THE KINETICS OF THE ACID-CATALYZED HYDROLYSIS OF AMINE DISULFONATE ION. THE THIRD IONIZATION CONSTANT OF AMINE DISULFONIC ACID

Thesis

by

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Abstract

The rate of the acid-catalyzed hydrolysis of amine disulfonate ion, $HN(SO_3)_2^=$, in water solution has been thoroughly studied over the temperature range 25–45° C. The effect of varying the concentration of reactants, the effect of ionic strength (neutral salt effect), and the effect of temperature have been studied. All results at constant ionic strength confirm the rate equation

$$-\frac{d(HN(SO_3)_2^=)}{dt} = k(H^+)(HN(SO_3)_2^=)$$

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 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 internal energy of activation, $\Delta E^{\ddagger}$, was found to be 23.5 ± 1 Kcal., and the entropy of activation, $\Delta S^{\ddagger}$, was found to be $+7.2 \pm 1.5$ e.u. for the reaction at zero ionic strength.

A mechanism involving an activated complex of amine disulfonate ion and hydronium ion may be invoked to explain these results.

In addition, the ionization function (classical ionization constant) for the equilibrium

$$HN(SO_3)_2^{=} \rightleftharpoons H^+ + N(SO_3)_2^{\equiv}$$

was measured in a sodium chloride solution at an ionic strength of 1.00 at 25° C. It was found that

$$\frac{(H^+)(N(SO_3)_2^{\equiv})}{(HN(SO_3)_2^{=})} = 3.2 \times 10^{-9} .$$

Introduction

Amine disulfonate ion (imidodisulfonate ion) is known to hydrolyze irreversibly and quantitatively in dilute acid at a measurable rate according to the equation

$$HN(SO_3)_2^{=} + H_2O \overset{H^+}{=} HSO_4^- + H_2NSO_3^- \quad ^{1,2,3} .$$

Wagner[4] in the course of his study on the kinetics of the hydrolytic decomposition of the sulfur-nitrogen acids did one experiment on the hydrolysis of amine disulfonate in the presence of hydrochloric acid at 42°C. 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. In his analysis of his results he did not take the equilibrium between sulfate and hydrogen ions into account. Sisler and Audrieth[2] followed the course of hydrolysis with time of amine trisulfonate ion (nitrilosulfonate ion) to amine monosulfonate ion (sulfamate ion) at several different temperatures. The reaction goes by two steps, the first step being the hydrolytic reaction

$$N(SO_3)_3^{\equiv} + H_2O = HN(SO_3)_2^{=} + H^+ + SO_4^{=} ,$$

and the second step the slower hydrolysis of the amine disulfonate ion to amine monosulfonate ion. They did not

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[1] Audrieth, Sveda, Sisler and Butler, Chem. Rev., <u>26</u>, 49 (1940).

[2] Sisler and Audrieth, J. Am. Chem. Soc., <u>60</u>, 1947 (1938).

[3] Raschig, Ann., <u>241</u>, 161 (1887).

[4] Wagner, Z. phys. Chem. <u>19</u>, 678 (1896).

attempt an analysis of the kinetics of the reactions. However, their study brought out some valuable information concerning the relative rates of the two successive hydrolytic reactions.

Because of the lack of quantitative data it was thought desirable to investigate thoroughly the kinetics of this reaction.

Materials

Distilled Water

All distilled water used in the hydrolysis reaction mixtures, in the standard solutions, and in the stock solutions had been previously boiled free of dissolved gases and stored in a *Pyrex* siphon carboy with a soda lime guard tube.

Standard Base

Solutions of sodium hydroxide were made up from an 18 N solution of C.P. pellet sodium hydroxide which had been centrifuged clear of sodium carbonate and kept in a wax-lined bottle. The 0.02 N base was kept in a *Pyrex* siphon bottle with a soda lime guard tube. The stronger solutions, although they were kept in a soft glass siphon bottle, were used very soon after preparation while the dilute 0.02 N solution was kept several months while in continuous use.

Standard Acid

Solutions of hydrochloric acid were made by dilution of C.P. acid with distilled water. The 0.02 N. acid was kept in a *Pyrex* siphon with a soda lime guard tube. It was thought that in such dilute acid solution atmospheric carbon dioxide would be nearly as soluble as in water.

Sodium Chloride

C.P. sodium chloride, which was used to adjust ionic strength, was dried four hours at 200°C. to drive off most of the water. There is about 0.1 per cent residual moisture which is not driven off by this procedure[5]. The salt was dissolved in distilled water to make a five molal stock solution.

Sodium Sulfate

C.P. anhydrous sodium sulfate was ignited 1½ hours at 700-800°C. driving off any traces of water[6]. A one molal stock solution was made up and used as a source of sulfate ion.

Indicators

To follow the reaction, samples were withdrawn from the reaction mixture and analyzed for total acid by titration with dilute base. However, the pH at the equivalence point in solutions containing appreciable quantities of amine disulfonate ion is low because of the third acid dissociation of the ion. One may estimate the pH at the equivalence point using the value of the ionization function at an ionic strength of 1.00 for disulfonate ion,

$$\frac{(H^+)(N(SO_3)_2^{\equiv})}{(HN(SO_3)_2^{=})} .$$

The measurement of this quantity will be described later.

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[5] Sorensen, Z. Anal. Chem., 44, 149 (1905).

[6] Remy and Siegmund, Z. anal. Chem., 93, 321 (1933).

To calculate the hydrogen ion concentration the equation

$$(H^+) = \sqrt{K_o \frac{f_{HN(SO_3)_2^=}}{f_{H^+} \times f_{N(SO_3)_2^\equiv}} (HN(SO_3)_2^=)} \quad ,$$

where $(HN(SO_3)_2^=)$ was taken as very closely equal to the total disulfonate concentration was used. The value of the product of the ionization constant K_o, and the activity function,

$$\frac{f_{HN(SO_3)_2^=}}{f_{H^+} f_{N(SO_3)_2^\equiv}} \quad ,$$

was estimated by using the equation

$$\log f_i = - \frac{A z_i^2 \Gamma^{1/2}}{1 + \Gamma^{1/2}} + \beta_i \Gamma \tag{1}$$

which is an approximation to the complete Debye-Hückel equation with salting out correction, to calculate the activity coefficient and using the known value of the ionization function at an ionic strength of 1.00 to estimate K_o,

$$K_o = \frac{f_{H^+} f_{N(SO_3)_2^\equiv}}{f_{HN(SO_3)_2^=}} \times \frac{(H^+)(N(SO_3)_2^\equiv)}{(HN(SO_3)_2^=)} \quad .$$

In these equations

f_i = activity coefficient of ith ion

A = Debye-Hückel coefficient

z_i = electronic charge of ith ion

Γ = ionic strength (strictly ional strength, i.e., $\Gamma = \frac{1}{2}\sum_i c_i z_i^2$ where c_i is in moles per liter)

$\beta_i =$ a constant characteristic of the i^{th} ion and of the electrolytes contributing to the ionic strength. In calculating K_0 the linear term in (1) was neglected in calculating the activity coefficients. If one presupposes two extreme cases in order to estimate the range of pH likely to be encountered at the equivalence point one has: 1. 10 ml. of a 0.05 formal solution of disulfonate that is 0.005 formal in hydrochloric acid and at an ionic strength of 1.00 is titrated with 0.02 normal base to give a final volume of 20 ml. (including wash water). This has a calculated pH of 5.4 at the equivalence point. 2. A 10 ml. volume of a 0.005 formal solution of disulfonate which is 50 per cent hydrolyzed, initially 0.005 normal in acid, and having no added neutral salt is titrated to a final volume of 20 ml. This has a calculated pH of 6.3 at the equivalence point. These figures suggest an indicator changing in the neighborhood of pH 5 to 6. The indicator selected was bromcresol green-methyl red mixed indicator with a sharp distinct end point at pH 5.1. The indicator was made up according to the directions of Kolthoff and Sandell[7].

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[7] Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis", p. 429, Macmillan, 1937).

Preparation, Analysis and Acid Constant of Potassium Amine Disulfonate.

Preparation

Potassium amine disulfonate was prepared by hydrolysis of potassium amine trisulfonate,

$$N(SO_3)_3^{\equiv} + H_2O \overset{H^+}{=} HN(SO_3)_2^{=} + HSO_4^{-} .$$

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[2] of Claus and Koch's method),

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

A solution of 642 g. of C.P. potassium hydroxide pellets dissolved in 1280 ml. of distilled water was saturated with sulfur dioxide. This solution was divided into three portions, put into three four-liter beakers, and heated to about 60-70°C. One third of a solution of 214 g. of C.P. potassium nitrite in 855 ml. of distilled water was added slowly with vigorous stirring to each of the beakers. The mixture became boiling hot and crystals began to form almost immediately. The mixture was allowed to stand an hour and then distilled water was added to bring the volume in each beaker to 4 liters. The mixture was then heated to near boiling to bring the potassium amine trisulfonate into solution. During the course of the formation and redissolving of the salt, it was found necessary to add ca. 10 g. of solid potassium hydroxide pellets to each of the beakers to keep the pH of the solution greater than 7 and thus repress hydrolysis. The solutions were cooled and allowed to stand until recrystallization seemed complete. The yield of crystals was favored by the low solubility of this salt, about 2 g. per 100 g. of water at 23°C.[8] The solid salt from each beaker was filtered from the mother liquor onto a sintered glass filter and washed several times with successive portions of 250 ml. of ice-cold distilled water mixed with 2 ml. of concentrated ammonium hydroxide. The three portions of the salt were sucked as dry as possible and all three were transferred into a large crystallizing dish. To hydrolyze the trisulfonate to the disulfonate the moist salt was mixed with 250 ml. of 2 per cent sulfuric acid to form a pasty mass and allowed to stand 24 hours. It was then filtered and washed with successive portions of one liter of ice-cold distilled water. The crude disulfonate was dissolved by heating in about 4 liters of dilute ammonium hydroxide (1:6), and filtered while hot through a preheated sintered glass filter to remove lint, solid silica, etc. The solution was allowed to cool to room temperature and then it was chilled to 15°C. and the crystals filtered off. The disulfonate is also not very soluble, 1.6 g. of salt per 100 g. of water at 23°C.[9] The crystals were washed three times with ice-cold distilled water, and then a sufficient additional

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[8] Yost and Russell, "Systematic Inorganic Chemistry", p. 99, Prentice Hall, 1944.

[9] Yost and Russell, loc. cit., p. 100.

number of times to give a wash water free of sulfate ion. The crystals were then washed three times with absolute anhydrous C.P. ethanol, three times with anhydrous C.P. ethyl ether, and sucked dry. The disulfonate was spread out in a shallow dish and placed in a vacuum desiccator over concentrated sulfuric acid. The desiccator was pumped on with a water aspirator for several hours to evaporate most of the ether. The sulfuric acid was then replaced by Drierite, and the salt vacuum desiccated to constant weight within 0.1 per cent for successive periods at 1-2 mm. Hg. The yield was 295.5 g. or 64 per cent of quantitative yield based on potassium nitrite. It is noteworthy that this yield is greater than that of Sisler and Audrieth[2]. This is probably due to the greater efficiency of the larger scale synthesis.

