on initial concentrations of reactants determined. The dependence of initial rate on initial hydrochloric acid concentration for two initial disulfonate concentrations (0.0500 and 0.0200 *F*) is shown in Fig. 1. The dependence of initial rate on initial disulfonate concentration for two initial hydrochloric acid concentrations (0.099 and 0.0593 *F*) is exhibited in Fig. 2.

These results suggest the rate equation

$$-d[HN(SO_3)_2^-]/dt = k[H^+][HN(SO_3)_2^-] \quad (c)$$

In an experiment for 34,000 min. at a *p*H of 8 in which $[HN(SO_3)_2^=] = 0.045\ M$ and $[N(SO_3)_2^{\equiv}] = 0.005\ M$, the observed change in titer of the solution corresponded to hydrolysis of 0.2% of the disulfonate and a calculated average rate of 3×10^{-9} mole/liter × minute. There was therefore no significant uncatalyzed hydrolysis in the experiments at moderate acidities.

In order to establish whether the hydrolysis of disulfonate is specifically catalyzed by hydronium ion (H_3O^+), or is also catalyzed by other acids, in particular by the bisulfate ion formed during the reaction, a series of experiments was performed (at 25.00° and $\mu = 1.00$) at constant initial disulfonate concentration and constant initial hydrochloric acid formality, but with varying initial amounts of added sulfate. In the hydronium ion concentration range with which we are concerned the disulfonate ion is not appreciably converted to $N(SO_3)_2^{\equiv}$. We assume further that it is not appreciably converted to $HN(SO_3)/(SO_3H)^-$. Evidence bearing on this point will be discussed more fully in a later section. In addition, the amine monosulfonic acid formed on hydrolysis is completely ionized.[13]

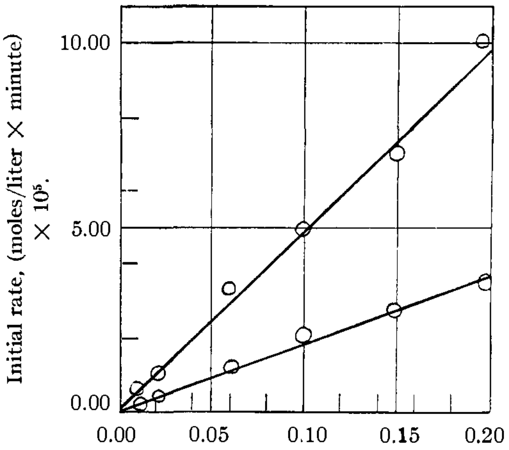

Fig. 1.—The dependence of the initial rate of hydrolysis of amine disulfonate on hydrochloric acid concentration at an ionic strength of 1.00 and at 25.00°; upper curve, $[HN(SO_3)_2^-] = 0.0500$; lower curve, $[HN(SO_3)_2^-] = 0.0200$.

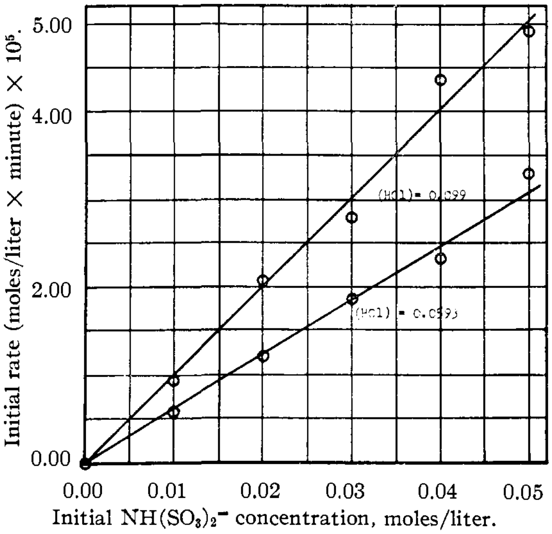

Fig. 2.—The dependence of the initial rate of hydrolysis of amine disulfonate on amine disulfonate concentration at an ionic strength of 1.00 and at 25.00°.

