

Iron-Catalyzed Reaction between Nitrosyl Disulfonate and Hydroxylamine Monosulfonate Ions*

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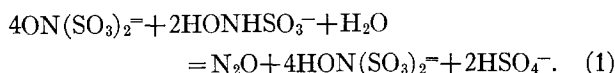
An investigation of the kinetics of the iron-catalyzed reaction between the purple-colored, paramagnetic nitrosyl disulfonate ($\text{ON}(\text{SO}_3)_2^-$) ions and hydroxylamine monosulfonate (HONHSO_3^-) ions has been made. [W. J. Ramsey and D. M. Yost, *J. Chem. Phys.* **21**, 957 (1953)]. At a temperature of 20°C, an ionic strength of 0.026, and total added iron concentrations less than 3.5×10^{-7} *VF*, the initial rate of disappearance of $\text{ON}(\text{SO}_3)_2^-$ is well represented by the equation:

$$-\frac{d(\text{ON}(\text{SO}_3)_2^-)}{dt} = 2 \left\{ \frac{k_2 h_1 (\text{H}^+) + k_3 h_1 h_2}{(\text{H}^+)^2 + h_1 (\text{H}^+) + h_1 h_2} \right\} (\Sigma \text{Fe}^{+3}) (\text{HONHSO}_3^-),$$

where h_1 and h_2 are the first and second hydrolysis constants for ferric iron and where k_2 and k_3 are the specific second-order rate constants for the reactions of HONHSO_3^- with $\text{Fe}(\text{OH})^{++}$ and $\text{Fe}(\text{OH})_2^+$, respectively. Under the above conditions, and if a value of 3×10^{-3} is assumed for h_1 ; h_2 , k_2 , and k_3 have the values, 7×10^{-4} l. mole⁻¹, $13.7 \pm 1.0 \times 10^4$ l. mole⁻¹ · min⁻¹, and $1.5 \pm 0.5 \times 10^4$ l. mole⁻¹ · min⁻¹, respectively.

INTRODUCTION

THE iron catalyzed reaction between the purple-colored, paramagnetic nitrosyl disulfonate ions and hydroxylamine monosulfonate ions, $\text{ON}(\text{SO}_3)_2^-$ and HONHSO_3^- , respectively, is interesting for two reasons. First, the concentration of iron necessary to cause the reaction to proceed at an easily measurable rate is on the order of 10^{-7} mole per liter. Second, the ability of iron to catalyze the reaction is dependent upon hydrogen-ion concentration in a way that indicates that predominantly one of the hydrolyzed species of iron (III), $\text{Fe}(\text{OH})^{++}$, is responsible for the catalysis. The stoichiometry of the reaction is,



This iron-catalyzed reaction was investigated as part of a study of the autocatalytic decomposition of nitrosyl disulfonate ion. However, the iron-catalyzed reaction is of interest by itself, and further, is of little or no significance in the autocatalytic decomposition. A kinetic investigation of the autocatalytic decomposition of nitrosyl disulfonate ion has been reported in some detail by Murib and Ritter¹; our own independent, unpublished study is in substantial agreement with the results of Murib and Ritter.

For the above reasons, the details of our investigation of the iron-catalyzed reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions are described below.

* Taken in part from a thesis by William J. Ramsey submitted in partial fulfillment of the requirements for the Ph.D. degree at the California Institute of Technology in 1952.

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¹ J. H. Murib and D. M. Ritter, *J. Am. Chem. Soc.* **74**, 3394 (1952).

EXPERIMENTAL

Reagents

Potassium nitrosyl disulfonate was prepared by the method of Raschig,² and the preparation was further purified by recrystallizing it from 0.1-*VF* (formula weights per liter of solution) potassium hydroxide between 40° and 0°C. The resulting orange-colored crystalline product was washed three times with absolute alcohol and three times with absolute ether, and was then stored in a vacuum desiccator. In this way, a salt of purity greater than 99% is obtained.³

Anhydrous sodium hydroxylamine monosulfonate was prepared by the method of Raschig.⁴ Salt samples thus prepared were found by iodometric titration to be about 75% pure, the principal impurity being sodium sulfate. Further purification was obtained by equilibrating the impure material with a 50-50 weight percent solution of methanol and water. Excess solid material was filtered off, and the relatively pure (93-97%) product was precipitated by adding excess absolute methanol. Again the main impurity was sodium sulfate as indicated by testing with barium chloride solution.

Iron-free potassium perchlorate, used to adjust the ionic strength, was prepared by adding a ten percent excess of concentrated perchloric acid to a saturated solution of potassium chloride. The precipitate was filtered, and washed several times with ice water and then recrystallized from water.

Standard 0.0167-*VF* lanthanum perchlorate solution was prepared by weighing out just 5.43 gm of lanthanum sesquioxide, just dissolving and neutralizing this solid with standard 0.100-*VF* perchloric acid, and diluting

² F. Raschig, *Schwefel- und Stickstoffstudien* (Verlag Chemie, G. m. b. H., Leipzig-Berlin, 1924), pp. 148-9.

