The high temperature form was indexed from powder diffraction charts on the basis of an orthorhombic unit cell with $a = 5.149$ Å., $b = 5.436$ Å., $c = 14.688$ Å. If finely divided rhodium powder is heated in air above 600°, it converts to the high temperature form directly. The optimum temperature for the formation of Rh_2O_3 is 1000°. However, above 1100° Rh_2O_3 decomposes to the metal.

Goldschmidt[5] has shown that the perovskite-type structure is stable only if a tolerance factor, t, defined by $(r_A + r_O) = t\sqrt{2}(r_B + r_O)$, has an approximate range of $0.8 < t < 1$. The values for r_A, r_B, and r_O are the Goldschmidt radii of the respective ions. Megaw[6] has tabulated the tolerance factor of a large number of perovskites and found that if $0.8 < t < 0.9$, a cooperative buckling and enlargement of the unit cell occurs. The values of t are given for several rare earth rhodium oxides in Table III. These values are based on the rare earth radii reported by Templeton and Dauben[7] and a radius of 0.69 for trivalent rhodium (coordination number six). The decrease in the value for t as one proceeds from lanthanum to neodymium is accompanied by greater difficulty in the preparation of the rare earth rhodium oxide. Neodymium rhodium oxide does not form unless the oxides are allowed to react in an oxygen atmosphere at 1100°. Neodymium rhodium oxide also possesses a greater distortion than lanthanum rhodium oxide, although for both compounds $a < c/\sqrt{2} < b$ (O structure). Calculations based on X-ray data and comparison with $GdFeO_3$[8] show that $NdRhO_3$ probably belongs to the space group D_{2h}^{16} Pbnm, with four formula weights per unit cell. The lattice constants are $a = 5.402$ Å., $b = 5.772$ Å., $c = 7.816$ Å. Attempts to prepare samarium and yttrium rhodium oxides were unsuccessful, and it can be seen from Table III that formation of these compounds necessitates a further decrease in the value of t. It is apparent that for the radii chosen a minimum value of t (0.810) is reached for $NdRhO_3$. A further decrease in t results in the lack of formation of a perovskite structure. Since both lanthanum and neodymium rhodium oxides possess the O structure, it can be concluded that the only factor to be considered for the formation of rare earth rhodium perovskites is the ionic size effect. The lack of formation of an O′ structure ($c/\sqrt{2} < a < b$) indicates that this type of distortion must be caused by a superposition of electron-ordering as was suggested by Goodenough.[4]

TABLE III

VALUES OF t FOR $MRhO_3$

Compound	t
$LaRhO_3$	0.832
$NdRhO_3$	.810
$SmRhO_3$	.800
$YRhO_3$	.785

Acknowledgment.—It is a pleasure to thank Dr. John B. Goodenough for his many valuable suggestions.

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[6] H. D. Megaw, *Proc. Phys. Soc.* (London), **58**, 133 (1946).

[7] D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

[8] S. Geller, *J. Chem. Phys.*, **24**, 1236 (1956).

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Decomposition of Nitrosyl Disulfonate Ion in Mildly Alkaline Solution[1]

BY BYRON J. WILSON[2] AND D. M. RITTER

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Decomposition of nitrosyl disulfonate ion between 25 and 90° in the pH range 6 to 11 gives the products found by Divers and Haga in amounts now found quantitatively and a still unrecognized anion, probably divalent with N/S = 1.0. The stoichiometry and kinetics were consistent with two decomposition paths involving initial rupture of the radical anion into the free radicals SO_3^- (k_1) and NO (k_2), respectively. These are also proposed as the reactions which initiate the material chain process in acid solution. Assuming the reactions actually to be S_N2 involving water, the rate constants for color disappearance could be expressed by $k_1 = (kT/h) \exp(1 - (32900/RT) + (18.8/R))$ and $k_2 = (kT/h) \exp(1 - (29800/RT) + (9.5/R))$ independent of pH and initial concentration and subject to only a secondary salt effect. Rates of nitrite ion formation and liberation of acid were proportional to the rate of color disappearance.