Analysis

The purity of potassium amine disulfonate prepared by the above described method was determined by a rather complete analysis of the product of a previously made smaller batch of disulfonate. The salt was analyzed for sulfur, nitrogen, and material not volatile on ignition with sulfuric acid (taken as potassium sulfate).

Potassium

To determine potassium the procedure of Remy and Siegmund[6] was used. A 0.2 g. sample was weighed into a weighed and ignited porcelain crucible and hydrolyzed to potassium and ammonium sulfates by dissolving in 10 ml. of water and 1 ml. of concentrated sulfuric acid and slowly evaporating to dryness at 60-80°C. Some of the sulfuric acid was driven off by heating slowly to 250°C. and holding at that temperature until fuming ceased. In order to decompose the ammonium salt and drive off more sulfuric acid, it was then heated to a higher temperature until the sample lost enough sulfuric acid to solidify. The crucible was cooled, 0.1 g. of powdered C.P. ammonium carbonate was added, and the heating to 250°C. repeated to destroy any pyrosulfate which might have been formed. The cooling, addition of ammonium carbonate, and reheating was repeated until no fumes were given off on heating. Then the crucible was ignited at 600-700°C. for one hour, cooled in a desiccator, and weighed. It was then ignited to constant weight by successive one half hour ignition periods at 600-700°C. The gain in weight of the crucible was taken as potassium sulfate.

Nitrogen

The analysis for nitrogen was done by a semi-micro Kjeldahl procedure according to E.C.Wagner[10] using an apparatus of the type devised by C.E.Redemann[11]. A 0.1 g. sample of the salt was digested with sulfuric acid with selenium as a catalyst. The ammonia was distilled from the digestion mixture made alkaline into boric acid

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[10] Wagner, Ind. Eng. Chem., Anal. Ed. 12, 771 (1940).

[11] Redemann, Ind. Eng. Chem., Anal. Ed. 11, 635 (1939).

solution, and titrated with 0.02 normal hydrochloric acid using methyl red as indicator. A color standard was used. A blank was run and found to be negligible.

Sulfur

The disulfonate was hydrolyzed and oxidized to sulfate by hot concentrated nitric acid,

$$HN(SO_3)_2^{=} + H_2O \overset{H^+}{=} H_2N(SO_3)^- + HSO_4^-$$

$$H_2N(SO_3)^- + HNO_3 = N_2O + HSO_4^- + H_2O$$ [1,12]

To ensure complete oxidation, some hydrochloric acid was added to give chlorine and nitrosyl chloride which might be more reactive in oxidizing the amine monosulfonate. The excess nitric acid was destroyed by repeated evaporation to dryness with concentrated hydrochloric acid for it would have interfered with the determination of sulfate as barium sulfate by coprecipitation. The sulfate was then determined by the usual barium sulfate method, specifically, according to the directions of Kolthoff and Sandell[13].

A 0.3 g. sample of the disulfonate was weighed into a 400 ml. beaker covered with a watch glass, evaporated twice to dryness with a mixture of 10 ml. of concentrated nitric acid and 1 ml. of concentrated hydrochloric acid, and then evaporated twice to dryness with 10 ml. of concentrated hydrochloric acid on a thermostatted hot plate. The sample

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[12] Cupery, Ind. Eng. Chem. <u>30</u>, 627 (1938).

[13] Kolthoff and Sandell, loc. cit., p. 319.

was then dissolved by heating with 1 ml. of concentrated hydrochloric acid and 25 ml. of water, and the solution was filtered on a small paper filter to take out a trace of silica from the glassware. The paper was washed several times with warm water until the washings showed no test for chloride ion. The filtrate was then treated by the usual procedure for the determination of sulfate.

The results of the analysis are shown in Table 1. These results indicate a purity of somewhere between 97.6 - 98.5 per cent.

Table 1

Analysis of potassium amine disulfonate

		Found %	Calc. %	Dev. from theoretical %
Potassium	1	30.43	30.87	-1.4
	2	30.38		-1.6
Nitrogen	1	5.55	5.53	0.4
	2	5.50		-0.5
	3	5.44		-1.6
Sulfur	1	24.74	25.31	-2.3
	2	24.75		-2.4

Another method of analysis was used to determine the extent of deterioration, if any, with time. A weighed sample of the salt was dissolved in dilute base and the solution adjusted to the equivalence point by adding acid. A known amount of acid was then added, and the disulfonate was hydrolyzed completely by heating to 85-95°C. for an hour, cooled, and titrated with standard base. The hydrolysis of sulfamic acid if it occurs to any extent during the heating will not interfere appreciably, for

$$NH_2SO_3^- + H_2O \overset{H^+}{=} NH_4^+ + SO_4^= \quad .$$

The results of such analyses of the second large batch of salt done at various times are shown in Table 2. This shows that there is no appreciable decomposition in three months if the disulfonate is kept in a vacuum desiccator over <u>Drierite</u>. The reason for the high values given by this method of analysis is not known. The second batch of salt appears to be purer than the first.

Table 2

Analysis of potassium amine disulfonate by total hydrolysis

Time	Per cent disulfonate				Comment
	I	II	III	IV	
2/9/47	-	-	-	-	Salt synthesized
4/8/47	98.4	99.6	-	-	Analysis not carefully done
7/8/47	99.9	100.2	100.2	100.2	Carefully done analysis

The Acid Constant

In the course of preliminary experiments on titrating acid in the presence of amine disulfonate ion it was found that with an indicator with a pH range in the neighborhood of pH = 6-7, e.g. bromthymol blue, an amount of base greatly in excess of that equivalent to the acid present was required to produce the indicator color change. This was thought to be caused by the partial neutralization of a third active hydrogen

$$HN(SO_3)_2^{=} \rightleftharpoons H^+ + N(SO_3)_2^{\equiv}.$$

In support of this is the fact that salts of the formula $K_3[N(SO_3)_2]$ have been prepared[1]. The determination of an approximate acid constant for this equilibrium became advisable because: 1. it would be useful in deciding what indicator to use to indicate the equivalence point 2. it might be of importance in the initial mechanism of hydrolysis of the disulfonate in solutions to which no acid had been added and 3. it is in itself an interesting datum. The value of the ionization function,

$$\frac{(H^+)(N(SO_3)_2^{\equiv})}{(HN(SO_3)_2^{=})}, \qquad (2)$$

where the parentheses indicate molar concentrations, was determined at an ionic strength of 1 and at 25°C. by measuring with a Beckman pH meter the pH of a dilute buffer solution made by partially neutralizing the imide hydrogen with sodium hydroxide and adjusting the ionic strength to 1.00 by addition of sodium chloride. The pH of dilute hydrochloric acid solutions also adjusted to an ionic strength of 1.00 by sodium chloride were also measured.

In the latter solutions the hydrogen ion concentration was taken equal to the stoichimetric concentration of hydrochloric acid and the activity coefficient of hydrogen ion was taken to be the same as in the buffer solutions. On the basis of these assumptions the concentrations of hydrogen ion in the buffer solution were easily calculated and from this the value of the function (2). To check the method, the value of the ionization function

$$\frac{(H^{+})(HPO_4^{=})}{(H_2PO_4^{-})} \qquad (3)$$

was determined by the same means and compared with the values calculated from the second ionization constant of phosphoric acid[14] and the use of the approximate equation (1) for the activity of ions, neglecting the term linear in the ionic strength. This method of determining the value of the ionization function was suggested by the precise method of Harned and Ehlers for determining ionization constants of weak acids[15,16]. The data are given in Table 3.

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[14] Nims, J.Am.Chem.Soc. 55, 1946 (1933).

[15] Harned and Ehlers, J.Am.Chem.Soc. 54, 1350 (1932).

[16] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions", p. 497, Reinhold, 1943.

Table 3

Ionization Functions at 25° C.

Amine Disulfonate Ion: Ionic Strength, 1.00

Formality $K_2HN(SO_3)_2$	Formality NaOH	Molality HCl	Molality NaCl	pH	Molality H	Ionization Function x 10^{-9}
		0.01123	0.989	1.82	0.01123	
		0.001123	0.999	2.83	0.001123	
0.0200	0.0999		0.910	8.39	3.02×10^{-9}	3.0
.0200	$.00499^5$		0.925	7.91	9.11 x	3.0
.0200	.01498		0.892	8.82	1.12 x	3.4
.0100	$.00499^5$		0.955	8.34	3.38 x	3.4
.0100	$.00199^8$		0.964	7.78	12.3 x	3.1
.0100	.00699		0.949	8.68	1.55	3.6

Dihydrogen Phosphate Ion: Ionic Strength, 1.00

Formality NaH_2PO_4	Formality NaOH	Molality HCl	Molality NaCl	pH	Molality H	Ionization Function Found x 10^{-7}	Ionization Function Calc. x 10^{-7}
0.0200	0.00999		0.960	6.20	4.67×10^{-7}	4.67	6.4
.0100	$.00499^5$		.980	6.20	4.67 x	4.67	6.4
					Ionic Strength, 0.150		
		0.001123	.149	2.98	0.001123		
.0200	0.00999		.110	6.71	2.09×10^{-7}	2.1	2.3
.0100	$.00499^5$		.130	6.68	2.24 x	2.2	2.3

An average value of the ionization function for disulfonate is about 3.2×10^{-9}. The values of the function for dihydrogen phosphate ion agree satisfactorily with the calculated values if one takes into consideration the approximate nature of the calculation.

To confirm this estimation of the ionization function, and to find if the other ionization constants of amine disulfonic acid were large enough so it might be treated as having two completely ionized hydrogens, a titration curve was run. A solution 0.0500 formal in disulfonate, 0.2 formal in hydrochloric acid, and 0.75 molal in sodium chloride (to give an ionic strength of 1.00) was made up. A 250 ml. portion of this solution was titrated rapidly at 25°C. with 1.0 molal sodium hydroxide immediately after having been made up. The pH of the solution was followed during the titration by means of a Beckman pH meter. The duration of the experiment (40 minutes over all) was so short that no appreciable hydrolysis could have taken place. The result of this experiment is shown in Figure 1. The cross bars on the curve mark the calculated equivalence points from the value of the ionization function of the disulfonate ion, the value of the ionization function of water in sodium chloride at an ionic strength of 1.00[17], and the activity coefficient for hydrogen ion at an ionic strength of 1.00 and at 25°C. calculated by equation (1). It is evident that the other ionization constants of amine disulfonic acid are larger than about 0.5. The error in calculating the hydrogen ion

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[17] Harned and Owen, loc.cit., p. 488.