³ H. J. Tauber and G. Jellinek, *Naturwiss.* **38**, 259 (1951).

⁴ Raschig, see reference 2, pp. 154-5.

the resulting solution to 1.00 liter. The lanthanum sesquioxide was labeled 99.9% pure and was obtained from Research Chemicals, Incorporated, Burbank, California.

Tap-distilled water was redistilled from alkaline permanganate in an all-pyrex still. Water thus purified had a specific conductance of about 5×10^{-5} mho, and a *pH* value of about 6.5. This water was stored in a bottle fitted with a soda-lime tube.

A solution of ferric perchlorate was prepared in the following way. Reagent-grade ferric chloride was twice resublimed. To the resulting solid was added a 20% excess of concentrated perchloric acid, and the mixture was fumed almost to dryness. More concentrated perchloric acid was added, and the mixture again fumed almost to dryness. Excess perchloric acid was then filtered off, and the precipitate was weighed and dissolved in enough 0.1-*VF* perchloric acid to make the solution obtained 0.1 *VF* in ferric perchlorate. This solution gave a negative test for chloride with silver nitrate.

A dilute solution of ferric perchlorate was prepared by adding one milliliter of the 0.1-*VF* solution to a liter of 1.0×10^{-3} *VF* perchloric acid. The authors are indebted to Mr. J. K. Rowley, who standardized the dilute stock solution by a coulometric method. This dilute stock solution underwent no significant change with time, as was indicated by the constancy of rate measurements made at the beginning and end of the period of its use.

A standard 0.0100-*VF* perchloric acid solution was prepared by diluting concentrated, vacuum-distilled perchloric acid, and was standardized against recrystallized borax, using a Beckman Model H *pH* meter to determine the end point.

Iron in the various reagents was tested for by the method of Appleman.⁵ This test is sensitive to about one part per million of iron and, therefore, was useful only when relatively large amounts of iron were present.

Apparatus

All rate runs were carried out in a Beckman Model DU spectrophotometer, in ten-centimeter optical cells. A solution to be used in any rate run was first thermostated in a water bath. The cell compartment of the spectrophotometer was carefully thermostated. Temperature variations were within 0.05°C, provided that the temperature of the room was not more than a few degrees from the thermostating temperature.

Glassware was carefully cleaned in the following way. First the object was rinsed with chromic-acid cleaning solution, then with tap-distilled water, then with concentrated hydrochloric acid, then with acidified Versene Fe-3 Specific, then with more distilled water, and finally with several portions of redistilled water. When working

⁵ See reference 8 in paper by Ramsey, Colichman, and Pack, *J. Am. Chem. Soc.* **68**, 1695 (1946).

with very small concentrations of iron, it was found desirable to rinse the reaction vessels in advance with a solution of the same concentration of iron (III) as that to be used in a rate run. This procedure largely eliminated any effects which may have been due to surface-adsorbed iron.

OPTICAL PROPERTIES OF POTASSIUM NITROSYL DISULFONATE SOLUTIONS

Extinction coefficients of the purple solutions of potassium nitrosyl disulfonate were measured over a range of wavelengths and of concentrations. Values obtained for the coefficients are shown graphically in Fig. 1 and are in substantial agreement with those found in the visible region by Murib and Ritter.³ There is a shoulder on the curve of coefficient *vs* wavelength at 2450 Å, at which point it has the value 1690 ± 15 l·mole⁻¹·cm⁻¹. At 2450 Å, the value of the extinction coefficient is independent of the concentration of potassium nitrosyl disulfonate in the range of concentrations between 2 and 6×10^{-5} *VF*.

Procedure for Rate Runs

In running any particular rate, all of the solutions to be used in establishing the conditions of the run, exclusive of that containing potassium nitrosyl disulfonate, were mixed in a reaction vessel, and the vessel was placed in the thermostat. A blank solution was prepared which was identical to the reaction mixture except that the volume of potassium nitrosyl disulfonate solution to be used was replaced by the same volume of water. Blank solutions were always placed in the same optical cell. The cell which was to contain the reaction mixture was first allowed to stand in the thermostated cell compartment for several minutes. An appropriate quantity of potassium nitrosyl disulfonate solution was then added to the reaction mixture, and the clock was started. Reaction mixtures were rapidly stirred, and portions were then placed in the reaction cell. First measurements of optical density

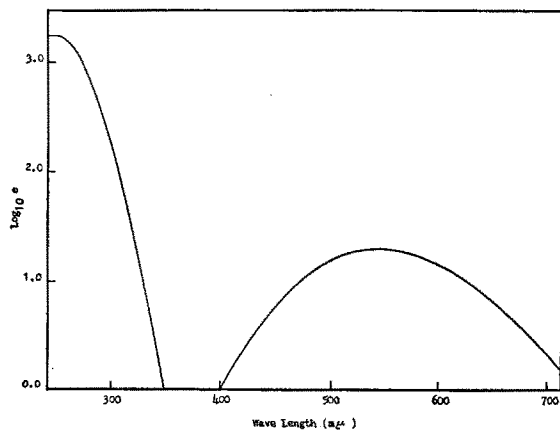


FIG. 1. Logarithm of extinction coefficient (l·mole⁻¹·cm⁻¹) of nitrosyl disulfonate ion *vs* wavelength (mμ).

were usually obtained one and one-half minutes after the addition of the potassium nitrosyl disulfonate solution. Readings of optical density were made periodically, and the dark current and "zeroing" of the spectrophotometer were checked at appropriate intervals.

