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

Decomposition of Nitrosyl Disulfonate Ion. V. The Reaction with Sulfite Ion[1]

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The reaction of nitrosyl disulfonate ion with sulfite ion has been found to be first order with respect to each substance. This was deduced from the effect of initial concentrations upon the reaction velocity with a correction for the reversion of hydroxylamine disulfonate. The ionic strength (0.034 to 1.25) dependence and the temperature (10 to 40°) dependence of the rate were observed. The following rate law reproduces the data obtained from reactions in 1 *M* NaCl solutions: $-\mathrm{d}\ln((SO_3)_2NO^{=})/\mathrm{d}t = 2k_1(SO_3^{=})$ where $k_1 = (kT/h)\ \exp.\ (1 - 13{,}530/RT - 18.6/R)$. The extrapolated value of k_1 at zero ionic strength was found to be between 0.02 to 0.03 l./mole min. at 25°.

In order to explain the spontaneous decomposition of nitrosyl disulfonate ion in alkaline solution at elevated temperature, the complications due to sulfite ion from hydroxylamine disulfonate ion must be studied. Haga[2] found the stoichiometry of the reaction of nitrosyl disulfonate ion with sulfite ion to be as

$$2(SO_3)_2NO^{=} + SO_3^{=} + H_3O^{+} \longrightarrow (SO_3)_2NOH^{=} + (SO_3)_2NOSO_3^{\equiv} + H_2O \qquad (1)$$

but the kinetics and mechanism of this reaction remained unknown. It is the purpose of this report to establish a possible mechanism from the kinetics of the reaction. The results will be applied later to the spontaneous decomposition of nitrosyl disulfonate ion in alkaline solutions.

Experimental Part

The rate of color disappearance was observed spectrophotometrically as described before.[3] Freshly recrystallized potassium nitrosyl disulfonate was dissolved in 1 *M* NaOH, 1 *M* NaCl or pure water at a *p*H value where the spontaneous decomposition was very slow. It was then added to a sodium or potassium sulfite solution with a concentration determined immediately before mixing.

Results and Discussion

The Reaction of Nitrosyl Disulfonate Ion with Sulfite Ion in 1 *M* NaOH Solution.—The reaction in dilute alkaline solutions was found to be very slow but it became fast when the concentration of NaOH was increased. Therefore the kinetics of the reaction in 1 *M* NaOH solution were first studied. After careful examination of the data from about twenty runs as measured by color disappearance with a wide range of initial concentrations, the following mechanism was proposed

$$(SO_3)_2NO^{=} + SO_3^{=} \xrightarrow{k_1} (SO_3)_2NO^{\equiv} + SO_3^{-} \qquad (2)$$

$$(SO_3)_2NO^{=} + SO_3^{-} \xrightarrow{\text{fast}} (SO_3)_2NOSO_3^{\equiv} \qquad (3)$$

$$(SO_3)_2NO^{\equiv} \xrightarrow{k_2} 2SO_3^{=} + NO^{+} \qquad (4)$$

Reactions shown by equations 2 and 3 can be combined to give the correct stoichiometry found by Haga as shown in equation 1. The reaction shown by equation 4 was found by Divers and Haga[4] as the reversal in highly alkaline solutions of the formation of hydroxylamine disulfonate ion. The reversion was found[4] to be complicated by hydrolysis and side reactions. Since in this case the reversion was much slower than the reaction between nitrosyl disulfonate ion and sulfite ion, these complications could be neglected.

The mechanism can be analyzed as follows: Let *A* be the concentration of nitrosyl disulfonate ion and *B* that of $(SO_3)_2NO^{\equiv}$ at any time *t*. Then

$$-\frac{\mathrm{d}A}{\mathrm{d}t} = 2k_1A(SO_3^{=}) \qquad (5)$$

$$-\frac{\mathrm{d}(SO_3^{=})}{\mathrm{d}t} = k_1A(SO_3) - 2k_2B \qquad (6)$$

$$\frac{\mathrm{d}(NO_2^{-})}{\mathrm{d}t} = k_2B \qquad (7)$$

To solve these simultaneous differential equations is difficult. An approximate numerical method has been based upon the fact that the reaction shown by equation 4 is much slower than the reaction shown by equation 2 so that the concentration of nitrite ion produced is practically negligible as compared to the concentration of $(SO_3)_2NO^{\equiv}$. Therefore the concentration of $(SO_3)_2NO^{\equiv}$ can be taken as $(A_0 - A)/2$ with A_0 equal to the initial concentration of nitrosyl disulfonate ion. The concentration of nitrite ion at any time *t* can then be calculated from integration of equation 7

$$(NO_2^{-}) = \frac{k_2}{2}\int_0^t (A_0 - A)\,\mathrm{d}t \qquad (8)$$

Thus the concentration of sulfite ion at any time *t* is

$$(SO_3^{=}) = (SO_3^{=})_0 - \frac{(A_0 - A)}{2} + k_2\int_0^t (A_0 - A)\,\mathrm{d}t \quad (9)$$