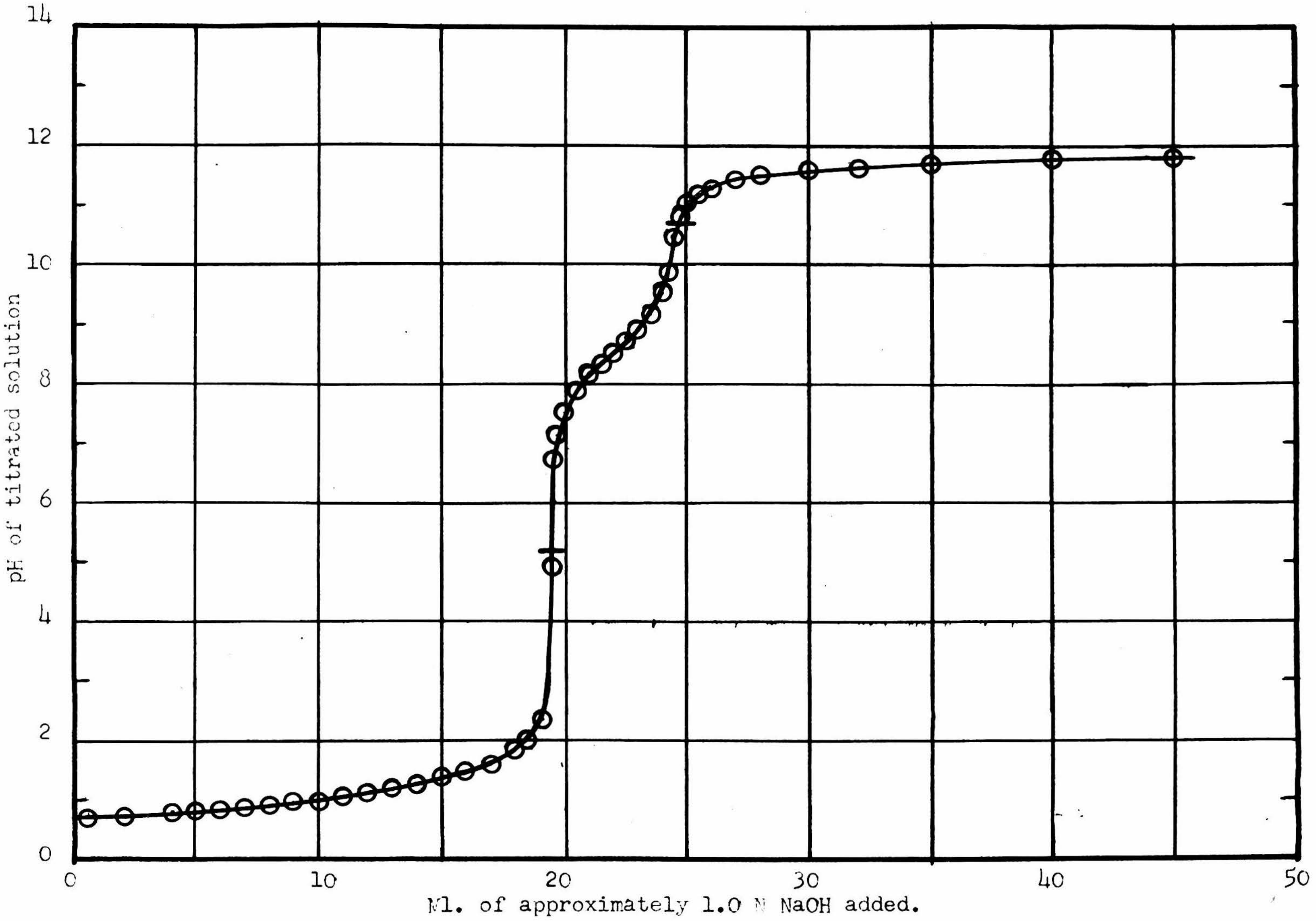

Fig. 1. Titration curve of 0.05 molal disulfonate in 0.2 normal acid at 25° C. and an ionic strength of 1.00.

concentration on the assumption that these constants are infinite is therefore less than 10 per cent under the least favorable conditions to be encountered in the rate experiments.

Rate Determination Procedure

The thermostat in which the reactions were run was an electronically controlled water thermostat capable of being held within 0.03°C. of the desired temperature. The temperature-sensitive element was an Aminco *Metastatic* mercury thermoregulator.

The reaction was followed by titrating samples taken from the reaction mixture for total strong acid. The reaction mixtures were made up in 250 ml. glass-stoppered volumetric flasks, using stock solutions of all materials except the potassium amine disulfonate which was weighed out as the solid. The required quantities of stock solutions were measured into the volumetric flasks and the latter nearly filled to the mark with distilled water. They were then placed in the thermostat along with a reservoir bottle of distilled water. After temperature equilibrium had been established, the weighed portion of disulfonate was rapidly washed into the flask and the flask filled up very close to the mark with water from the reservoir bottle. The volumetric flask was stoppered and shaken violently for 1-2 minutes to dissolve the salt. (In the later experiments at higher temperatures, the salt was ground in an agate mortar to speed up the rate of solution; thus the time of solution was cut down to 1/2 minute.) The flask was then reimmersed in the thermostat and the volume made up exactly to the mark and the contents agitated thoroughly. It was then emptied into 500 ml. glass-stoppered Erlenmeyer flasks immersed in the thermostat. Two 10 ml. samples were taken and analyzed immediately to fix the initial hydrogen ion concentration, and then 10 ml. samples were taken at appropriate intervals. The pipettes used to take the samples had been previously calibrated under exactly the same conditions including the temperature of the sample. In the later runs, two final samples were hydrolyzed completely by heating to 80-90°C. for one hour to check on the disulfonate concentration.

For runs at 25°C. the samples were analyzed by running the sample into a 125 ml. Erlenmeyer flask, adding two drops of bromcresol green-methyl red mixed indicator and titrating rapidly with 0.02 normal sodium hydroxide and 0.02 N hydrochloric acid. The samples which had been hydrolyzed completely were titrated using bromthymol blue indicator because of the change of the pH at the equivalence point due to the absence of disulfonate ion. Samples taken during rate experiments done at temperatures higher than 25°C. were pipetted into an excess of 0.02 normal base, and the excess base back titrated with 0.02 normal hydrochloric acid, using the same indicator.

Results and Discussion

Rate Studies at an Ionic Strength of 1.00

To establish the mechanism, a series of experiments was done with the ionic strength kept at a constant value of 1.00. This high ionic strength was chosen because it is in the neighborhood of the minimum of the activity coefficient for many electrolytes[18] thus minimizing any effect of the change of ionic strength during the reaction, and because the concentration of neutral salt (sodium chloride) added to give this ionic strength was much greater than the concentration of reactants and products in most of the experiments, which also tended to minimize any effect due to a change of ionic strength during the course of the reaction.

Initial Rates

To establish tentatively the rate law, the average initial rates over the first ten per cent 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 in minutes $= x$) and the dependence of the initial rates on initial concentrations of reactants determined. These initial rates are shown in Table 4. The dependence of initial rate on initial hydrochloric acid concentration at constant initial disulfonate concentration is shown in Fiture 2 for two initial disulfonate concentrations. The dependence of initial rate on initial disulfonate concentration at constant initial hydrochloric acid concentration is shown in Figure 3 for two initial hydrochloric acid concentrations.

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[18] Harned and Owen, loc. cit., p. 444.

Table 4

The Results of the Determination of Initial Rates at

t = 25.00°C. and $\Gamma = 1.00$

Run No.	Initial Concentrations Molarity HCl	 Molarity $K_2HN(SO_3)_2$	 Molarity NaCl	Initial Rate $\frac{\Delta x}{\Delta t}$ moles/l. x min. x 10^{-5}
28	0.01000	0.02000	0.930	0.21^{5}
26	.01967	.02000	.920	$.42^{1}$
23	$.0593^{3}$	.02000	.880	1.19
18	.0988	.02000	.840	2.06
14	.1466	.02000	.790	2.78
12	.1973	.02000	.740	3.51
27	.01018	$.0500^{0}$	.840	0.60^{6}
25	.02001	$.0500^{0}$	.830	1.07
20	$.0590^{0}$	$.0500^{0}$	.790	3.29
15	.0984	$.0500^{0}$	.750	4.9^{1}
13	.1478	$.0500^{0}$	.700	7.0^{4}
11	.1955	$.0500^{0}$	.650	10.2
24	$.0592^{8}$	.01000	.910	0.58^{1}
22	$.0593^{5}$	$.0300^{0}$	.850	1.84
21	$.0595^{8}$	$.0400^{0}$	.820	2.32
19	.0988	.01000	.870	0.93^{5}
17	.0990	$.0300^{0}$	.810	2.78
16	.0978	$.0400^{0}$	.780	4.3^{5}

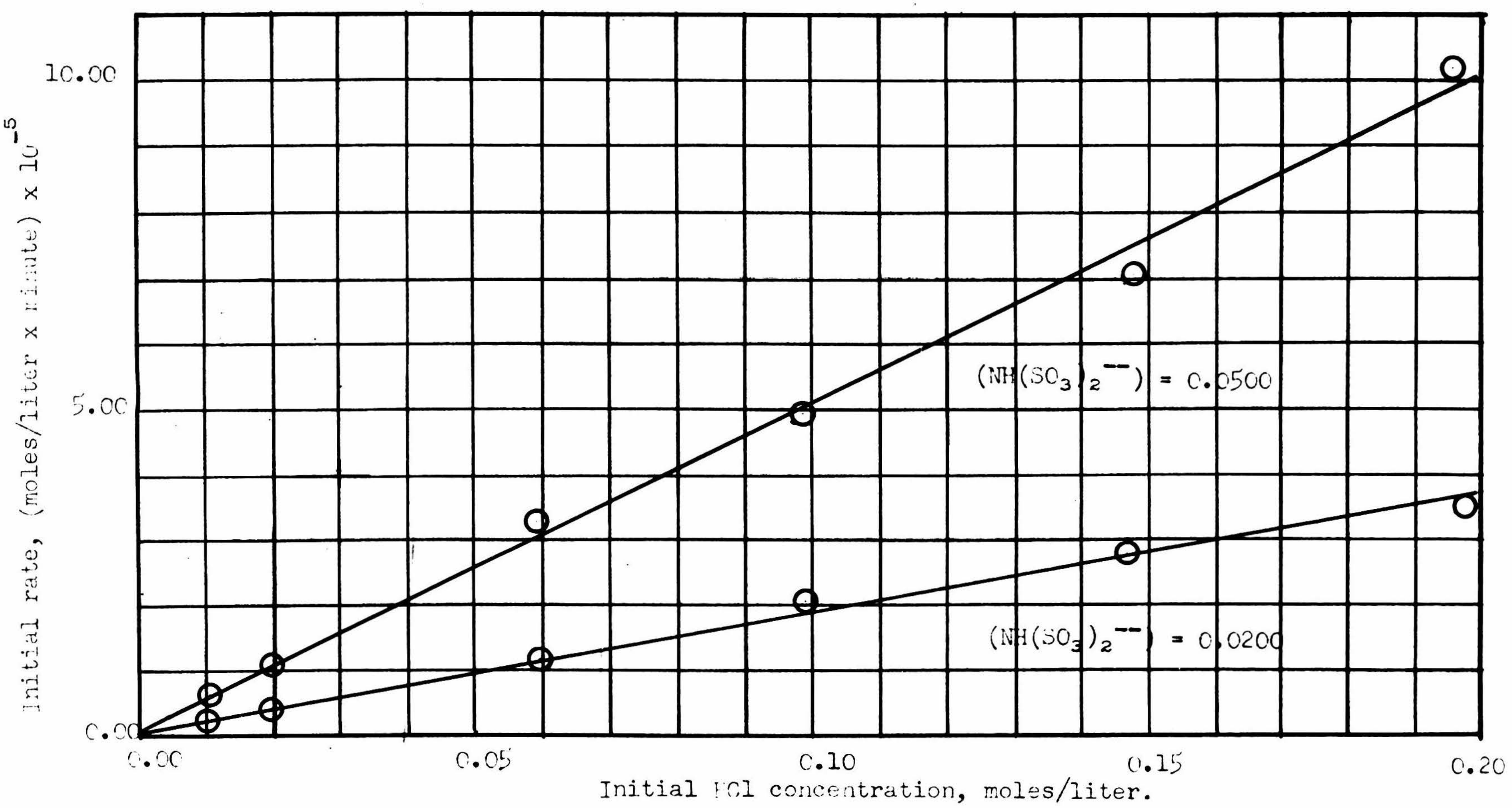

Fig. 2. Graph showing dependence of initial rate of hydrolysis of $NH(SO_3)_2^{--}$ on HCl concentration at an ionic strength of 1.00 and at 25.00° C.