During the period of preparing for a rate run, and during the run itself, room temperature was kept within 2°C of the temperature at which the run was to be carried out.

Nitrosyl disulfonate ion undergoes slow, autocatalytic decomposition in dilute aqueous solution, and therefore solutions of this ion are used within one hour after their preparation.

Rates of disappearance of nitrosyl disulfonate were measured under the following initial conditions: Perchloric acid concentration, between 2.5×10^{-4} and 2.5×10^{-3} *VF*; ferric perchlorate, as high as 1.46×10^{-6} *VF*; sodium hydroxylamine monosulfonate, between 1.03 and 4.59×10^{-5} *VF*; potassium nitrosyl disulfonate, between 1.4 and 4.7×10^{-5} *VF* (determined spectrophotometrically); various concentrations of potassium perchlorate and lanthanum perchlorate to adjust the ionic strength; and the thermostating temperature, 20.00 ± 0.03 or 30.00 ± 0.03 °C. In Table I are presented the time and concentration data for two typical experiments.

DISCUSSION

A reaction takes place between iron (III) and hydroxylamine monosulfonate which is entirely analogous to the reaction between iron (III) and hydroxylamine.⁶ This reaction is,

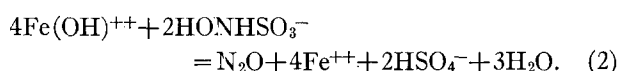


TABLE I. Representative time-concentration data for rate measurements at 20°C.

Experiment No. 56 initial conditions		Experiment No. 88 initial conditions	
$(\text{H}^+) = 5.0 \times 10^{-4}$ <i>VF</i>		$(\text{H}^+) = 5.0 \times 10^{-4}$ <i>VF</i>	
$(\text{HONHSO}_3^-) = 4.60 \times 10^{-5}$ <i>VF</i>		$(\text{HONHSO}_3^-) = 4.58 \times 10^{-5}$ <i>VF</i>	
$(\Sigma\text{Fe}^{+3})_a = 1.4_6 \times 10^{-7}$ <i>VF</i>		$(\Sigma\text{Fe}^{+3})_a = 3.6_6 \times 10^{-7}$ <i>VF</i>	
$(\text{KClO}_4) = 2.50 \times 10^{-2}$ <i>VF</i>		$(\text{KClO}_4) = 2.50 \times 10^{-2}$ <i>VF</i>	
$(\text{ON}(\text{SO}_3)_2^-) = 1.83 \times 10^{-5}$ <i>VF</i>		$(\text{ON}(\text{SO}_3)_2^-) = 2.21 \times 10^{-5}$ <i>VF</i>	
Time (min)	$(\text{ON}(\text{SO}_3)_2^-)$ $\times 10^5$ <i>VF</i>	Time (min)	$(\text{ON}(\text{SO}_3)_2^-)$ $\times 10^5$ <i>VF</i>
1.50	1.71	1.50	1.85
2.00	1.65	2.00	1.72
2.50	1.60	2.50	1.60
3.00	1.54	3.00	1.49
3.50	1.49	3.50	1.37
4.00	1.43	4.00	1.26
4.50	1.37	4.50	1.14
5.00	1.32	5.00	1.05
5.50	1.26	5.50	0.93
6.00	1.20	6.00	0.82

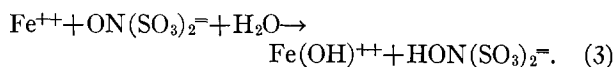
⁶ Bray, Simpson, and MacKenzie, *I. Am. Chem. Soc.* 41, 1363 (1919).

TABLE II. Values of *R'* at various concentrations of reactants (temperature 20°C; solutions 0.025 *VF* in KClO₄) initial concentrations (*VF*).

