For reactions of long duration the rate increased compared to the initial parabolic rate, this change was probably due to volume changes of the metal phase. The rate constants are sensitive to the origin of zirconium samples.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

The Kinetics of Hydrolysis of the Sulfamate Ion

BY SAMUEL H. MARON AND ALAN R. BERENS

Sulfamic acid in aqueous solution and at elevated temperatures hydrolyzes according to the scheme[1]

$$NH_2SO_2OH + H_2O \longrightarrow NH_4HSO_4$$

The extents of hydrolysis of the acid in fairly concentrated solutions were measured by Cupery[2] and by Oberhauser and Urbina,[3] but these men made no attempt to analyze the kinetics of the reaction.

Neutral or alkaline aqueous solutions of salts of this acid are stable even when boiled. However, on acidifying such solutions hydrolysis is again observed. It would appear, therefore, that the presence of hydrogen ions is necessary for hydrolysis of the sulfamate ion. The purpose of the present study was to investigate this effect of hydrogen ions on the rate of hydrolysis, and to elucidate the kinetics of the reaction.

Experimental

The rate of hydrolysis was followed by periodic removal of samples of reaction mixtures and analyzing them for sulfamate content. The analytical procedure employed was titration with standard sodium nitrite according to the procedure of Bowler and Arnold,[4] using starch iodide solution as an external indicator.

Materials.—The sulfamic acid and ammonium sulfamate used were the "Pure, Standardized" products of the Lamotte Chemical Co. After drying for twenty-four hours under vacuum at 40°, the sulfamic acid was found to be 100.0% pure by titration with standard sodium hydroxide.

The standard 0.05 molar solutions of sodium nitrite were made slightly alkaline with sodium hydroxide to prevent loss of nitrous acid. Nitrite solutions so prepared were stable for several months. They were standarized against a potassium permanganate solution according to the procedure given by Kolthoff and Sandell.[5]

The starch iodide solution used as indicator was prepared as follows. Five grams of starch and 20 g. of zinc chloride were dissolved slowly in 100 ml. of water. After the mixture was boiled for two hours, 2 g. of potassium iodide was added, the solution filtered through sintered glass, and then diluted to one liter. The resulting indicator solution was of such sensitivity that 0.02 ml. of 0.05 molar sodium nitrite solution in 100 ml. of dilute sulfuric acid was sufficient to give a distinct blue coloration in a spot-test. The indicator blank correction was therefore negligible.

Apparatus.—The thermostat was an oil-bath controlled by a sensitive mercury thermoregulator to within ±0.05° in the range 80–100°. Reaction vessels were rubber-stoppered 500 and 1000 ml. erlenmeyer flasks. All volumetric apparatus was calibrated at each temperature employed.

Procedure.—To prepare reaction mixtures, weighed amounts of sulfamic acid, or sulfamic acid and ammonium sulfamate, were dissolved in distilled water or hydrochloric acid solutions preheated to the desired temperature in the thermostat. The reaction mixture was immediately stirred and the first sample pipetted out. Successive samples were withdrawn, as necessary, at intervals ranging from one-half to four hours. The samples were discharged into iodine flasks containing about 50 ml. of cold water to stop the reaction.

In runs in which the starting sulfamate and hydrogen ion concentrations were not equal, two initial samples were taken, one to be titrated for sulfamate content and the other with standard base for the initial hydrogen ion concentration.

Runs were made at 80.35, 90.00 and 98.00°, and at concentrations ranging from 0.005 to 0.04 molar in sulfamate ion. Depending upon the speed of the hydrolysis, the extents of reaction followed varied from 20 to 50%.

Results

Preliminary kinetic experiments showed that the hydrolysis proceeds as a first order reaction with respect to sulfamate and to hydrogen ions. If we designate the initial sulfamate and hydrogen ion concentrations by *a* and *b*, and the concentration of sulfamate decomposed at any time *t* by *x*, then the concentrations of sulfamate, hydrogen, ammonium, and bisulfate ions at time *t* will be, respectively, $a - x$, $b - x$, x and x. However, due to the dissociation of the bisulfate ion, hydrogen ions removed by reaction are partly regenerated. Hence the hydrogen ion concentration at time *t* is $b - x + y$, and that of the bisulfate ion is $x - y$, where *y* is the decrease in concentration of the bisulfate ion due to dissociation. We obtain thus for the over-all reaction and the concentrations of the various ions at time *t*

$$\begin{array}{ccccccccc} H_2NSO_2O^- & + & H_3O^+ & \longrightarrow & NH_4^+ & + & HSO_4^- & & \\ (a-x) & & (b-x+y) & & (x) & & (x-y) & & (1) \\ & & & & & & \uparrow\downarrow & & \\ & & & & & & SO_4^{--} & + & H_3O^+ \\ & & & & & & (y) & & (b-x+y) \end{array}$$

