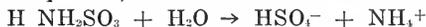# The Hydrolysis of Sulfamic Acid[1]

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Introduction

The slow hydrolysis of sulfamic acid in aqueous solution may be represented by the equation,

$$H\ NH_2SO_3 + H_2O \rightarrow HSO_4^- + NH_4^+$$

This reaction has proven to be useful in analytical chemistry because, when carried out in the presence of certain cations, it serves as the basis for the precipitation of insoluble sulfates from homogeneous solution (2, 4). The reaction has proven to be of special interest in this laboratory in conjunction with research on the physicochemical aspects of nucleation and crystal growth (1). In order to use the reaction for this purpose, however, it became necessary to obtain kinetic data. Only a few isolated measurements had heretofore been reported in the literature (1, 3), but these were inadequate for the present purpose.

The rate constant may be expressed by the equation,

$$rate = \frac{-d\ [HNH_2SO_3]}{dt} = k\ [HNH_2SO_3]^m$$

in which t is time, k is the rate constant and m is the order of reaction with respect to the concentration of sulfamic acid. The water molecule concentration need not appear as a variable in this equation, as it remains essentially constant in the aqueous solutions of interest in this study. Experimental measurements of rate data could be based upon determinations of sulfamic acid, or of sulfate ion, or of ammonium ion, each in the presence of the others. Sulfate determinations were selected.

Experimental Methods and Results

The reaction was run under controlled conditions, duplicate aliquots were withdrawn periodically, the reaction in each was quenched by cooling, and each was analyzed for sulfate ion by a conventional gravimetric procedure. All hydrolyses were run in the research laboratory, but all sulfate determinations were performed by students in a beginning course in quantitative analysis. The overall plan of the project was discussed with the students in advance, and the final results were subsequently discussed with and evaluated by the entire group. No student knew at the time of his analysis what the "hydrolysis history" of his sample was, nor did he even know that some one else had a duplicate of his sample.

The analytical data are summarized in table 1. Each reported value is a rounded-off arithmetic mean of triplicate determinations performed by one student. (Each student also reported his precision in terms of 50% confidence limits, but these data are not listed in table 1.) The data for

the hydrolysis runs were then analyzed both by a graphical method and by a half-reaction time method, from both of which it was found that the hydrolysis reaction rate is first-order with respect to sulfamic acid concentration. The rate constants, also listed in table 1 for the seven runs, were obtained by a graphical method, and are expressed with time units as hours and with the sulfamic acid concentration in uits of "mg.SO_4 yet to form per ml. of hydrolyzing solution." These units were selected because they arose directly from the analytical data.

TABLE 1. ANALYTICAL DATA

Run No.	Temp. (°C.)	Initial Sulfamic Concn.	Time (Hrs.)	MG. SO_4/ML.			Rate Constant For this Run
				1	2	AVE	
1	99.5	1%	1	2.36	. . .	2.36	0.26
			2	4.27	. . .	4.27	
			4	6.32	6.49	6.41	
2	99.9	0.5%	1	0.83	0.96	0.89	0.18
			2	1.67	1.61	1.64	
			4	. . .	2.17	2.17	
3	100	1%	1¼	0.32	0.44	0.38	0.025
		(in 0.1 M.	2¼	0.68	0.75	0.72	
		NaOH)	4½	10.03+	1.05	1.02	
4	99.5	1%	1	3.53	. . .	3.53	0.51
		(in 0.1 M.	2	6.70	7.43	7.07	
		HCl)	4	8.39	8.72	8.56	
5	70	1%	1	0.13	0.13	0.13	0.012
			2	0.29	. . .	0.29	
			4	. . .	0.47	0.47	
6	80	1%	1	. . .	0.41	0.41	0.035
			2	0.82	0.73	0.77	
			3½	1.33	4.4++	1.33	
7	99.5	2%	1	6.56	0.46++	6.56	0.35
			2	10.55	10.46	10.51	
			4	. . .	14.28	14.28	

+ This result appears to contain a decimal-point error and was so considered in calculating the average.
++ These two results are clearly inconsistent with their duplicate aliquots and with the general trend of the hydrolysis, so they were discarded.

Several observations may be made from the data of table 1.

(1) The rate constant is increased considerably by the presence of excess acid (hydrochloric) and is decreased considerably by the presence of excess base (sodium hydroxide), as shown by comparison of runs 1, 3 and 4.