To determine the concentration of hydronium ion $[H^+]$, in the presence of added sulfate, it was necessary to know the ionization function of

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[16] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 94, 129.

[17] Brønsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1922)

HSO_4^- at an ionic strength of 1.00. This was calculated from the ionization constant[18] of HSO_4^- by multiplying by the ratio of the ionization function of $H_2PO_4^-$ at $\mu = 1.00$ measured by us to the ionization constant[15] of $H_2PO_4^-$

$$K(HSO_4^-, \mu = 1) = \frac{K(H_2PO_4^-, \mu = 1)}{K_0\ (H_2PO_4^-)} K_0\ (HSO_4^-) = \frac{4.67 \times 10^{-7}}{6.23 \times 10^{-8}} \times 1.20 \times 10^{-2} = 0.090$$

This calculation is based on the assumption that the ionic strength effects depend mostly on the charge types of the ions, and the small contributions of specific effects are nearly the same for the two acids. In treating the data, the procedure used above of calculating the average initial rate over the first 10% of hydrolysis was adopted. It is evident from the presentation of the data in Table III that the addition of sulfate decreases the rate of hydrolysis because it converts the hydronium ion to bisulfate. The hydrolysis is specifically catalyzed by hydronium ion.[19]

TABLE III

THE EFFECT OF INITIAL SULFATE CONCENTRATION ON INITIAL RATE AT 25.00° AND μ = 1.00

Initial HCl volume molality, 0.0197; initial $HN(SO_3)_2^=$ volume molality, 0.02000

Na_2SO_4, *F*	NaCl, *M*	Initial rate, $\Delta x/\Delta t$ mole/liter × min. × 10^5	$[H^+]$, calcd.	$k = (\Delta x/\Delta t)/[H^+][HN(SO_3)_2^=] \times 10^{+2}$
0.0200	0.860	0.334	0.0166	1.005
.0400	.800	.288	.0143	1.005
.0500	.740	.260	.01250	1.04
.0800	.680	.222	.01107	1.00
.1000	.620	.190	.00985	0.965

The values of *k*, the specific rate constant at 25.00° and at $\mu = 1.00$, calculated from the slopes of Figs. 1 and 2 and from Table III, that is, from all the initial rate data, are presented in Table IV. Considering the approximate nature of initial rate calculations, the agreement amongst the various series of experiments is good, and tends to confirm the proposed rate equation (c).

The Course of the Reaction at 25.00° and μ = 1.00.—To further confirm the validity of the rate equation (c), analysis of the progress of the reaction with time was carried out. These calculations are rather complicated because one must allow for the varying degree of dissociation of bisulfate (from sulfate added initially and from the hydrolysis of the disulfonate) during the course of the reaction.

TABLE IV

SPECIFIC RATE CONSTANT AT 25.00° AND AT μ = 1.00 ESTIMATED FROM INITIAL RATE DATA

Description of experiments	*k*, liter/moles × min. × 10^2
Varying HCl concentration, $[HN(SO_3)_2^=]$ = 0.02000 *M*	1.00
Varying HCl concentration, $[HN(SO_3)_2^=]$ = 0.05000 *M*	0.93
Varying $HN(SO_3)_2^=$ concentration, [HCl] = 0.0593 *M*	1.04
Varying $HN(SO_3)_2^=$ concentration, [HCl] = 0.099 *M*	1.02
Varying $SO_4^=$ concentration, [HCl] = 0.0197 *M*, $[HN(SO_3)_2]^=$ = 0.0200 *M*	1.01

The method chosen to treat most of the data is based on the equation (d)

$$k = \frac{2(x_2 - x_1)}{\int_{t_1}^{t_2} [((s + K - a)^2 + 4K(a + x))^{1/2} - (s + K - a)](d - x)dt} \tag{d}$$

In this relation: x = increase in acid titer due to the reaction (moles/liter) (reaction variable); K = ionization function of bisulfate ion; a = initial formality of hydrochloric acid (moles/liter); d = initial concentration of disulfonate; s = initial formality of sulfate. The equation (d) is derived in a straightforward manner from the rate equation (c). For the experiments at 25.00° and at $\mu = 1.00$, the integral in the denominator of (d) was evaluated by: (1) smoothing the data (*x vs. t*) graphically, (2) calculating the values of the integrand from the smoothed data, (3) plotting the integrand against time, and (4) evaluating the integral with a polar planimeter.