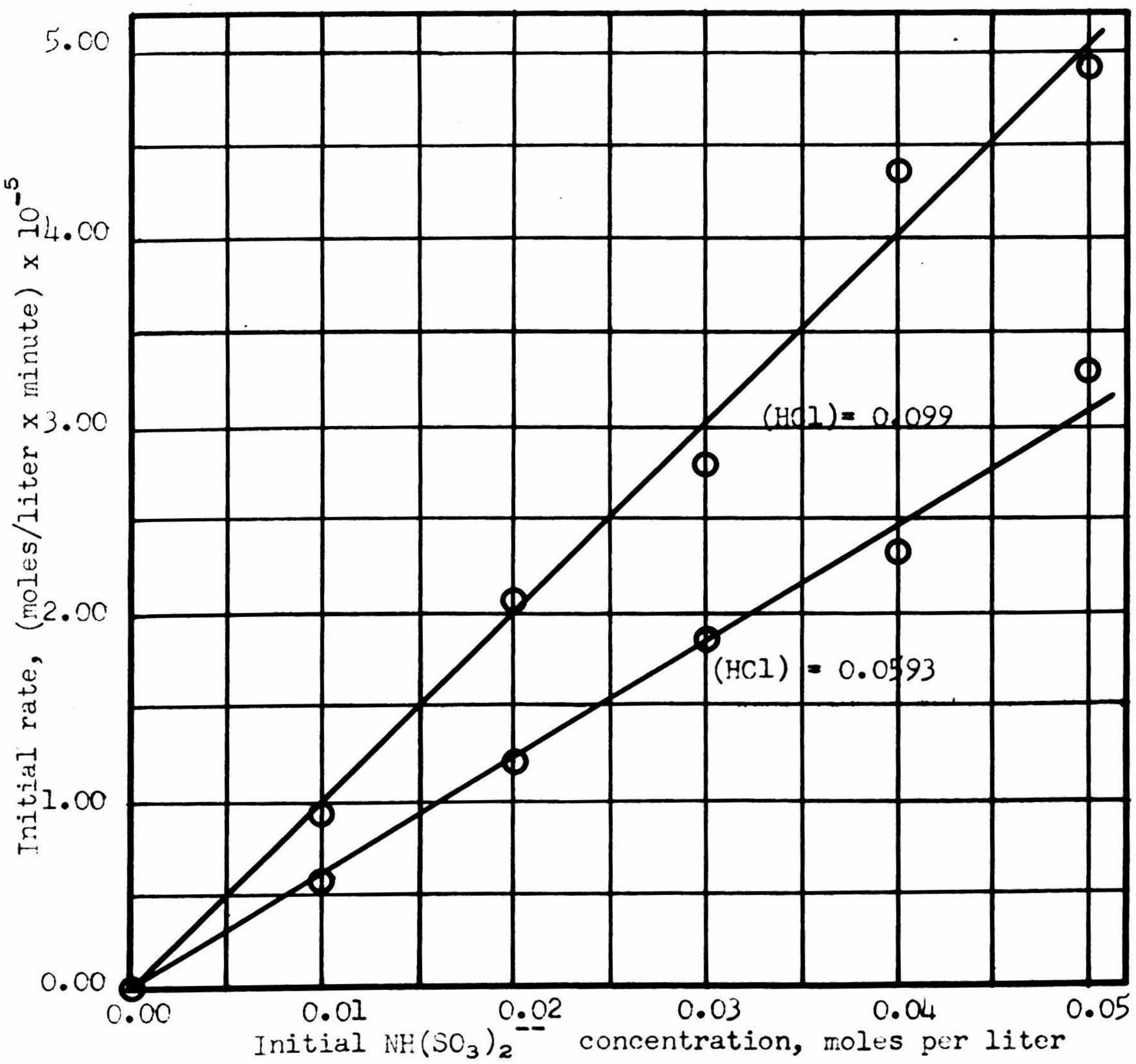

Fig. 3. Graph showing dependence of initial rate of hydrolysis of $NH(SO_3)_2^{--}$ on $NH(SO_3)_2^{--}$ concentration at an ionic strength of 1.00 and at 25.00° C.

This suggests the rate equation

$$-\frac{d\ (HN(SO_3)_2^{=})}{dt} = k\ (H^+)\ (HN(SO_3)_2^{=}) \quad . \qquad (3)$$

The small finite intercepts in Figure 1 suggest a possible slow hydrolysis not catalyzed by hydrochloric acid. The possibility that this is caused by the small hydrogen ion concentration due to the dissociation of disulfonate ion itself is eliminated by a simple calculation of the hydrogen ion concentration prevailing in solutions of disulfonate with $\Gamma = 1$, and at 25°C; it is much too small to give the intercepts in Figure 1. The remaining possibility of a relatively slow reaction with water not catalyzed by hydrogen ion was checked by attempting to follow the reaction in alkaline medium. A reaction mixture 0.05 molar in disulfonate and 0.005 molar in sodium hydroxide with sufficient sodium chloride to give $\Gamma = 1.00$ was allowed to stand at 25°C. for 34,000 minutes during which time it was analyzed periodically. Such a solution is approximately 0.045 molar in $HN(SO_3)_2^{=}$, 0.005 molar in $N(SO_3)_2^{\equiv}$, 10^{-8}normal in H and 10^{-6} normal in OH^-. The observed change in titer of the solution corresponded to hydrolysis of 0.2 per cent of the disulfonate and the calculated average rate is 3×10^{-9} moles/liter x minute. The hydrogen ion catalyzed rate, judging from the slope of the line in Figure 1, is 4×10^{-12}moles/liter x minute. The uncatalyzed rate calculated in this manner is probably an upper limit to the actual rate because of the inevitable decrease in titer of an alkaline solution on standing for a long period of time, and the possibility of a base catalyzed reaction. From this upper limit it was concluded that the uncatalyzed reaction at 25°C. is so slow as to be negligible at any hydrogen ion concentration at which the acid catalyzed reaction has a rate fast enough to be measured in a reasonable length of time, and that the intercepts of Figure 1 are due to a combination of experimental and drafting errors.

If one accepts equation (3) as expressing correctly the results of the initial rate studies, the question of the effect of the products of the reaction on the rate arises. The assumption was made that amine disulfonic acid, and amine monosulfonic acids are strong acids. This assumption is experimentally supported in the case of amine monosulfonic acid[12]. The disulfonic acid is thought to be a strong dibasic acid because of the observation that often when two hydrogen atoms are attached to relatively widely separated oxygens the two successive acid constants are much less widely separated than such constants for hydrogens attached to oxygens which are close together and because the assumption was made that the first acid dissociation constant of the disulfonic acid is about as strong as that of the monosulfonic acid. In addition, there is the experimental evidence of the titration curve of an acid solution of disulfonate - see Figure 1. Therefore, the sulfate ion presents the only likely possibility of appreciable effect on the rate. If it is assumed that the HSO_4^- ion does not catalyze the reaction, the differential equation

$$-\frac{dx}{dt} = k\,\frac{\sqrt{(s + K - a)^2 + 4K(a + x)} - (s + K - a)}{2}\,(d - x), \qquad (4)$$

is easily derived from equation (3) and the equilibrium expression for the ionization of HSO_4^- ion. In this equation

x = concentration of acid produced by the reaction, moles/liter of solution (the reaction variable);

t = time in minutes,

k = specific rate constant, liter/moles x minute;

s = concentration of sulfate added at t 0;

K = ionization function of bisulfate ion,

$$= \frac{(H^+)(SO_4^=)}{(HSO_4^-)} \quad ;$$

a = concentration of hydrochloric acid, moles/liter of solution at t = 0;

d = concentration of disulfonate at t = 0, moles/liter.

To test the validity of (4) insofar as it expresses the dependence of rate on initial total sulfate concentration the average initial rate at 25°C. and at $\Gamma = 1.00$ over the first 10 per cent of hydrolysis of a series of reaction mixtures in which the only variable was initial sulfate concentration was determined from graphically smoothed data. The results are given in Table 5.

To estimate the value of the ionization function, K, for HSO_4^- at $\Gamma = 1.00$ and at 25°C. the value of the ionization constant of HSO_4^- obtained by Hamer[19] was multiplied by the ratio of the ionization function of $H_2PO_4^-$ at $\Gamma = 1.00$ to the

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[19] Hamer, J. Am. Chem. Soc. 56, 860 (1934).

Table 5

The Effect of Initial Sulfate Concentration on Initial Rate at 25.00°C. and $\Gamma = 1.00$. Initial HCl Molarity, 0.0197; Initial $HN(SO_3)_2^{=}$ Molarity, 0.02000.

Run No.	Molarity Na_2SO_4	Molarity NaCl	Initial Rate, $\frac{\Delta x}{\Delta t}$ moles/l. x min.	$\left(\frac{\partial(H^+)}{\partial K}\right)_{0.09}$	$\frac{\Delta x}{\Delta t} \Big/ \left(\frac{\partial(H^+)}{\partial K}\right)_{0.09}$ x 10^{-6}	$(H^+) \Big/ \left(\frac{\partial(H^+)}{\partial K}\right)_{0.09}$
33	0.0200	0.860	$0.33^4 \times 10^{-5}$	0.0252	133	0.660
34	.0400	.800	$.28^8$ x	.0395	72.9	.362
35	.0500	.740	$.26^0$ x	.0469	55.4	.266
36	.0800	.680	$.22^2$ x	.0517	42.9	.214
37	.1000	.620	$.19^0$ x	.0524	36.2	.188

ionization constant of $H_2PO_4^-$,[14]

$$K(HSO_4^-, \Gamma=1) \simeq \frac{K(H_2PO_4^-, \Gamma=1)}{K_o(H_2PO_4^-)} \times K_o(HSO_4^-) \qquad (5)$$

$$\simeq \frac{4.6^7 \times 10^{-7}}{6.23 \times 10^{-8}} \times 1.20 \times 10^{-2} = 0.090$$

Here K = ionization function, and K_o = ionization constant of the acid in question. This 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.

