[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

Decomposition of Nitrosyl Disulfonate Ion. IV. The Reaction of Sulfamate Ion with Nitrous Acid[1]

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RECEIVED MAY 16, 1953

The reaction between sulfamate ion and nitrous acid has been studied and found first order with respect to each of the substances in an acetate buffer solution. As derived from the *p*H (3.3–5.6), ionic strength (0.05–0.48) and temperature (15–35°) dependences of the rate, the following rate law reproduces all the data presented here: $d(N_2)/dt = k'(HNO_2)(H_3O^+)(^-SO_3NH_2)$ moles/l. min. and $\log k' = 5.037 + (\theta - 25)/31.2 - 0.72\sqrt{\mu}/(1 + \sqrt{\mu})$ where θ is the temperature in centigrade degrees and concentrations are in molarities. Using this and the kinetics of decomposition deduced in the third paper of this series,[2] the inhibition of decomposition of nitrosyl disulfonate ion by sulfamate ion is discussed.

As found previously[2] the spontaneous decomposition of nitrosyl disulfonate ion occurs principally through the reaction with nitrous acid, and it is inhibited by the addition of sulfamate ion.[3] When first tested the inhibition was assumed to occur because a sufficient amount of sulfamate ion reacted with nitrous acid faster than did nitrosyl disulfonate ion itself. In order to confirm the assumption and to establish the inhibition on a more quantitative basis, the reaction between sulfamate ion and nitrous acid has been studied, and the results have been applied to explain some details of the inhibited decomposition of nitrosyl disulfonate ion.

Experimental Part

The rate of reaction between sulfamate ion and nitrous acid was measured by observing the rate of evolution of nitrogen in an apparatus previously described for measurement of nitrous oxide. Most of the measurements were made without previously sweeping the apparatus with N_2 or NO. However, the results obtained agreed completely with observations made on systems under an atmosphere of NO. This indicated that both the spontaneous decomposition and the autoöxidation of nitrous acid were negligible under the conditions employed in this work.

Sulfamic acid from Eastman Kodak Co., recrystallized from water and dried in vacuum, was dissolved in 0.2 *M* potassium acetate used to make up the buffer solution. Aliquots were mixed with sodium nitrite solution to start the reaction. The total volume of solution was 30 to 40 ml.

The nitrogen evolved was measured at one-minute intervals in the 10 ml. micro-buret to ±0.01 ml. The total volume of gas evolved was usually within ±1% of the stoichiometric quantity. The *p*H values of the solutions remained unchanged throughout the reaction.

Results and Discussion

Demonstration of the Second-order Kinetics.—In a buffer solution of *p*H 4.03, μ 0.17, sulfamate ion 0.0753 *M* and the stoichiometric concentration of nitrous acid 0.0122 *M*, the reaction was second order as shown in Fig. 1 by a plot of $\log [(^-SO_3NH_2)/(\Sigma HNO_2)]$ *vs.* *t*, where the concentrations of sulfamate ion and nitrous acid at any time *t* were calculated from the amount of nitrogen evolved.

In another case with a solution of *p*H 3.55, μ 0.17, sulfamate ion and nitrous acid each 0.0119 *M*, the reaction was also found second order as shown in Fig. 2 by a plot of $1/(V_f - V)$ or $1/[(\Sigma HNO_2).RTv/p]$ *vs.* *t*, with V_f equal to the total volume of nitrogen evolved, *V* the volume at any time *t*, in milliliters, *p* the partial pressure of nitrogen and *v* the volume of solution. These were only two typical examples. About 30 other runs were carried out at different concentrations, *p*H values, ionic strengths and temperatures; in each case second-order kinetics was found.

