the parameter k_3 would itself be a function of (CH_3), (CH_4), the pressure of the gas and the detailed nature of the discharge. If we ignore such factors as the effect of turbulence, we can write for the average rates

$$\bar{r}_2 \sim 2\bar{r}_3$$

and

$$\bar{r}_3 \propto \bar{r}_1 \propto (CH_4)$$

If the average rate of methane disappearance, $\overline{d(CH_4)/dt}$, could be equated to $\bar{r}_2$, we might then reach the rather satisfactory conclusion that $\overline{d(CH_4)/dt}$ would be approximately first order in (CH_4). Actually, we note that $\overline{d(CH_4)/dt} = \bar{r}_2 - \bar{r}_5$ and that the last term is not small relative to $\bar{r}_2$ when the amount of hydrogen present is high (*cf.* section 3.3). Thus, from the viewpoint of kinetic requirements the best that can be said about the mechanism proposed is that it does not obviously violate the need that the average rate of methane decomposition be first order in methane. In section 4.3 it has been shown that increase in the "first-order constant" on dilution with hydrogen is consistent with the theory of the electrical discharge.

The mechanism given suggests that carbon and polymer formed result from secondary reactions on acetylene, a result consistent with the report of Vasil'ev[8] that relatively less acetylene is formed with increased residence time. If anything, our results show an opposite effect (*cf.* Table II) but it is possible that this result is attributable to still another secondary effect; *i.e.*, the effect of atomic hydrogen on carbon deposits, which have been formed rather plentifully in our work.

Yet one other pair of reactions must be assumed to explain the totality of the results observed, namely

$$CH_2 + CD_4 \longrightarrow CH_2D_2 + CD_2 \qquad (6a)$$

$$CD_2 + CH_4 \longrightarrow CH_2D_2 + CH_2 \qquad (6b)$$

These reactions do not involve any great rearrangement of atoms in the activated complex, which probably involves a rather sticky collision. They are required to explain the almost exclusive yield of CH_2D_2 among mixed methanes formed in the discharge-induced reaction between methane and methane-d_4 (*cf.* section 3.4).

The general absence of CH_3D and CD_3H, the predominance of CH_2D_2, and the preferential excitation of CH_2 in the discharge (*cf.* section 4.3) all are consistent with a C–H bond dissociation energy in free methyl substantially lower than that in methane.

This reaction scheme has neglected consideration of many other obvious radical reactions. However, the conclusion for all those examined was that they could not have contributed importantly to the reaction scheme.

NOTRE DAME, IND.

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

Decomposition of Nitrosyl Disulfonate Ion. III. Reaction with Nitrous Acid and its Relation to the Mechanism in Acid Solution[1]

BY JAMES C. M. LI AND D. M. RITTER

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The spontaneous decomposition of nitrosyl disulfonate ion has been further studied by observations in 1 *M* sodium acetate buffer solutions with and without added nitrous acid. With sufficient nitrous acid the rates of color fading and nitrous oxide evolution were proportional to $(\Sigma HNO_2)^2((SO_3)_2NO^-)^0$; the nitrous acid was regenerated by the reaction, and extra nitrous acid was formed. The spontaneous decomposition (no added nitrous acid) in the high capacity, high ionic strength buffer solution proceeded throughout by the branching chain mechanism previously reported, but with a scarcely observable initiating step. A mechanism was deduced in which the formation of N_2O_3 from nitrous acid was the rate determining step with $k_{N_2O_3} = k_1 = (kT/h)\, e^{-20{,}070/RT}\, e^{16.28/R}$.

In previous work[2] nitrous acid was found to act as an important intermediate in the branching-chain decomposition of nitrosyl disulfonate ion as observed in mildly acidic buffer solutions. Part of the evidence was the *p*H dependence of the chain-branching constant which could be interpreted as being related to the concentration of molecular nitrous acid. The investigation reported here had the object of inquiring further into the action of nitrous acid. This was accomplished by observing the reaction of that substance with nitrosyl disulfonate ion within a *p*H range where the spontaneous decomposition was slow. The reaction was best observed in high capacity buffer solutions[3] and thus required a restudy of the spontaneous decomposition under those conditions in order to compare the kinetics. With these data available it became possible to account for the spontaneous decomposition in unbuffered solutions.