It should be mentioned that in the form $-d[HN(SO_3)_2^=]/[H^+][HN(SO_3)_2^=] = k dt$, the rate equation may be integrated analytically by applying the method of integration by partial fractions after suitable transformation. The cumbersome expressions resulting therefrom have been used in representative cases to check the method

TABLE V

VALUES OF THE RATE CONSTANT OBTAINED BY GRAPHICAL INTEGRATION

Temperature, 25.00°; ionic strength, 1.00

t_1, min.	t_2, min.	x_1, moles/liter	x_2, moles/liter	(*k*, liter/moles × min.) × 10^2
Run No. 28, *a* = 0.01000, *d* = 0.02000, *s* = 0 (NaCl) = 0.930				
0	2000	0	0.00440	1.05
1500	4000	0.00325	0.00855	1.02
3500	6000	.00760	.01205	0.97
5000	9000	.01040	.01575	0.98
Run No. 37, *a* = 0.01970, *d* = 0.02000, *s* = 0.1000; (NaCl) = 0.620				
0	3000	0	0.00575	1.01
2000	5000	.00380	.00920	1.05
4000	8000	.00760	.01305	0.99
7000	9000	.01190	.01400	0.95

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[18] Hamer, THIS JOURNAL, **56**, 860 (1934).

[19] After carrying out the calculations outlined here, it was called to our attention that on p. 580 of "The Physical Chemistry of Electrolytic Solutions" (Reinhold Publishing Corp., New York, N. Y., 1943) Harned and Owen recommend the privately communicated value of 0.0101 for the ionization constant of HSO_4^- instead of the 0.0120 we have used. Since the correction to an ionic strength of 1.0 is uncertain, and since a difference of 20% would produce less than a 10% change in the calculated rate constants, we have not recalculated our results using the newer data.

described above.[1] Table V exhibits the results of representative experiments, analyzed by the graphical integration method.

For the experiments listed in the table and for most of the many other runs that were made, there was a definite downward trend in the calculated rate constants especially after about 50% of the disulfonate initially present had hydrolyzed. It is not known to what this was due. The trend could not be correlated with any of the known variables. In spite of these trends, the calculated constants are so nearly constant under a wide variety of initial conditions that, taken in conjunction with the results of the initial rate study, they indicate that the proposed rate equation (c) is essentially correct.

The fact that the calculated values of the rate constant, as exhibited in Tables IV and V, are constant and independent of the calculated concentrations of hydronium ion and disulfonate ion strongly suggests that no appreciable fraction of these ions reacts to form an acid-disulfonate ion $[H_2N(SO_3)_2]^-$ or $HN(SO_3H)(SO_3)^-]$ (that is, an isomer of the activated complex postulated in a later section). If as is indicated in Fig. 1 the rate constant calculated at an H^+ concentration of 0.20 mole/liter is the same within 10% as that at lower acidities so that less than 20% of the disulfonate has been converted to the acid-disulfonate ion in 0.2 *M* acid, a lower limit for the second ionization function of amine disulfonic acid is 0.2 × 9 = 1.8.

Dependence of the Specific Rate Constant on Ionic Strength at 25.00°.—The effect of varying the ionic strength is of interest because the theoretical interpretation gives a clue to the identity of the reacting species in the rate-controlling reaction, that is, it gives the sign and a good idea of the magnitude of the product of the charges of the reacting ions. As is well known, the use of equation (b) for the variation of activity with ionic strength in conjunction with Brønsted's theory yields the equation (e)

$$\log_{10} k = \log_{10} k_0 + \frac{2Az_1z_2\mu^{1/2}}{1+\mu^{1/2}} + \beta\mu \qquad \text{(e)}$$

where z_1 and z_2 are the charges of the reacting ions, k_0 is the limiting specific reaction constant as the ionic strength approaches zero, and β is a constant at constant temperature.

