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Subject: Docket Number 070-03098
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Mixed Oxide (MOX) Fuel Fabrication Facility
References Concerning HAN

Reference: (1) P. S. Hastings (DCS) letter to Document Control Desk (NRC), DCS-NRC-000140, dated 30 May 2003, *Response to DSER Open Items AP-10 and CS-2*

Enclosures (1) through (8) are provided herein. These are most of the references of the Reference (1) response to DSER Open Item CS-02. Copyright issues have been resolved for these references, but such issues have not yet been resolved for the remaining references of the Open Item.

If you have any questions, please feel free to contact me at (704) 373-7820.

Sincerely,

Peter S. Hastings, P.E.
Manager, Licensing & Safety Analysis

Enclosures:
(1) Dukes, E.K.; *Kinetics and Mechanisms for the Oxidation of Trivalent Plutonium by Nitrous Acid*, **82**, pp 9-13 (1960).
(2) Biddle, P.; McKay, H.A.C.; Miles, J.H.; *The Role of Nitrous Acid in the Reduction of Plutonium(IV) by Uranium(IV)in TBP Systems*, Proc. Int. Conf. on Solvent Extraction of Metals, Harwell, Macmillan, London, pp 133-60 (1965).
(3) Garley, M.S.; Phelan, K.G.; Stedman, G.; *Nitrogen Tracer Studies, on the Decomposition of Hydroxylamine in Nitric Acid*, Chem. Soc. Dalton Trans., pp 2835-37 (1984).

PO Box 31847
Charlotte, NC 28231-1847

128 South Tryon Street, FC12A
Charlotte, NC 28202

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(4) Bennett, M.R.; Brown, G.M.; Maya, L.; Posey, F.A.; *Oxidation of Hydroxylamine by Nitrous and Nitric Acids*, Inorg. Chem., **21**, pp 2461-68 (1982).
(5) Gowland, R.J.; Stedman, G.; *Kinetic and product Studies on the Decomposition of Hydroxylamine in Nitric Acid*, Journal of Inorganic Nuclear Chemistry, **43**, pp 2859-62 (1981).
(6) Fitzpatrick, J.; Meyer, T.A.; O'Neill, M.E.; Williams, D.L.H.; *Comparison of the Reactivity of Nine Nitrous Acid Scavengers*, Chem. Soc. Perkin Trans. II, pp 927-32 (1984).
(7) Karraker, D.G.; *Oxidation of Hydrazine by Nitric Acid*, Inorg. Chem., **24**, pp 4470-77 (1985).
(8) Maya, B.M.; Stedman, G.; *Decomposition of Hydrazoic Acid in Nitric Acid*, J. Chem. Soc. Dalton Trans. (1983).

xc (with enclosure):
David Alberstein, NNSA/HQ
Kenneth L. Ashe, DCS
David D. Brown, USNRC/HQ
Andrew Persinko, USNRC/HQ
Donald J. Silverman, Esq., DCS
PRA/EDMS: Corresp\Outgoing\NRC\2003 NRC\DCS-NRC-000149

xc (without enclosure):
Marc Arslan, DCS
David A. Ayres, USNRC/RII
Timothy S. Barr, NNSA/CH
Jean-Marc Belmont, DCS
Edward J. Brabazon, DCS
James R. Cassidy, DCS
Sterling M. Franks, III, NNSA/SR
Kathy H. Gibson, USNRC/HQ
Robert H. Ihde, DCS
James V. Johnson, NNSA/HQ
Eric J. Leeds, USNRC/HQ
J. David Nulton, NNSA/HQ
Robert C. Pierson, USNRC/HQ
Luis A. Reyes, USNRC/RII
Patrick T. Rhoads, NNSA/HQ
Brian W. Smith, USNRC/HQ
Thomas E. Touchstone, DCS
Martin J. Virgilio, USNRC/HQ

TABLE III

RELATIVE VALUES OF THE MOLAR EXTINCTION COEFFICIENT OF $C_6H_6 \cdot I$ AT 4200 AND 4000 Å.

$(k/\epsilon_c) \times 10^{-6}$ (cm./sec.)

Cell	4200	4000	$\epsilon_{4000}/\epsilon_{4200}$
E	7.3	3.7	0.51
F	7.6	3.9	.51
G	7.1	3.5	.50
A-3	6.0	3.1	.53

A very small deflection was also measured at 6000 Å. indicating slight absorption by the complex at this wave length but was too small to permit the accurate calculation of k/ϵ_{c6000} after the deflections were corrected for stray light of other wave lengths transmitted by the filter

Discussion

The calculated extinction coefficients in Table II, although large, are to be expected from Mulliken's theory of intermolecular charge-transfer interaction.[8] The several simplifications of the theory[22,23] used to explain certain regularities between the ionization potential of the donor molecules and the observed maximum of the charge-transfer spectrum involving molecular iodine should not hold with this system because the constants involved are considerably different for different acceptors.[24] Qualitatively, though, the complex involving I atoms might be expected to be more stable than the corresponding I_2 complex because of the larger electron affinity of the I atom, so that ϵ_{max} should shift toward longer wave lengths. The data of Table III and the observed very slight absorption at 6000 Å., admittedly very scanty, suggest that a maximum exists between 4000 and 5000 Å. This shift is quite large compared to that of only 200 Å. for quite different acceptor molecules.[22]

Increased stability of the complex theoretically should also lead to an increase in the intensity of the charge-transfer spectrum, although the results of Benesi and Hildebrand[7] indicate that ϵ_{max} decreases with increasing complex stability in the methylated benzene series. (Orgel and Mulliken,[25] however, have suggested that the observed intensities are composed of both "contact" and "complex" charge-transfer spectra. When an appropriate division is made between the two possibilities, an increase in ϵ_c with increasing complex stability can be calculated.) Thus the values given in Table II for ϵ_c are reasonable, especially at the larger values of ϕ, even though 4200 Å. is obviously not the wave length of maximum absorption.

Even the smallest possible value for the rate of complex combination (*i.e.*, 1.02×10^{11} l. mole^{-1} sec.$^{-1}$, when $\phi = 1$) is about 18 times larger than the recombination of iodine atoms in carbon tetrachloride.[3] This is surprising, for if the rate of combination is diffusion-controlled as presumed[6] then k should be *smaller* for the complexed atom (with its larger diffusion diameter) than for the free atom. The fact that both ϵ_c and k are large at $\phi = 1$, and increase markedly to unreasonable values with decreasing ϕ, supports the view that the formation of the complex stabilizes the I atoms so that most of them escape recombination into the parent molecule in contrast to the caging effect and low degree of dissociation of I_2 in inert solvents.

Acknowledgments.—The authors are indebted to Dr. J. W. Hollingsworth, Mr. W. G. McClintock and Mr. S. Tsao, of the Computer Laboratory, Rensselaer Polytechnic Institute, for their assistance in the solution of the differential equation with the IBM-650 computer.

Support in part by National Science Foundation grant NSF G-4181 is gratefully acknowledged.

TROY, NEW YORK

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[22] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, 21, 66 (1953).

[23] S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, 75, 2901 (1953).

[24] R. S. Mulliken, *Rec. trav. chim.*, 75, 845 (1956).

[25] L. E. Orgel and R. S. Mulliken, THIS JOURNAL, 79, 4839 (1957).

[CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY, E. I. DU PONT DE NEMOURS & COMPANY]

Kinetics and Mechanisms for the Oxidation of Trivalent Plutonium by Nitrous Acid[1]

More recent?