Experimental Part

The color disappearance of nitrosyl disulfonate ion during reaction was measured at 540 mμ with a Beckman DU spectrophotometer using a ground-stoppered cell of one centimeter thickness placed in a chamber built in the light path of the spectrophotometer. The chamber was filled with water to about the shoulder of the cells, and the water was circulated continuously from a thermostated bath. The temperature variation in the chamber was ±0.01° at room temperature and ±0.02° at 35° and 10°.

For the collection of N_2O gas where reaction velocities were determined by observing that substance, the apparatus was similar to that described by Schubert.[4] All-glass seals were used and the 10 ml. micro-buret, the temperature equalizer and the water-filled differential manometer were

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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. H. Murib and D. M. Ritter, THIS JOURNAL, **74**, 3394 (1952).

[3] 1 *M* sodium acetate as compared with 0.045 *M* previously used.

[4] W. M. Schubert, THIS JOURNAL, **71**, 2639 (1949).

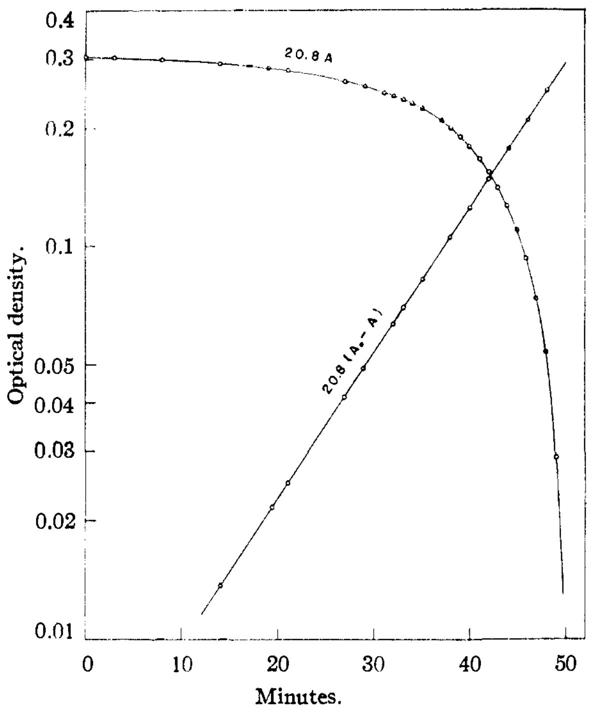

Fig. 1.—Spontaneous decomposition in 1 *M* sodium acetate buffer solution.

all sealed into the same water jacket. The reaction vessel was also similar to Schubert's,[4] except that a stopcock-closed inlet tube was sealed to the bulb above the liquid level. This was used to admit N_2O gas for sweeping and saturating the system before reaction. The reaction vessel was placed on a shaker mounted in a thermostated bath, where it was connected to the gas measuring buret through a bath-immersed 10-cm. diameter spiral wound from five mm. glass tubing. The reaction bath temperature was controlled to ±0.01° and the temperature of the gas collecting ensemble was maintained by circulating through its jacket the water from a second bath maintained at 25 ± 0.02°. A run was started after the whole system had reached thermal and mechanical equilibrium. The period of each run was so chosen that the variation of atmospheric pressure and room temperature would not affect the result.

For kinetic runs based on color disappearance, purified potassium nitrosyl disulfonate was kept in a vacuum desiccator no longer than one week between recrystallizations. It was dissolved in 1 *M* sodium acetate buffer solution of known concentration of nitrous acid and transferred to a cell which was then placed in the chamber of the Beckman DU spectrophotometer where optical densities were read at proper time intervals. To study the rate of N_2O evolution, the potassium nitrosyl disulfonate was dissolved in 1 *M* sodium acetate and placed in the bulb of the reaction vessel. The second bulb contained a solution of nitrous acid in acetic acid and sodium acetate in such proportions that, after mixing, the resulting solution would have the desired *p*H. To study the spontaneous decomposition in unbuffered solution, recrystallized potassium nitrosyl disulfonate was dissolved in distilled water and the residual alkali which usually caused the solution to have *p*H 8 or 9 was carefully neutralized by very dilute sulfuric acid to *p*H about 4. Then the rate of color disappearance was measured.