To study this effect, experiments were done at a series of ionic strengths varying from 0.020 to 0.25. The hydrolysis was followed until more than 50% of the disulfonate had hydrolyzed. The data were smoothed and a rate constant calculated by a tabular integration method using the trapezoid rule. The time intervals of the integrals were taken over the first portion of the reaction but they did not include the region about t = 0, thus eliminating the effects of the disturbances involved in starting the reaction. The value of the ionization function of bisulfate ion at different ionic strengths, which is involved in the calculation, was estimated by assuming the validity of the equation (b), and that the value of K, 0.090, at μ = 1.00 was accurate. This taken in conjunction with Hamer's value of K_0 at 25.00°[18] gives the equation

$$\log K = \log K_0 + \frac{4A\mu^{1/2}}{1+\mu^{1/2}} + \gamma\mu \qquad \text{(f)}$$

where, at 25.00°, K_0 = 0.0120, A = 0.5065, and γ = −0.137 for sodium chloride solutions. The rate constants are shown in Table VI.

TABLE VI

DEPENDENCE OF THE RATE CONSTANT ON IONIC STRENGTH AT 25°

Moles/liter HCl	Moles/liter $HN(SO_3)_2^=$	Moles/liter NaCl	$\mu^{1/2}$ $\left(\frac{\text{moles}}{\text{liter}}\right)^{1/2}$	K, moles/liter	k, liter/moles × min.
0.00479	0.00500	0.00	0.140$_7$	0.021$_2$	0.047$_8$
.00482	.00500	.0100	.172$_6$	.023$_9$	.043$_6$
.00978	.01000	0.0	.199$_3$	.025$_7$	.039$_5$
.00987	.01000	.0500	.300$_0$	.034$_0$	.028$_7$
.00985	.01000	.1200	.400	.043$_1$	.023$_3$
.00985	.01000	.2100	.500	.052$_5$	.018$_9$
.01000	.02000	.930	1.000	.090$_0$	.010$_2$

In order to estimate the value of z_1z_2 in (e), log k was plotted against $0.5065\mu^{1/2}/(1+\mu^{1/2})$ and a smooth curve drawn through the points as shown in Fig. 3. From smoothed data read from the curve, the slope of the curve was calculated, and divided by 2 to give an approximation to z_1z_2. The values thus obtained differed from −2 by about 5–10%. To fit equation (e) to the data, the value of −2 for z_1z_2 was assumed and log k + $[(4 \times 0.5065\ \mu^{1/2}/(1+\mu^{1/2})]$ was plotted against μ, as shown in Fig. 4, to evaluate β. It was found that β = +0.09$_2$ and k_0 = 0.085$_2$. This value of β is a reasonable one. The conclusion may be drawn that the most probable value of z_1z_2 is −2 which suggests a rate-determining reaction between amine disulfonate ion and hydronium ion. This is consistent with the experimental rate equation.

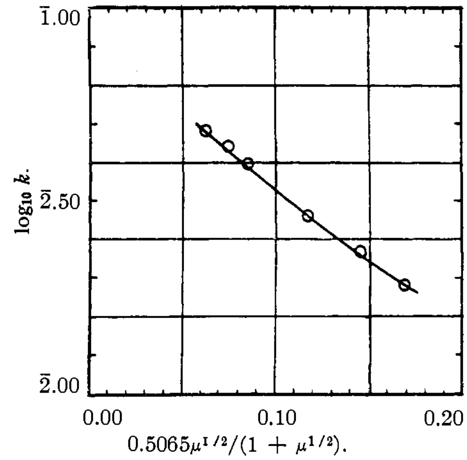

Fig. 3.—The dependence of the reaction constant on ionic strength at 25.00°.