The data of Table 5 are plotted in Figure 4 as initial rate/$\left(\frac{\partial(H^+)}{\partial K}\right)_{K=0.09}$ versus $(H^+)_{K=0.09}/\left(\frac{\partial(H^+)}{\partial K}\right)_{K=0.09}$. From (3) the equation which ought to govern the results of this particular set of experiments is

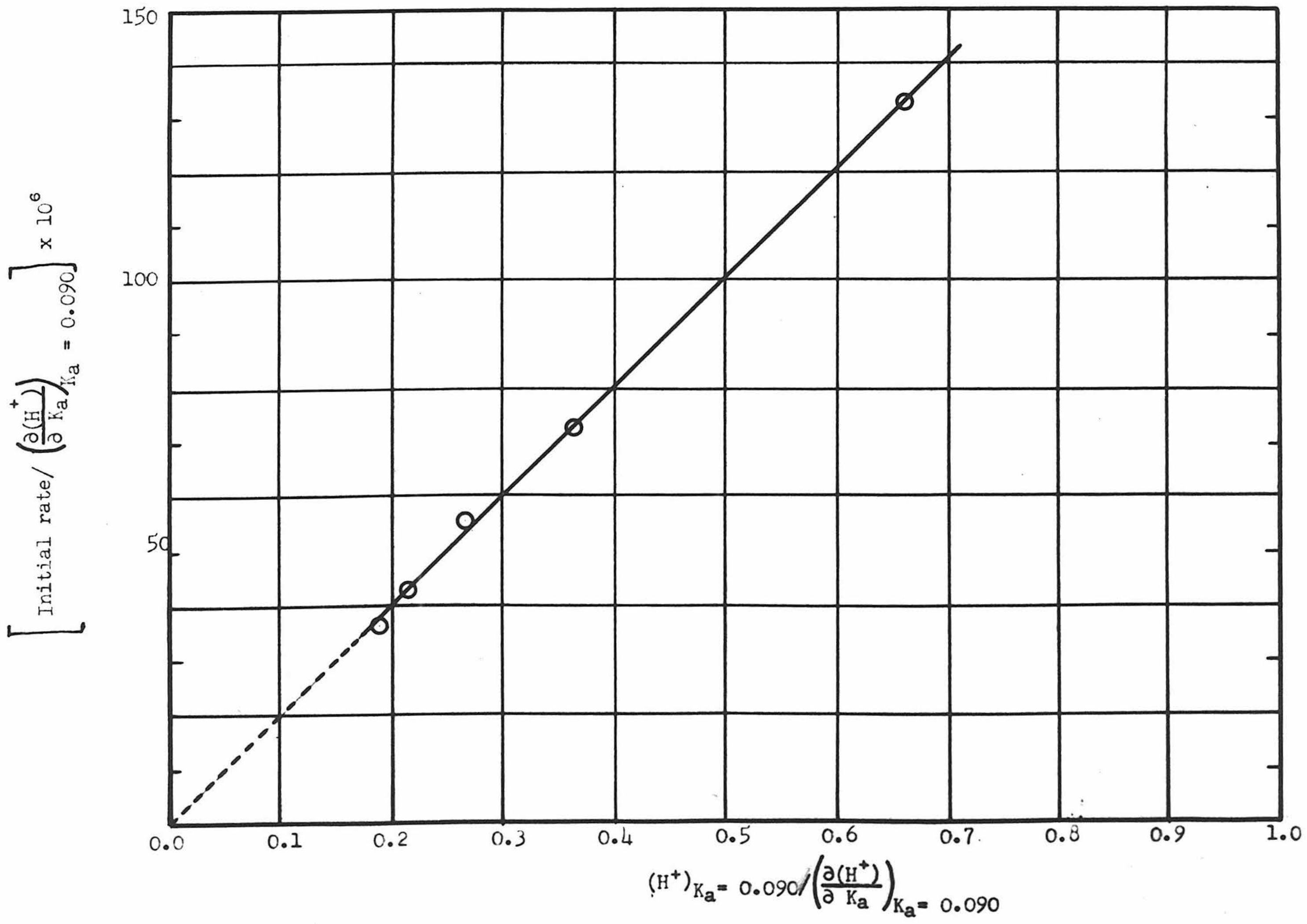

Fig. 4. Graph showing the effect of added sulfate ion upon the initial rate and the correctness of the assumed value of the acid dissociation constant of the HSO_4^- ion. Ionic strength= 1.00. Temperature = 25.00° C.

$$-\left[\frac{d(HN(SO_3)_2^{=})}{dt}\right]_{t=0} = \left[k(HN(SO_3)_2^{=})\right]_{t=0}\cdot(H^+)_{t=0} \qquad (6)$$

If it is assumed that there is a small inaccuracy δK in the estimated value (5) of K, then

$$(H^+) = (H^+)_{K=0.09} + \left(\frac{\partial(H\ )}{\partial K}\right)_{K=0.09}\cdot\ \delta K$$

and

$$-\frac{\left[\frac{d(HN(SO_3)_2^{=})}{dt}\right]_{t=0}}{\left(\frac{\partial(H^+)}{\partial K}\right)_{K=0.09}} = \left[k(HN(SO_3)_2^{=})\right]_{t=0}\cdot\left[\frac{(H^+)_{K=0.09}}{\left(\frac{\partial(H^+)}{\partial K}\right)_{K=0.09}} + \delta K\right] \qquad (7)$$

The value of $\left(\frac{\partial(H^+)}{\partial K}\right)_{K=0.09}$ is easily calculated from the equilibrium expression for the ionization of HSO_4^- ion which gives

$$\frac{\partial(H^+)}{\partial K} = \frac{a-(H^+)}{s+K+(H^+)-\left[a-(H^+)\right]}\ . \qquad (8)$$

The values of these various quantities are tabulated in Table 5 and the fit to equation (7) shown in Figure 4. It is evident that δK is negligibly small and that HSO_4^- has no detectable effect in catalyzing the reaction. From the slope and the possible error in the intercept it is possible to estimate that the value of δK is less than 5×10^{-3}, that is, K is in error by less than 6 per cent.

The values of k, the specific rate constant at 25.00°C. and at $\Gamma = 1.00$ calculated from the slopes of Figure 2, 3, and 4, that is to say, from initial rate data, are tabulated in Table 6. Considering the approximate nature of initial rate calculations, the agreement amongst the various series of experiments is rather good, and tends to confirm the proposed rate equation (3).

Table 6

Specific Rate Constant at 25.00°C. and at $\Gamma = 1.00$ Estimated From Initial Rate Data.

Description of Experiments	k, liter/moles x min.
Varying HCl molarity, $(HN(SO_3)_2^{=}) = 0.02000$ molar	1.00×10^{-2}
Varying HCl molarity, $(HN(SO_3)_2^{=}) = 0.05000$ molar	0.93×10^{-2}
Varying $HN(SO_3)_2^{=}$ molarity, $(HCl) = 0.059^{3}$ molar	1.04 x
Varying $HN(SO_3)_2^{=}$ molarity, $(HCl) = 0.099$ molar	1.02 x
Varying $SO_4^{=}$ molarity, $(HCl) = 0.0197$ molar, $(HN(SO_3)_2^{=}) = 0.0200$ molar	1.01 x

Analysis of Data

From the results of the initial rate studies it was virtually certain that equation (3) is the correct rate equation. To confirm this, the analysis of the progress of the reaction with time was carried out on the basis of (3). This could have been done in any of several ways.

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

$$k = \frac{x_2 - x_1}{\int_{t_1}^{t_2} \frac{\sqrt{(s+K-a)^2 + 4K(a+x)} - (s+K-a)}{2} (d-x)\, dt} \qquad (9)$$

which may be easily derived from (4) by integration. To show the validity of (3) it was only necessary to compute the value of the right hand side of (9) for several successive intervals of time during a run for several runs and thus show that it is a constant during a run, and constant for all runs at the same ionic strength and temperature. The integral was evaluated by one of two methods. The method used for all runs at $\Gamma = 1.00$ and at 25°C. was to smooth the data, graphically, calculate the values of the integrand from the smoothed data, plot the integrand against time, and graphically evaluate the definite integral by means of a polar planimeter. For runs under other conditions, a tabular method of evaluating the integral utilizing the trapezoid rule was used.

Another possibility is to solve the differential equation (4) and test the fit of the data to the result. The variables may be separated to give

$$\int \frac{dx}{(d-x)\,\dfrac{\sqrt{(s+K-a)^2 + 4K(a+x)} - (s+K-a)}{2}} = kt + C \,, \qquad (10)$$

where C is the constant of integration. The integral may be expressed in terms of logarithmic functions by making the transformation

$$\frac{s + K - a}{2} = \alpha \,, \quad \left(\frac{s + K - a}{2}\right)^2 + K(a + d) = \gamma^2, \quad \left(\frac{s+K-a}{2}\right)^2 + K(a+x) = z^2,$$

and applying the method of integration by partial fractions to the result. This gives

$$\frac{1}{\alpha-\gamma} \ln(\gamma - z) + \frac{1}{\alpha+\gamma} \ln(\gamma + z) - \frac{2\alpha}{\alpha^2-\gamma^2} \ln(z-\alpha) = kt + C$$

and this may be written

$$\left.\begin{aligned} -\frac{1}{(H^+)_\infty} \log\left[(H^+)_\infty - (H^+)_t\right] + \frac{1}{2\alpha + (H^+)_\infty} \log\left[2\alpha + (H^+)_t + (H^+)_\infty\right] \\ + \frac{2\alpha}{K(a+d)} \log (H^+)_t = \frac{k}{2.303} t + C \end{aligned}\right\} \qquad (11)$$

where $(H^+)_t$ is the hydrogen ion concentration at time t, and $(H^+)_\infty$ is the hydrogen ion concentration at completion of the reaction. The fit of (11) to the data was tested by calculating the value of the left hand side for unsmoothed data and plotting against t. The closeness of fit of the plotted points to a straight line is the criterion of how closely the data fit the proposed rate equation and the slope of the best straight line through the points yields a value of the specific rate constant, k. This method was used on several representative runs to illustrate graphically the fit to (3).

The results of the analysis of the data at 25.00°C. and an ionic strength of one by the graphical integration method based on (9) are shown in Table 7.