Dependence on *p*H and Possible Mechanism.—In each buffer solution, a second-order constant *k* could be attached to a run as

$$\frac{d(N_2)}{dt} = k(^-SO_3NH_2)(\Sigma HNO_2) \qquad (1)$$

At constant ionic strength, the *p*H dependence of *k* was found to follow the relation

$$k = \frac{k'[H^+]^2}{K + \gamma_+[H^+]} \qquad (2)$$

with *K* equal to the dissociation constant of nitrous acid, γ_+ the activity coefficient and $[H^+]$ the activity of hydronium ions, as was demonstrated by the plot of $1/[H^+]$ *vs.* $[H^+]/k$. From the intercept of the straight line, $K/\gamma_+ = 7.15 \times 10^{-4}$ was obtained. If γ_+ was taken as that of an HCl solution, namely, 0.773, the value $K = 5.5 \times 10^{-4}$ was very close to that given in the literature.[4,5] This implied that the following rate law applied

$$\frac{d(N_2)}{dt} = k'(HNO_2)(H^+)(^-SO_3NH_2) \qquad (3)$$

with (HNO_2) equal to the concentration of molecular nitrous acid, assuming the activity coefficients of (H^+) and (NO_2^-) to be the same. Table I shows the *p*H dependence of *k* at ionic strength 0.17; k'/γ_+ was calculated at each *p*H using $K/\gamma_+ = 7.15 \times 10^{-4}$ from equation 2. Introducing the equilibrium

$$HNO_2 + H_3O^+ \rightleftharpoons H_2O + H_2NO_2^+ (\text{or } NO^+) \qquad (4)$$

TABLE I

DEPENDENCE OF RATE CONSTANT ON *p*H

*p*H	*k*, l./mole min.	$(k'/\gamma_+) \times 10^{-4}$, (l./mole)^2 min.$^{-1}$	*p*H	*k*, l./mole min.	$(k'/\gamma_+) \times 10^{-4}$, (l./mole)^2 min.$^{-1}$
5.59	8.6×10^{-4}	9.40	3.81	2.50	9.12
4.93	1.75×10^{-2}	9.24	3.54	7.85	9.65
4.26	0.360	9.22	3.49	9.59	9.52
4.20	0.470	9.24	3.35	15.3	9.00
4.03	0.97	9.05	3.26	22.2	9.32

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[1] Abstracted from a thesis by J. C. M. Li, submitted to the Graduate School of the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1953.

[2] J. C. M. Li and D. M. Ritter, THIS JOURNAL, **75**, 5823 (1953).

[3] J. H. Murib and D. M. Ritter, *ibid.*, **74**, 3394 (1952).

[4] Alfons Klemenc and Erich Hayek, *Monatsh.*, **54**, 407 (1929).

[5] H. Schmid, R. Marchgraber and F. Dunkl, *Z. Elektrochem.*, **43**, 337 (1937).

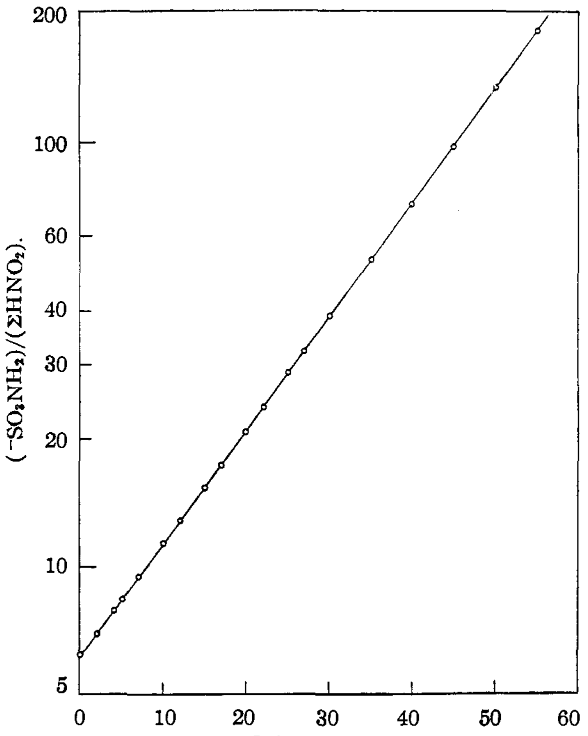

Fig. 1.—Second-order plot for the reaction of unequal amount of sulfamate ion and nitrous acid.