While a certain amount was learned concerning the behavior of nitrous acid as a chain carrier during previous observation of nitrosyl disulfonate ion decomposition in acid solution, the reaction had such complexity that no conclusion could be reached concerning the initiating reaction. In the pH range 6–11 the reaction is much slower,[3] and the inventory of products[4] made long ago lent encouragement that suitable observations of alkaline solutions might indicate the initiating reactions. Since our last paper other such experiments

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[1] Paper VI of a series in which the most recent is J. C. M. Li and D. M. Ritter, *J. Am. Chem. Soc.*, **75**, 5831 (1953).

[2] Based on the doctoral thesis of Byron J. Wilson, University of Washington, 1961. Work was done under NSF Grant G-11397, an assistance gratefully acknowledged.

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

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

have been made[5] without any clearly interpretable result. So through an improved examination of the product stoichiometry and with kinetic diagnosis we undertook to discover what the decomposition in alkaline solution might reveal. As preliminary to this an intermediate reaction had been examined, that between nitrosyl disulfonate ion and sulfite ion, inescapably the source of the hydroxylamine trisulfonate ion formed in the decomposition.[1]

Experimental

Preparations.—Potassium hydroxylamine disulfonate was prepared by Raschig's method.[6] Potassium hydroxylamine trisulfonate was prepared as described by Haga[4] and potassium nitrosyl disulfonate was prepared by Raschig's method as modified by Murib and Ritter.[3]

Analytical Methods.—Nitrite ion was determined by Raschig's iodometric method,[7] which worked satisfactorily in the presence of hydroxylamine disulfonate ion, but nitrosyl disulfonate ion interfered. To remove the interference sulfite ion was added to the solution buffered by saturation with sodium borate. When the color of nitrosyl disulfonate ion disappeared the excess sulfite was titrated with iodine to a pale blue end point. The solution was then acidified and analyzed for nitrite, the liberated iodine being titrated with standard thiosulfate to the same pale blue end point.

Nitrous oxide was determined by manipulation under high vacuum as described previously.[3]

Total nitrogen was estimated by the Dumas method.[8]

Sulfate ion was determined gravimetrically as barium sulfate, without the addition of other salts often added to prevent the precipitation of barium hydroxylamine di- and trisulfonates. If the solution was kept basic at room temperature, only barium sulfate precipitated. After filtration the precipitate was washed with a small volume of hot dilute hydrochloric acid to dissolve any barium carbonate or hydroxide which may have formed.

The ferric salt oxidation method[9] was used for the determination of hydroxylamine obtained from the hydrolysis of hydroxylamine disulfonate, but hydroxylamine trisulfonate and nitrite were interfering ions. Hydroxylamine trisulfonate ion was determined from the sulfate content after hydrolysis of solutions in which that substance was the only source of sulfate ion. A similar assay was used for hydroxylamine disulfonate.

Separation by Ion Exchange.—An ion-exchange procedure was used to separate the anions expected from the decomposition of nitrosyl disulfonate ion, namely, nitrite, sulfate, and hydroxylamine disulfonate and trisulfonate ions. A strongly basic resin, Duolite A-40, was pulverized and sieved to select the particle size 80–170 mesh. The column was prepared in a 25-ml. buret with a capacity of about 20 mequiv. After each run the column was repacked, regenerated with about 150 ml. of 5 *N* potassium hydroxide, and washed with water until the eluate was hydroxide-free. The flow rate was about 1.5 ml./min. The concentration of potassium chloride required to elute each of the ions with 100 ml. of eluent was separately established and the solution containing the expected ions in known concentration was prepared in the same buffer (pH 9) used in many of the nitrosyl disulfonate ion decompositions. An aliquot of this solution was placed on the column, and its components were removed by 100-ml. portions of each of the eluting potassium chloride solutions. The components were determined as previously described with the results given in Table I.

TABLE I

EVALUATION OF ION-EXCHANGE SEPARATION

Ion	Concn. of eluent, *M*	Amounts, mmoles	
		Added	Found
NO_2^-	0.2	1.297	1.304
SO_4^{-2}	0.2	1.201	1.205
$HON(SO_3)_2^{-2}$	0.5	0.958	0.959[a]
			0.946[b]
$ON(SO_3)_3^{-3}$	1.0	1.290	1.281[b]

[a] Ferric ion method. [b] From sulfate determined after hydrolysis.