BY E. K. DUKES

RECEIVED APRIL 6, 1959

The rate of oxidation of plutonium(III) by nitrous acid was investigated in nitric, hydrochloric and perchloric acids. The rate expressions obtained were in HCl or $HClO_4$, $-d[Pu(III)]/dt = K_1[Pu(III)][H^+][HNO_2]$; in HNO_3, $-d[Pu(III)]/dt = K_2[Pu(III)][H^+][NO_3^-][HNO_2]$ where $K_1 = 18 \pm 3.5$ moles^{-2} min.$^{-1}$ and $K_2 = 90 \pm 20$ moles^{-3} min.$^{-1}$. The proposed mechanisms for the oxidation of Pu(III) by nitrous acid involve N_2O_4 as an intermediate in HNO_3 and NO^+ as an intermediate in HCl or $HClO_4$. Activation energies of 14.0 ± 0.6 and 6.0 ± 0.3 kcal./mole were found for K_1 and K_2. Studies were made with solutions 10^{-6} to 10^{-4} molar in plutonium and the change in distribution coefficient of plutonium into 30 vol. % tributyl phosphate (TBP) was used to follow the reaction.

Introduction

Nitrous acid oxidizes trivalent plutonium to tetravalent plutonium in acid solutions by the reaction

$$Pu(III) + H^+ + HNO_2 \longrightarrow Pu(IV) + NO + H_2O$$

The rate of this reaction is measurable at tracer concentrations of Pu but no data have been published. This paper reports the results of a study of the

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[1] The information contained in this report was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

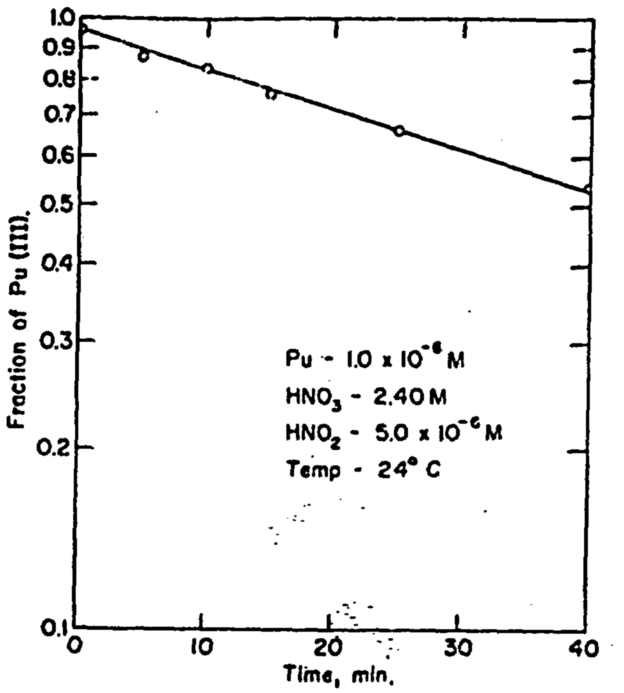

Fig. 1.—Typical curve.

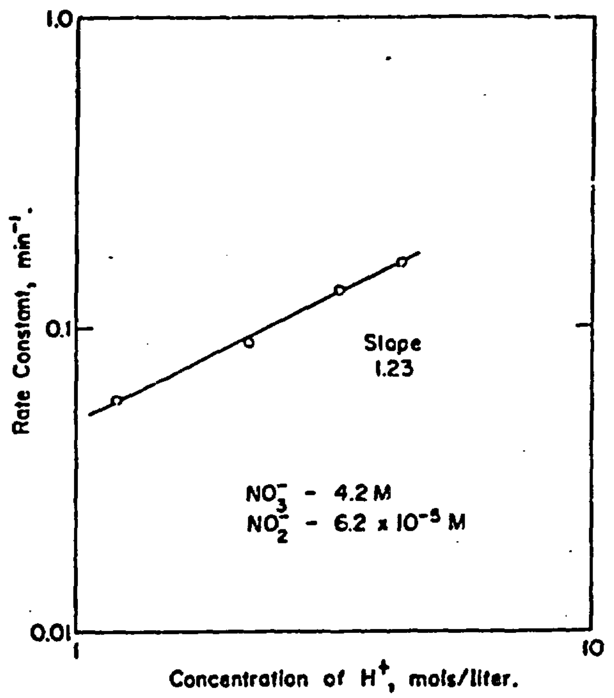

Fig. 3.—Effect of hydrogen ion concentration.

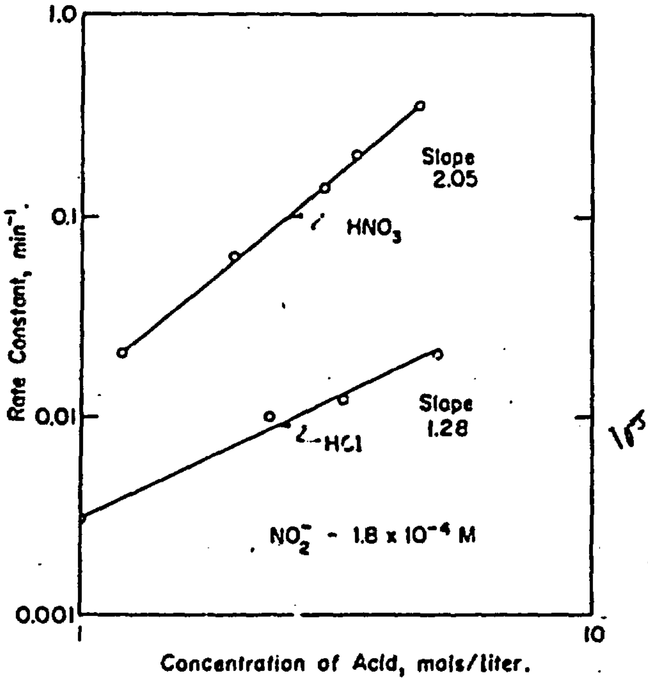

Fig. 2.—Effect of HCl and HNO_3.

kinetics of the Pu(III)–HNO_2 reaction in HNO_3, HCl and $HClO_4$.

Preparation of Reagents

Tetravalent Plutonium.—Solvent extraction or ion exchange was used to purify solutions of Pu(IV). In the solvent extraction method, plutonium(IV) was extracted from 4 *M* nitric acid into a solution of 30 vol. % tributyl phosphate (TBP) in *n*-dodecane. The extract was scrubbed three times with 4 *M* nitric acid and the plutonium(IV) was back-extracted into 0.5 *M* nitric acid. In the anion-exchange method, plutonium(IV) was absorbed from 8 *M* nitric acid on "Dowex" 21-K resin and was eluted with 0.5 *M* nitric acid. The ion-exchange procedure also was used to prepare solutions of plutonium(IV) in hydrochloric acid.

Trivalent Plutonium.—Solutions of trivalent plutonium were prepared from solutions of Pu(IV) in HNO_3 or HCl by the hydrogen reduction of plutonium(IV) with a strip of platinized platinum as a catalyst.[2] Analyses of these solutions by solvent extraction showed that the plutonium(III) content averaged 94%. The low concentration of plutonium(IV) in these solutions was not important because each solution was analyzed immediately before use.

Tributyl Phosphate and *n*-Dodecane.—TBP was purified by crystallization of its uranyl nitrate addition compound from *n*-hexane.[3] Thirty volume per cent. (1.09 *M*) solutions of TBP in *n*-dodecane were used throughout the study. The *n*-dodecane, olefin free grade, was obtained from the Humphrey-Wilkinson Co. and was used without further treatment.