From expression (1), the rate of decomposition of the sulfamate ion follows as

$$dx/dt = k(a - x)(b - x + y) = k_0f(a - x)(b - x + y) \tag{2}$$

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(1) E. Divers and T. Haga, *J. Chem. Soc.*, **69**, 1634 (1896).

(2) M. E. Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938).

(3) Oberhauser and Urbina, *Anales facultad filisof. y educacion, Univ. Chile, seccion quim.*, **3**, 119 (1946).

(4) W. W. Bowler and E. A. Arnold, *Anal. Chem.*, **19**, 336 (1947).

(5) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1936, p. 574.

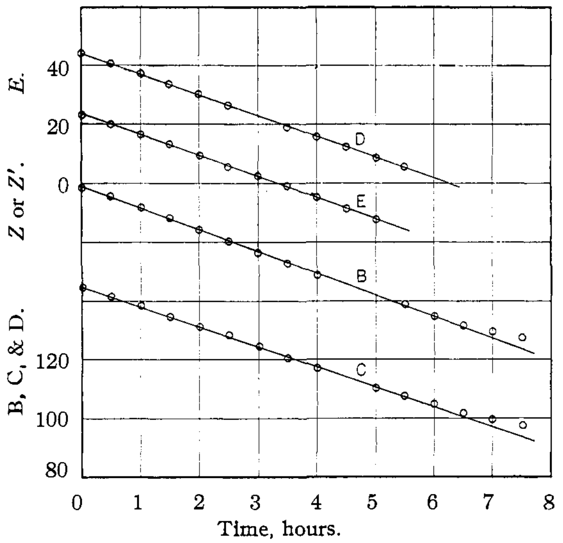

Fig. 1.—Plots of Z or Z' *vs.* t at 98.0°: B, $a = b = 0.01003$ molar; C, $a = b = 0.01570$ molar; D, $a = 0.00973$, $b = 0.00722$ molar; E, $a = 0.00996$, $b = 0.01444$ molar.

where $k = k_0 f$, k_0 being the true rate constant and f a factor giving the anticipated primary salt effect.

If the sulfate ion concentration is small compared to that of hydrogen ions, *i. e.*, if $(b - x + y) \cong (b - x)$, then the concentration ionization constant of the bisulfate ion

$$K_i = \frac{(b - x + y)(y)}{(x - y)} \cong \frac{(b - x)(y)}{(x - y)} \qquad (3)$$

may be used to eliminate y from equation (2), yielding

$$\frac{dx}{dt} = k(a - x)\left[\frac{(b - x)^2 - bK_i}{b - x + K_i}\right] \qquad (4)$$

Upon integration this equation becomes

$$Z = \beta \log_{10}\left[\frac{(a - x)^2}{(b - x)^2 + bK_i}\right] - \frac{\gamma}{\alpha}\tan^{-1}\left(\frac{b - x}{\alpha}\right) = I - kt \qquad (5)$$

Here I, the constant of integration, is given by

$$I = \beta \log_{10}\left(\frac{a^2}{b^2 + bK_i}\right) - \frac{\gamma}{\alpha}\tan^{-1}\left(\frac{b}{\alpha}\right) \qquad (6)$$

and the factors α, β and γ, which are constant for any given run, by

$$\alpha = \sqrt{bK_i} \qquad (7)$$

$$\beta = \frac{2.303(b - a + K_i)}{2(b - a)^2 + 2bK_i} \qquad (8)$$

$$\gamma = \frac{(b - a)(b - a + K_i)}{(b - a)^2 + bK_i} - 1 \qquad (9)$$

For the special case of hydrolysis of sulfamic acid alone, $a = b$, and equation (5) reduces to

$$Z' = \frac{1}{\alpha}\tan^{-1}\left(\frac{a - x}{\alpha}\right) - \frac{2.303}{2a}\log_{10}\left[1 + \frac{aK_i}{(a - x)^2}\right] = I' - kt \qquad (10)$$

where

$$I' = \frac{1}{\alpha}\tan^{-1}\left(\frac{a}{\alpha}\right) - \frac{2.303}{2a}\log_{10}\left(1 + \frac{K_i}{a}\right) \qquad (11)$$

and α is again given by equation (7).