Experiment number ^a	$(\text{H}^+) \times 10^3$	$(\Sigma\text{Fe}^{+3})_a$ $\times 10^6$	(HONHSO_3^-) $\times 10^5$	$(\text{ON}(\text{SO}_3)_2^-)$ $\times 10^5$	$R' \times 10^2$ (min ⁻¹)
1	2.45	1.46	1.08	2.68	14.2
2	2.45	1.46	1.08	3.41	14.5
3	2.45	1.46	1.08	3.04	14.2
4	2.45	1.46	2.21	2.55	14.0
5	2.45	1.46	2.21	3.10	14.2
40-43	2.45	0.73	1.15	3.42	9.5
9-12	2.45	0.73	2.27	1.88	9.24
13-16	2.45	0.36 ₅	2.28	2.96	5.12
36-39	2.45	0.36 ₅	4.58	3.78	5.04
17-19	2.45	0.14 ₅	2.30	1.93	2.32
28-31	2.45	0.14 ₅	4.60	2.88	2.26
20-23	2.45	0.00	2.31	1.42	0.24
194-195	1.94	1.46	2.21	3.94	15.0
192-193	1.94	0.73	2.27	4.14	9.7
184-187	1.94	0.36 ₅	4.58	3.32	5.44
180-183	1.94	0.14 ₅	4.60	2.07	2.30
188-191	1.94	0.00	4.61	3.43	0.24
162-163	1.55	1.46	2.21	3.31	15.6
160-161	1.55	0.73	2.27	3.37	10.5
168-171	1.55	0.36 ₅	4.58	2.80	5.76
164-167	1.55	0.14 ₅	4.60	2.07	2.36
140-143	0.99	1.46	2.21	4.60	18.6
136-139	0.99	0.73	2.27	3.02	10.3
132-135	0.99	0.36 ₅	4.58	3.22	5.60
44-51	0.99	0.14 ₅	4.60	2.06	2.44
96-98	0.50	1.46	2.21	4.65	18.6
99	0.50	1.46	2.21	4.02	18.5
116-119	0.50	0.73	2.27	1.82	9.8
92-95	0.50	0.73	2.27	2.52	9.8
88-91	0.50	0.36 ₅	4.58	2.21	5.12
56-59	0.50	0.14 ₅	4.60	1.83	2.44
100-103	0.50	0.00	4.61	3.14	0.48
128-131	0.25	1.46	2.21	2.82	17.7
120-123	0.25	0.73	2.27	2.07	9.4
112-115	0.25	0.36 ₅	4.58	1.82	4.96
104-111	0.25	0.14 ₅	4.60	2.34	2.58

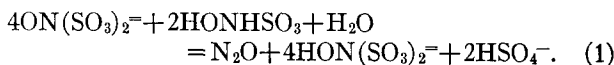
^a Where a series of experiments is indicated, the initial conditions were the same for the series, and the value of *R'* is the average for the series.

A rapid reaction takes place between iron (II) and nitrosyl disulfonate ion in neutral or acid solutions:



A quantitative determination of nitrosyl disulfonate ion could be based upon this reaction were it not for an indirect slow reaction between iron (III) and hydroxylamine disulfonate ion, $\text{HON}(\text{SO}_3)_2^-$.

Thus the stoichiometry of the iron-catalyzed reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions is obtained from Eqs. (2) and (3).



In the majority of experiments the *initial* rate of disappearance of nitrosyl disulfonate ion was measured because of the complex reactions between the various products and the initial reactants. The value of the initial rate was determined by one of two methods. When the hydroxylamine monosulfonate ion concentration was greater than that of the nitrosyl disulfonate ion, the rate of disappearance of the latter was very

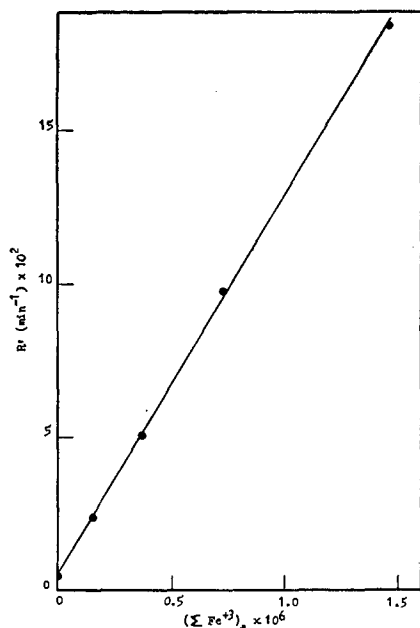


FIG. 2. R' vs $(\Sigma\text{Fe}^{+3})_a$, slope equals k_0 . ($(\text{H}^+) = 0.50 \times 10^{-3}$ VF; $(\text{KClO}_4) = 0.0250$ VF; $t = 20^\circ\text{C}$.)

nearly constant for the first three minutes of the reaction. Therefore, since spectrophotometric determinations of nitrosyl disulfonate ion concentration were made every half minute, the average amount disappearing in half a minute determined the rate. When the hydroxylamine monosulfonate ion concentration was not greater than the nitrosyl disulfonate ion concentration, a plot of the latter concentration vs time was constructed. This plot was extrapolated to zero time, and the slope at zero time was taken as the initial rate of the reaction.

When the initial concentration of nitrosyl disulfonate ion was of the same order of magnitude as that of the hydroxylamine monosulfonate ion, the initial rate of disappearance of the former ion was independent of its own concentration.

Initial rates were found to be proportional to initial concentrations of hydroxylamine monosulfonate ion. A quantity, R' , is defined as the *initial* rate of disappearance of nitrosyl disulfonate ion divided by the initial concentration of hydroxylamine monosulfonate ion.