Other Chemicals.—All other solutions were prepared from reagent grade chemicals and were used without further purification.

10^{-5} to 10^{-6} M

Experimental Procedure

These studies were made at Pu concentrations of 10^{-5} to 10^{-6} *M* to minimize interferences from peroxide produced by α-particles and from disproportionation reactions that might occur at high concentrations of Pu. An excess of nitrous acid was used in all experiments to diminish the importance of an autocatalytic effect that arises from the production of 1.5 moles of HNO_2 for each mole of HNO_2 consumed by the reaction.

Measurements of the reaction rate were made by determination of the Pu(III) in acidic solutions by solvent extraction with 30 vol. % TBP. Under the experimental conditions, only Pu(III) and Pu(IV) were present; the fraction of

$$\text{Pu(III)} = \frac{\text{Pu(III)}_{aq} + \text{Pu(III)}_{org}}{\text{Pu(III)}_{aq} + \text{Pu(III)}_{org} + \text{Pu(IV)}_{aq} + \text{Pu(IV)}_{org}}$$

The distribution coefficient (E_s) of a mixture of Pu(III) and Pu(IV) is

$$E_s = \frac{\text{Pu(IV)}_{org} + \text{Pu(III)}_{org}}{\text{Pu(IV)}_{aq} + \text{Pu(III)}_{aq}}$$

The distribution coefficients of pure Pu(III) and pure Pu(IV) are

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(2) G. T. Seaborg, J. J. Katz and W. M. Manning, "The Transuranium Elements," (National Nuclear Energy Series IV-14B), McGraw-Hill Book Co., New York, N. Y., 1949.

(3) E. K. Dukes, "The Formation and Effects of Dibutyl Phosphate in Solvent Extraction," E. I. du Pont de Nemours & Co., Savannah River Laboratory, DP-250, November, 1957.

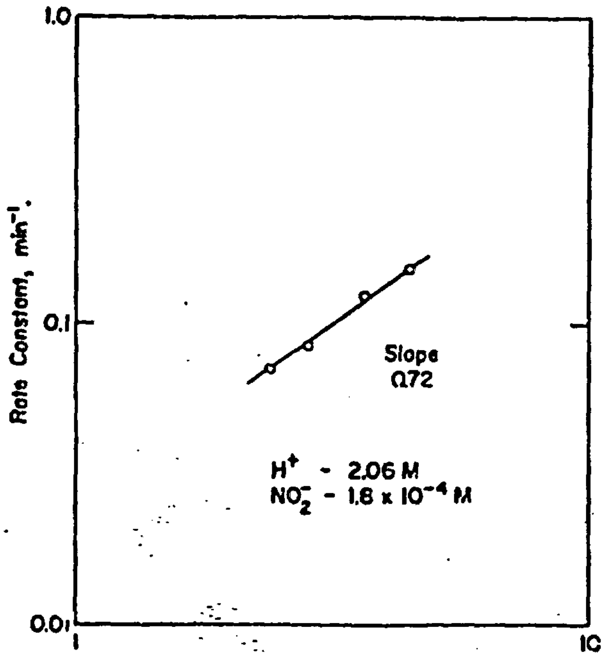


Fig. 4.—Effect of nitrate ion concentration.

$$E_{(III)} = \frac{Pu(III)_{org}}{Pu(III)_{aq}} \qquad E_{(IV)} = \frac{Pu(IV)_{org}}{Pu(IV)_{aq}}$$

Simultaneous solution and algebraic manipulation yield an expression for the fraction, $F(III)$, of Pu(III) in a mixture of Pu(III) and Pu(IV)

Fraction of III

$$F_{(III)} = \frac{(E_{IV} - E_{x})(E_{III} + 1)}{(E_{x} + 1)(E_{IV} - E_{III})}$$

This expression is valid when the volumes of the aqueous and organic phases are equal. With this equation, the determination ~~of Pu(III)~~ in a mixture of Pu(III) and Pu(IV) requires determination of the distribution coefficient of the mixed Pu(III) and Pu(IV), and knowledge of the distribution coefficient of pure Pu(III) and pure Pu(IV) under the same conditions of acidity, temperature, etc.

Distribution coefficients were determined in the following manner: A solution of Pu (10^{-6} to 10^{-4} M) and an equal volume of 30% TBP in *n*-dodecane were mixed thoroughly. Equilibrium was reached in less than 20 seconds of mixing. The phases were separated by centrifugation, and the plutonium content of each phase was determined by α-count of an aliquot. This distribution coefficient was the ratio of the α-activity in the organic phase to the α-activity in the aqueous phase. All distribution coefficients were determined at 0°. Tables I and II contain distribution coefficients for pure Pu(III) and pure Pu(IV) in solutions with

TABLE I

DISTRIBUTION OF PLUTONIUM(III) AT 0°

HNO_3 (M) concn. (aq.)	1.05	1.57	2.70	3.60	4.60
Distribution coefficient (org./aq.)	0.042	0.052	0.058	0.056	0.049

TABLE II

DISTRIBUTION OF PLUTONIUM(IV) AT 0°

HNO_3 (M) concn. (aq.)	1.03	1.40	2.16	3.10	3.80	5.30
Distribution coefficient (org./aq.)	2.20	3.90	6.60	11.00	15.50	25.00

Not Applied

compositions of interest to the rate determination. The proper valence was ensured by adding ferrous sulfamate for Pu(III) or $NaNO_2$ for Pu(IV).

In the determination of reaction rates, an aliquot of a stock solution of Pu(III) was added to the acid solution of the desired composition, and the solution was analyzed by solvent extraction to determine the initial fraction of Pu(III). A measured amount of sodium nitrite was added to start the reaction. Aliquots of the solution were withdrawn at timed intervals, chilled at 0° to decrease the rate of the reaction, and the fraction of Pu(III) determined by solvent extraction.

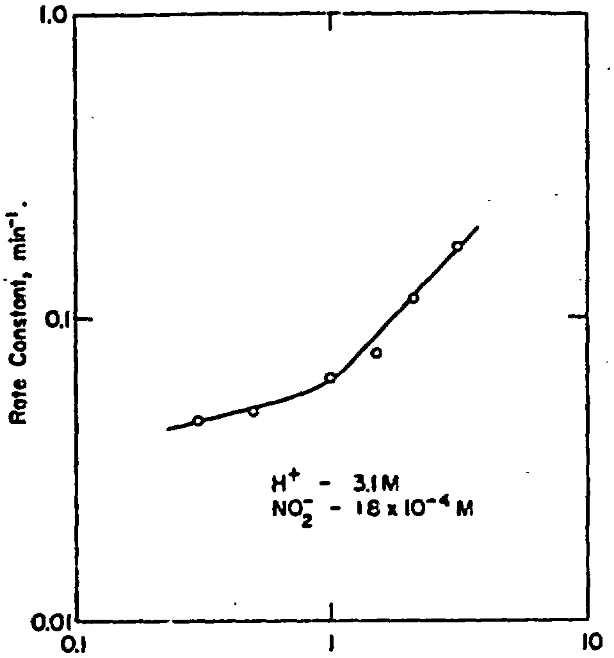


Fig. 5.—Effect of nitrate ion in HCl.