Knowing a, b, K_i and x at various values of t, it is possible to calculate values of Z according to (5) or Z' according to (10). Then if such values of Z or Z' be plotted against t, straight lines should be obtained for each run with slopes equal to $-k$, and intercepts equal to I or I', respectively.

The requisite K_i's were obtained with the aid of the Debye–Hückel limiting law from the thermodynamic ionization constants of the bisulfate ion as given by Hamer.[6] The values of the Debye–Hückel constants employed were those given by Manov.[7]

In Fig. 1 curves B and C are typical plots of Z' against t obtained in runs on the hydrolysis of solutions of sulfamic acid. The good linearity of the plots confirms the validity of equation (10). In general the above treatment of the data was found to give plots linear up to 30 to 40% decomposition. Thereafter deviations from linearity were observed due to the breakdown of the assumption

TABLE I

RATE CONSTANTS FOR HYDROLYSIS OF SULFAMIC ACID SOLUTIONS

Concentration, moles/liter; time/hours

Temp., °C.	$a \times 10^3$	k	k_0
80.35	5.06	1.07	1.30
	7.59	1.00	1.26
	11.21	1.02	1.35
	11.92	1.00	1.34
	14.17	1.02	1.39
	15.85	0.976	1.36
	22.94	0.886	1.32
	30.27	0.729	(1.15)
	38.76	0.700	(1.18)
	Average	± 2.5%	1.33 ± 0.03
90.00	4.98	3.54	4.29
	6.94	3.47	4.35
	9.64	3.06	3.99
	12.33	3.09	4.18
	14.72	3.06	4.25
	16.29	2.91	4.11
	18.79	2.74	3.97
	26.50	2.39	(3.71)
	31.29	2.32	(3.74)
	Average	± 2.9%	4.16 ± 0.12
98.00	4.80	9.50	11.5
	7.19	8.78	11.1
	10.03	7.69	10.1
	10.97	7.69	10.3
	12.70	8.01	10.9
	13.73	7.11	9.8
	15.70	7.03	10.0
	19.53	7.00	10.3
	26.55	6.70	10.5
	29.85	6.46	10.4
	38.58	5.99	10.3
	Average	± 3.7%	10.5 ± 0.4

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(6) W. J. Hamer, THIS JOURNAL, **56**, 860 (1934).

(7) G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, *ibid.*, **65**, 1765 (1943).

embodied in equation (4), that $b - x + y \cong b - x$, and also due to the change in ionic strength of the reaction mixture as the concentration of sulfate ions becomes appreciable.

Table I gives the values of k calculated by the method of least squares from values of Z' and t for runs on sulfamic acid at three temperatures. It is seen that k at each temperature exhibits a gradual decrease with increasing concentration caused by the anticipated primary salt effect. This drift in the k's can be eliminated in the more dilute solutions by calculation of the true rate constant, k_0, with the aid of the Debye–Hückel limiting law from the relation

$$\log_{10}k_0 = \log_{10}k + 2A\sqrt{\mu} \qquad (12)$$

where A is a constant and μ the ionic strength. The values of k_0 thus calculated, and shown in the last column of Table I, are seen to be satisfactory constants at each temperature up to an ionic strength of 0.02 at 80 and 90°, and up to 0.04 at 98°.

In order to test the more general rate equation (5), several runs were made on reaction mixtures containing hydrogen and sulfamate ions in unequal concentrations. Curves D and E in Fig. 1 show that plots of Z *versus* t thus obtained are again excellent straight lines, giving further evidence of the correctness of the mathematical treatment.

In Table II are summarized the rate constants observed with such mixtures. Again k_0, calculated from k as before, is a satisfactory constant in good agreement with that found with pure sulfamic acid solutions.