with the equilibrium constant, K_4, equation 3 could also be written as

$$\frac{d(N_2)}{dt} = \frac{k'}{K_4}(NO^+)(^-SO_3NH_2) \quad (5)$$

in agreement with Dusenbury and Powell.[6] Hence the mechanism proposed by them is also applicable here

$$^-SO_3NH_2 + NO^+ \longrightarrow H_2SO_4 + N_2 \quad (6)$$

Ionic Strength Dependence.—Since the dependence of K_4 on ionic strength is probably small, the ionic strength dependence of k' may be expected to follow the usual relation.[7] In studying the relation between k' and μ, k' was calculated from k in each run by means of equation 2. Table II shows some of the results. It was found that the following relation reproduced k' as a function of ionic strength

$$\log k' = 5.037 - 0.72\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \quad (7)$$

TABLE II

IONIC STRENGTH DEPENDENCE OF THE RATE CONSTANT

μ	pH	k, l./mole min.	$k' \times 10^{-4}$, (l./mole)^2 min.$^{-1}$
0.052	3.35	17.0	7.85
.081	3.49	9.6	7.50
.17	4.03	0.97	6.90
.21	3.95	1.29	6.55
.27	4.91	1.68×10^{-2}	6.20
.40	4.93	1.43×10^{-2}	5.70
.48	5.59	6.6×10^{-4}	5.50

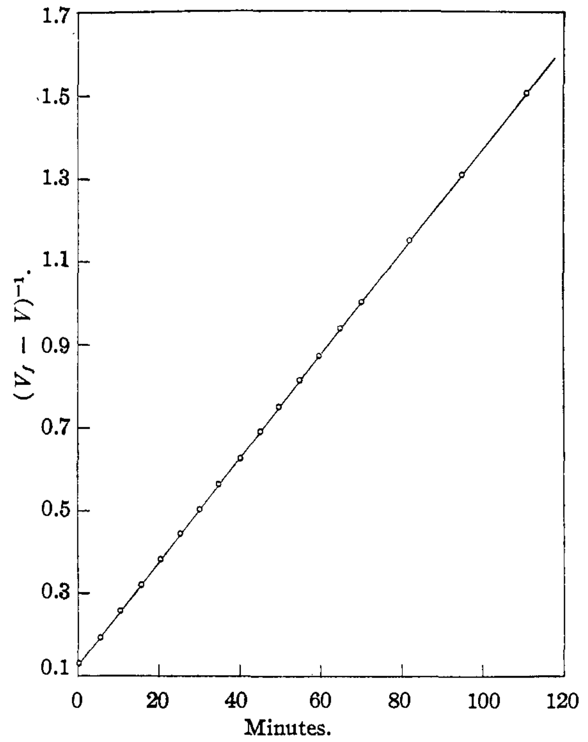

Fig. 2.—Second-order plot for the reaction of equivalent amount of sulfamate ion and nitrous acid.

The slope was somewhat less than the limiting value, but it might have gradually increased to that theoretical value had the solutions been further diluted.

Temperature Dependence.—The effect of temperature on k' was observed over the range 15–35° in a buffer solution of pH 3.95 (measured at 25°), ionic strength 0.21, concentration of sulfamate ion 0.05 M and the stoichiometric concentration of nitrous acid 0.01 M. The small variation of pH with temperature was corrected by applying the dissociation constant of acetic acid[8] as a function of temperature. The dissociation constant of nitrous acid at other temperatures was obtained by drawing a curve parallel to that of Schmid, Marchgraber and Dunkl[5] through the point 5.5×10^{-4} at 25°. It was found that the curve so drawn passed though the 12.5 and 35° points obtained by Klemenc and Hayek.[4] The activity coefficient of hydronium ion was taken as that of a solution of hydrochloric acid.