Table 7

Values of the Rate Constant Obtained by Graphical Integration; Temperature, 25.00°C.; Ionic Strength, 1.00.

t_1 min.	t_2 min.	x_1 $\frac{\text{moles}}{\text{liter}}$	x_2 $\frac{\text{moles}}{\text{liter}}$	k $\frac{\text{liter}}{\text{moles x min.}}$
Run No. 28, a = 0.01000, d = 0.02000, s = 0, (NaCl) = 0.930				
0	2000	0	0.00440	1.05×10^{-2}
1500	4000	0.00325	0.00855	1.02 x
3500	6000	0.00760	0.01205	0.97 x
5000	9000	0.01040	0.01575	0.98 x
Run No. 26, a = 0.01967, d = 0.02000, s = 0, (NaCl) = 0.920				
0	1000	0	0.00410	1.09×10^{-2}
750	2500	0.00315	0.00905	1.01×10^{-2}
2000	4000	0.00755	0.01300	1.03 x
3500	5000	0.01165	0.01525	1.26 x

t_1 min.	t_2 min.	x_1 $\frac{\text{moles}}{\text{liter}}$	x_2 $\frac{\text{moles}}{\text{liter}}$	k $\frac{\text{liter}}{\text{moles x min.}}$
Run No. 23, a = 0.0593^{3}, d = 0.02000, s = 0, (NaCl) = 0.880				
0	500	0	0.00552	1.06 x 10^{-2}
250	1000	0.00292	.00982	1.09 x
750	1500	.00778	.01292	1.12 x
1250	2000	.01102	.01469	0.91 x
Run No. 18, a = 0.0988, d = 0.02000, s = 0, (NaCl) = 0.840				
0	250	0	0.00472	1.07 x
100	750	.00207	.01101	1.04 x
500	1000	.00828	.01319	1.03 x
750	1750	.01101	.01689	1.02 x
Run No. 14, a = 0.1466, d = 0.02000, s = 0, (NaCl) = 0.790				
0	200	0	0.00539	1.06 x
100	400	.00281	.00948	1.10 x
300	750	.00766	.01412	1.08 x
500	1250	.01092	.01698	1.01 x
750	1500	.01412	.01782	0.88 x
Run No. 12, a = 0.1973, d = 0.02000, s = 0, (NaCl) = 0.740				
0	150	0	0.00552	1.08 x
100	300	.00363	.00967	1.17 x
200	500	.00712	.01317	1.06 x
300	700	.00967	.01563	1.06 x
500	800	.01317	.01630	1.03 x

Table 7 (cont.)

t_1 min.	t_2 min.	x_1 moles/liter	x_2 moles/liter	k liter/moles x min.
Run No. 27, a =0.01018, d =0.0500^{0}, s = 0, (NaCl)= 0.840				
0	2000	0	0.01310	0.99 x 10^{-2}
1500	3000	.00955	.02065	0.96 x
2500	4500	.01685	.03060	0.95 x
4000	5500	.02760	.03580	0.91 x
Run No. 25, a = 0.02001, d = 0.0500^{0}, s = 0, (NaCl)= 0.830				
0	1250	0	0.01350	1.00 x
1000	2000	.01080	.02115	0.96 x
1750	3500	.01870	.03325	0.93 x
3000	4250	.02985	.03715	0.85 x
Run No. 20, a = 0.0590^{0}, d =0.0500^{0}, s = 0, (NaCl)= 0.790				
0	400	0	0.01195	1.09 x
300	800	.00935	.02120	1.01 x
600	1500	.01685	.03290	1.00 x
1000	1750	.02495	.03560	0.98 x
Run No. 15, a =0.0984, d = 0.0500^{0}, s = 0, (NaCl)= 0.750				
0	300	0	0.01390	1.07 x
200	600	.02472	.01510	1.08 x
500	1000	.02136	.03347	1.01 x
800	1500	.02995	.04008	0.88 x

Table 7 (cont.)

t_1 min.	t_2 min.	x_1 moles/liter	x_2 moles/liter	k liter/(moles x min.)
Run No. 13, $a = 0.1478$, $d = 0.0500^{0}$, $s = 0$, $(NaCl) = 0.700$				
0	200	0	0.01337	1.03×10^{-2}
100	400	.00705	.02330	1.03 x
300	800	.01873	.03580	0.99 x
600	1200	.03070	.04205	0.92 x
Run No. 11, $a = 0.1955$, $d = 0.0500^{0}$, $s = 0$, $(NaCl) = 0.650$				
0	200	0	0.01817	1.13 x
100	300	.00985	.02475	1.16 x
200	500	.01817	.03380	1.11 x
400	1000	.02970	.04453	1.08 x
600	1300	.03717	.04740	1.07 x
Run No. 24, $a = 0.0592^{8}$, $d = 0.01000$, $s = 0$, $(NaCl) = 0.910$				
0	500	0	0.00270	1.05 x
300	1000	.00170	.00468	1.04 x
750	1750	.00382	.00668	1.00 x
1250	2000	.00541	.00712	1.00 x
Run No. 22, $a = 0.0593^{5}$, $d = 0.03000$, $S = 0$, $(NaCl) = 0.850$				
0	500	0	0.00827	1.04 x
300	1000	.00535	.01462	1.03 x
750	1500	.01168	.01888	0.99 x
1000	1750	.01462	.02059	0.94 x
Run No. 21, $a = 0.0595^{8}$, $d = 0.04000$, $s = 0$, $(NaCl) = 0.820$				
0	400	0	0.00910	1.03 x
300	1000	.00695	.01937	1.00 x
750	1500	.01545	.02570	1.00 x

Table 7 (cont.)

t_1 min.	t_2 min.	x_1 $\frac{\text{moles}}{\text{liter}}$	x_2 $\frac{\text{moles}}{\text{liter}}$	k $\frac{\text{liter}}{\text{moles x min.}}$
Run No. 19, a = 0.0988, d = 0.01000, s = 0, (NaCl) = 0.870				
0	300	0	0.00271	1.06×10^{-2}
200	500	.00185	.00422	1.14 x
300	1000	.00271	.00668	1.11 x
750	1250	.00559	.00728	0.97 x
Run No. 17, a = 0.0990, d = 0.03000, s = 0, (NaCl) = 0.810				
0	250	0	0.00682	1.03 x
150	750	.00417	.01649	1.04 x
500	1000	.01235	.01957	1.00 x
750	1250	.01649	.02198	0.97 x
Run No. 16, a = 0.0978, d = 0.04000, s = 0, (NaCl) = 0.780				
0	200	0	0.00802	1.13 x
100	500	.00433	.01708	1.07 x
400	1000	.01433	.02662	1.01 x
750	1500	.02257	.03247	1.02 x
Run No. 33, a = 0.01973, d = 0.02000, s = 0.02000, (NaCl) = 0.860				
0	1500	0	0.00495	1.03 x
750	3000	.00250	.00920	1.03 x
2000	6000	.00640	.01500	1.02 x
5000	7250	.01330	.01625	0.99 x
Run No. 34, a = 0.01977, d = 0.02000, s = 0.04000, (NaCl) = 0.800				
0	2000	0	0.00560	1.02 x
1500	4000	.00425	.01030	1.03 x
3000	7000	.00820	.01495	0.98 x
5000	9000	.01210	.01675	0.96 x

Table 7 (cont.)

t_1 min.	t_2 min.	x_1 moles/liter	x_2 moles/liter	k liter/(moles x min.)
Run No. 35, a = 0.01972, d = 0.02000, s = 0.0600^0, (NaCl) = 0.740				
0	3000	0	0.00735	1.04 x 10^{-2}
1500	6000	.00385	.01270	1.02 x
3000	7000	.00735	.01400	1.00 x
4000	8500	.00935	.01560	1.00 x
Run No. 36, a = 0.01980, d = 0.02000, s = 0.0800^0, (NaCl) = 0.680				
0	3000	0	0.00660	1.04 x
2000	6000	.00455	.01160	0.99 x
5000	8000	.01010	.01415	1.01 x
6000	8500	.01160	.01465	1.02 x
Run No. 37, a = 0.01970, d = 0.02000, s = 0.1000, (NaCl) = 0.620				
0	3000	0	0.00575	1.01 x
2000	5000	.00380	.00920	1.05 x
4000	8000	.00760	.01305	0.99 x
7000	9000	.01190	.01400	0.95 x

It is noteworthy that there is in most cases a definite downward trend in the calculated rate constants especially after about fifty per cent 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. It could possibly be due to any one of a number of causes, e.g., specific ion interaction effects of the products of the reaction on the reactants, and the activated complex, definite interference in the mechanism by the products, impure reactants, some systematic undetected experimental error, or a relatively slow side reaction.

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 (3) is essentially correct.

To illustrate graphically the fit to the rate equation (3), the function on the left hand side of (11) plotted against time for several representative runs at 25°C. and ionic strength of 1.00 is shown in Figure 5. The specific rate constants derived from the slope of the straight lines in Figure 5 agree rather well with those calculated by the graphical integration method as may be seen by comparison of Tables 7 and 8.

Table 8

Specific Rate Constants at 25°C. and at Γ= 1.00 Calculated From the Slopes of the Lines of Figure 5.

Run No.	Specific Rate Constant liter/moles x minutes
28	1.00×10^{-2}
12	1.12 x
27	0.97 x
11	1.11 x
37	1.01 x

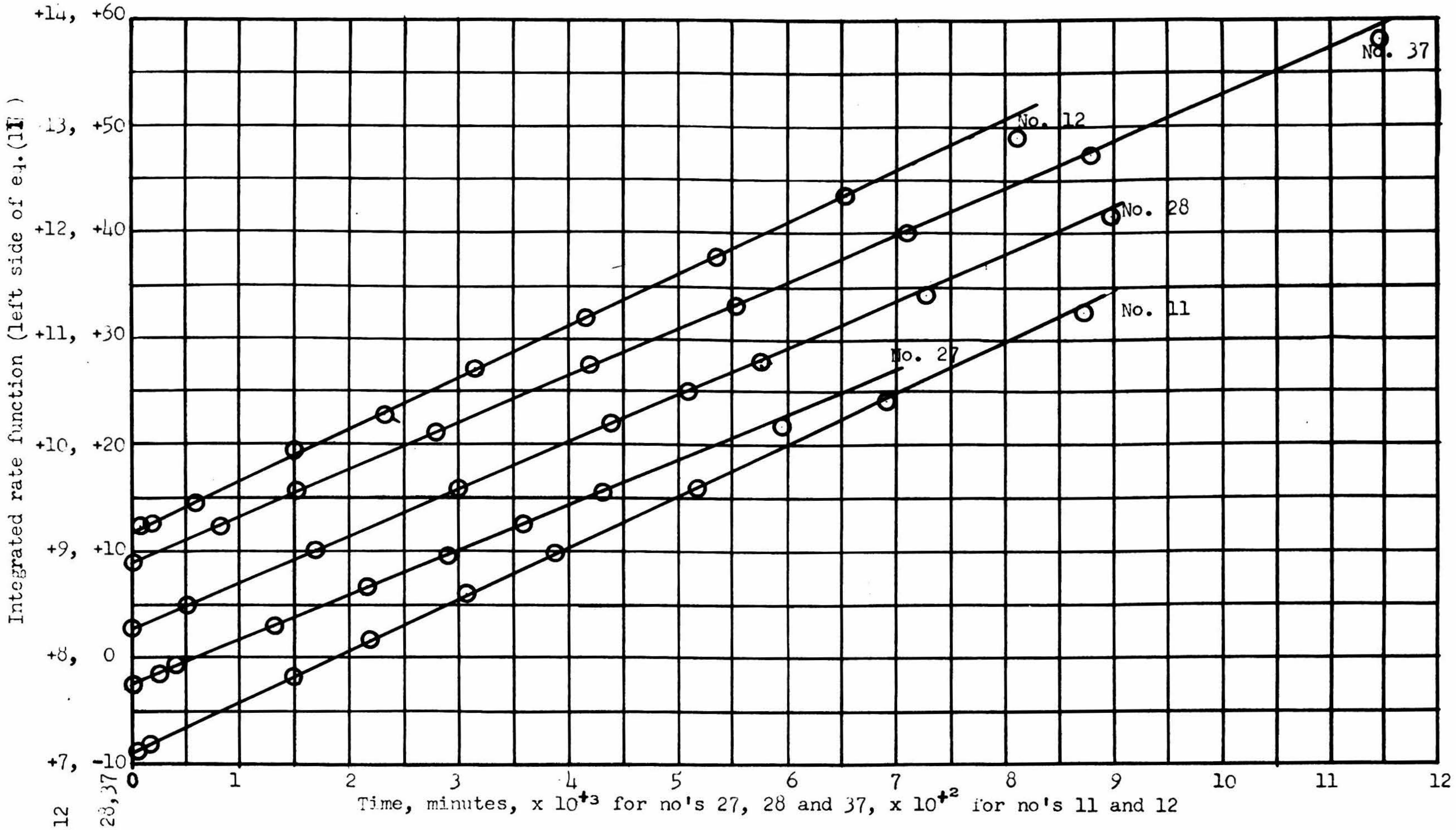

Fig. 5. Plot of experimental data to illustrate fit to eq. (11) for several representative experiments.