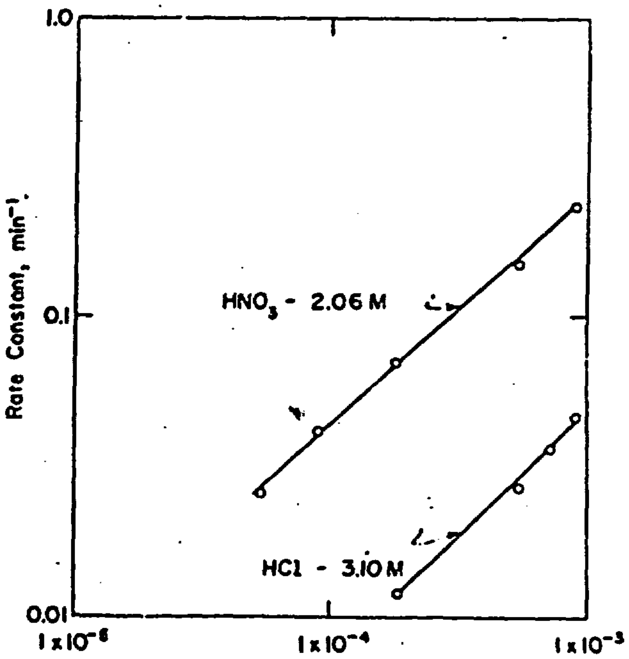


Fig. 6.—Effect of HNO_2.

The distribution data obtained with Pu in HNO_3 also were used to analyze for Pu(III) in HCl or $HClO_4$. Aliquots of the samples were diluted in nitric acid before the equilibration with TBP. Low concentrations of HCl or $HClO_4$ in nitric acid did not cause significant changes in the distribution coefficients for pure nitric acid. The remainder of the procedure was the same as the procedure in nitric acid.

$\frac{dPu(III)}{dt} = -Pu(III)[NO_3^-]^2$

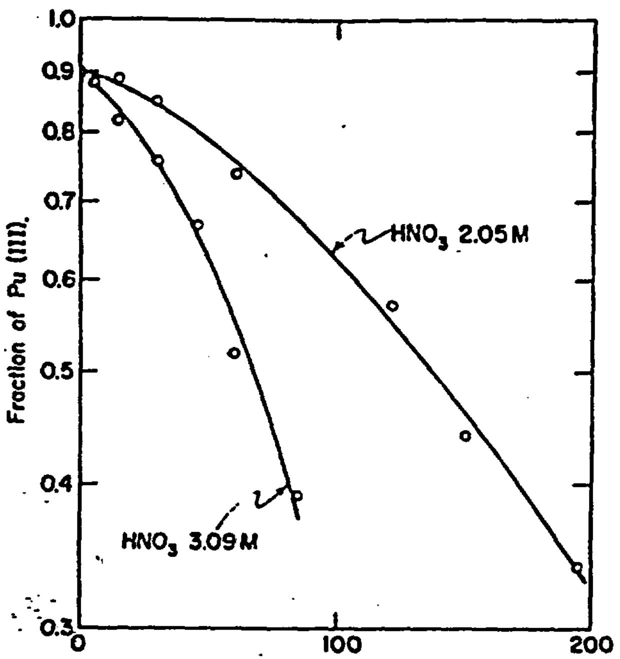
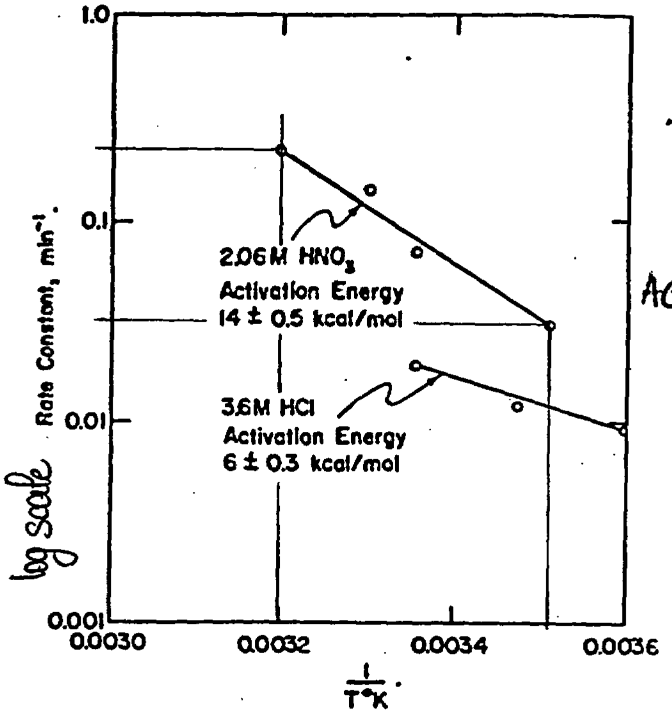


Fig. 7.—Oxidation of Pu(III) in HNO_3.



$Ae^{-H/1.98x}$

Fig. 8.—Effect of temperature on oxidation of Pu(III) to Pu(IV).

Results

Effect of Concentration of Plutonium.—The oxidation of trivalent plutonium by nitrous acid was first order with respect to plutonium. Rate constants were the same at 1.0×10^{-4} *M* as at 5.0×10^{-5} *M* Pu. Typical data are shown in Fig. 1.

Dependence on HNO_3, HCl and $HClO_4$.—The rates of oxidation of Pu(III) depended on the second power of the concentration of HNO_3 and the first power of the concentration of HCl (Fig. 2). Rates were slower in HCl than in comparable concentrations of HNO_3.

The dependence on the concentration of HNO_3 was due to the combined effects of the hydrogen and nitrate ions. Variations of the hydrogen ion concentration, with $NaNO_3$ added to maintain a constant nitrate concentration, showed that the hydrogen ion dependence of the reaction was approximately first power (Fig. 3). Rate determinations in solutions of constant acidity, with varied sodium nitrate concentrations, showed an approximate first power dependence on the nitrate ion (Fig. 4). Determination of the rates in mixtures of $HCl—HNO_3$, at constant ionic strength, showed an exact first power dependence of the rate on nitrate concentrations above 1 *M* in nitrate. At lower nitrate concentrations the reaction apparently was less dependent on nitrate concentration (Fig. 5). These data suggested that at least two mechanisms were involved in the oxidation of Pu(III).

Pu(III)

The rates of oxidation were identical in HCl and $HClO_4$ (Table III); therefore, either the chloride ion and the perchlorate ion had the same effect on the reaction rate, or neither affected the reaction rate. It was assumed in this study that neither the chloride ion nor the perchlorate ion affected the reaction rate.

Dependence on Nitrous Acid.—Rates of oxidation depended on the first power of the concentration of HNO_2 in HNO_3 and HCl (Fig. 6). Oxidation of Pu(III) was autocatalytic in solutions of nitric acid if the concentration of HNO_2 was less than or equal to the concentration of plutonium (Fig. 7). Uniform rates of oxidation were obtained by maintaining an excess of HNO_2. In some experiments nitrous acid was lost during the reaction; however, the loss of nitrous acid was slow enough to allow the determination of rate constants from initial rates of oxidation.