The quantity $(\Sigma\text{Fe}^{+3})_a$ is defined as the total concentration of added iron, i.e., it is the formula weights of ferric perchlorate added per liter of reaction mixture, while (ΣFe^{+3}) represents the total concentration of iron in the reaction mixture including the relatively small amounts in the other reagents.

In Table II are presented the values of R' obtained. The independence of R' upon the nitrosyl disulfonate ion concentration is shown by the first five and twenty-sixth through twenty-ninth entries in the table. The independence of R' upon hydroxylamine monosulfonate

ion concentration is shown by the first eleven entries in the table.

At each of the lower hydrogen-ion concentrations, 2.5 and 5.0×10^{-4} VF, the values of R' are directly proportional to the total iron concentration, as shown for the latter case in Fig. 2. At higher hydrogen-ion concentrations, plots of R' vs $(\Sigma\text{Fe}^{+3})_a$ are not linear. At low total iron concentrations the plots are very nearly linear, but at higher total iron concentrations they deviate considerably from linearity. An example of this behavior is shown in Fig. 3. At these higher hydrogen ion concentrations, the slope of the curve of R' vs $(\Sigma\text{Fe}^{+3})_a$ was measured at $(\Sigma\text{Fe}^{+3})_a$ equal zero. This slope is defined as k_0 . In the case of the linear plots of R' vs $(\Sigma\text{Fe}^{+3})_a$, obtained for the lower hydrogen-ion concentrations, the slope of the line is k_0 .

There is at present no certain explanation of the curvature of the plots of R' vs $(\Sigma\text{Fe}^{+3})_a$. The curvature is not due to any slowness of the reaction between ferrous ion and nitrosyl disulfonate ion because the rate of disappearance of the latter is independent of its own concentration. Also, it is not due to complex formation between iron (III) species and hydroxylamine monosulfonate ion because the values of R' were independent of the concentration of the latter ion. It would seem to be due to the removal of Fe^{+++} , because the curvature increases with increasing hydrogen-ion concentration, and indeed, vanishes at low hydrogen-ion concentration.

The intercept of the extrapolated curve of R' vs $(\Sigma\text{Fe}^{+3})_a$ on the abscissa axis is numerically equal to the amount of iron due to the reagents. That amount was, on the average, 3×10^{-8} VF.

That the rate-determining step in this iron-catalyzed reaction is the reaction between iron (III) and hydroxylamine monosulfonate ion is proved by the following facts. The rate is independent of nitrosyl disulfonate ion

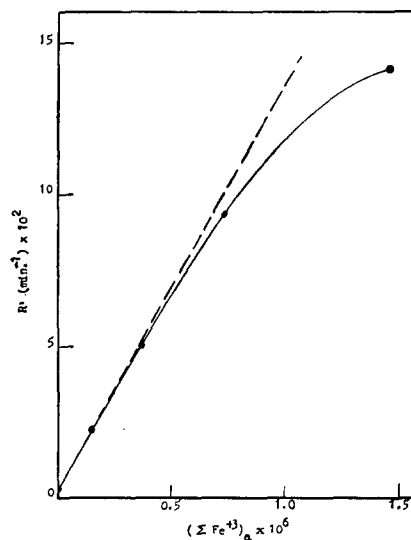


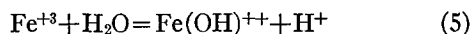
FIG. 3. R' vs $(\Sigma\text{Fe}^{+3})_a$, slope of dashed line equals k_0 . ($(\text{H}^+) = 2.54 \times 10^{-3}$ VF; $(\text{KClO}_4) = 0.0250$; $t = 20^\circ\text{C}$.)

concentration; it is directly proportional to hydroxylamine monosulfonate ion concentration, and at low concentrations of added iron, the rate is directly proportional to these concentrations. Thus, at a given hydrogen-ion concentration, temperature, and ionic strength, and at total iron concentrations less than 3.5×10^{-7} *VF*, the rate of disappearance of nitrosyl disulfonate ion is well represented by the equation,

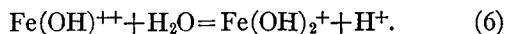
$$-\frac{d(\text{ON}(\text{SO}_3)_2^-)}{dt} = k_0(\Sigma\text{Fe}^{+3})(\text{HONHSO}_3^-). \quad (4)$$

Dependence of k_0 in Eq. (4) upon hydrogen-ion concentration, as shown graphically in Fig. 4, indicates that predominantly one of the hydrolyzed species of iron (III) is responsible for the catalysis. Since k_0 has a maximum value at a *pH* of about three, $\text{Fe}(\text{OH})^{++}$ must be the principal catalytic species.