Dependence of the Specific Rate Constant on Ionic Strength at 25.00°C.

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. The use of equation (1) for the variation of activity with ionic strength in conjunction with Brønsted's theory yields the equation

$$\log_{10} k = \log_{10} k_0 + \frac{A\,2 z_1 z_2 \Gamma^{1/2}}{1 + \Gamma^{1/2}} + \beta \Gamma \qquad (12)$$

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 per cent of the disulfonate had hydrolyzed. The data were smoothed and a rate constant calculated by the 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 (1), and that the value of K at $\Gamma = 1.00$, 0.090, was accurate. This taken in conjunction with Hamer's value of K_o at 25.00°C.[19] gives the equation

$$\log K = \log K_o + \frac{4A\Gamma^{1/2}}{1 + \Gamma^{1/2}} + \gamma\Gamma \qquad (13)$$

where, at 25.00°C., $K_o = 0.0120$, $A = 0.5065$, and $\gamma = -0.137$ for sodium chloride solutions. The rate constants are shown in Table 9.

Table 9

Dependence of the Rate Constant on Ionic Strength at 25°C.

Exp. No.	(HCl) $\frac{\text{moles}}{\text{liter}}$	$(HN(SO_3)_2^{=})$ $\frac{\text{moles}}{\text{liter}}$	(NaCl) $\frac{\text{moles}}{\text{liter}}$	$\Gamma^{\frac{1}{2}}$ $\frac{\text{moles}^{\frac{1}{2}}}{\text{liter}}$	K $\frac{\text{moles}}{\text{liter}}$	k $\frac{\text{liter}}{\text{moles x min.}}$
38	0.00479	0.00500	0.0	0.140^7	0.021^2	0.047^8
39	.00482	.00500	.0100	$.172^6$	$.023^9$	$.043^6$
40	.00978	.01000	0.0	$.199^3$	$.025^7$	$.039^5$
41	.00987	.01000	.0500	$.300^0$	$.034^0$	$.028^7$
42	.00985	.01000	.1200	.400	$.043^1$	$.023^3$
43	.00985	.01000	.2100	.500	$.052^5$	$.018^9$
28	.01000	.02000	.930	1.000	$.090^0$	$.010^2$

In order to estimate the value of z_1z_2 in (12), log k was plotted against $0.5065\Gamma^{\frac{1}{2}}/(1 + \Gamma^{\frac{1}{2}})$ and a smooth curve drawn through the points as shown in Figure 6. 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

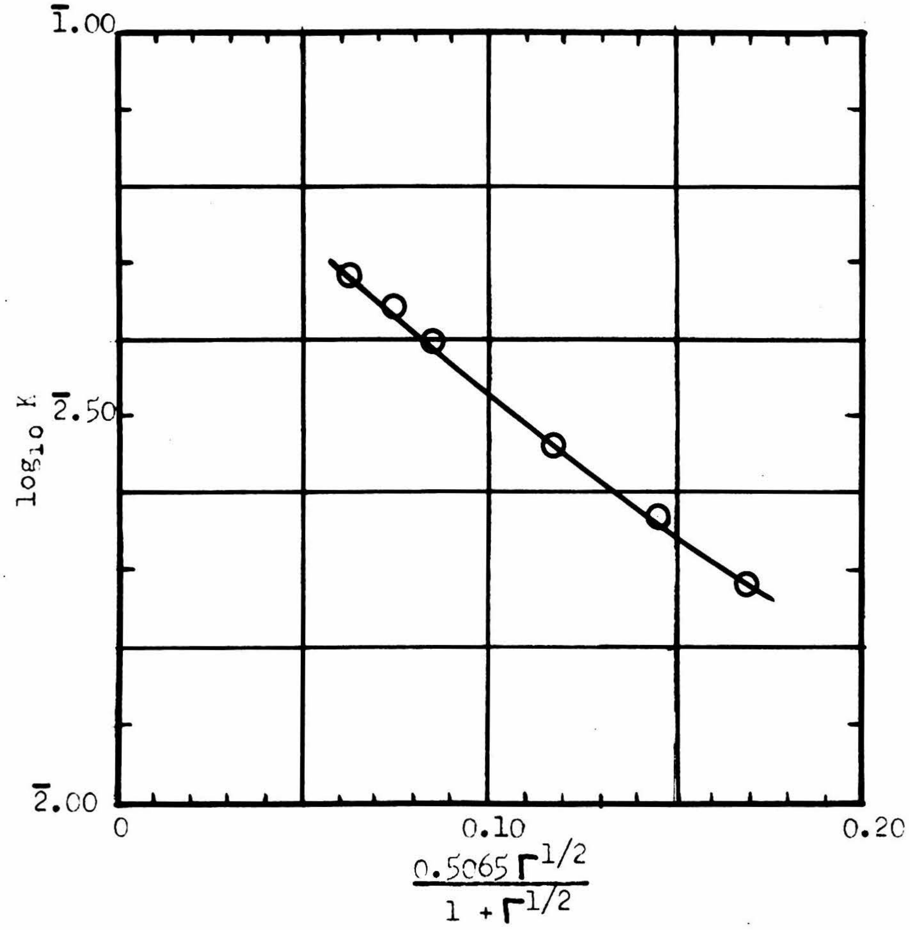

Fig. 6. Dependence of reaction constant on ionic strength at 25.00° C.

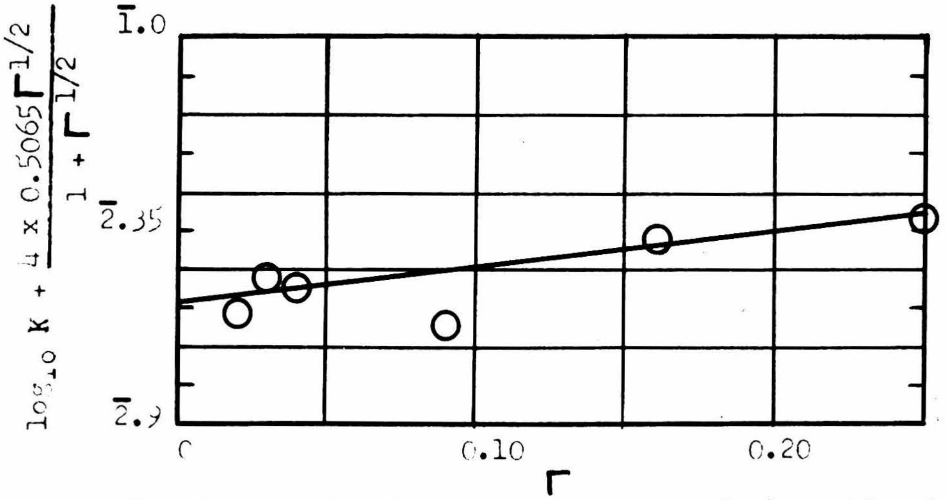

Fig. 7. Graphical evaluation of β in (12) at 25.00° C.

by about 5 - 10 per cent. To fit equation (12) to the data, $\log k + \frac{4 \times 0.5065 \Gamma^{1/2}}{1 + \Gamma^{1/2}}$ was plotted against Γ, as shown in Figure 7, to evaluate β. It was found that $\beta = +0.09^2$ 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 hydrogen ion. This is consistent with the experimental rate equation.

The Effect of Temperature on the Rate

To estimate the energy and entropy of activation, two series of experiments were done, one at 35°C., the other at 45°C. Each series consisted of three experiments at decreasing ionic strength to facilitate the extrapolation to $\Gamma = 0.00$, two experiments to spot check the rate law at constant ionic strength, and one experiment in alkaline medium (added base equivalent to 10 per cent 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 10. The rate constant was calculated by the tabular integration method 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

Table 10

Dependence of Reaction Constant on Temperature and Ionic Strength.

Run No.	(HCl) moles/liter	$(HN(SO_3)_2^{=})$ moles/liter	(NaCl) moles/liter	Γ moles/liter	$\Gamma^{1/2}$ $\left(\frac{\text{moles}}{\text{liter}}\right)^{\frac{1}{2}}$	K for HSO_4^-	k liter/(moles x min.)
		Experiments at 34.55°C., K_0 = 0.0106					
44	0.00954	0.01000	0.0	0.0395	0.1988	0.0234	0.143
45	.00974	.01000	.0225	.0622	.2495	.0275	.117
46	.00984	.01000	.0500	.0898	.2999	.0318	.101
47	.01962	.01000	.0400	.0896	.2997	.0318	.099
48	.00970	.02000	.0200	.0897	.2998	.0318	.100
		Experiments at 44.77°C., K_0 = 0.00892					
50	.00469	.01000	.00500	.0397	.1991	.0205	.479
51	.00488	.01000	.0275	.0624	.2499	.0236	.416
52	.00488	.01000	.0350	.0699	.2642	.0246	.390
53	.00976	.01000	.0500	.0898	.2999	.0274	.364
54	.00469	.02000	.0250	.0897	.2998	.0274	.341

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.

The values of the ionization function of bisulfate ion were estimated by neglecting the term linear in Γ in the equation (13) previously derived from equation (1). This approximation is adequate because of the low ionic strengths and the relative insensitivity of the values of the rate constant to the value of the ionization function. Values of

K_o were taken from Hamer's values[19] and the small corrections to the exact temperature of the experiments made by the equation

$$\delta K_o = \frac{\Delta H_i K_o \delta T}{RT^2} \tag{14}$$

using values of ΔH_i, the enthalpy of ionization, given by Hamer.

To extrapolate to $\Gamma = 0$, the procedure used in the ionic strength studies at 25°C. was applied. The graphical evaluation of the constants β and log k_o of equation (12) is shown in Figure 8.