Decomposition Products.—These were observed on aliquots from solutions originally containing about 1 g. of potassium nitrosyl disulfonate dissolved in 100 ml. of appropriate double capacity phosphate or borate buffer solution. The decompositions were carried out at temperatures regulated ±0.01°. The pH was determined before and after each experiment. Before ion-exchange separation an aliquot was deposited on the column followed by a water rinse until the eluate was neutral. Then each component was removed by passage of 100 ml. of potassium chloride eluent. Following this 10-ml. portions were individually tested to assure completeness of elution. No more than 120 ml. was ever required. The results are given in Table II.

Volatile Substances.—Gases produced in the decomposition were determined by the method previously reported.[3] The material found had the volatility of nitrous oxide but the amount was too small to identify by the infrared spectrum. The quantity, 0.009 mmole, corresponded to about the lower limit of accuracy, 0.01 mmole of nitrous oxide per mmole of decomposed nitrosyl disulfonate, found in previous experiments.

Reaction Kinetics.—The rate of color disappearance was observed at the higher concentrations as previously reported.[3,10] In low concentration the rates were determined in 20-cm. long cells fitted in a suitable temperature-regulated bath attached to the Beckman DU spectrophotometer. The pH was controlled by use of phosphate and borate buffers and the ionic strength was regulated by suitable additions of potassium nitrate. The results of the rate determinations on color disappearance are given in Tables III, IV, and V and Fig. 1.

The kinetics of nitrate ion formation was determined by iodometric analysis for nitrite in the presence of nitrosyl disulfonate ion. This was accomplished by removal of nitrosyl disulfonate through reaction with sulfite ion in solutions saturated with sodium borate buffer. The result is shown in Fig. 2.

The development of hydrogen ion was studied by observing the hydroxide ion consumption at a constant pH. The solution was prepared by adding solid potassium nitrosyl disulfonate slowly to the solvent with simultaneous addition of hydroxide ion to maintain slight basicity. Manual stirring was used to avoid erratic pH readings. The reaction flask was lowered into an oil bath and after 25 min. the temperature of the contents reached 70.0°, where it was maintained ±0.1°. Sodium hydroxide solution was added periodically to maintain the pH at about 9.18. The 3.55 mmoles of nitrosyl disulfonate ion initially present required a total of 2.00 mmoles of hydroxide ion to maintain the initial basicity during decomposition. The results are plotted in Fig. 3.

Results and Discussion

The substances measured directly, entered in Table II, have all been identified previously,[4] but never have they been measured very precisely. To a first approxi-

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[5] H. Gehlen and J. Cermak, *Z. anorg. Chem.*, **275**, 113 (1954).

[6] D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry of the Non-metallic Elements of the 5th and 6th Groups," Prentice-Hall, New York, N. Y., 1946, p. 91.

[7] F. Raschig, *Ber.*, **38**, 3911 (1905).

[8] A. Steyermark, "Quantitative Organic Microanalysis," The Blakiston Co., Philadelphia, Penna., 1951.

[9] W. C. Bray, M. E. Simpson, and A. A. MacKenzie, *J. Am. Chem. Soc.*, **41**, 1363 (1919).

[10] J. C. M. Li and D. M. Ritter, *ibid.*, **75**, 5823 (1953).

TABLE II

PRODUCTS OF NITROSYLDISULFONATE DECOMPOSITION IN ALKALINE SOLUTION[a]

				Eluates from ion-exchange resin by Cl^-					Calcd. quantities			
	pH			0.2 *M*		0.5 *M*		1 *M*				
Temp., °C.	Initial	Final	Decompn. time, hr.	NO_2^-	SO_4^{-2}	SO_4^{-2}[e]	$HON(SO_3)_2^{-2}$	$ON(SO_3)_3^{-3}$	OH^-	N_2O	$[HON(SO_3)]_2^{-2}$[h]	Sulfur matl. bal.
25	7.80[b]	7.06	1440	0.219	0.406	0.672	...	...	...			
25	9.02[c]	8.53	1440	.193	.366	.592	0.242	0.350	0.598	0.053	0.054	2.01
50	7.80[b]	7.08	39	.203	.324	.548	...	.384	...			
50	8.96[c]	8.47	32	.174	.336	.502	.170	.373	.635	.060	.081	1.96
70	7.65[b]	7.07	3.2	.193	.306	.536	...	.384	...			
70	8.94[b]	..	...	.173	.355	.444[g]	.123	.390	.737	.058	.099	1.97
70	9.13[d]	9.13	...	.191	.355	.536	.206	.392	.563[f]			
90	7.80[b]	7.05	0.5	.193	.321	.488	...	.389	...			
90	8.96[c]	8.43	.5	.166	.348	.408	.079	.408	.672	.048	.125	1.98