TABLE II

RATE CONSTANTS FOR SULFAMATE ION HYDROLYSIS AT 98.00°

Concentration: moles/liter; time, hours

$a \times 10^3$	$b \times 10^3$	k	k_0
6.90	10.00	7.75	10.3
9.73	7.22	7.18	9.5
9.74	18.57	7.42	10.9
9.96	14.44	7.26	10.2
14.22	10.03	7.25	10.1
	Average	± 3.0%	10.2 ± 0.3

The plot of log k_0 *vs.* $1/T$ was found to be an excellent straight line with slope corresponding to the unusually high activation energy of 30,500 calories, or $\Delta H^* = 29{,}800$ calories. Utilizing this value of ΔH^*, the entropy of activation, ΔS^*, was calculated from the Theory of Absolute Reaction Rates[8] to be 9.69 entropy units, again an unusually large positive value. Quite evidently the very slow reaction rate to be expected for the hydrolysis from the large value of ΔH^* is compensated for by the large positive value of ΔS^*.

Mechanism of the Hydrolysis.—The unusually large values of ΔH^* and ΔS^* suggest that the mechanism of the reaction is more complex than indicated by equation (1). Suppose we postulate that the reaction proceeds according to the sequence

$$H_2NSO_2^- + H_3O^+ \rightleftarrows X \xrightarrow{k_1} NH_4^+ + HSO_4^- \qquad \mathbf{(13)}$$

where the reactants are in equilibrium with an intermediate, X, whose decomposition leads to formation of the products. On this basis the rate of the over-all reaction is given by

$$dx/dt = k_1 fK(H_2NSO_2O^-)(H_3O^+) \qquad (14)$$

where k_1 is the velocity constant for the decomposition of intermediate X, f is the Brönsted activity coefficient factor, and K is the thermodynamic constant for the indicated equilibrium, namely

$$K = \frac{a_X}{a_{H_2NSO_2O^-}\, a_{H_3O^+}} \qquad (15)$$

Equation (14) gives the correct dependence of the rate on the concentrations of the reacting ions, and shows that the corrected experimental rate constant, k_0, is the product of a velocity constant and an equilibrium constant

$$k_0 = k_1 K \qquad (16)$$

If such be the case, then

$$RT^2\frac{d\ln k_0}{dT} = RT^2\frac{d\ln k_1}{dT} + RT^2\frac{d\ln K}{dT}$$

and hence

$$\Delta H^* = \Delta H_1^* + \Delta H \qquad (17)$$

On this basis ΔH^* is the sum of the activation energy for the decomposition of the intermediate, X, and the heat of reaction, ΔH, for the postulated equilibrium. If the latter quantity is appreciable and positive, then the high observed value of the energy of activation is understandable.

Extension of the argument to the entropy of activation shows that the observed ΔS^* will also be the sum of two terms, ΔS_1^*, for the decomposition of X, and ΔS for the equilibrium step. While a large positive entropy of activation seems unreasonable, ΔS may well be positive and sufficiently large to bring the over-all ΔS^* up to its observed value of 9.69 entropy units.

Although the proposed mechanism furnishes a reasonable explanation of the observed facts, a suggestion may be in order as to the nature of the intermediate, X. Suppose that the equilibrium reaction involves the transfer of a proton from H_3O^+ to the amino group of the sulfamate ion. The product will then be $H_3N^+\cdot SO_2O^-$, a dipolar ion analogous to the well-known zwitterion of a sulfanilic acid. Reaction of this ion with a molecule of water will lead then to formation of an ammonium and a bisulfate ion, the products of the hydrolysis.

Summary

The rates of hydrolysis of sulfamic acid at 80, 90 and 98°, and of sulfamic acid in presence of excess sulfamate or hydrogen ions at 98°, have been measured by a titration method.

The rate has been found to be first order with

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[8] W. F. K. Wynne-Jones and Eyring, *J. Chem. Phys.*, **3**, 492 (1935).

respect to sulfamate and hydrogen ion concentrations, and to be accompanied by a primary salt effect of the expected magnitude.

A mechanism is proposed for the hydrolysis, in which the formation of an intermediate dipolar ion in equilibrium with the reactants is postulated. With the aid of this mechanism it is possible to explain the high values found for the energy and entropy of activation.