In Table 11, 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 11

Summary of the Dependence of the Rate Constant on Ionic Strength and Temperature

Temperature °C.	Temperature °K.	A	β	k_o $\frac{\text{liters}}{\text{moles x min.}}$
24.00	298.16	0.506	.09[2]	0.085[2]
34.55	307.71	.517	-.32	0.321
44.77	317.93	.528	.13	1.06

The variation of k_o with temperature was interpreted by the Activated Complex Theory. This theory yields the equation

$$k_o = \frac{\kappa T}{h} e^{-\frac{\Delta F^{\ddagger}}{RT}} \tag{15}$$

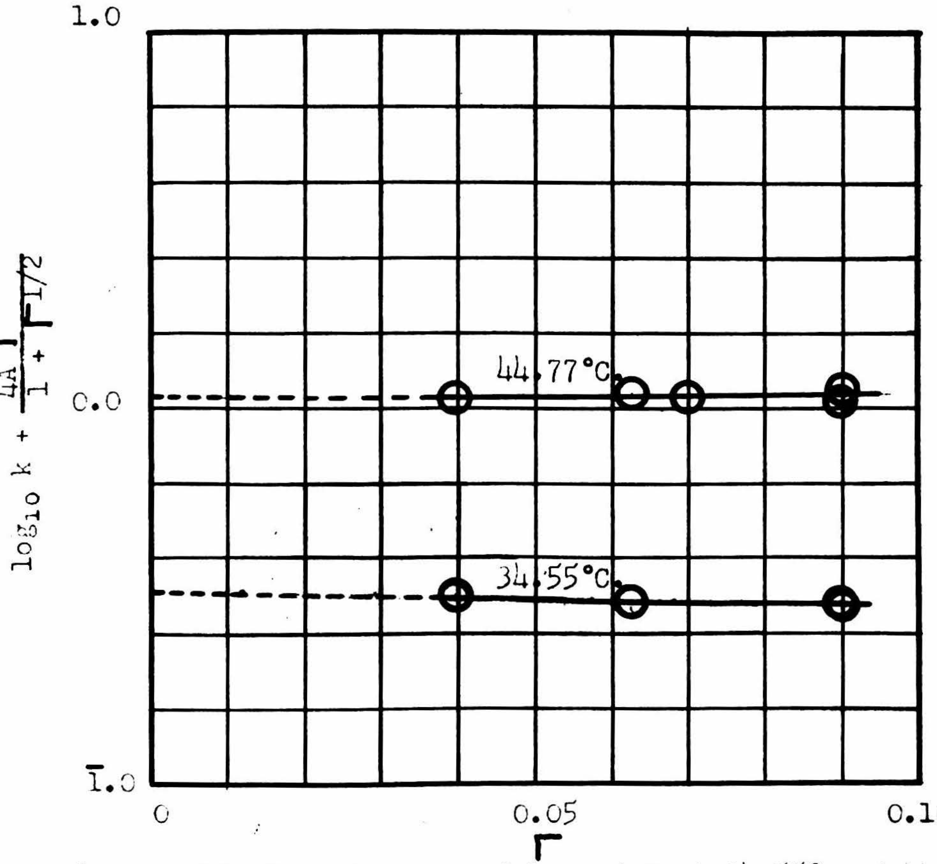

Fig. 8. Graphical evaluation of k_o and β at 34.55° and 44.77° C.

where k_0 is the rate constant in liters/mole x second, κ is Boltzmann's constant, h is Planck's constant, and $\Delta F^{\ddagger}$ is the free energy of activation per mole[20]. As the volume change of activation, $\Delta v^{\ddagger}$, is presumed to be negligible, (15) yields

$$\log \frac{k_0}{T} = \log\left(\frac{\kappa}{h} e^{\frac{\Delta S^{\ddagger}}{R}}\right) - \frac{\Delta E^{\ddagger}}{2.303\ RT} \quad , \qquad (16)$$

where $\Delta S^{\ddagger}$ is the entropy of activation, and $\Delta E^{\ddagger}$ is the energy of activation. To evaluate $\Delta E^{\ddagger}$, a plot of log k_0/T versus 1/T was made and is shown in Figure 9. From the slope of the straight line, it was found that $\Delta E^{\ddagger} = 23{,}500$ cals. with an estimated error of the order of ±1000 cals.

The value of the entropy factor, $e^{\frac{\Delta S^{\ddagger}}{R}}$, was calculated for the three values of k_0 shown in Table 12.

Table 12

Values of the Entropy of Activation

Temperature °C.	k_0 $\frac{\text{moles}}{\text{liter x min.}}$	$e^{\frac{\Delta S^{\ddagger}}{R}}$
25.00	0.0852	38
34.55	.321	42
44.77	1.06	35
	Ave.	38

$$\Delta S^{\ddagger} = 7.2 \text{ e.u.}$$

The average value of $e^{\frac{\Delta S^{\ddagger}}{R}} = 38$, giving $\Delta S^{\ddagger} = 7.2$, is not

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[20] Glasstone, Laidler, and Eyring, "The Theory of Rate Processes", McGraw-Hill Book Co., Inc. 1941.

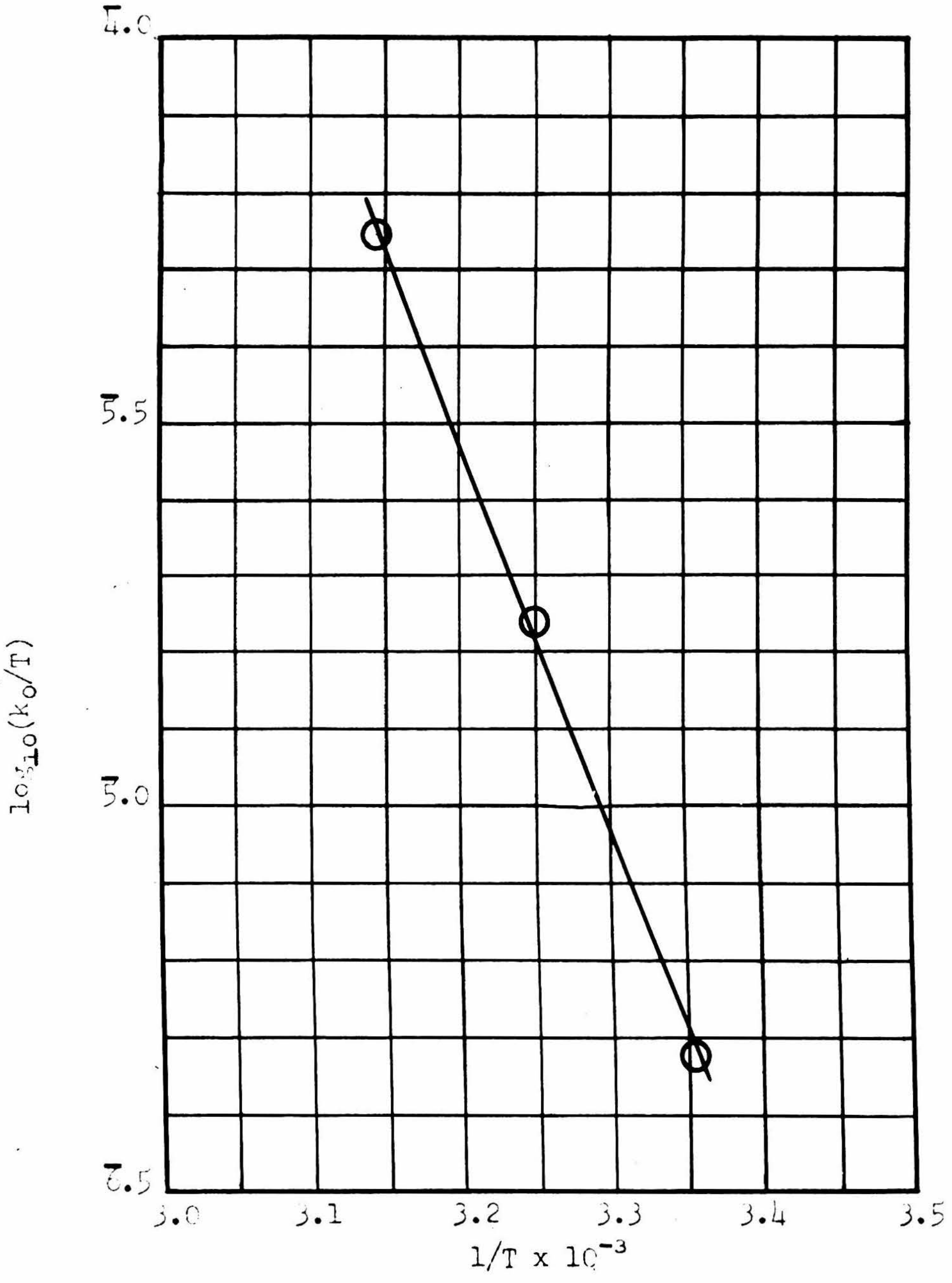

Fig. 9. Dependence of k_o on temperature.

unreasonable for a reaction of charge product -2. For, if the results of Scatchard's arguments[21] based on a model of the activated complex consisting of two charged spheres at distance r apart are utilized to calculate the contribution to the entropy of activation due to electrostatic interaction between dielectric medium and charged ion alone, it is found that

$$\Delta S_D^{\ddagger} = \frac{\epsilon^2 z_A z_B}{rD^2}\left(\frac{\partial D}{\partial T}\right)_p \quad .$$

Here $\Delta S_D^{\ddagger}$ = the dielectric contribution to the entropy of activation, ergs/degree x ion of activated complex,

ϵ = magnitude of electronic charge in e.s.u.,

z_A, z_B = valences of reacting ions,

D = dielectric constant of medium,

T = absolute temperature,

and p = pressure[22]. For water this yields

$$\Delta S_D^{\ddagger} \simeq \frac{-20 z_A z_B}{r\ (\text{in Å})} \qquad \text{e.u./mole,}$$

and, in particular

$$7.2 \simeq \frac{-20 \times (-2)}{5.5} \quad .$$

This is not to be taken to imply that the distance r is 5.5 Å. but it is intended to indicate the order of magnitude of this contribution to $\Delta S^{\ddagger}$ which is probably the greatest contribution in this case.

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[21] Scatchard, J. Am. Chem. Soc., 52, 52 (1930).

[22] Glasstone, Laidler, and Eyring, loc. cit., especially pp. 434-435.

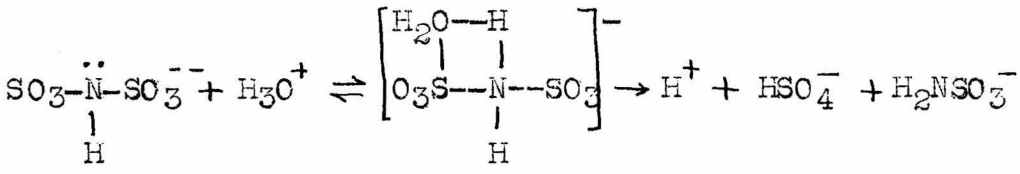
Mechanism of the Reaction

All of the experimental evidence is in favor of the formation of an activated complex from hydronium ion and amine disulfonate ion which then decomposes to give the reaction products. The simplest such mechanism is

$$H_3O^+ + HN(SO_3)_2^{=} \rightleftharpoons \{H_3O,\ HN(SO_3)_2\}^-$$
$$\{H_3O,\ HN(SO_3)_2^{=}\}^- \rightarrow HSO_4^- + H_2NSO_3^- + H^+ \ .$$

The configuration of the activated complex can be only a subject of conjecture as far as the experimental evidence obtained in this investigation is concerned.

For example, one may think of the reaction as occurring through a four-center reaction with hydronium ion,



$$SO_3\text{-}\underset{\underset{H}{|}}{\overset{\cdot\cdot}{N}}\text{-}SO_3^{--} + H_3O^+ \rightleftharpoons \left[\begin{array}{ccc} H_2O & \text{—} & H \\ | & & | \\ O_3S & \text{--} & N\text{--}SO_3 \\ & & | \\ & & H \end{array}\right]^- \rightarrow H^+ + HSO_4^- + H_2NSO_3^-$$

activated complex

If one presupposes a similar mechanism for the hydrolysis of N-substituted sulfamic acids, the relative ease of hydrolysis of aryl substituted sulfamic acids as compared with alkyl substituted acids[1] may be correlated with the influence of the substituent on the ionic character of the N-S bond, indicating that this may be the dominant factor in their effect on the reaction rate rather than their effect on the attraction of the disulfonate for the hydronium ion for which the effect of the substituents is in the opposing direction to the experimental observations.