Results and Discussion

The Spontaneous Decomposition in 1 *M* Sodium Acetate Buffer Solution.—The rate of color fading in the buffer solution was reexamined and unlike the prior observation,[2] the first-order part was found negligible. The following equation described the color fading almost exactly with deviation only in the initial 2–3%

$$-\frac{dA}{dt} = \phi(A_0 - A) \qquad (1)$$

with A equal to the concentration of nitrosyl disulfonate ion at any time t, A_0 the initial concentration of the same and ϕ a constant.

The rate of N_2O evolution was observed also, where the following rate law was applied

$$\frac{d(N_2O)}{dt} = -\frac{1}{4}\frac{dA}{dt} = \frac{\phi}{4}(A_0 - A) = \phi(N_2O) \qquad (2)$$

Figure 1 shows a typical plot of log A and log $(A_0 - A)$ *vs.* t at *p*H 3.59 where ϕ can be calculated from the slope of the straight line. Table I shows some values of ϕ obtained by both methods. The constant is independent of the initial concentration of nitrosyl disulfonate ion, but dependent upon the *p*H of the buffer solution. The values of ϕ lack agreement with those obtained before[2] because of higher ionic strength and much higher acetic acid content, but it is seen that they are of the same order of magnitude. Equation 2 shows that every four ions of $(SO_3)_2NO^=$ which disappear give one molecule of N_2O immediately. Thus the intermediate compound proposed previously[2] appears very unstable, if it exists at all. This observation is rather important because it enables treatment of the data for spontaneous decomposition in unbuffered solution.

TABLE I

SPONTANEOUS DECOMPOSITION IN 1 *M* SODIUM ACETATE BUFFER SOLUTION

*p*H	A_0, *M*	ϕ, min.$^{-1}$	*p*H	A_0, *M*	ϕ, min.$^{-1}$
3.55[a]	0.0152	0.093	4.00[b]	0.0229	0.036
3.59[b]	.0384	.085	4.00[b]	.0149	.036
3.59[b]	.0312	.086	4.05[a]	.0312	.033
3.59[b]	.0147	.086			

[a] From N_2O evolution. [b] By spectrophotometric method.

The Reaction with Nitrous Acid in 1 *M* Sodium Acetate Buffer Solution.—In a buffer solution of *p*H high enough to render the spontaneous decomposition negligible, the nitrosyl disulfonate ion was found to react with a sufficient amount of nitrous acid in the following way The rate of color disappearance was constant in a single run until near the end of the reaction, where the nitrosyl disulfonate ion concentration fell below 0.001 *M*. A typical example shown in Fig. 2 was observed at *p*H 5.02 with the initial concentration of nitrosyl disulfonate ion at 0.0130 *M* and with the stoichiometric nitrous acid concentration equal to 0.0100 *M*. The concentration of nitrous acid relative to the nitrosyl disulfonate ion concentration had to be high enough that the accumulation of extra nitrous acid as a reaction product was negligible. The rate was also independent of the initial concentration of nitrosyl disulfonate ion, but it was proportional to the square of the initial stoichiometric concentration of nitrous acid. This conclusion was drawn from experiments at several *p*H values within the range 4.00 to 6.60 in which the initial nitrosyl disulfonate ion concentration was varied about tenfold at each *p*H, and all the runs covered the concentration range 0.003–0.057 *M*. In these same runs the initial stoichiometric nitrous acid concentration was varied

