ARH-SA-97

CONF-710658--1

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June, 1971

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THE REACTION OF HYDROXYLAMINE WITH NITROUS ACID

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To be presented at the

26th Northwest Regional American Chemical Society Meeting
June 16, 17, and 18, 1971
Bozeman, Montana

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ABSTRACT

The kinetics of the reaction

have been studied in aqueous nitric acid media (ionic strength = 2.0) using stopped-flow techniques. The reaction is first order with respect to hydroxylamine, nitrous acid, and hydrogen ion. The acid-catalyzed reaction is the only important mechanism at the acid concentrations studied (0.30 to 2.0M). Nitrate ion is shown to have a negligible effect on the rate. The marked increase in rate with increasing ionic strength and the negative value of the activation entropy are consistent with a mechanism in which the conjugate acid of hydroxylamine is attacked by H_2NO_2^+ or, possibly, NO^+ . A discussion of possible intermediates is given. The Arrhenius activation energy is 11.5 ± 0.5 kcal/mol. The rate constant at 30° is $10.0 \pm 0.8 \text{M}^{-2} \text{sec}^{-1}$ and $\Delta S_{30}^\ddagger$ is -18 ± 2 e.u.

THE REACTION OF HYDROXYLAMINE WITH NITROUS ACID

INTRODUCTION

The recent application of hydroxylamine as a reductant for plutonium(IV) in the nuclear fuel reprocessing industry has generated interest in the reaction between hydroxylamine and nitrous acid. Organic process streams containing plutonium(IV) frequently also contain appreciable amounts of nitrous acid. When the organic phase contacts the aqueous phase containing hydroxylamine in nitric acid, the reaction occurs.

The objective of this study was to determine the stoichiometry, mechanism, and rate constants for the reaction in nitric acid solution. These data will then be used to optimize process parameters. Previous kinetic studies have been performed in either perchloric acid⁽¹⁻³⁾ at unspecified ionic strengths or acetate-buffered solutions.⁽⁴⁾ There have been two isotopic tracer studies^(5,6) of the reaction which have provided information on the mechanism of the reaction at low acid concentrations. Although data from these studies are useful, they do not provide an adequate description of the reaction in nitric acid solution. Also, the effects of temperature and ionic strength on the reaction rate are not presented in enough detail to be of use.

SUMMARY AND CONCLUSIONS

The reaction between hydroxylamine nitrate and nitrous acid in 0.30 to 2.00M HNO₃ has been studied at an ionic strength of 2.00. A rate law,

$$\frac{-d[\text{HNO}_2]}{dt} = k[\text{HNO}_2][\text{NH}_3\text{OH}^+][\text{H}^+]$$

has been derived which adequately describes the rate within the range of acid concentrations studied. The rate constant, k , is $10.0 \pm 0.8 M^{-2} \text{ sec}^{-1}$ at 30°C and the Arrhenius activation energy is $11.5 \pm 0.5 \text{ kcal/mol}$. The entropy of activation, $\Delta S^\ddagger$, is $-18 \pm 2 \text{ e.u.}$ at 30°C . An increase in ionic strength produced a marked increase in the rate constant. Nitrate ion is not involved in any rate-determining mechanism and does not appear in the rate law. A mechanism is proposed in which hydroxylammonium ion is attacked by nitrous acidium ion. This reaction produces the intermediate, N-nitrosohydroxylamine, which then rapidly decomposes to form nitrous oxide and water. The stoichiometry of the reaction is consistent with the reaction

EXPERIMENTAL

REAGENTS

Stock solutions of the appropriate molarity were made from each of the following: NaNO_2 (reagent grade, Baker and Adamson [B&A]), HNO_3 (reagent grade, Mallinckrodt), NaNO_3 (reagent grade, B&A), and NaClO_4 (reagent grade, G. F. Smith Chemical Company). All solutions were made from either quartz-distilled or doubly-deionized water. Fresh NaNO_2 stock solutions were made daily because of their instability. A hydroxylamine nitrate stock solution was prepared by converting reagent grade hydroxylamine hydrochloride (B&A) by ion exchange using 20 to 50 mesh Dowex 50W-X8 (Dow Chemical Company) cation exchange resin. Hydroxylamine concentration was determined by the Rashig method.⁽⁷⁾ The stability of the hydroxylamine stock solution at room temperature and at 50°C was checked by analyzing portions of the solutions frequently. No change in hydroxylamine molarity was observed over a period of six

months at room temperature or four hours at 50 °C (the acid concentration was 1.0M).