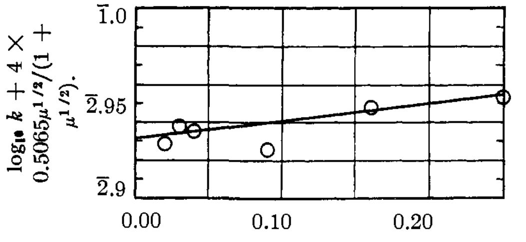

Fig. 4.—Graphical evaluation of k_0 and β of equation (e) at 25.00°

The Effect of Temperature on the Rate.—To estimate the energy and entropy of activation, two additional series of experiments were done, one at 35°, the other at 45°. Each series consisted of three experiments at decreasing ionic strength to facilitate the extrapolation to $\mu = 0.00$, two experiments to spot check the rate law at constant ionic strength, and one experiment in alkaline medium (added base equivalent to 10% of the disulfonate) to find if an uncatalyzed reaction with water becomes appreciable at the higher temperatures.

The results of these experiments are shown in Table VII. The rate constant was calculated by a tabular integration method utilizing the trapezoid rule over an early time interval which did not include the initial time. No attempt was made in these series to check the rate law by calculating the rate constant over different time intervals for the same experiment as the agreement of the values of the constant calculated for the two spot check experiments was taken as adequately showing the validity of the rate law at the temperature in question. No detectable reaction was found in alkaline media at these temperatures during time intervals comparable with the duration of the other experiments of the same series.

TABLE VII

DEPENDENCE OF REACTION CONSTANT ON TEMPERATURE AND IONIC STRENGTH

Moles/liter HCl	Moles/liter $HN(SO_3)_2^=$	Moles/liter NaCl	$\mu^{1/2}$, $\left(\frac{\text{moles}}{\text{liter}}\right)^{1/2}$	K for HSO_4^-	k, liter/moles × min.
		34.55°, K_0 = 0.0106			
0.00954	0.01000	0.0	0.1988	0.0234	0.143
.00974	.01000	.0225	.2495	.0275	.117
.00984	.01000	.0500	.2999	.0318	.101
.01962	.01000	.0400	.2997	.0318	.099
.00970	.02000	.0200	.2998	.0318	.100
		44.77°, K_0 = 0.00892			
.00469	.01000	.00500	.1991	.0205	.479
.00488	.01000	.0275	.2499	.0236	.416
.00488	.01000	.0350	.2642	.0246	.390
.00976	.01000	.0500	.2999	.0274	.364
.00469	.02000	.0250	.2998	.0274	.341

The values of the ionization function of bisulfate ion were estimated by neglecting the term linear in μ in the equation (f) previously derived from equation (b). This approximation is adequate because of the low ionic strengths and the relative intensitivity of the values of the rate constant to the value of the ionization function. Values of K_0 were taken from Hamer's values[18] and the very small corrections to the exact temperature of the experiments made using values of ΔH_{i}, the enthalpy of ionization, given by Hamer.

To extrapolate to $\mu = 0$, the procedure used in the ionic strength studies at 25° was applied. The graphical evaluation of the constants β and log k_0 of equation (e) is shown in Fig. 5.

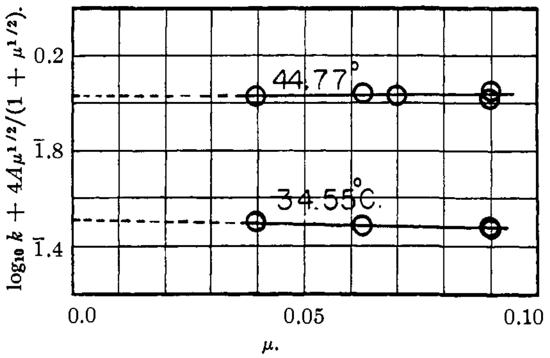

Fig. 5.—Graphical evaluation of k_0 and β at 34.55° and 44.77°.

• In Table VIII the behavior of the rate constant with ionic strength and temperature is summarized. The values of A are the theoretical ones calculated from the expression given by the Debye–Hückel theory.