[a] Millimoles of product per one millimole of nitrosyldisulfonate decomposed. [b] In 0.1 *M* dihydrogen phosphate buffer. [c] In 0.1 *M* borate buffer. [d] No buffer; OH^- added during decomposition. [e] Total sulfate after hydrolysis. [f] Measured. [g] Total nitrogen by Dumas method 0.350. [h] Hypothetical product.

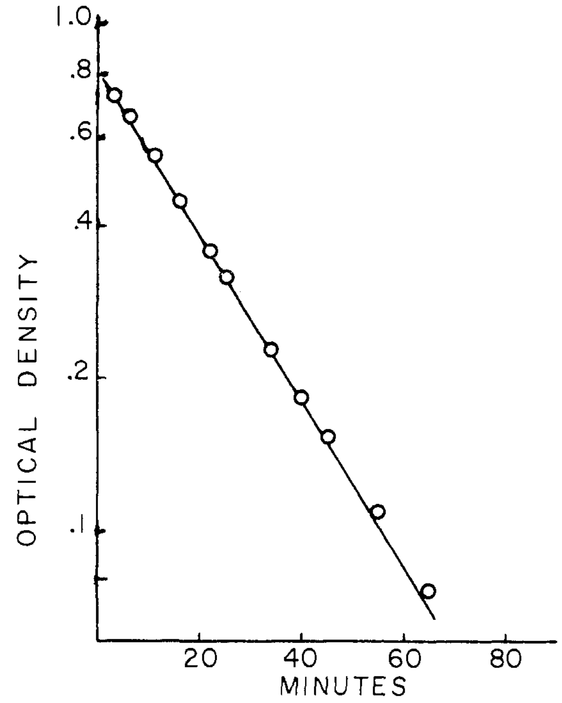


Fig. 1.—Color fading: 70.6°, pH 9.0.

mation the quantities found are best accounted for by the sum of reactions 1 and 2 in proportions linearly variable with the temperature, modified by side reactions of which (1c) is an example. Reactions of sulfite radical and sulfite anions and of nitric oxide with nitrosyl disulfonate anion are involved but not written.

TABLE III

TEMPERATURE AND pH DEPENDENCE OF VELOCITY CONSTANTS, *k*, (MIN.$^{-1}$) FOR COLOR FADING

pH[a]	25° $k \times 10^5$	50.1° $k \times 10^3$	70.6° $k \times 10^2$	80.6° $k \times 10^1$	90.6° $k \times 10^1$
6.48[b]	3.6	1.34	2.68	0.89	
7.23[b]	2.7	1.62	3.20	1.05	
7.86[b]	2.7	1.71	3.60	1.10	2.05
8.96[c]	2.6	1.62	3.76	1.31	2.94
9.32[c]	2.4	1.60	3.54	1.32	
9.86[c]	1.9	1.44	2.90	1.20	
10.72[d]	2.3	1.33	3.80	1.15	

[a] Ionic strength 0.405–0.409. [b] Buffer anion $H_2PO_4^-$. [c] Buffer anion $H_2BO_3^-$. [d] Buffer anion HPO_4^{-2}.

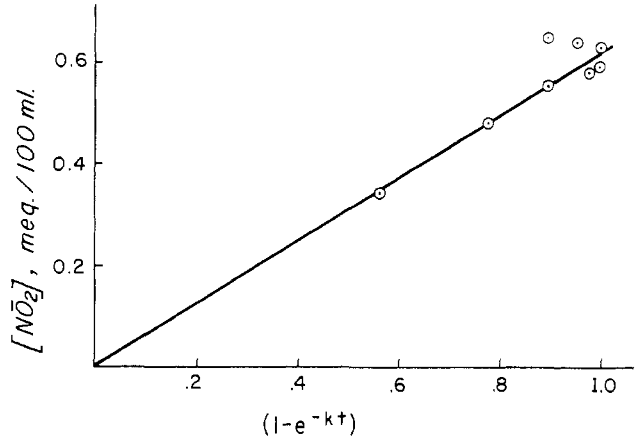


Fig. 2.—Nitrite formation: 70.6°, pH 9.0, $k = 4k'$.