? (2)

?

actually $HNO_2 < Pu$

TABLE III

COMPARISON OF RATES OF OXIDATION IN HCl AND $HClO_4$

Acid	Concn., *M*	HNO_2, *M*	Rate, min.$^{-1}$
HCl	3.60	5.4×10^{-4}	0.034
$HClO_4$	3.60	5.4×10^{-4}	.031
HCl	3.06	1.8×10^{-4}	.012
$HClO_4$	3.06	1.8×10^{-4}	.013
HCl	1.60	5.4×10^{-4}	.013
$HClO_4$	1.60	5.4×10^{-4}	.019

Discussion

The oxidation of Pu(III) by nitrous acid fits the rate expressions

$\frac{dy}{dt} = -ay$

in HCl or $HClO_4$

$$-\frac{d[Pu(III)]}{dt} = K_1[Pu(III)][H^+][HNO_2] \quad (1)$$

in HNO_3

$$-\frac{d[Pu(III)]}{dt} = K_2[Pu(III)][H^+][NO_3^-][HNO_2] \quad (2)$$

The contribution of expression 1 to the rate of oxidation is small at concentrations of nitrate ion greater than 1.0 *M* but expressions 1 and 2 must be combined at lower concentrations of nitrate.

Observed rates were used in (1) and (2) to calculate an average value of 18 ±3.5 moles^{-2} min.$^{-1}$ for K_1 and 90 ±20 moles^{-3} min.$^{-1}$ for K_2.

$.3 = A e^{-14/1.98 \cdot (273+30)}$

From the data in Fig. 8 the activation energy was calculated to be 6.0 ± 0.3 kcal./mole for (1) and 14.0 ± 0.5 kcal./mole for (2).

Different rate constants and activation energies for the different acids suggest at least two mechanisms for the oxidation of Pu(III) by nitrous acid. More complicated mechanisms may be involved but two possible mechanisms that are in accord with the results are

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O;\ \text{rapid reversible} \quad (3)$$
$$NO^+ + Pu(III) \longrightarrow NO + Pu(IV);\ \text{rate controlling}$$
$$HNO_2 + HNO_2 \rightleftharpoons N_2O_3 + H_2O;\ \text{rapid, reversible} \quad (4)$$
$$N_2O_3 + Pu(III) \longrightarrow NO_2^- + NO_2 + Pu(IV);\ \text{rate controlling}$$

In (3) the oxidation of Pu(III) by NO^+ is analogous to the mechanism proposed by Abel[4] for the oxidation of Fe(II) by HNO_2 *in acid media*. It is proposed that in solutions of nitric acid oxidation occurs through both mechanisms. Studies in HCl showed that (3) becomes important only at low concentration of the nitrate ion.

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[4] E. Abel, *Monatsh.*, 80, 379 (1949).

AIKEN, SOUTH CAROLINA

[CONTRIBUTION FROM GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

The Oxidation of Captive Oxalate

BY PATRICIA SAFFIR AND HENRY TAUBE

RECEIVED JUNE 20, 1950

The oxidation of $(NH_3)_5CoC_2O_4^+$ by Ce(IV) takes place with almost perfect stoichiometry, one Ce(IV) being consumed for each mole of the Co(III) complex, and one Co^{++} being formed. Co^{+++} aq. and $S_2O_8^=$ with Ag^+ as catalyst behave similarly. *However,* H_2O_2 *catalyzed by Mo(VI), and* Cl_2 *act to preserve the oxidation state of Co(III) and* $(NH_3)_5CoOH_2^{+++}$ *is formed. The difference in behavior of the two classes of oxidizing agents is ascribed to this: Ce(IV), Co(III) and some intermediate in the* $S_2O_8^= + Ag^+$ *system act by extracting one electron at a time, while the other two act in a manner which is equivalent to extracting two electrons simultaneously.*

In many systems it has been observed that metal ions though present in small amounts may alter the kinetics and even the course of oxidation-reduction reaction. Usually the studies have been done with metal ions which are substitution-labile and the interpretation of the results is made difficult because the way the metal ion is combined in the various stages of the reaction in which it is active is not known. The experiments reported in this paper, on the reaction of oxidizing agents with a reducing agent bound to a substitution-inert metal ion center, are relevant to this subject. The reducing agent–metal ion complex we chose for study is $(NH_3)_5CoC_2O_4^+$, and the feature of particular interest was to learn whether and when the Co(III) takes part in the oxidation of the bound oxalate brought about by external oxidizing agents.

Materials.—The $(NH_3)_5CoC_2O_4H(ClO_4)_2$ was prepared by warming a solution of $(NH_3)_5CoH_2O(ClO_4)_3$ with a slight excess of oxalic acid. The solid which separated on cooling was recrystallized and submitted for analysis (analysis reported at 16.02% N and 16.35% Cl to be compared with the theoretical values of 16.21 and 16.41%, respectively). The solution containing Co^{+++} aq. was prepared by the method of Weiser.[1] The carbonato complex is prepared in saturated $NaHCO_3$ using H_2O_2 as oxidant on a cobaltous salt. The solution is added slowly to a cooled solution of $HClO_4$ aq.

All other reagents were standard C.P. or A.R. chemicals.

Results

Reaction with Ce(IV) Perchlorate.—In a typical experiment, a solution was used which was 0.025 *M* in $(NH_3)_5CoC_2O_4H(ClO_4)_2$, 0.047 *M* in Ce(IV) and 1 *M* in $HClO_4$. The progress of the reaction was followed by titrating Ce(IV) with Fe^{++} (the cobalti complex does not react rapidly with this reducing agent). The reaction of Ce(IV) with the cobalti complex is very much slower than it is with uncomplexed oxalate, and a period of *ca.* 20 hr. is required to ensure complete reaction at room temperature at the concentrations obtaining in our present experiments; for the uncomplexed oxalate, a few minutes would suffice.

There is apparently a slow loss of Ce(IV) even after the oxalato complex has disappeared; this loss is perhaps attributable to the oxidation of water by Ce(IV), catalyzed by Co^{++}. The effect is much reduced at 10°, and at this temperature clear-cut results on the stoichiometry are obtained. After 73 hr., the oxalato complex has disappeared and the ratio of Ce(IV) consumed to total oxalato complex is 1.01, after 140 hr. the ratio is 1.02 and after 250 hr., 1.04. Correcting for the continued slow loss of Ce(IV), the conclusion follows that the reaction of Ce(IV) with the oxalato complex takes place with almost perfect stoichiometry, *one* Ce(IV) being required for each oxalate. The cobalt product is not $(NH_3)_5CoOH_2^{+++}$ as would be expected if the cobalt oxidation state were preserved, but Co^{++}. The net change can be represented by the equation

$$(NH_3)_5CoC_2O_4H^{++} + Ce(IV) + 4H^+ = Co^{++} + Ce^{+++} + 2CO_2 + 5NH_4^+$$

Reaction with Co^{+++}.—The observations with Co^{+++} aq. as oxidizing agent are complicated by the reaction of Co^{+++} aq. to liberate O_2 from water but the intrinsic stoichiometry in the reaction of interest can nevertheless be fairly well established. In an experiment with $(NH_3)_5CoC_2O_4H(ClO_4)_2$ at 0.0021 *M*, Co^{+++} initially at 0.0041 *M* and $HClO_4$ at 2 *M*, at 10° and in the dark, after 144 hr. the total amount of Co^{+++} aq. consumed (as determined by titration) compared to the initial amount of the oxalato complex was 1.28. After this time, the extinctions of the solution at λ's = 4020 and 6020 Å. could be accounted for quantitatively by the residual Co^{+++} shown by titration and the Co^{++} resulting from the reduction of Co^{+++} and the Co(III) complex. If $(NH_3)_5Co(OH_2)^{+++}$ or $(NH_3)_5CoC_2O_4H^{++}$ were present, it would contribute appreciably to the extinction at 4020 Å.; at most 5% of an ammino complex remains. We conclude that in this reaction also, the oxidation of the bound oxalate by the external oxidizing agent brings about the reduction of Co(III) in the complex. The consumption of Co^{+++} aq. in excess of that prescribed by this stoichiometry is attributable to the spontaneous oxidation of H_2O by Co^{+++} aq., rather than to the $2e^-$ oxidation of the oxalato complex by the Co^{+++} aq.