TABLE VIII

SUMMARY OF THE DEPENDENCE OF THE RATE CONSTANT ON IONIC STRENGTH AND TEMPERATURE

Temperature, °C.	A	β	k_0 liters/moles × min.
25.00	0.506	0.092	0.0852
34.55	.517	−.32	0.321
44.77	.528	.13	1.06

The Thermodynamics of the Activated Complex.—The variation of k_0 with temperature was interpreted by the activated complex theory. This theory yields the equation (g)[20]

$$k_0 = (\mathbf{k}T/h) \exp(-E^*/RT)\exp(\Delta S^*/R) \quad \text{(g)}$$

for the specific rate constant of a reaction in solution. In this relation, **k** and h are Boltzmann's and Planck's constants, respectively, and the starred quantities are the internal energy and entropy of activation.

Figure 6 is a plot of log k_0/T *versus* $1/T$. From the slope of the straight line, $\Delta E^* = 23{,}500$ cal., with an estimated error of the order of ±1000 cal.

Using this value for the activation energy, the values of $(\mathbf{k}T/h)$ exp $(\Delta S^*/R)$ (A in the Arrhenius equation, $k_0 = A \exp(-E^*/RT)$) and of the

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[20] Glasstone, Laidler and Eyring "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 198, 199; eqns. 167, 178.

entropy of activation listed in Table IX were calculated.

TABLE IX

VALUES OF THE ENTROPY OF ACTIVATION

T	k_0, ml./mole sec.	(kT/h) exp $(\Delta S^*/R)$	ΔS^*, e. u.
25.00	1.42	2.4×10^{17}	21.2
34.55	5.18	2.67×10^{17}	21.6
44.77	17.66	2.55×10^{17}	21.1
	Av.	2.54×10^{17}	21.3

The frequency factor is about 10^3 times larger than that calculated on the basis of the simple collision theory for a bimolecular reaction.[21] This is to be expected for a reaction between two ions when $z_1z_2 = -2$. For if the results of Scatchard's arguments[22] based on a model of the activated complex consisting of two charged spheres at a distance r apart are used to calculate the contribution (ΔS^*_D) to the entropy of activation due to electrostatic interaction between dielectric medium and charged ion, it is found that

$$\Delta S^*_D = \frac{\epsilon^2 z_1 z_2}{rD}\left(\frac{\partial \ln D}{\partial T}\right)_p$$

Here, ϵ = electronic charge (e. s. u.); z_1,z_2 = charges of reacting ions; D = dielectric constant of medium; T = absolute temperature; p = pressure.[23] For water this yields

$$\Delta S^*_D = -20 z_1 z_2 / r \text{ (A) e. u./mole} \qquad \text{(h)}$$

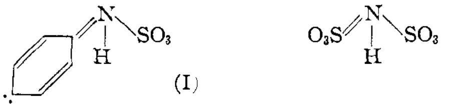
The value of $\mathbf{k}T/h$ is 1.7×10^{13} at $T = 298°K$. Since the collision factor has a value of *ca.* 2.8×10^{14} sec.$^{-1}$ when concentrations are expressed in moles/ml.,[23] a reaction with a "normal" collision factor has an entropy of activation of *ca.* 5.6 e. u. For the reaction in question, we may therefore attribute approximately 15.7 e. u. to the electrostatic interaction, corresponding on the basis of equation (*h*) to a separation of the charges in the activated complex of 2.5 Å. This argument is not presented to prove that in the activated complex, the charges of the reaction ions are separated by exactly 2.5 Å.; it does indicate that it is reasonable to expect a positive entropy of activation of the order of magnitude of that observed.

The Mechanism of the Reaction.—The kinetic evidence indicates that the reaction proceeds via the formation of an activated complex from hydronium ion and amine disulfonate ion which then decomposes to give the reaction products.

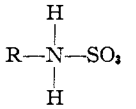
$$H_3O^+ + HN(SO_3)_2^= \rightleftarrows (H_3O, HN(SO_3)_2)^-$$

$$H_2O + (H_3O, HN(SO_3)_2)^- \longrightarrow HSO_4^- + H_2NSO_3^- + H_3O^+$$

In speculating about the detailed mechanism of the reaction, it is pertinent to recall that N-alkyl sulfamic acids (*e. g.*, H_3CNHSO_3H) are quite resistant to hydrolysis, but that the N-aryl sulfamic acids (*e. g.*, $C_6H_5NHSO_3H$) have not been prepared because they hydrolyze readily in acid media; salts of the type $C_6H_5NHSO_3Na$ can be prepared.[24] The base strength of the electron pair on the nitrogen in disulfonate or phenylsulfamate is less than that of the corresponding electron pair in methyl sulfamate because the addition of a proton destroys the possibilities of resonance of the normal structure with structures of the type (I).