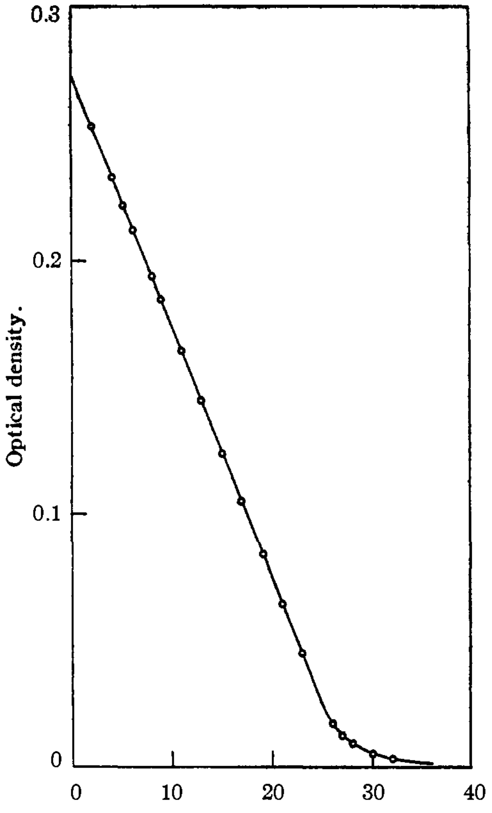

Fig. 2.—The reaction with nitrous acid, showing zero-order dependence on nitrosyl disulfonate ion concentration.

about 3- to 5-fold at each *p*H, and the concentration range covered was 0.001 to 0.1 M.

Thus the rate law is

$$-\frac{dA}{dt} = k(\Sigma HNO_2)^2 \qquad (3)$$

where (ΣHNO_2) is the concentration of all nitrous acid species (including both HNO_2 and NO_2^-) and k is a *p*H dependent rate constant. Figure 3 showing this relation at *p*H 4.25 is a plot of log $(-dA)/dt$ *vs.* log (ΣHNO_2). The straight line has a slope of exactly 2.0 and $k = 146$ can be obtained from the intercept. The *p*H dependence of k follows the relation

$$k = \frac{k'}{\left\{1 + \frac{K}{[H^+]\gamma_-}\right\}^2} \qquad (4)$$

where k' is a constant independent of *p*H, K the dissociation constant of nitrous acid, $[H^+]$ the activity of hydronium ions and γ_- the activity coefficient of NO_2^-. This implies that molecular nitrous acid is involved, thus

$$-\frac{dA}{dt} = k'(HNO_2)^2 \qquad (5)$$

As in the spontaneous decomposition this reaction was followed also by observing the evolution of N_2O gas. Then the rate law becomes

$$\frac{d(N_2O)}{dt} = -\frac{1}{4}\frac{dA}{dt} = \frac{k}{4}(\Sigma HNO_2)^2 \qquad (6)$$

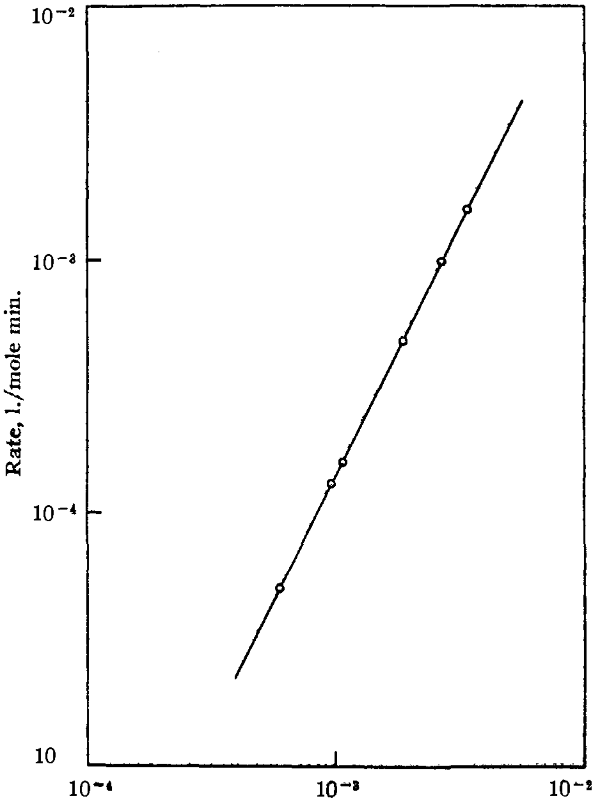

Fig. 3.—The reaction with nitrous acid, showing second-order dependence on nitrous acid concn.