APPARATUS

The reaction was followed spectrophotometrically using an Aminco-Morrow stopped-flow apparatus (American Instrument Company) coupled to a Beckman DU monochromator (Beckman Instruments). The disappearance of the 356 nm absorbance of nitrous acid was followed by recording the percent transmittance versus time curve on a Tektronix 564B storage oscilloscope (Tektronix, Inc.). The curves were then photographed using Polaroid film (Polaroid Corporation). Water at constant temperature (± 0.1 °C) was circulated through cavities surrounding the driving syringes of the stopped-flow apparatus.

PROCEDURE

Ten milliliter volumes each of hydroxylamine nitrate and HNO_2 were prepared from stock solutions. Ionic strength was maintained at 2.00 by addition of NaClO_4 solution. For most runs a 10-fold molar excess of hydroxylamine was used in order to obtain pseudo-first-order rate constants. The two prepared solutions were brought to the desired temperature in a separate water bath and then placed in the thermostated driving syringes of the stopped-flow apparatus. The solutions were then mixed and the reaction followed spectrophotometrically. At least three runs were recorded for each pair of solutions. The time required for the mixed solutions to reach the observation cell is estimated to be ~ 5 milliseconds.

The stoichiometry of the reaction was investigated by adding a measured amount of NaNO_2 solution to a molar excess of hydroxylamine. The reaction was allowed to go to completion and hydroxylamine concentration in the resulting solutions was determined.

RESULTS AND DISCUSSION

STOICHIOMETRY

The reaction between hydroxylamine and nitrous acid has been shown to occur according to the stoichiometric equation

in perchloric, hydrochloric, hydrobromic, and acetic acids. Although the different anions can affect the reaction rate, the stoichiometry of the reaction apparently remains the same in these acids. In order to confirm this same stoichiometry for the reaction in nitric acid, several experiments were performed. The results for the reaction in 1.0M HNO_3 are given in Table I.

TABLE I
STOICHIOMETRY OF REACTION

<u>Initial mmoles of NH_3OH^+</u>	<u>Initial mmoles of HNO_2</u>	<u>Reaction Ratio</u>
5.22	0.50	0.80
4.64	1.00	0.89
4.06	1.50	0.78
3.48	2.00	0.97

The expected stoichiometry shown by the above equation is confirmed. Although the reaction ratio (mmoles NH_3OH^+ consumed/initial mmoles of HNO_2) is somewhat lower than one, all values are within the error limits of the experiments.

REACTION ORDERS

Reaction orders for hydroxylamine, HNO_2 , and H^+ were obtained at zero time so that any products or intermediates of the reaction would not interfere. Absorbance versus time data were fit to a cubic polynomial equation using a least-squares computer program. Initial reaction rates ($-\text{d}A_0/\text{d}t$) were then determined by differentiating this equation at zero time.

Values for the initial rates at various initial concentrations of HNO_2 , hydroxylamine, and H^+ are given in Table II.

TABLE II
INITIAL REACTION RATES^a

<u>$[\text{HNO}_2], M$</u>	<u>$[\text{NH}_3\text{OH}^+], M$</u>	<u>$[\text{H}^+], M$</u>	<u>$-\text{d}A_0/\text{dt}, \text{sec}^{-1}$</u>
0.0050	0.107	1.86	0.207
0.0100	0.107	1.86	0.352
0.0250	0.107	1.86	0.700
0.0500	0.107	1.86	1.85
0.100	0.107	1.86	2.97
0.100	0.0535	1.88	0.276
0.100	0.0803	1.88	0.456
0.100	0.107	1.88	0.486
0.100	0.134	1.88	0.605
0.100	0.161	1.88	0.722
0.100	0.107	0.90	0.465
0.100	0.107	0.70	0.355
0.100	0.107	0.50	0.271
0.100	0.107	0.30	0.130

^aTemperature = 30 °C, $\mu = 2.00$, and $[\text{NO}_3^-] = 2.00$.