TABLE IV

EFFECT OF IONIC STRENGTH AND INITIAL CONCENTRATION OF NITROSYL DISULFONATE ION ON RATE CONSTANTS FOR COLOR FADING AT 70.0°

Concn., $M \times 10^3$	Ionic strength $\times 10^2$	$k \times 10^2$, min.$^{-1}$
1.77[a]	0.63	2.87
1.77[a]	1.11	3.03
0.89[b]	1.37	2.84
.89[b]	2.32	2.97
.89[b]	3.28	2.84
.89[b]	5.17	2.86
.89[b]	8.02	2.74
.65[c]	0.28	3.07
.65[c]	9.81	2.75

[a] Borate buffer 0.00250 *M*, pH 8.78. [b] Borate buffer 0.003 *M*, pH 8.82. [c] Borate buffer 0.00195 *M*, pH 8.90.

TABLE V

EFFECT OF INITIAL CONCENTRATION AND IONIC STRENGTH UPON DECOMPOSITION IN ACID SOLUTION AT 25.40°

$ON(SO_3)_2^{-2}$, *M*	Ionic strength	$k \times 10^4$, min.$^{-1}$	$\phi \times 10^2$
0.000925[a,e]	0.00500	4.1	2.09
.000925[b,e]	.00697	3.1	2.06
.000925[b,e]	.0170	4.5	2.04
.000925[b,e]	.107	4.0	1.49
.00545[c,e]	.0362	5.0	2.16
.00109[c,e]	.0386	3.0	2.70
.000218[c,e]	.0390	—	1.54
.0152[d,f]	.0682	15.5	5.80
.0097[d,f]	.0683	11.9	4.90
.0055[d,f]	.0682	7.4	3.40

[a] In 0.00210 *M* acetate buffer, pH 3.85. [b] In 0.0040 *M* acetate buffer, pH 3.84. [c] In 0.022 *M* acetate buffer, pH 3.84. [d] In 0.0224 *M* acetate buffer, pH 3.80. [e] 20-cm. cells. [f] 10-cm. cells.

TABLE VI

EQUATION COEFFICIENTS AND MATERIAL BALANCES[a]

		NO_2^-		$HON(SO_3)_2^{-2}$			$ON(SO_3)_3^{-3}$		SO_4^{-2}			H_3O^+	
T, °C.	x	C^b	m^c	C^b	m^c	Σ^d	C^b	m^c	C^b	m^c	Σ^e	C^b	m^c
25	0.40	0.25	0.19	0.40	0.24	0.35	0.35	0.35	0.15	0.37	0.38	0.80	0.60
50	.49	.25	.17	.37	.17	.33	.38	.37	.13	34	.41	.76	.63
70	.56	.25	.17	.36	.12	.36	.39	.39	.11	.35	.33	.72	.74
90	.63	.25	.17	.34	.08	.33	.41	.41	.09	.35	.34	.69	.67

[a] Based upon one mmole of nitrosyl disulfonate ion. [b] Coefficient in sum of eq. 1 and 2. [c] Amount of substance found in Table II. [d] $(SO_4^{-2})_{0.5m\,Cl^-} - HON(SO_3)_2^{-2}$ = original $HON(SO_3)_2^{-2}$. [e] $C_{SO_4^{-2}} + (C - m)_{NO_2^-} + (C - m)_{HON(SO_3)_2^{-2}}$ as SO_4^{-2} from reaction 2 and side reactions.