Table II shows the *p*H-dependence of k evaluated from color disappearance and N_2O evolution The dissociation constant for nitrous acid, K/γ_- was evaluated from equation 4 by means of a plot of $1/\sqrt{k}$ *vs.* $1/[H^+]$ and found to be 5×10^{-4} which was used in the calculation of k' at each *p*H. The average value of k' was also obtained from the plot to be 1.42×10^4 Between *p*H 4 and 5, each value of k listed in Table II as determined spectrophotometrically was obtained from a plot of at least 5

TABLE II

THE DEPENDENCE OF k ON *p*H

*p*H	k, l./mole min.	$\left\{1 + \frac{K}{[H^+]\gamma_-}\right\}^2$	$k' \times 10^{-4}$, l./mole min.
4.00^b	7.25×10^2	1.93×10^a	1.40
4.25^b	1.46×10^2	9.75×10	1.42
4.53^b	4.40×10	3.20×10^2	1.41
4.53^c	4.42×10	3.20×10^2	1.42
4.65^b	2.56×10	5.44×10^2	1.39
4.81^b	1.28×10	1.11×10^3	1.42
4.92^b	7.67	1.82×10^3	1.40
4.93^c	7.64	1.87×10^3	1.44
5.02^b	4.80	2.85×10^3	1.36
5.33^c	1.20	1.16×10^4	1.40
5.54^b	4.70×10^{-1}	2.98×10^4	1.40
5.93^c	7.60×10^{-2}	1.81×10^5	1.38
6.07^b	4.00×10^{-2}	3.45×10^5	1.38
6.55^b	4.45×10^{-3}	3.12×10^6	1.39

[a] This value was calculated using a value of 3.4×10^{-4} for K/γ_- instead of 5×10^{-4} used for the others since a decrease of K might be expected when a solution contained about 1/5 glacial acetic acid by volume. (The solution of *p*H 4.25 contained only about 1/10 acetic acid by volume.) [b] Spectrophotometric method. [c] From N_2O evolution.

sets of data similar to those shown in Fig. 3. The rest of the k values were from single runs calculated by equation 3 or 6.

Relation between the Spontaneous Decomposition and the Reaction with Nitrous Acid.—If it is assumed that the decomposition occurs mainly through the reaction with nitrous acid, the quantity, A, can be eliminated from equations 1 and 3 by first equating them and differentiating with respect to time, then by again equating the result with equation 3 to obtain

$$\frac{\mathrm{d}(\Sigma \mathrm{HNO_2})}{\mathrm{d}t} = \frac{\phi}{2}(\Sigma \mathrm{HNO_2}) \qquad (7)$$

This says that there is a way to produce nitrous acid during the decomposition and that the rate of production is proportional to the stoichiometric nitrous acid concentration in a buffer solution. This makes it possible to treat the data of spontaneous decomposition in the presence of a small added amount of nitrous acid. The concentration of nitrous acid will then increase during decomposition to accelerate the rate of color fading. At any time t, the stoichiometric concentration of nitrous acid can be calculated through integration of equation 7

$$(\Sigma \mathrm{HNO_2}) = (\Sigma \mathrm{HNO_2})_0 e^{\phi t/2} \qquad (8)$$

where $(\Sigma \mathrm{HNO_2})_0$ is the initial stoichiometric concentration of added nitrous acid. Therefore the rate of color fading at any time t can be predicted by substitution of equation 8 into equation 3. The resultant differential equation can be integrated to give

$$\ln\left[A_0 - A + \frac{k}{\phi}(\Sigma \mathrm{HNO_2})_0{}^2\right] = \ln\frac{k}{\phi}(\Sigma \mathrm{HNO_2})_0{}^2 + \phi t \qquad (9)$$

This relation was examined thoroughly at pH 4.00 with different added amounts of nitrous acid. In each run, the left hand side of equation 9 was plotted against t using $k/\phi = 2 \times 10^4$ as the first trial value. From the slope and intercept of the line, first approximate values were found for ϕ and k. A second or third approximation was often required in order to find exact values. It was found that equation 9 held at various values of $(\Sigma \mathrm{HNO_2})_0$ as shown in Table III. The values of ϕ and k obtained agreed with the previous values found in the spontaneous decomposition (Table I) and the reaction with a sufficient amount of nitrous acid (Table II).

To show that the decomposition occurred mainly through the reaction with nitrous acid, the production of nitrous acid which was obviously at the expense of nitrosyl disulfonate ion had to be small. An estimation of the amount of nitrous acid produced was made using equation 8 and the experimental over-all reaction time t_f with results also shown in Table III. This showed that in the spontaneous decomposition most of the color disappeared as described by the rate equation 3 and only a small fraction reacted to produce extra nitrous acid; hence the treatment appeared valid.