(2) The rate constant is increased somewhat by an increase in initial concentration of sulfamic acid, as shown by comparison of runs 2, 1 and 7. This fact appears at first to contradict the conclusion

that the reaction is truly first-order. However, this difference is likely again due to the acidity factor, as the hydrogen ion concentration necessarily increases as the sulfamic acid concentration is increased. The acidity should remain essentially constant during any one run, because the H NH_2SO_3 reactant and the HSO_4 product are of comparable acid strength.

(3) The rate constant decreases considerably as the temperature is decreased, as shown by comparison of runs 1, 6 and 5. An Arrhenius plot of log k vs. 1/T for these three runs yielded a straight line, the slope of which is a measure of the activation energy.

It is of interest to speculate as to which ionic or molecular form of sulfamic acid reacts with water in the hydrolysis reaction. There are four possible species.
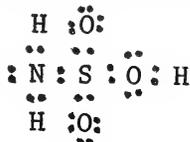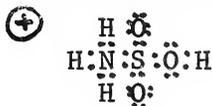
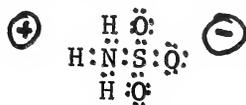a. sulfamic acid molecule   b. sulfamate ion
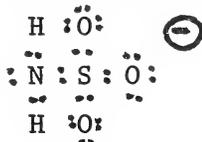
c. zwitter-ion form of sulfamic acid molecule


d. zwitter-ion form of sulfamate ion

For hydrolysis to sulfate and ammonia to occur, the N : S bond must be broken. Furthermore, the electrons in this bond must go with the N atom, in order to form the products which are obtained. In examining these four species, we would expect this pair of electrons to be attended most strongly to the N in the order d>b, c<a, with no evident basis for predicting a difference between b and c. This consideration at least should rule out a. as the reactive species.

At very low pH, we would expect the fully protonated species, c, to predominate, and the least protonated form, b, to be formed at very high pH. Species a. and d. are singly protonated so would be more formed at intermediate acidities. The experimental observation that the rate is enhanced at a greater acidity would seem to rule out b, at least, as the reactive species.

This leaves c and d as possibilities. Sulfamic acid is quite strong, the listed acid ionization constant being 10^2. Ths means that we would hardly expect to find the doubly protonated species, c, even in very acidic

media. Therefore, it may be concluded with reasonable confidence that it is d, the zwitter-ion form of the sulfamate ion, which reacts with the water molecule during hydrolysis.
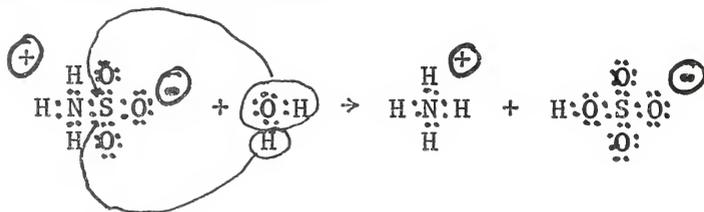
Summary

The hydrolysis reaction rate of sulfamic acid in aqueous solution to form sulfate and ammonium ions is first order with respect to sulfamic acid concentration. Excess acid (hydrochloric) markedly increases the rate, and excess base decreases it. An Arrhenius plot by log k vs.1/T yielded a straight line, the slope of which is a measure of the activation energy. It was further deduced that the form of sulfamic acid which actually reacts with the water molecule is the zwitter-ion form, $^{+}H_3N\text{-}SO_3{}^{-}$.

In addition to providing useful new data on the kinetics of the hydrolysis of sulfamic acid, this study proved to be a successful part of the laboratory work in quantitative analysis. Each student performed a gravimetric sulfate determination, merely starting with a solution unknown rather than with a conventional solid, powdered unknown. The interest and the enthusiasm of the students was enhanced by being a part of a group research problem, and the students gained some familiarity with reaction kinetics as a by-product of their quantitative work.

Literature Cited

1. FISCHER, R. B. 1960. Anal. Chem. Acta **22**: p. 501 and 508.
2. GORDON, L., M. L. SALUTSKY, and H H. WILLARD. 1959. "Precipitation from Homogeneous Solution"; John Wiley and Sons, New York.
3. KORCHMARCK, J. A. and O. A. KHAN. 1955. Izvest, Akod. Nauk Kazakh. S.S.R. Ser. Khim., No. 8, p. 60. (As abstracted in Chemical Abstracts, 1955, **49**:1293.)
4. WAGNER, W. F. and J. A. WUELLNER. 1952. Anal. Chem. **24**: 1031.