$$ON(SO_3)_2^{-2} \xrightarrow{k_1} SO_3^- + ONSO_3^- \qquad (1a)$$

$$3H_2O + ONSO_3^- \xrightarrow{k_{1a}} SO_3^{-2} + NO_2^- + 2H_3O^+ \qquad (1b)$$

$$ONSO_3^- + 2H_2O \longrightarrow SO_4^{-2} + NOH + H_3O^+ \qquad (1c)$$

$$x[ON(SO_3)_2^{-2} + 0.75H_2O \longrightarrow 0.25NO_2^- + 0.25HON(SO_3)_2^{-2} + 0.50ON(SO_3)_3^{-3} + 0.50H_3O^+] \qquad (1)$$

$$ON(SO_3)_2^{-2} + 3H_2O \xrightarrow{k_2} SO_3^{-2} + SO_4^{-2} + NO + 2H_3O \qquad (2a)$$

$$(1 - x)[ON(SO_3)_2^{-2} + H_2O \longrightarrow 0.25NO_2^- + 0.50HON(SO_3)_2^{-2} + 0.25ON(SO_3)_3^{-3} + 0.25SO_4^{-2} + 0.5H_3O^+] \qquad (2)$$

The amount of nitrite ion expected is the same in either reaction, but the hydroxylamine trisulfonate yields differ. The stability of that salt, the accuracy with which it can be separated and determined, and the simple monotonic variation of its amount at different temperatures suggested that the algebra for partitioning the products between reactions 1 and 2 could be based upon it. Consequently the factors x and $1 - x$ were determined from the relation

$$0.5x + 0.25(1 - x) = ON(SO_3)_3^{-3}$$

with the results entered in Table VI. When certain logically valid corrections were considered the agreement between this scheme and the quantities found was rather good and better than any of the alternatives tested.

The corrections involved the fact that nitrite ion and hydroxylamine disulfonate ion yields were notably lower than predicted. Reaction 1c, leading to nitrous oxide, is an example. In addition to hydroxylamine disulfonate ion there was found in the 0.5 *M* chloride ion eluate nitrogenous anionic material estimated to have a ratio N/S = 1.0 and to be divalent. The inverse relation between these two substances suggested that the unknown came from hydroxylamine disulfonate and the amount of the substance calculated (*cf.* Table VI, footnote *d*) on that basis matches the amount expected. It was assumed that the side reactions generated sulfate ion in an amount equimolar in proportion to the product diverted. These together with the sulfate ion predicted in the reaction scheme (*cf.* Table VI, footnote *e*) gave quantities close to the sulfate ion found.

Rate studies showed that between 25 and 90° in the pH range 6 to 11 color disappearance followed a first-order rate law as illustrated in Fig. 1 with constants shown in Table III. The velocity constants were independent of pH and initial concentration of nitrosyl disulfonate ion within the limits of observation,[2] while the influence of ionic strengths was no more than that for the secondary salt effect in a noncatalyzed system as shown in Table IV. Rates of product formation were closely related to color disappearance.

Results of rate measurements on nitrite formation and the release of hydronium ion are shown in Fig. 2 and 3, respectively. The abscissa in Fig. 2 is derived from the integrated expression for $[NO_2^-]$ in terms of $[ON(SO_3)_2^{-2}]$. The velocity constant for the formation of nitrite ions was 6.54×10^{-3} min.$^{-1}$, almost identical with the value calculated from color disappearance and the reactant product ratio. The constant for consumption of hydroxide ion was 3.10×10^{-2} min.$^{-1}$, 82% of the color-related rate, compared with about 75% predicted by the reactant product ratio.

Kinetic equations derived from the reaction scheme, idealized by ignoring side reactions, are consistent with the experimental results. Rate-controlling reactions are 1a and 2a with constants k_1 and k_2. Reactions with SO_3^-, SO_3^{-2}, and NO are assigned velocity constants k_3, k_4, and k_5, respectively.

$$-\frac{d[ON(SO_3)_2^{-2}]}{dt} = [ON(SO_3)_2^{-2}]\{k_1 + k_2 + k_3[SO_3^-] + k_4[SO_3^{-2}] + k_5[NO]\} \qquad (3)$$