The problem of the dependence of k_0 upon hydrogen-ion concentration, may be treated mathematically in the following way. Let the three species, Fe^{+3} , $\text{Fe}(\text{OH})^{++}$, and $\text{Fe}(\text{OH})_2^+$, react with hydroxylamine monosulfonate ion with specific rate constants, k_1 , k_2 , and k_3 , respectively. Further, let h_1 and h_2 be the equilibrium constants, respectively, for the two reactions,



and



Under the conditions of these experiments, and assuming no $\text{Fe}(\text{OH})_3$ to be present,

$$(\Sigma\text{Fe}^{+3}) = (\text{Fe}^{+++}) + (\text{Fe}(\text{OH})^{++}) + (\text{Fe}(\text{OH})_2^+). \quad (7)$$

Making use of the equilibrium constants, and assuming that enough acid is present so that the hydrolysis of the iron does not change the hydrogen-ion concentration significantly, the following are obtained for the concen-

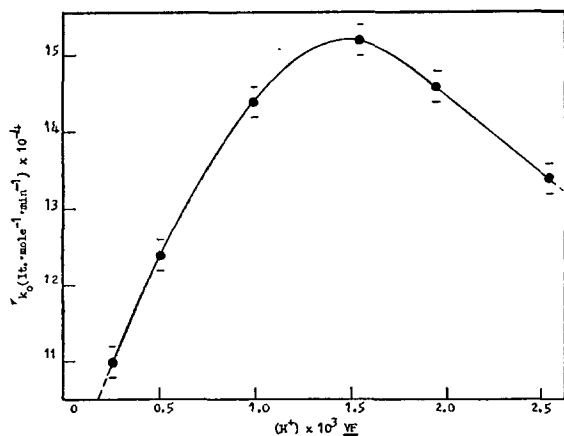


FIG. 4. k_0 vs (H^+) , bars above and below point are equivalent to $\pm 2\%$ error in k_0 . ($(\text{KClO}_4) = 0.0250$ *VF*; $t = 20^\circ\text{C}$.)

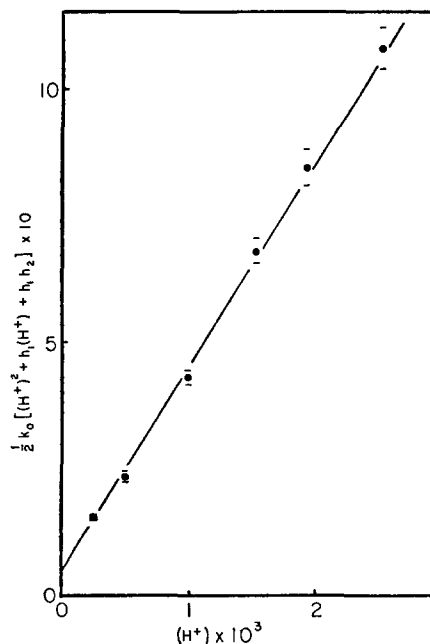


FIG. 5. A plot of the function $\frac{1}{2}k_0[(\text{H}^+)^2 + h_1(\text{H}^+) + h_1h_2]$ vs (H^+) . Bars above and below the points represent an error in k_0 of $\pm 4\%$.

trations of the various iron (III) species:

$$(\text{Fe}^{+++}) = \frac{(\text{H}^+)^2(\Sigma\text{Fe}^{+3})}{(\text{H}^+)^2 + h_1(\text{H}^+) + h_1h_2}, \quad (8)$$

$$(\text{Fe}(\text{OH})^{++}) = \frac{h_1(\text{H}^+)(\Sigma\text{Fe}^{+3})}{(\text{H}^+)^2 + h_1(\text{H}^+) + h_1h_2}, \quad (9)$$

$$(\text{Fe}(\text{OH})_2^+) = \frac{h_1h_2(\Sigma\text{Fe}^{+3})}{(\text{H}^+)^2 + h_1(\text{H}^+) + h_1h_2}. \quad (10)$$

As shown above, the rate-determining step is the reaction between the various iron (III) species and hydroxylamine monosulfonate ion, also according to the stoichiometry of the over-all reaction (Eq. (1)), two moles of nitrosyl disulfonate ion are reduced per mole of the monosulfonate reacting with iron (III). Therefore, the rate of disappearance of nitrosyl disulfonate ion will be twice the rate of reaction between iron (III) and hydroxylamine monosulfonate ion, and

$$\frac{1}{2}k_0(\Sigma\text{Fe}^{+3}) = k_1(\text{Fe}^{+++}) + k_2(\text{Fe}(\text{OH})^{++}) + k_3(\text{Fe}(\text{OH})_2^+). \quad (11)$$

By substituting Eqs. (8), (9), and (10) into Eq. (11), and simplifying, k_0 is related to the hydrogen-ion concentration by the expression,

$$\frac{1}{2}k_0 = \frac{k_1(\text{H}^+)^2 + k_2h_1(\text{H}^+) + k_3h_1h_2}{(\text{H}^+)^2 + h_1(\text{H}^+) + h_1h_2}. \quad (12)$$

If it is assumed that both k_1 and k_3 are zero, k_0 will have a maximum value when (H^+) is equal to $\sqrt{h_1h_2}$.

TABLE III. Effect of ionic strength on k_0 .