CLEVELAND, OHIO RECEIVED JANUARY 3, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Rates of Ionization of Pseudo-acids. III. Forward and Reverse Reactions for Nitroethane

BY RALPH G. PEARSON AND ROBERT L. DILLON

The rate of the water-catalyzed ionization of nitroethane has now been measured over a range of temperatures[1] by following the rates of bromination and iodination in aqueous solution. These rates have turned out to be the same showing that the rate determining step in each case is the ionization.

$$C_2H_5NO_2 + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_2H_4NO_2^- + H_3O^+ \quad (1)$$

The rates were measured both by the usual titration technique and by the conductimetric method mentioned in paper II of this series.[2] A range of temperatures from 15 to 35° enables us to calculate the heat and entropy of activation. Moreover, from the relationship $k_1/k_2 = K_{eq} = K_{ion}$, one can calculate the rate constant k_2 for the recombination of ions and the attendant heat and entropy of activation. The value of K_{ion} is known from 18 to 30° by the work of Turnbull and Maron,[3] being 3.50×10^{-9} at 25°.

It is of interest to extrapolate the calculated value of k_2 down to 0° since Maron and La Mer[4] attempted a direct measurement of this quantity at that temperature. The procedure used by Maron and La Mer was to make a solution of the barium salt of nitroethane and to acidify it with an equivalent amount of sulfuric acid. This produced the aci-form which isomerized to the nitro-form at a measurable rate. Since the aci-form is a stronger acid than the nitro-form, the isomerization is accompanied by a decrease in the ionic concentration and an increase in resistance. Maron and La Mer measured the resistance and found it to be linear with the time. By several assumptions they were able to justify this linearity as being consistent with the mechanism

$$H_2O + C_2H_4NO_2H \rightleftarrows C_2H_4NO_2^- + H_3O^+ \xrightarrow{k_2} C_2H_5NO_2 + H_2O \quad (2)$$

The aci-form is in mobile equilibrium with its ions which react together slowly to give the nitro compound. They then calculated a value of 144 for k_2 at 0°. From measurements at 5° they also computed the heat and entropy of activation. Tables I and II give a compilation of the data gathered in this work and by Maron and La Mer.

The discrepancy between a rate constant of 26 and 144 is not too alarming since the values depend upon an extrapolation of several quantities (including the ionization constant of the aci-form of nitroethane) from room temperature down to 0°. The disagreement between the heats and entropies of activation is serious, however, since these quantities should be nearly independent of temperature over a small range.

Accordingly the data of Maron and La Mer were re-examined and it became evident that they had incorrectly identified the conductance with the concentration of unreacted aci-nitroethane. The conductance, of course, should be identified with the concentration of the ions resulting from the aci-compound. Since the latter is a weak acid comparable to acetic acid, $K_A = 3.6 \times 10^{-5}$ at 0° (ref. 3), one can derive the equation

$$[H_3O^+] = [C_2H_4NO_2^-] = K_A^{1/2}[C_2H_4NO_2H]^{1/2} = K_A^{1/2}(a - x)^{1/2} \quad (3)$$

where K_A is the ionization constant of the aci-form and $(a - x)$ has its usual kinetic meaning. Since the reciprocal of the resistance is proportional to the concentration of ions, the experimental fact that the resistance is linear with the time is equivalent to saying that $1/(a - x)^{1/2}$ is linear with the time. This corresponds to a rate expression of the form

$$dx/dt = k\,(a - x)^{3/2} \quad (4)$$

which is satisfied by either of the two mechanisms

$$H_3O^+ + C_2H_4NO_2H \xrightarrow{k_3} H_3O^+ + C_2H_5NO_2 \quad (5)$$

$$C_2H_4NO_2^- + C_2H_4NO_2H \xrightarrow{k_4} C_2H_5NO_2 + C_2H_4NO_2^- \quad (6)$$

Mechanism (5) can be ruled out by the principle of microscopic reversibility since there is no acid catalysis for the ionization of nitroethane (the reverse of reaction (5) would be an acid-catalyzed ionization). The mechanism shown in (6), however, is a reasonable and indeed an expected one

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[1] Junell, *Arkiv. Kemi, Mineral. Geol.*, **11B**, 30 (1934), has measured the rate of ionization at 69.85° in 1 molar hydrochloric and hydrobromic acids.

[2] Pearson and Mills, THIS JOURNAL, **72**, 1692 (1949).

[3] Turnbull and Maron, *ibid.*, **65**, 212 (1943).

[4] Maron and La Mer, *ibid.*, **61**, 692 (1939).