The free radicals NO and SO_3^- will react rapidly with another radical

$$\frac{d[NO]}{dt} = k_2[ON(SO_3)_2^{-2}] - k_5[ON(SO_3)_2^{-2}][NO] = 0 \qquad (4)$$

$$[NO] = k_2/k_5 \qquad (5)$$

$$\frac{d[SO_3^-]}{dt} = k_1[ON(SO_3)_2^{-2}] + k_4[ON(SO_3)_2^{-2}][SO_3^{-2}] - k_3[ON(SO_3)_2^{-2}][SO_3^-] = 0 \qquad (6)$$

$$[SO_3^-] = \frac{k_1 + k_4[SO_3^{-2}]}{k_3} \qquad (7)$$

Potassium nitrosyl disulfonate (0.0376 *M*) reacting with SO_3^{-2} (0.070 *M*) required about 53 min. to go from optical density 0.306 to 0.010 at room temperature.[1] At the same concentration with no initial sulfite present, the solution required about 2 months to become colorless. Thus the steady-state treatment can be applied to $[SO_3^{-2}]$

$$\frac{d[SO_3^{-2}]}{dt} = k_{1a}[ONSO_3^-] + k_2[ON(SO_3)_2^{-2}] - k_4[ON(SO_3)_2^{-2}][SO_3^{-2}] + k_r[HON(SO_3)_2^{-2}][OH^-]^2 = 0 \qquad (8)$$

$$[SO_3^{-2}] = \frac{k_{1a}[ONSO_3^-] + k_2[ON(SO_3)_2^{-2}] + k_r[HON(SO_3)_2^{-2}][OH^-]_2}{k_4[ON(SO_3)_2^{-2}]} \qquad (9)$$

with

$$\frac{d[ON(SO_3)]}{dt} = k_1[ON(SO_3)_2{}^{-2}] - k_{1a}[ONSO_3{}^-] = 0 \qquad (10)$$

$$[ONSO_3{}^-] = \frac{k_1[ON(SO_3)_2{}^{-2}]}{k_{1a}} \qquad (11)$$

also since it has been found[2] $k_r << k_1$ or k_2 then

$$[SO_3{}^{-2}] = \frac{k_1 + k_2}{k_4};\ [SO_3{}^-] = \frac{k_1 + k_1 + k_2}{k_3} \qquad (12)$$

$$-\frac{d[ON(SO_3)_2{}^{-2}]}{dt} = [ON(SO_3)_2{}^{-2}]\{k_1 + k_2 + k_1 + k_1 + k_2 + k_1 + k_2 + k_2\} = 4(k_1 + k_2)[ON(SO_3)_2{}^{-2}] \qquad (13)$$

For nitrite ion formation, justifiably neglecting accretion from reversion of hydroxyl amine disulfonate,[2] with $(k_1 + k_2) = k'$ and $[ON(SO_3)_2{}^{-2}] = C_t$

$$\frac{d[NO_2{}^-]}{dt} = k''[ON(SO_3)_2{}^{-2}];\ C_t = C_0e^{-4k't} \qquad (14)$$

$$\frac{d[NO_2{}^-]}{dt} = k''(C_0e^{-4k't});\ [NO_2{}^-] = -{}^1/_4k''C_0e^{-4k't} + C \qquad (15)$$

and, from $t = 0$, $[NO_2{}^-] = 0$; $C = {}^1/_4(k''/k')C_0$

$$[NO_2{}^-] = -{}^1/_4\frac{k''}{k'}C_0e^{-4k't} + {}^1/_4\frac{k''}{k'}C_0 \qquad (16)$$

$$= {}^1/_4\frac{k''}{k'}C_0(1 - e^{-4k't})$$

The temperature dependence could be expressed as the Antoine equations with k in units of min.$^{-1}$

$$\log k_1 = -\frac{7182.7 \pm 40}{T} + 19.1258 \qquad (17)$$

$$\log k_2 = -\frac{6517.3 \pm 30}{T} + 17.0780 \qquad (18)$$

From these constants were calculated the values $\Delta H_1{}^* = 32.9$ kcal./mole, $\Delta S_1{}^{0*} = 18.8$ e.u., $\Delta H_2{}^* = 29.8$ kcal./mole, $\Delta S_2{}^{0*} = 9.5$ e.u. using the second-order form of the absolute reaction rate equation.