The results are shown in Table III. A plot of $\log k'$ *vs.* $1/T$ gave a straight line from which 13.0 kcal. for the heat of activation was obtained. From equation 5 it can be seen that $\Delta H_6^{\ddagger} + \Delta H_4^0 =$

TABLE III

TEMPERATURE DEPENDENCE OF THE RATE CONSTANT

Temp., °C.	$K \times 10^4$, moles/l.	k, l./mole min.	$k' \times 10^{-4}$, (l./mole)^2 min.$^{-1}$
35	6.4	2.32	13.8
30	6.0	1.71	9.35
25	5.5	1.29	6.55
20	5.1	0.92	4.37
15	4.8	0.69	3.14

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[6] J. H. Dusenbury and R. E. Powell, THIS JOURNAL, **73**, 3266, 3269 (1951).

[7] See for example, Edward S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, p. 73.

[8] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **55**, 652 (1933).

13 kcal. where $\Delta H_6^{\ddagger}$ is the heat of activation of the reaction shown by equation 6 and ΔH_4^0 is the standard enthalpy change of the reaction shown by equation 4. Since ΔH_4^0 is not known, it is only possible to say that $\Delta H_6^{\ddagger} < 13$ kcal. assuming ΔH_4^0 to be positive.

Sulfamate Inhibition of the Decomposition of Nitrosyl Disulfonate Ion.—With the kinetics of decomposition and the reaction of sulfamate ion with nitrous acid known, it becomes possible to discuss the effect of sulfamate ion on the decomposition. At any time *t*, let *A* be the concentration of nitrosyl disulfonate ion and *B* that of sulfamate ion. The former will disappear through three reactions: The first is the proposed initiation step[3]

$$(SO_3)_2NO^- + H_3O^+ \longrightarrow \alpha HNO_2, \text{ etc.} \quad (8)$$

with the rate equal to $k_8A[H^+]$; the second is the reaction[2] with N_2O_3

$$2(SO_3)_2NO^- + 2HNO_2 \longrightarrow 2SO_4^- + 2NO^+ + NOH + (SO_3)_2NOH^- \quad (9)$$

at the rate of $k_9(HNO_2)^2$ and the third is the chain branching[2] reaction

$$\beta(SO_3)_2NO^- + HNO_2 \longrightarrow 2HNO_2, \text{ etc.} \quad (10)$$

with the rate equal to $\beta(HNO_2)(\phi_0/2)$. If the rates of the color disappearance through the reactions 9 and 10 are negligible in comparison with that through reaction 8, the initiation step can be studied through color disappearance without the complication due to nitrous acid. Then the maximum allowable concentration of molecular nitrous acid can be calculated from the relative rates of the three reactions. Let us suppose that the sum of the rates of the reactions 9 and 10 is only 1% of the rate of reaction 8, it is seen

$$k_9(HNO_2)^2 + \beta(HNO_2)(\phi_0/2) = 0.01k_8A[H^+] \quad (11)$$

Solving for (HNO_2)

$$(HNO_2) = \sqrt{0.01\frac{k_8}{k_9}A[H^+] + \left(\frac{\beta\phi_0}{4k_9}\right)^2} - \frac{\beta\phi_0}{4k_9} \quad (12)$$

There are four reactions which involve nitrous acid: The first is the reaction 8 which will produce nitrous acid at the rate of $\alpha k_8A[H^+]$; the second is the reaction 9 which will preserve nitrous acid; the third is reaction 10 which will produce nitrous acid at the rate of $(HNO_2)(\phi_0/2)$ and the fourth is due to sulfamate ion which will consume nitrous acid at the rate of $k''B(HNO_2)[H^+]$. Assuming that there is no reaction between sulfamate ion and nitrosyl disulfonate ion, the over-all rate of production of nitrous acid is

$$\frac{d(\Sigma HNO_2)}{dt} = \alpha k_8A[H^+] + (HNO_2)\frac{\phi_0}{2} - k''B(HNO_2)[H^+] \quad (13)$$