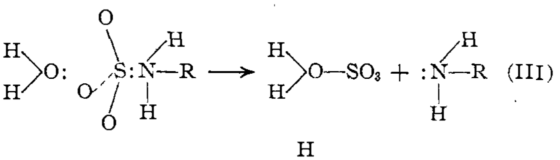

(I)

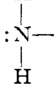
Consequently an activated complex of the type (II)



$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}-SO_3 \qquad \text{(II)}$$

will exist in smaller concentration for R = C_6H_5 or SO_3 than for R = CH_3. However, in such an activated complex, the attack of a water molecule depicted in (III)


(III)

causes the liberation of  $:\overset{\displaystyle H}{\underset{\displaystyle H}{N}}-R$ which is stabilized by resonance for R = C_6H_5 or $-SO_3^{\bullet-}$. The experimental evidence indicates that this latter ef-

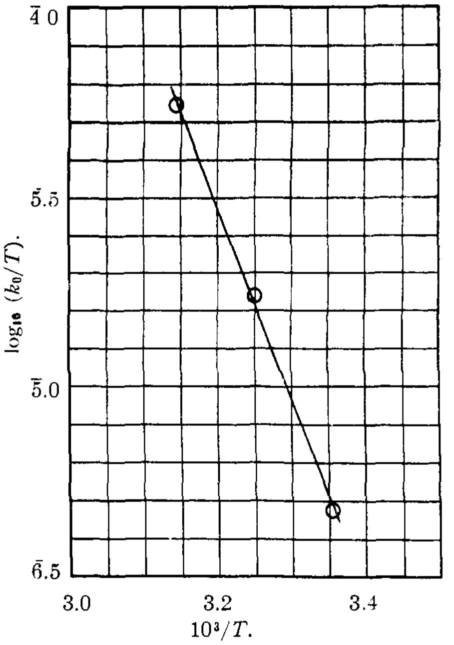


Fig. 6.—The dependence of k_0 on temperature.

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(21) See, for example, Moelwyn-Hughes "Kinetics of Reactions in Solution," 2d edition, Oxford University Press, 1947, Chapter III.

(22) Scatchard, THIS JOURNAL, **52**, 52 (1930).

(23) Glasstone, Laidler and Eyring, *loc. cit.*, pp. 434–435. A similar equation is given in ref. 21, p. 93.

(24) Ref. 5, p. 69.

fect is greater than the effect of resonance on the acid strengths of the activated complexes. It is not necessary to think of the addition of a proton and the attack by a water molecule as steps taking place in series; in a single attack by a hydronium ion, the same factors would affect the relative reactivities of disulfonate, N-alkyl and N-aryl sulfamates.

An uncatalyzed reaction with water like (III) would require the liberation of the unstable ion; $:\underset{\cdot\cdot}{\overset{\overset{H}{|}}{N}}\text{—}R$ and hence does not take place. If the activated complex for the acid catalyzed reaction were $HO_3S\text{—}\underset{\cdot\cdot}{\overset{H}{N}}\text{—}R$ the same unfavorable factor would affect the reaction.

Acknowledgment.—We are indebted to Professor Don M. Yost for proposing this problem to us. Professors N. Kharasch and S. Winstein of the University of Southern California and The University of California, respectively, have made stimulating suggestions as to the mechanism of the reaction.

Summary

The rate of the acid catalyzed hydrolysis of amine disulfonate ion, $HN(SO_3)_2^{=}$, in water solution has been studied over the temperature range 25–45°. The results at constant ionic strength conform to the rate equation

$$-\,d[HN(SO_3)_2^-]/dt = k[H^+][HN(SO_3)_2^-]$$

if the equilibrium between sulfate ion and hydrogen ion is taken into account. The uncatalyzed hydrolysis was found to have an undetectable rate compared to the rate of the acid catalyzed reaction.