Substituting equation 9 into equation 5, the simplified form for the case of $A_0 = 2(SO_3^{=})_0$ is

$$\frac{\mathrm{d}(1/A)}{\mathrm{d}t} = k_1 + \frac{2k_1k_2}{A}\int_0^t (A_0 - A)\,\mathrm{d}t \qquad (10)$$

and for other cases, it is

$$-\frac{\mathrm{d}\ln A}{\mathrm{d}t} = k_1[2(SO_3^{=})_0 - (A_0 - A)] + 2k_1k_2\int_0^t (A_0 - A)\,\mathrm{d}t \quad (11)$$

These forms are specially chosen to subject the mechanism to direct test using the data from color disappearance.

Equation 10 was first tested in a case where $A_0 = 0.0314$ *M* and $(SO_3^{=})_0 = 0.0157$ *M* in a solution of 1 *M* NaOH. Optical densities measured at one-minute intervals were recorded as shown partly in Table I. If there were no complication from the reaction shown by equation 4, the quantity $\mathrm{d}(1/A)/\mathrm{d}t$ should have been constant throughout the

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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) T. Haga, *J. Chem. Soc.*, **85**, 78 (1904).

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

(4) E. Divers and T. Haga, *J. Chem. Soc.*, **65**, 523 (1894).

TABLE I

CORRECTION OF THE REVERSION OF HYDROXYLAMINE DISULFONATE ION IN 1 M NaOH

t, min.	$20.8A$	$d(1/20.8A)/dt$, min.$^{-1}$	$A^{-1}\int_0^t(A_0 - A)dt$, min.	$k_1/20.8$	$20.8\ (NO_2^-)$
0	0.653	...	....	...	.....
1	.486	0.508	0.17	0.508	0.00008
3	.328	.507	1.74	.507	.00057
5	.245	.525	5.30	.514	.00130
7	.192	.570	11.3	.546	.00217
9	.157	.580	19.9	.537	.00313
11	.132	.600	31.4	.534	.00415
13	.111	.640	46.9	.540	.00521
15	.097	.690	65.4	.547	.00631
17	.085	.740	87.4	.548	.00743
19	.075	.800	114	.555	.00857
21	.067	.843	145	.533	.00973
23	.060	.930	182	.538	.0109
25	.054	1.04	224	.550	.0121
27	.049	1.12	273	.523	.0133
29	.044	1.29	334	.550	.0145
31	.039	1.40	403	.533	.0157

run. Actually it increased during the reaction as seen in the third column of Table I. According to equation 10, $d(1/A)/dt$ was plotted against $A^{-1}\int_0^t(A_0 - A)\,dt$, where the integral was evaluated graphically. An approximate straight line was actually obtained, and from it both k_1 and k_2 were found. Since reaction 4 was slow in comparison with reaction 2, k_2 could be evaluated only approximately from the experimental data. However, with the value of k_2 found from the plot, k_1 was calculated at 2-minute intervals by means of equation 10 as shown in the fifth column of Table I. Since a large error in k_2 would cause only a small error in k_1, the standard deviation of the 16 values of k_1 was only ±2.7%.

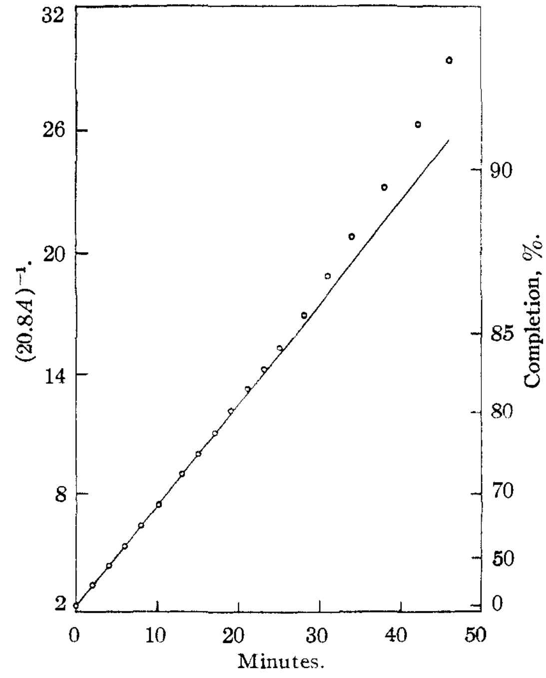

Fig. 1.—The reaction of nitrosyl disulfonate ion with sulfite ion in one molar NaCl solution.