Plots of $\ln(-\text{d}A_0/\text{dt})$ versus $\ln [\text{HNO}_2]$, $\ln [\text{NH}_3\text{OH}^+]$, and $\ln [\text{H}^+]$ (Figure 1) gave straight lines with slopes of 0.92, 0.96, and 1.1, respectively. The reaction order for each of these reactants is, therefore, equal to one at the beginning of the reaction. The rate law for the initial reaction can thus be expressed as follows:

$$\frac{-\text{d}[\text{HNO}_2]}{\text{dt}} = k[\text{HNO}_2][\text{NH}_3\text{OH}^+][\text{H}^+]$$

Plots of $\ln (A_t - A_\infty)$ versus time (where A_t = absorbance at time, t , and A_∞ = absorbance at infinite time) for runs where hydroxylamine and acid were in large excess gave straight lines over greater than 90% completion of the reaction (Figure 2). The reaction order of one for HNO_2 therefore holds true throughout the reaction. A summary of the kinetic data obtained at 30 °C under pseudo-first-order conditions is given in Table III. Values for the observed rate constant, k_o , were

obtained by fitting $\ln (A_t - A_\infty)$ versus time data to a first order polynomial using a least squares method computer program. The rate constant, k , was calculated using the relationship,

$$k = \frac{k_0}{[\text{NH}_3\text{OH}^+][\text{H}^+]}$$

TABLE III
RATE CONSTANTS FOR THE REACTION^a AT 30 °C

<u>$[\text{NH}_3\text{OH}^+]$, M</u>	<u>$[\text{H}^+]$, M</u>	<u>k_0, sec⁻¹</u>	<u>k, M⁻² sec⁻¹</u>
0.107	1.89	1.94	9.64
0.134	1.86	2.06	8.27
0.161	1.83	2.73	9.27
0.107	1.40	1.50	10.01
0.107	1.20	1.43	11.14
0.107	1.00	1.11	10.37
0.107	0.90	0.996	10.34
0.107	0.70	0.759	10.13
0.107	0.60	0.671	10.45
0.107	0.50	0.576	10.77
0.107	0.30	0.312	9.72

^aIonic strength = 2.00, $[\text{NO}_3^-] = 2.00$, and $[\text{HNO}_2] = 0.010M$.

Analysis of the data at 30.0 ± 0.1 °C results in a value for k equal to $10.0 \pm 0.8 M^{-2} \text{ sec}^{-1}$ at $\mu = 2.00$. A plot of k_0 versus $[\text{H}^+]$ (Figure 3) gives a straight line with an intercept at $k_0 \approx 0$. Because of the intercept at the origin of the plot, the acid catalyzed reaction is the only important mechanism in this range of acid concentrations (0.30 to 1.40M). Hughes and Stedman⁽¹⁾ give evidence for a different mechanism at $[\text{H}^+] < 0.1M$ in which free hydroxylamine is attacked by dinitrogen tetroxide. However, at higher acidities, the acid catalyzed reaction predominates.

Several different anions (Br^- , SCN^- , and CH_3COO^-) have been shown to catalyze the reaction. The reactive intermediate for these reactions has been postulated to be a nitrosyl compound containing the anion; *e.g.*, NOBr . An analogous intermediate

for the present reaction is nitrosyl nitrate, ONONO_2 . This compound has been reported⁽⁸⁾ to be highly unstable, although small concentrations might exist in aqueous solution. A more likely N(III) intermediate reactive species is either H_2NO_2^+ or NO^+ . Experiments in which the nitrate concentration was varied from 1.00 to 2.00M gave no significant change in the k_0 value. Therefore, nitrate ion is not involved in any rate-determining mechanism and a nitrosyl nitrate intermediate is untenable.