$(H^+) \times 10^3 VF$	$\mu \times 10^2$	$k_0 \times 10^{-4}$ 1·mole ⁻¹ ·min ⁻¹
1.94	2.70 (KClO ₄ , 2.5×10 ⁻² VF)	14.6
1.94	2.70 (La(ClO ₄) ₃ , 4.17×10 ⁻³ VF)	14.4
1.94	0.20	18.7
0.50	2.55 (KClO ₄ , 2.5×10 ⁻² VF)	12.5
0.50	2.55 (La(ClO ₄) ₃ , 4.17×10 ⁻³ VF)	12.5
0.50	0.06	19.8

The maximum value of k_0 occurs when (H^+) equals $1.5 \times 10^{-3} VF$. Although there is general disagreement about the value of h_1 ,⁷ a value of about 3×10^{-3} is reasonable for a temperature of 20°C and an ionic strength of 0.025. Therefore, if k_1 and k_3 are zero, h_2 has the value, 7×10^{-4} . This value of h_2 might appear to be higher than expected, but recently, a value for the ratio of h_1 to h_2 of only 1.67 for somewhat different conditions has been reported.⁸

Using the values of h_1 and h_2 stated above, a plot of $\frac{1}{2}k_0[(H^+)^2 + h_1(H^+) + h_1h_2]$ vs (H^+) was constructed, and is shown in Fig. 5. That the plot is very nearly linear indicates that Fe^{+++} is insignificant in the catalysis. The slope of the curve is equal to k_2h_1 , and the intercept is equal to $k_3h_1h_2$. The least-squares method was used to fit the line. Calculated values of k_2 and k_3 are $13.7 \pm 1.0 \times 10^4$ 1·mole⁻¹·min⁻¹ and $1.5 \pm 0.5 \times 10^4$ 1·mole⁻¹·min⁻¹. The limits of error in the rate constants are estimated on basis of the accuracy of the least-squares calculation.

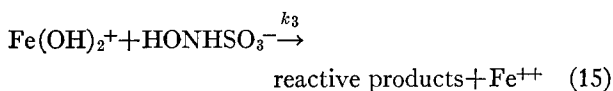
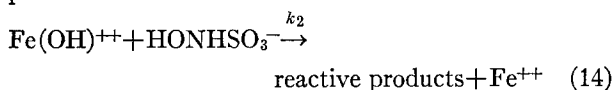
Values of k_2 and k_3 obtained by the above calculations depend critically upon the value chosen for h_1 , and since there does exist disagreement about the value of h_1 , the values of k_2 and k_3 must remain tentative.

A value other than zero for k_3 would be expected to change the value found for h_1h_2 , and, therefore, change the evaluation of k_3 . However, when k_3 is not zero the maximum value of k_0 occurs at,

$$(H^+) = \left[\frac{k_3^2 h_2^2}{k_2^2} + \frac{h_1 h_2}{k_2} (k_2 - k_3) \right]^{\frac{1}{2}} - \frac{k_3 h_2}{k_2} \quad (13)$$

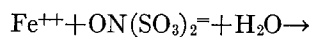
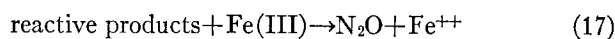
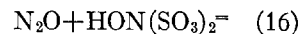
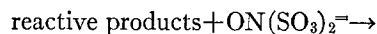
Using the values determined above for k_2 , k_3 , h_1 , and h_2 , k_0 should have a maximum value when the hydrogen-ion concentration is $1.4 \times 10^{-3} VF$, which agrees with the experimental value within the limits of experimental error.

The following mechanism is in accord with the experimental data:



⁷ T. H. Siddall, III, and W. C. Vosburgh, J. Am. Chem. Soc. **73**, 4270 (1951).

⁸ B. O. A. Hedström, Arkiv Kemi **6**, 1 (1953).



Equation (17) summarizes the reactions which may take place between various species of iron (III) and the reactive products of the initial oxidation of hydroxylamine monosulfonate ion. The reactions represented by Eqs. (3) and either (16), (17), or both must be fast compared to those represented by Eqs. (14) and (15).

Effects of ionic strength upon the rate of reaction would be expected to be complex, because of the nature of k_0 . Further, there is disagreement about the quantitative effect of "inert" electrolytes upon the hydrolysis of ferric ion^{9,10} and upon ionic reactions in general.¹⁰ Therefore, the experimental results summarized in Table III are useful primarily in determining the magnitude of any errors resulting from small changes in ionic strength. From the values shown it is evident that a change in ionic strength of ten percent would cause a change of about one percent in the value of k_0 . Also, there is no measurable difference between the effects of lanthanum perchlorate and potassium perchlorate at the same ionic strength.

Effects of temperature changes upon the rates of the reaction would be expected to be complex, again because of the nature of k_0 . Effects of a ten degree change in temperature upon the values of k_0 obtained at hydrogen-ion concentrations of 1.94 and $0.50 \times 10^{-3} VF$ are shown in Table IV. Also, an apparent activation energy, ΔE_a , has been calculated by use of the equation,

$$\Delta E_a = \frac{-R\Delta \ln k_0}{\frac{1}{\Delta T}} \quad (18)$$

TABLE IV. Effect of temperature on k_0 (KClO₄ = $2.5 \times 10^{-2} VF$).