The Ag^+ Catalyzed Reaction with $S_2O_8^=$.—The reaction of $S_2O_8^=$ with $(NH_3)_5CoC_2O_4^+$ is very slow, but when Ag^+ is present (~ 0.1 *M* $AgClO_4$ was used), reaction takes place immediately and Co^{++} is formed. A blank experiment with $(NH_3)_5CoOH_2^{+++}$ in place of the oxalato complex shows that the aquo ion survives this treatment. We can conclude

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[1] D. W. Weiser, Ph.D. Dissertation, University of Chicago, 1950.

The Role of Nitrous Acid in the Reduction of Plutonium(IV) by Uranium(IV) in TBP Systems

P. BIDDLE, H. A. C. McKAY & J. H. MILES
Atomic Energy Research Establishment, Harwell, Berks., U.K.

A rotating platinum microelectrode has enabled plutonium(III) or plutonium(IV) to be determined polarographically, in either an aqueous or a TBP-diluent phase, at very low levels (6 × 10^{-6}M *in aqueous phases,* 10^{-4}M *in organic). It has also been used to make rough measurements on the concentration of stabilizers in organic phases. The rate of reduction of plutonium(IV) by uranium(IV) in organic phases has been measured at* 0°C *and* 11°C *and an expression has been derived for the overall rate in a mixed phase system in terms of the rate in each phase. The rate of reduction in such systems containing nitric acid depends also on the autocatalytic rate of reaction of plutonium(III) with nitrous acid and on the rate of reaction of nitrous acid with stabilizers. Both of these rates have been measured in the organic phase.*

The separation of small concentrations of plutonium from much larger concentrations of uranium in the aqueous reprocessing of nuclear fuels is usually effected by reduction of the plutonium to the trivalent state. Ferrous sulphamate has been used almost exclusively for this purpose. The possibility of using uranium(IV) and hydrazine in place of ferrous sulphamate was suggested[1] in the days of the bismuth phosphate process but has only recently been carefully investigated or used on a plant.[2-6] The following advantages were expected:

(a) Both the reductant uranium(IV) and its oxidation product uranium(VI) would be extracted into the organic phase and would not add extraneous material to either product stream, *cf.* ferric and sulphate ions.

(b) The redox potentials indicate virtually complete reduction in a single stage with only a small excess of uranium(IV) reductant, even in presence of large amounts of uranium(VI). With iron, on the other hand, the reduction is incomplete (say <99·9% complete) unless a sufficiently large iron(II):iron(III) ratio is maintained.

In practice[3–6] in a multi-stage contactor the expectation (b) has not been fulfilled. The highest decontamination factor[3] of the uranium stream (organic) from plutonium so far achieved has only reached 1·4 × 10^4 whereas in theory a factor of the order of 10^9 should have been obtainable under the conditions used.

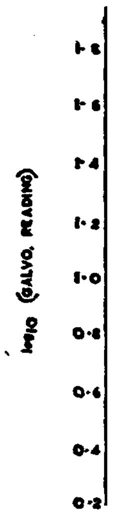
McKay, Streeton and Wain[4] ascribed the low decontamination factors they obtained to low stage efficiencies in their mixer-settlers, but also drew attention to uncertainties in our knowledge of the rate of the plutonium(IV)–uranium(IV) reaction, especially in the organic phase. The present work was undertaken to fill this gap.

RESULTS IN AQUEOUS SOLUTIONS

Newton[7] has studied the rate of reduction of plutonium(IV) by uranium(IV) in aqueous perchloric acid in the range 0–30°C using a spectrophotometric technique. He showed that the rate was approximately first order in uranium(IV) and plutonium(IV) concentrations and that the variation with acidity (almost inverse square at high acid concentration) was consistent with attack of UOH^{3+} on PuOH^{3+}. The variation of rate with temperature gave a good Arrhenius plot, the activation energy being 24·9 kcal/mole. The spectrophotometric technique requires about 2 × 10^{-3}M plutonium whichever species, plutonium(III) or plutonium(IV), is followed; the reactions at low acidities are then too fast to measure conveniently by conventional methods. It is also difficult to use a sufficiently high range of reactant concentrations to establish the order of the reaction unequivocally.

We have therefore used a very sensitive polarographic method based on a rotating platinum wire microelectrode. The technique is sensitive to 10^{-6}M plutonium(III) or plutonium(IV) in the aqueous phase and is readily adaptable to thermostat and fume hood working. A typical rate plot is shown in Fig. 1. Our results in aqueous phases will be published elsewhere.[8] In aqueous perchloric acid we found rates 3–5 times faster than those of Newton, and in aqueous nitric acid, about one-half of those in perchloric acid. The most striking feature of the aqueous phase work was the discovery of significant catalysis by chromium(III) and other metal ions and pronounced catalysis by traces of phosphate ion. The rate was doubled both by 7 × 10^{-3}M chromium(III) and by 6 × 10^{-6}M phosphate.

These results confirm that aqueous phase rates are sufficiently fast to complete the reduction of plutonium(IV) within a normal mixer residence time (*ca.* 1 min).



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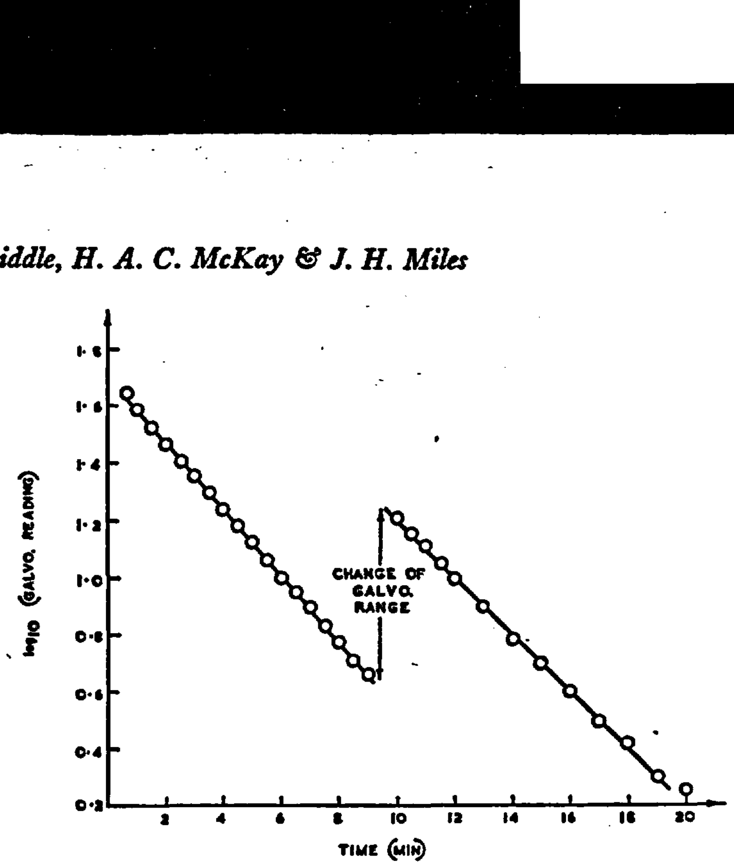

FIG. 1—Reduction of Pu(IV) by U(IV) in Aqueous Nitric Acid at 0°C.