The condition that reaction 4 be slow, upon which the approximate numerical solution is based, was confirmed by computing the quantity of nitrite formed in the side reaction. This was done by graphical integration of equation 8 using the value of k_2 obtained previously. The amount of nitrite which appeared during a reaction of 31 minutes duration as described in Table I was only 5.2% of the $(SO_3)_2NO^=$ formed.

Equation 11 was then tested for the case where A_0 was different from $2(SO_3^=)_0$. In each case, k_1 was evaluated numerically at 2-minute intervals and the average value was recorded as shown in Table II. Within the range of the ratio of $A_0/(SO_3^=)_0$ from 13.5 to 0.37, the average of all the values of k_1 obtained from 16 runs was 10.80 ± 0.30 l./mole min. at 25°.

TABLE II

THE EFFECT OF INITIAL CONCENTRATIONS ON THE SECOND-ORDER RATE CONSTANT, k_1

A_0, M	$(SO_3^=)_0$, M	$A_0/(SO_3^=)_0$	l./mole min.
0.0298	0.0022	13.5	10.4
.0365	.0030	12.1	10.8
.0234	.0025	9.4	10.4
.0361	.0045	8.0	10.8
.0327	.0052	6.3	10.6
.0191	.0035	5.5	10.4
.0350	.0075	4.7	10.8
.0330	.0083	4.0	10.8
.0394	.0151	2.61	11.3
.0314	.0157	2.00	11.1
.0233	.0290	0.80	11.1
.0394	.0517	0.76	10.9
.0165	.0221	0.75	11.1
.0273	.0480	0.57	11.2
.0216	.0483	0.45	10.4
.0189	.0517	0.37	10.4

The Ionic Strength Dependence.—Since the proposed mechanism consisted only of pH independent reactions, the slow rates in dilute alkaline solutions could be ascribed only to the effect of ionic strength. As expected, the reaction in 1 M NaCl solution proceeded at the same rate as in 1 M NaOH solution. In this case, however, the reaction shown by equation 4 was negligible until the latter part of each run, when the pH of the solution was high enough that a significant portion of hydroxylamine disulfonate ion was converted to its conjugate base, $(SO_3)_2NO^=$. In a case of A_0 = 0.0200 M, $(SO_3^=)_0$ = 0.0100 M and initial pH = 9.95, a plot of $(20.8\,A)^{-1}$ *vs.* t was made as shown in Fig. 1. The deviation from second-order plot was only significant after about 82% completion, and the second-order constant, k_1, could be easily evaluated from the first 80% of the reaction. Some results are shown in Table III.

At other salt concentrations, k_1 should show a dependence on ionic strength with a limiting slope of about 4.1 when its logarithm was plotted against the square root of ionic strength.[5] This was ac-

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(5) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 428.

TABLE III

THE SECOND-ORDER RATE CONSTANT IN 1 *M* SODIUM CHLORIDE SOLUTION

A_0, *M*	$(SO_3^=)_0$, *M*	$A_0/(SO_3^=)_0$	k_1, l./mole min.
0.0203	0.0048	4.23	10.8
.0218	.0062	3.36	10.8
.0200	.0100	2.00	10.6
.0145	.0130	1.12	10.6
.0133	.0245	0.54	10.9
.0139	.0256	0.54	10.8

tually found as shown in Fig. 2, where a plot of log k_1 *vs.* $\sqrt{\mu}/1 + \sqrt{\mu}$ was made. The reaction was carried out in slightly alkaline solutions with or without the addition of sodium chloride. The ionic strength changed slightly during a run as seen from equation 1, but no curvature in the second-order plot could be detected. Hence an average value of ionic strength was assumed throughout each run. The values of k_1 at the two lowest salt concentrations were obtained from the initial rates and were subject to large error because of the slow rates. Thus the extrapolation to zero ionic strength was rather arbitrary. The value of k_1 at infinite dilution lay between 0.02 to 0.03 l./mole min. at 25°. The consistency of the experimental data with the theory of the ionic strength effect on the reaction rate between ions supports the mechanism proposed.