$(H^+) \times 10^3 VF$	$t^\circ C$	$k_0 \times 10^{-4}$ 1·mole ⁻¹ ·min ⁻¹	$\Delta E_a = -\frac{R\Delta \ln k_0}{\frac{1}{\Delta T}}$
1.94	20.0	14.6	21.4 kcal
1.94	30.0	48.6	
0.50	20.0	12.5	
0.50	30.0	41.7	

⁹ A. R. Olson and T. R. Simonson, J. Chem. Phys. **17**, 1322 (1949).

¹⁰ A. R. Olsen and T. R. Simonson, J. Chem. Phys. **17**, 1167 (1949).

where T is the absolute temperature, and R the gas constant. That ΔE_a has the same value for the two hydrogen-ion concentrations is quite probably fortuitous.

An estimate of the possible error due to incomplete temperature control shows that a 0.08°C error in

temperature gives rise to an error of one percent in the value of k_0 .

The authors wish to express their appreciation to the Research Corporation, the Shell Oil Company, and E. I. Du Pont de Nemours and Company for grants which supported this work.

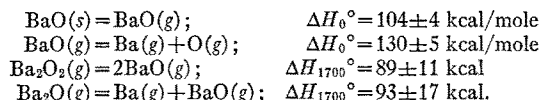
Mass Spectrometric Study of Barium Oxide Vapor*

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Ions formed by electron bombardment of the vapor in thermodynamic equilibrium with BaO solid have been studied mass spectrometrically. The BaO solid was heated in a Knudsen cell and a sample of the effusing vapor entered the ion source of a mass spectrometer. At cell temperatures between 1500°K and 1800°K , ion currents of Ba^+ , BaO^+ , Ba_2O^+ , Ba_2O_2^+ , and Ba_2O_3^+ were observed. The variations of ion intensities with temperature were measured and appearance potential curves were obtained. Possible mechanisms of ion formation were considered, and evidence for the existence of gaseous molecular species of BaO, Ba_2O , Ba_2O_2 , and Ba_2O_3 was obtained. The major molecular species, effusing from the Knudsen cell, was BaO. A thermodynamic treatment of ion currents yields the following heats of reaction



INTRODUCTION

THE species evaporating from heated metal surfaces coated with barium oxide have been studied by earlier workers employing mass spectrometric methods. These workers¹⁻⁴ found that BaO^+ was the predominant ion formed by electron bombardment of the vapor. This indicated that BaO gas is the principal vaporizing species. In addition to BaO^+ , Aldrich² observed less intense currents of Ba_2O^+ and Ba_2O_2^+ . Pelchowitch³ measured the temperature dependence of Ba_2O_2^+ and obtained further evidence that the oxide vaporizes to a small degree as gaseous Ba_2O_2 .

Our purpose has been to extend the work on barium oxide by studying the vapor in thermodynamic equilibrium with BaO solid inside a Knudsen cell. A sample of this vapor effusing from the Knudsen cell enters directly into an ion source of a mass spectrometer. With this experimental arrangement, observation of ions and measurements of ion currents offer both a means of identifying the molecular species in the vapor and of obtaining thermodynamic data for the gaseous equilibria inside the Knudsen cell. In this experiment the activities (or partial pressures) of the gaseous species involved in the equilibria are measured. Only

one assumption regarding the activity of a component is made. It is assumed that the activity of the BaO solid phase is nearly unity. Since BaO solid is present in large quantity, this should be a good assumption. Experimental evidence in support of the assumption can be obtained by x-ray and chemical examination of material removed from the inside of the cell after completion of an experiment. It is further assumed that the gaseous species reach equilibrium with each other and with the BaO solid phase. The use of a Knudsen cell with a large ratio of internal BaO surface area to effusion-hole area justifies this assumption.

This method of approach differs from the filament-type experiment in that here one is dealing with equilibrium concentrations of gases while the filament work deals principally with rates of vaporization. Thus, while the Knudsen cell method generally yields the true ΔH of vaporization, the surface-evaporation method yields only the activation energy of vaporization which may be equal to or greater than the true ΔH of vaporization. For calculation of such quantities as dissociation energies, it is, of course, necessary to know the true ΔH of vaporization.

EXPERIMENTAL

The Knudsen cell assembly for the mass spectrometer has been described earlier by Chupka and Ingram⁵

* This work was supported in large part by a grant from the National Science Foundation.

¹ R. H. Plumlee and L. P. Smith, *J. Appl. Phys.* **21**, 811 (1950).

² L. T. Aldrich, *J. Appl. Phys.* **22**, 1168 (1951).

³ I. Pelchowitch, *Philips Research Repts.* **9**, 42 (1954).

⁴ P. W. Bickel and L. V. Holroyd, *J. Chem. Phys.* **22**, 1793 (1954).

⁵ W. A. Chupka and M. G. Ingram, *J. Phys. Chem.* **59**, 100 (1955).