HNO_3	2·24M
U(IV)	$8{\cdot}5 \times 10^{-3}$M
Initial Pu(IV)	$2{\cdot}53 \times 10^{-4}$M
N_2H_4	0·05M

THE PLUTONIUM(IV)–URANIUM(IV) REACTION IN ORGANIC PHASES

Use of Rotating Platinum Microelectrode in Organic Phases

The rotating platinum microelectrode has been found to give useful results in the organic phase (either pure TBP or 30% TBP in hydrogenated propylene tetramer (HPT)). It is less sensitive than in the aqueous phase (10^{-4}M plutonium must be used) and the proportionality factor between current and plutonium(IV) concentration varies in an unexpected way. Currents for a given plutonium(IV) concentration are higher at 0°C than at 20°C and disappear almost completely at 25°C. The current per unit plutonium(IV) concentration is higher at high nitric acid concentrations. For the aromatic substituted hydrazine stabilizers the proportionality factor between current and concentration appears to remain constant for the few minutes of a rate study, but it has not been possible to obtain reproducible currents for different samples of the same solution or to plot current against concentration using separate samples of known concentration. Nitrous acid gave reproducible results (a reduction current) but a non-linear current concentration curve.

The aryl hydrazines gave oxidizing currents between 0·7 and 1·0 V against silver/silver chloride in 0·1M HCl in TBP. Nitrous acid and plutonium(IV) gave reducing currents between 0 and 0·4 V against the same standard. Inability to distinguish between currents due to nitrous acid and plutonium(IV) leads to difficulties in interpreting the results, as will be discussed.

Runs at 0°C

At this temperature it was possible to carry out runs more or less as in aqueous solution. All solutions were prepared by shaking the organic phase with an aqueous phase so that the results were directly applicable to consideration of a solvent extraction system. The effect of water concentration was checked in one independent experiment. Nitric acid solutions were used throughout and the solutions were stabilized by the addition of pure hydrazine to 0·06M. Table 1 shows the results of these runs and Fig. 2 shows the quality of the first run described.

It is seen that neither in 0·47M nitric acid nor in 1·60M nitric acid is the rate proportional to the uranium(IV) concentration. In the runs in

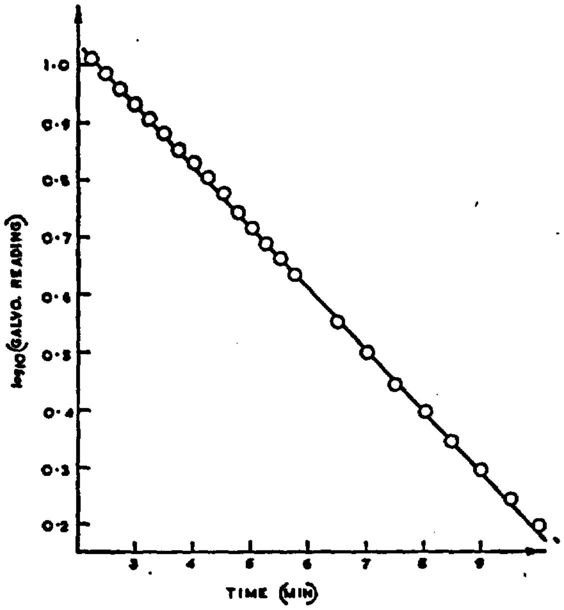

FIG. 2—Reduction of Pu(IV) by U(IV) in Pure TBP at 0°C.

HNO_3	0·47M
H_2O	*ca.* 3·5M
U(IV)	$7{\cdot}04 \times 10^{-4}$M
Initial Pu(IV)	$1{\cdot}17 \times 10^{-4}$M
N_2H_4	0·06M

1·60M nitric acid curved plots were obtained. This is in all probability due to failure of nitrous acid control (see below) and not to lack of proportionality of rate to plutonium(IV) concentration in the range considered ($<10^{-4}$M). The rate increases with decrease in acidity even more than the inverse square relationship found in aqueous solution would indicate. Comparing the fifth and sixth lines of the table one sees a large decrease in rate (by a factor of 6·6) on lowering the water concentration by a factor of 2·3. This may be the cause of the very steep increase in rate with decrease in nitric acid concentration, since in TBP solutions in equilibrium with aqueous solutions, an increase in acid concentration in the organic phase is, in the range considered, accompanied by a decrease in the water concentration.[9]

The last lines in the table describe runs in 30% TBP. The rate is about one order of magnitude slower than those in pure TBP and about two orders of magnitude slower than those in aqueous solutions of the same acid, uranium(IV) and plutonium(IV) concentrations.[7,8]

In spite of this, the reduction in many mixed phase systems occurs mostly in the organic phase. This can be demonstrated by calculating the absolute rate of reduction of plutonium(IV) in the two phases of a system at equilibrium. The composition of an aqueous phase in equilibrium with the solutions of Table 1 is first calculated from distribution data, and then the rate of reaction in this aqueous phase calculated from our aqueous phase results.[8] Multiplying the plutonium(IV) concentration by the rate constant appropriate to the composition of the phase then gives the rate of reduction per litre of phase. A solvent:aqueous phase volume ratio of 10 has been used in calculating the absolute rate of loss of plutonium(IV). The last column of Table 1 shows that between 50 and 370 times as much plutonium(IV) is being lost in the organic phase as in the aqueous phase. This large factor derives partly from the high phase volume ratio, and partly from the low distribution coefficient for nitric acid which is effectively squared in the rate calculation.

Rates in a Mixed Phase System

The results also enable us to calculate roughly the half-time of reaction in an actual mixer-settler system. It has to be assumed that, apart from depressing the nitric acid concentration in the organic phase, the heavy loading of uranium(VI) has no further effect on the rates.

Appendix 1 gives the derivation of the rate for a mixed phase system,

$$k = (DRk_o + k_a)/(DR + 1)$$

where k, k_a and k_o are the pseudo-first order rate constants (uranium(IV) in large excess) of the overall reaction, the reaction in the aqueous phase

TABLE 1—*Organic Phase Reaction Rates at* 0°C

All runs used 0·06M hydrazine as stabilizer and had an initial plutonium(IV) concentration of 1·17 × 10^{-4}M.
Phase volume ratio (organic:aqueous) = 10

Medium	$[HNO_3]_{org}$ (M)	$10^3[U(IV)]_{org}$ (M)	$[H_2O]_{org}$ (M)	Pseudo-First Order Rate Constant (min^{-1})	k_{aq}† (min^{-1})	Rate Ratio for Two Phases
TBP	0·47	0·704	3·5*	0·245	0·48	370
TBP	0·47	6·99	3·5*	0·542	4·8	82
TBP	1·60	0·943	2·7*	(9·44 × 10^{-3})‡	0·063	53
TBP	1·60	9·03	2·7*	(1·71 × 10^{-2})‡	0·61	100
TBP	0·80	37·3	1·34	0·088	2·5	—
TBP	0·80	37·3	3·14	0·579	2·5	—
30% TBP/OK	0·67	10·0	*	0·0307	3·4	50
30% TBP/HPT	0·73	10·0	*	0·0347	2·6	83

* Refers to solutions prepared by shaking with an aqueous phase. The values quoted for pure TBP are from Hesford and McKay.[9]

† k_{aq} refers to the first order rate which would have been obtained if the run had been conducted with the same concentrations of HNO_3, Pu(IV) and U(IV) in an aqueous phase. These values have been obtained from the data in ref. 8.