Hence the concentration of sulfamate ion required to keep the nitrous acid concentration constant is

$$B = \frac{\phi_0}{2k''[H^+]} + \frac{\alpha k_8A}{k''(HNO_2)} \quad (14)$$

Or the steady state concentration of molecular nitrous acid is

$$(HNO_2) = \frac{2\alpha k_8A[H^+]}{2[H^+]k''B - \phi_0} \quad (15)$$

But the minimum concentration of sulfamate ion required to keep the nitrous acid concentration below that expressed by equation 12 is more than that given by equation 14 because the maximum allowable concentration of molecular nitrous acid will decrease with the concentration of nitrosyl disulfonate ion as seen from equation 12. In the case of a buffer solution the ratio of (ΣHNO_2) to (HNO_2) is a constant and therefore by differentiating equation 12 with respect to *t* and comparing with equation 13, the extra sulfamate ion required in addition to that expressed by equation 14 in order to keep the nitrous acid concentration below that given by equation 12 is found to be

$$B' = \frac{0.02k_8^2A\{K + [H^+]\gamma_-\}}{[4k_9(HNO_2) + \beta\phi_0](HNO_2)k''} \quad (16)$$

For example, in a buffer solution of *p*H 3.6, $\mu = 0.15$, the constant can be taken as[9] $\phi_0 = 0.3$, $k'' = k'/\gamma_+ = 8.6 \times 10^4$ (l./mole)^2 min.$^{-1}$, $A = 0.033$ *M*, $k_9 = 1.4 \times 10^4$ l./mole min., $k_8 = 15$ l./mole min., $\alpha = 0.05$ and $\beta = 4$. The minimum concentration of sulfamate ion required to stop the chain branching as calculated from the first term on the right side of equation 14 is 0.007 *M* which can be compared to the experimental[3] value 0.00746 *M*. For the decomposition to occur entirely by the path of reaction 8, the maximum allowable concentration of molecular nitrous acid calculated from equation 12 is 2×10^{-6} *M*. So the minimum concentration of sulfamate ion as calculated from both equations 14 and 16 is 0.156 *M*. However, since the steady state concentration of nitrous acid will be proportional to the concentration of nitrosyl disulfonate ion as seen from equation 15, the reactions 8 and 10 appear as first order but reaction 9 appears as second order with respect to color. This explains why a concentration of sulfamate ion as low as 0.00746 *M* can cause the color to disappear through an approximately first-order path and also explains the upward concavity of the curves in Fig. 3, Part I.[3]

In another case, for a solution of *p*H 3.6, $\mu = 0.35$, taking all the constants as before except $k'' = 7.6 \times 10^4$ (l./mole)^2 min.$^{-1}$, the same calculation shows that the total sulfamate ion concentration required is 0.17 *M* at 25°. But at 30°, a calculation[10] using $\phi_0 = 0.6$, $k'' = k'/\gamma_+ = 1.1 \times 10^5$ (l./mole)^2 min.$^{-1}$, $k_9 = 2.6 \times 10^4$ l./mole min. and $k_8 = 22$ l./mole min. shows that the total sulfamate ion required is 0.25 *M*. Hence 0.2 *M* sulfamate ion can only stop the generation of nitrous acid below about 27°, exactly as found.[3]

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. Arthur Maki for a few of the experiments.

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[9] ϕ_0 is calculated from the *p*H dependence of ϕ as shown in Table III of Part I (ref. 3). k' is calculated from equation 7 of this paper using $\mu = 0.15$. γ_+ is taken as 0.8. A_0 is calculated from the optical density at $t = 0$ (ref. 3). k_9 is taken from the result of Part III (ref. 2.). k_8 is calculated from the *p*H dependence of *k* as shown in Table III of Part I (ref. 3). α is obtained from the fact that in the inhibited reaction, the ratio of N_2 to N_2O is about 1 to 9 (ref. 3). β is obtained through the valence balance of N assuming the product of reaction 10 to be either hydroxylamine disulfonate or trisulfonate.

[10] ϕ_0 is estimated from the temperature dependence of ϕ (ref. 3) k' is calculated by the equation shown in the abstract of this paper. γ_+ is taken as that of HCl solution. k_9 is estimated from the heat of activation (ref. 2). k_8 is obtained using the heat of activation of 14.5 kcal. (ref. 3).