The over-all time of reaction t_f can also be calculated from equation 9 putting A equal to zero. The calculated values of t_f are compared with the experimental ones in Table III and it is seen that they disagree when the initial concentrations of nitrous acid are very low. This is obviously because the initial reaction makes a significant contribution in those cases. By assuming that the initiation reaction will be negligible after the concentration of nitrous acid reaches 5×10^{-4} M, approximate values of the first-order constant, ζ, for the initial reaction can be calculated. This is defined as the ratio in which the rate of nitrous acid production is divided by the nitrosyl disulfonate ion concentration. The values are shown in Table III. As an example, when A_0 was 0.0149 M and $(\Sigma \mathrm{HNO_2})_0$ was 1.0×10^{-4} M, the experimental over-all reaction time was 87 minutes. If instead the initial concentration of nitrous acid was 5×10^{-4} M, the over-all reaction time would be only 38 minutes calculated from equation 9. So within 49 minutes, the concentration of nitrous acid must have increased from 1.0×10^{-4} M to 5.0×10^{-4} M through both initiation and the reaction described by equation 7. As an approximation, a constant term ζA_0 was added to the right hand side of equation 7 and ζ was evaluated to be 2.2×10^{-4} min.$^{-1}$ by substitution of experimental data into the integrated form. The agreement of the ζ's calculated for experiments with different initial concentrations of nitrous acid supports the validity of the treatment.

Table III

Spontaneous Decomposition in the Presence of Small Added Amounts of Nitrous Acid

A_0, M	$(\Sigma \mathrm{HNO_2})_0$, M	ϕ, min.$^{-1}$	$k/\phi \times 10^{-4}$, l./mole	t_f, min. Calcd.	t_f, min. Expt.	$\frac{(\Sigma \mathrm{HNO_2})_f - (\Sigma \mathrm{HNO_2})_0}{A_0}$	$\zeta \times 10^4$, min.$^{-1}$
0.0229	0.0×10^{-5}	0.0358	2.01	...	107	....	2.1
.0218	1.0×10^{-5}	.0364	2.01	254	105	0.0027	2.1
.0212	2.0×10^{-5}	.0362	2.01	218	104	.0052	2.0
.0149	1.0×10^{-4}	.0364	2.01	118	87	.0257	2.2
.0124	4.8×10^{-4}	.0359	2.07	35.6	35	.0338	...
.0214	9.1×10^{-4}	.0358	2.00	23.2	23	.0213	...
.0271	1.2×10^{-3}	.0364	1.94	18.6	19	.0184	...
.0572	1.7×10^{-3}	.0364	2.04	18.6	18	.0115	...

Spontaneous Decomposition in Unbuffered Solution.—The kinetic equation applied to observations in buffered solutions can be used to treat the data from unbuffered systems, if provision can be made for the autocatalysis by hydronium ion produced in the reaction. Inspection of equations 2 and 6 indicates that four ions of $(\mathrm{SO_3})_2\mathrm{NO^=}$ disappear to give one molecule of $\mathrm{N_2O}$, and the previously observed stoichiometry shows that two ions of $(\mathrm{SO_3})_2\mathrm{NOH^=}$ and four of $\mathrm{HSO_4^-}$ are formed also. Equation 7 which holds in buffered solutions can be modified by a substitution based upon the previously[2] observed relation between ϕ and the concentration of molecular nitrous acid (as expressed by the pH dependence of ϕ). This gives the equation

$$\frac{\mathrm{d}(\Sigma \mathrm{HNO_2})}{\mathrm{d}t} = \frac{\phi_0}{2}(\mathrm{HNO_2}) \qquad (10)$$

where ϕ_0 is pH independent. The nitrous acid concentration factor can then be eliminated from equations 5 and 10 by appropriate substitution of the equivalent equilibrium expression to give