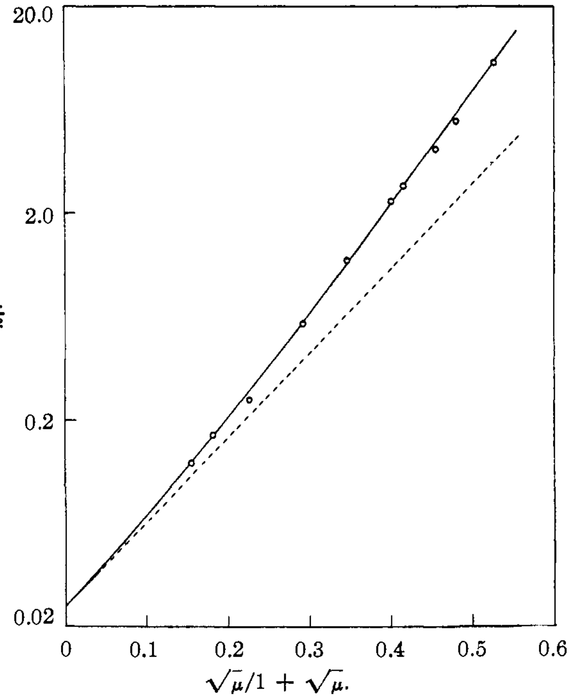

Fig. 2.—Ionic strength dependence of the rate constant k_1.

Temperature Dependence and the Heat and Entropy of Activation.—The second-order constant k_1 was obtained in 1 *M* NaCl solution at temperatures from 10 to 40°. A plot of log k_1 *vs.* $1/T$ gave a straight line as shown in Fig. 3 from which the experimental heat of activation was found to be 13.53 kcal. Based upon the absolute reaction rate theory, the following equation represents k_1 in 1 *M* NaCl solution as a function of temperature.

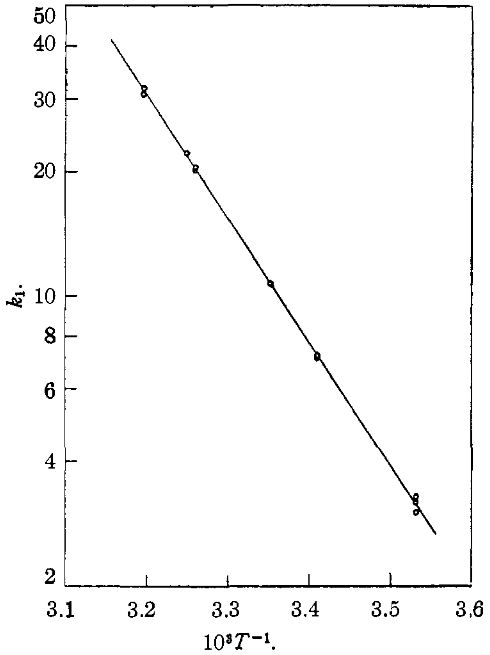

Fig. 3.—Arrhenius plot of the rate constant *vs.* $1/T$.

$$k_1 = \frac{kT}{h} \exp\left(1 - \frac{13{,}530}{RT} - \frac{18.6}{R}\right) \qquad (12)$$

The entropy of activation, −18.6 e.u., can be compared with that predicted by theory.[6] Assuming that the important contribution to the entropy of activation arises from electrostatic forces, it can be shown

$$\Delta S^{\ddagger} = \Delta S_{\mathrm{D}}^{\ddagger} + \Delta S_{\mu}^{\ddagger} = Z_{\mathrm{A}}Z_{\mathrm{B}}\left(7.24\frac{\sqrt{\mu}}{1 + 0.6\sqrt{\mu}} - 10\right) \qquad (13)$$

where the factor $\sqrt{\mu}/1 + 0.6\sqrt{\mu}$ enters from the fact that a plot of log k_1 *vs.* $\sqrt{\mu}/1 + 0.6\sqrt{\mu}$ with the data shown in Fig. 2 will give an approximate straight line with slope close to 4. This serves as a semi-empirical correction of the activity coefficients of the reactants and of the activated complex. With these considerations, substituting $z_{\mathrm{A}} = -2$, $z_{\mathrm{B}} = -2$ and $\mu = 1.25$ into equation 13, the theoretical value of $\Delta S^{\ddagger}$ calculated is −21 e.u. Considering that the non-electrostatic contribution to the entropy of activation was neglected, the agreement with experiment is satisfactory.

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(6) Reference 5, pp. 433–436, equations 78 and 82.