The variation of the rate constant with ionic strength implies that the charge product of the ions involved in the rate determining reaction is −2.

The variation of the rate constant at zero ionic strength with temperature is described by the equation

$$k_0(\text{ml./mole} \times \text{sec.}) = 2.54 \times 10^{17} \exp.\ (-23{,}500/RT)$$

The relatively large value of the frequency factor (as compared with that expected on the basis of collision theory for a bimolecular reaction between uncharged molecules) is explained on the basis of a large positive entropy of formation of the activated complex, due to its electrostatic interaction with the solvent.

A mechanism involving an activated complex of amine disulfonate ion and hydronium ion may be invoked to explain these results. A hypothesis to explain the relative stability toward hydrolysis of methyl sulfamic acid as compared with phenyl sulfamic acid or amine disulfonate is advanced.

In addition, the ionization function (classical ionization constant) for the equilibrium: $HN(SO_3)_2^{=} = H^+ + N(SO_3)_2^{\equiv}$ in a sodium chloride solution at an ionic strength of 1.00 at 25° was measured as 3.2×10^{-9}.

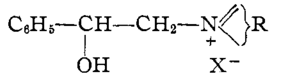
PASADENA, CALIF. RECEIVED JANUARY 3, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Reactions of 1,2-Epoxides with Salts of Organic Bases. I. Styrene Oxide[1,2]

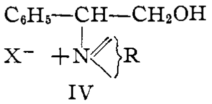
BY L. CARROLL KING, NEIL W. BERST AND F. N. HAYES

Styrene oxide (I) reacts with strong acid salts of certain organic bases to give a mixture of quaternary salts. For example, I reacted with pyridine hydriodide (II) to give a mixture of 2-phenyl-2-hydroxyethylpyridinium iodide (IIIa) and 1-phenyl-2-hydroxyethylpyridinium iodide (IVa).



$C_6H_5\text{—}\underset{\underset{OH}{|}}{CH}\text{—}CH_2\text{—}\underset{+}{N}\langle\rangle R \quad X^-$

III



$C_6H_5\text{—}\underset{\underset{X^-\ +N\langle\rangle R}{|}}{CH}\text{—}CH_2OH$

IV

(a) $X = I^-$; (b) $X = Br^-$; (c) $X = ClO_4^-$; (d) $X = {}^-O_3SC_6H_4CH_3$; $R = C_5H_5\text{—}$

In a series of reactions between I and II the over-all yield of mixed salts was quite constant, with IVa the principal product. The yields of IIIa were consistently low, except in the case where I was in excess. The requisite reaction time was five to ten minutes. Prolonged heating had little effect on the total yield or distribution of isomers except when I was in excess. In this case the products became tarry and the isolable yield of IVa was smaller.

The structure of IIIa was determined by comparison with authentic 2-phenyl-2-hydroxyethylpyridinium iodide, prepared by the method of Krohnke.[3] Further proof was obtained by oxidizing[4] 2-phenyl-2-hydroxyethylpyridinium perchlorate (IIIc), prepared from IIIa, to the known phenacylpyridinium perchlorate.[5] The structure assigned to IVa follows from its non-identity with IIIa and from its formation from the reaction of 2-phenyl-2-iodoethanol[6] with pyridine.

The generality of the reaction was established by allowing I to react with a number of acid salts

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(1) Presented before the Organic Division of the American Chemical Society, San Francisco, April, 1949.

(2) This investigation was supported in part by a research grant from the National Cancer Institute, U. S. Public Health Service.

(3) Krohnke, *Ber.*, **66**, 607 (1933).

(4) Krohnke, *ibid.*, **67**, 659 (1934).

(5) King, THIS JOURNAL, **66**, 894 (1944).

(6) Prepared by the method of Golumbic and Cottle, *ibid.*, **61**, 996 (1939).