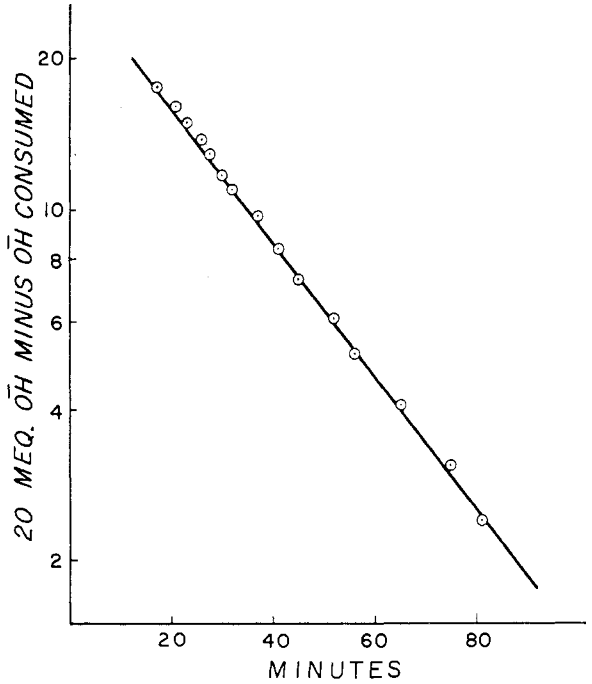
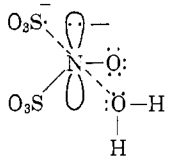
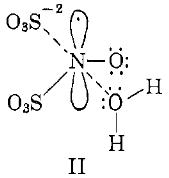


Fig. 3.—Hydroxide consumption: 70.6°, pH 9.2.

Perhaps now an effort can be made to explain reactions 1 and 2 and their relation to each other. Activation energies so close in value must belong to very similar transition states, which might be visualized as I and II.



I



II

These can be thought to be constructed from the sp^2-π ground state as deduced from the absorption spectra[11] of the ion[3,12] and of nitric oxide.[13] For I the representation is consistent with an interpretation of e.s.r. signals, where low intensity components have been observed for an odd electron in the neighborhood of the sulfur nucleus, and for II the representation is that corresponding to one canonical structure commonly assigned to nitrosyl disulfonate ion, to which are ascribed the most intense components in the e.s.r. spectrum.[14] By analogy with di-*sec*-butyl nitric oxide and with nitric oxide another canonical structure can be written with an odd electron on the oxygen.[15] Assisted by water from the solvent cage the ions depart in SN2 processes, which are only pseudo-first order. This makes more uncertain than usual exactly how to calculate the activation entropy, so the treatment for bimolecular reactions has been used. Thus the portion of $\Delta S_1{}^{0*}$ and $\Delta S_2{}^{0*}$ common to each could be just the reflection of the entropy increase arising from the participation of the hydration sphere. The difference between the two activation entropies, 9.4 e.u., is close to the $10Z_AZ_B$ e.u. calculated for union of single charges, positive in this case because the charges have been separated.

A number of questions remain unanswered concerning the decomposition in acid solution, including a fall-off in the initial first-order rate at very low concentration ($<10^{-3}$ M),[2] the absence of a primary salt effect in a reaction involving first-order catalysis by H_3O^+ (*cf.* Table V) and the hint of specific anion catalysis upon comparing Gehlen's results[5] in citrate buffer with those observed in acetate buffer. These are all very likely concerned with propagation of the material reaction chain and diminish very little the distinct possibility that the two pH-independent steps discernible in mildly alkaline solution are the initiating reactions in acid solution.

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(11) Comparison rests on the assumption that in each case there is involved a spin-forbidden π-π^* transition, ${}^4\pi \leftarrow x^2\pi$ in nitric oxide. In the ion this is displaced 1.2 e.v. to the red through perturbation by the ligand field from two $SO_3{}^-$ ions.

(12) S. Yamoda and R. Tshuchida, *Bull. Chem. Soc. Japan*, **32**, 721 (1959).

(13) Liquid nitric oxide has a continuous absorption at $\lambda \leq 4000$ Å. (3.1 e.v.) (H. J. Bernstein and G. Herzberg, *J. Chem. Phys.*, **15**, 77 (1947)) and a spin-forbidden ${}^4\pi \leftarrow x^2\pi$ transition has been calculated at 3.9 e.v. (H. Brion, C. Moser, and M. Yamayaki, *ibid.*, **30**, 673 (1959)).

(14) J. Townsend, S. I. Weissman, and G. E. Pake, *Phys. Rev.*, **89**, 606 (1953).

(15) J. C. Baird, *J. Chem. Phys.*, **37**, 1879 (1962).