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\{\left(-\frac{\mathrm{d}A}{\mathrm{d}t}\right)^{1/2}\left[1 + \frac{K}{(\mathrm{H^+})\gamma_+\gamma_-}\right]\right\} = \frac{\phi_0}{2}\left(-\frac{\mathrm{d}A}{\mathrm{d}t}\right)^{1/2} \qquad (11)$$

where γ_+ is the activity coefficient of hydronium ion whose concentration (H^+) can be calculated from the second dissociation constant K_s of sulfuric acid

$$(H^+) = (A_0 - A)\alpha \qquad (12)$$

and

$$\frac{\alpha^2}{1-\alpha} = \frac{K_s\gamma_-}{(A_0 - A)\gamma_+\gamma_-} \qquad (13)$$

Now 11, 12 and 13 can serve as the rate law for the spontaneous decomposition in unbuffered solutions. Since the integration of 11 proved difficult, ϕ_0 was evaluated numerically from experimental data. Because the initial stage of the decomposition was neglected, equation 11 obviously failed to apply during the initial few per cent. of color disappearance just as did equation 1. However, it was found that for about the remaining 95% of the color fading, the values of ϕ, calculated at 2-minute intervals, had ±12% standard deviation (for 20 values), which was reasonable considering that equation 11 involved the ratio of second and first derivatives. The average values of ϕ_0 calculated from runs at initial concentrations of nitrosyl disulfonate ion of 0.0231, 0.0184, 0.0118 and 0.0094 *M* were 0.112, 0.116, 0.114 and 0.112 min.$^{-1}$, respectively.

Proposed Mechanism for the Reaction with Nitrous Acid and the Heat and Entropy of Activation.—The rate of color fading in the reaction with nitrous acid remained constant in a single run, but it was proportional to the square of the initial concentration of nitrous acid. Thus it appeared that the reaction between nitrous acid and nitrosyl disulfonate ion regenerated the nitrous acid which it consumed, leaving the nitrous acid concentration constant. With this observation and the stoichiometry as the bases the following mechanism has been deduced[5]

$$2HNO_2 \xrightarrow{k_1} N_2O_3 + H_2O \qquad (14)$$

$$(SO_3)_2NO^- + N_2O_3 + 2H_2O \xrightarrow{\text{fast}} 2SO^- + NO + NO^+ + NOH + H_3O^+ \qquad (15)$$

$$(SO_3)_2NO^- + NO + H_3O^+ \xrightarrow{\text{fast}} (SO_3)_2NOH^- + NO^+ + H_2O \qquad (16)$$

with NO^+ and 2NOH giving nitrous acid and nitrous oxide, respectively.

The rate equation describing this mechanism is

$$-\frac{dA}{dt} = 2\frac{d(N_2O_3)}{dt} = 2k_1(HNO_2)^2 \qquad (17)$$

and

$$\frac{d(\Sigma HNO_2)}{dt} = 0 \qquad (18)$$

Comparing 17 with 5, it is seen $k_1 = k'/2$.

The temperature dependence of k_1 was studied from 10.3° to 35° in 1 *M* sodium acetate buffer solution of *p*H 4.81 (measured at 25°). The *p*H values at other temperatures were calculated assuming the activity coefficients to be the same as those at 25°. The dissociation constants of acetic acid were those obtained by Harned and Ehlers[6] as a function of temperature. The dissociation constants of nitrous acid at different temperatures were obtained through interpolation on a logarithmic scale of the data of Schmid, Marchgraber and Dunkl.[7] The rate constants k_1 thus calculated are shown in Table IV. A plot of log k_1 *vs.* $1/T$ gave a straight line from which the experimental heat of activation of 20,070 cal. was calculated. Based on the absolute reaction rate theory, the following relation expresses k_1 as a function of temperature

$$k_1 = \frac{kT}{h}\cdot e\cdot e^{-20{,}070/RT}e^{16.28/R} \qquad (19)$$

from which $\Delta H\ddagger$ = 19,490 cal. and $\Delta S\ddagger$ = 16.28 e.u.

TABLE IV

TEMPERATURE DEPENDENCE OF THE REACTION OF NITROSYL DISULFONATE ION WITH NITROUS ACID

Temp., °C.	$k_1 \times 10^{-3}$, l./mole min.	Temp., °C.	$k_1 \times 10^{-3}$, l./mole min.
10.3	1.08	25.0	7.10
15.0	1.96	30.0	13.1
20.1	3.88	35.0	24.3

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[5] For a similar mechanism in diazotization reactions, see L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 294.

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

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