EFFECT OF TEMPERATURE

Additional stopped-flow kinetic experiments were completed at 35, 40, 45, and 50 °C. The rate constants calculated for each temperature are given in Table IV.

TABLE IV

EFFECT OF TEMPERATURE ON THE RATE CONSTANT^a

<u>Temperature ± 0.1 °C</u>	<u>k, $M^{-2} \text{ sec}^{-1}$</u>
30	10.0 $\pm 0.8^b$
35	14.3 ± 1.2
40	20.1 ± 1.0
45	27.2 ± 1.4
50	35.6 ± 1.0

^aIonic strength = 2.00.

^bThe range is given as one standard deviation.

A plot of $\ln k$ versus $1/T, ^\circ\text{K}^{-1}$ (Figure 4) gives a straight line. The slope and intercept of the line was obtained by least-squares. The Arrhenius activation energy calculated from the slope is 11.5 ± 0.5 kcal/mol and the entropy of activation, $\Delta S^\ddagger$, is -18 ± 2 e.u. at 30 °C.

EFFECT OF IONIC STRENGTH

An increase in ionic strength produces a marked increase in k_o , as shown in Table V.

TABLE V
EFFECT OF IONIC STRENGTH^a

<u>Ionic Strength</u>	<u>k_o</u>
0.60	0.137
0.85	0.207
1.10	0.269
1.60	0.408
2.10	0.626

^aT = 30 °C, [HNO₂] = 0.010M, [NH₃OH⁺] = 0.107M,
[H⁺] = 0.50M.

A plot of $\log_{10} k_o$ versus $\sqrt{\mu}$ (Figure 5) gives a straight line with a slope of +0.91. The value of the slope is related to the charge, Z, on the two ions which form the activated complex by an equation derived by Bronsted.⁽⁹⁾ The slope is equal to $1.02Z_{\text{HNO}_2}Z_{\text{NH}_2\text{OH}}$. Therefore, the activated complex is formed by ions with the same sign (probably positive) and with ionic charges of one.

REACTION MECHANISM

Several isotopic tracer studies^(1,2,5,6) have shown that in acid solution the central atom of nitrogen in the reaction product, N₂O, is derived from HNO₂. This observation eliminates both nitroxyl, NOH; and hyponitrous acid, N₂O₂H₂, as possible intermediates. Bothner-By and Friedman⁽⁵⁾ have conjectured that the N₂O derives from N-nitrosohydroxylamine, ON-NHOH. These conclusions and the observed kinetics are consistent with the following mechanism:

Bunton and Stedman⁽¹⁰⁾ have concluded that when HNO_2 is used as an oxidant in aqueous solution, the active intermediate is $H_2NO_2^+$ rather than NO^+ . They offer evidence that NO^+ is only a good oxidant when covalently bonded, as in $NOCl$.

The calculated value for the activation entropy of -18 ± 2 e.u. is consistent with formation of the activated complex from $H_2NO_2^+$ and NH_3OH^+ . For reactions between ions of the same type, negative entropy values are expected since the system is more ordered than the initial reactants.

ACKNOWLEDGMENTS

The author expresses appreciation to G. E. Benedict for his interest in this work, to J. P. Martelli for his assistance with the experimental work, to D. F. Shepard for programming the least-squares analysis, and to Eleanore Earhart for her secretarial assistance.

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FIGURE 1

**REACTION ORDERS FOR (a) HNO_2 , (b) NH_3OH^+ ,
AND (c) H^+ FROM INITIAL REACTION RATES**

FIGURE 2

LOGARITHM OF ABSORBANCE AT 356 nm VERSUS TIME

FIGURE 3

EFFECT OF $[H^+]$ ON THE REACTION RATE

FIGURE 4

**ARRHENIUS PLOT FOR THE REACTION
AT IONIC STRENGTH EQUAL TO 2.00**

FIGURE 5

DEPENDENCE OF THE REACTION RATE
ON IONIC STRENGTH, μ

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