‡ The values for 1·60M acid have been placed in parentheses to indicate that they are initial rates of a curved plot.

TABLE 2—*Calculation of Overall Reaction Rates for Representative Stages of a Typical Mixer-Settler System (Run IC2, ref. 4)*

Stage No.	$[HNO_3]_{aq}$ (M)	$[U(IV)]_{aq}$ (M)	$[U(IV)]_{org}$ (M)	$D_{Pu(IV)}$	$[HNO_3]_{org}$ (M)	$10k_o$ min^{-1}	k_a min^{-1}	k' (0°C) min^{-1}	$t_{\frac{1}{2}}$ (0°C) min	k' (20°C) min^{-1}	$t_{\frac{1}{2}}$(20°) min
1	0·13	5×10^{-4}	8×10^{-5}				4·47				
3	0·57	5×10^{-3}	$1·3 \times 10^{-4}$	0·1	$4·27 \times 10^{-2}$	4·65	2·40	1·4	0·50	32	0·0218
5	0·95	8×10^{-3}	$2·5 \times 10^{-4}$	0·4	$6·65 \times 10^{-2}$	3·77	1·34	0·56	1·25	12·8	0·0545
7	1·2	$1·6 \times 10^{-2}$	$3·0 \times 10^{-4}$	0·6	$9·00 \times 10^{-2}$	2·41	1·68	0·44	1·59	10·1	0·0690
9	1·8	$1·7 \times 10^{-2}$	$4·0 \times 10^{-4}$	1·2	$13·5 \times 10^{-2}$	1·43	0·79	0·19	3·67	4·4	0·158
Batch[4] expt.	2·0	3×10^{-4}	$3·6 \times 10^{-4}$	20	$5·7 \times 10^{-1}$	0·073	0·0112	0·0073	96	0·29	2·4

(a) k', k_o and k_a are the pseudo-first order rate constants for the mixed phase system, the organic phase and the aqueous phase respectively.

(b) k_a is obtained from the table in ref. 8, by means of the expression $k_a = k[U(IV)]_{aq}/[H^+]^2_{aq}$.

(c) k_o is obtained by applying the expression $k_o = 6·5[U(IV)]_{org}/[H^+]^2_{org}$. This rate law is in fact known to be incorrect in the organic phase (see Table 1) but since the increase in rate with decrease in hydrogen ion is greater than a square law it is almost certain that the rates in the table are underestimates.

(d) Distribution data are 25°C values. These are not strictly correct for the 0°C calculations but probably not seriously in error.

(e) The last line in the table refers to calculations on the batch experiment of McKay, Streeton and Wain in which no uranium(VI) was present. This explains the much higher $D_{Pu(IV)}$ value.

(f) The 20°C rates are calculated by assuming that the mixed phase system rate has an activation energy of 24·9 kcal/mole as shown by the aqueous phase rate.

(g) Values in columns 5 and 6 from Geary.[18]

and the reaction in the organic phase respectively. *R* is the phase volume ratio and *D* the distribution coefficient for plutonium(IV). Table 2 shows the application of this formula to determine the half-periods of reaction in a typical mixer-settler system if run at 0°C (ref. 4, run IC2). Finally with the same value of the activation energy for the overall rate as was found by Newton[7] for the aqueous phase, half-times of reaction at 20°C are calculated. The half-times of reaction vary between 0·5 and 3·7 min at 0°C and 0·02 and 0·2 min at 20°C. It will be noted that the 20°C half-periods are adequate to provide complete reaction (say 10 half-periods) in a mixer-settler system having a residence time for the organic phase of 1 min. The use of the same activation energy for the overall rate as for the aqueous phase alone is in general incorrect, but appears by coincidence to be about right in this case, since Table 2 also shows these calculations applied to the mixed phase rate experiments of McKay *et al.*[4] The agreement between the calculated half-period, 2·4 min, and the experimental 1·5 min, is astonishingly good.

DRASTIC EFFECT OF NITROUS ACID IN THE ORGANIC PHASE

General

The results for the run described in the penultimate line of Table 1 are presented in Fig. 3. The current readings corresponding to the plutonium(IV) present levelled off, and then began to rise again, after about 70 min. After 130 min the current corresponded to 46% of the plutonium being in the IV-state, after a minimum value of 29%. At this point further hydrazine was added and the current resumed its downward trend. Examination of the cell showed precipitation of a small quantity of a semi-solid phase (probably hydrazine nitrate). Sulphamic acid and urea were also found to be insoluble in the organic phase. It would therefore appear that failure to destroy nitrous acid sufficiently rapidly is leading to re-oxidation of the plutonium.

Oxidation of plutonium(III) in nitrous acid–nitric acid mixtures has been studied by Dukes[10] in aqueous solution and found to be autocatalytic, i.e. in the presence of a large excess of nitric acid the reaction produces more of the reactive species than it consumes. Dukes believes that the principal reactive species in nitric acid media is N_2O_4, and formulates the rate-determining reaction as follows:

$$\mathrm{Pu(III)} + \mathrm{N_2O_4} \rightarrow \mathrm{Pu(IV)} + \mathrm{NO_2} + \mathrm{NO_2^-}.$$

The NO_2 and NO_2^- then rapidly regenerate N_2O_4 through the equilibria

$$2NO_2 \rightleftharpoons N_2O_4$$

$$H^+ + NO_2^- \rightleftharpoons HNO_2$$

$$HNO_2 + HNO_3 \rightleftharpoons N_2O_4 + H_2O$$

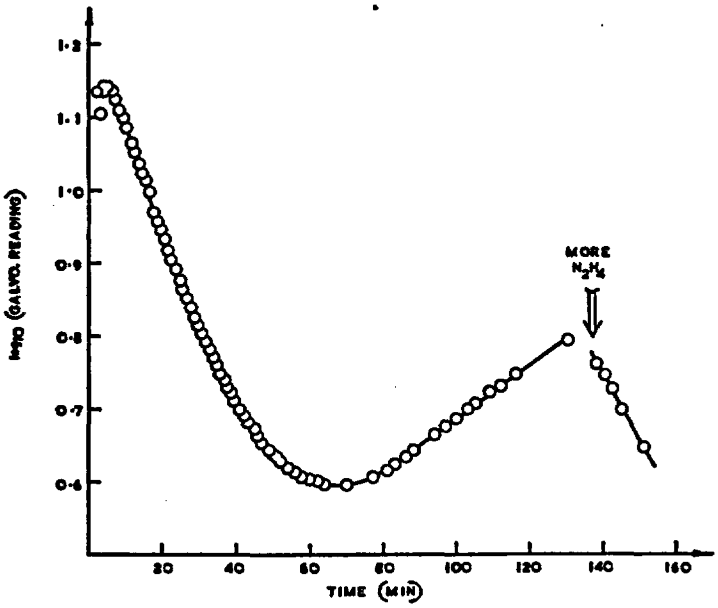

Fig. 3—Reduction of Pu(IV) by U(IV) in 30% TBP in OK at 0°C.

HNO_3	0·67M
U(IV)	$1·0 \times 10^{-2}$M
Initial Pu(IV)	$1·17 \times 10^{-4}$M
N_2H_4	0·06M

In other acid media, NO^+ may be the reactive species (*cf.* Abel[11]), but since N_2O_4 may behave like $NO^+.NO_3^-$ the difference is not of major significance. An autocatalytic reaction scheme can also be formulated with NO_2 as the reactive species. Whatever the details, it is to be expected that in the absence of stabilizer these reactions will oxidize the whole of the plutonium(III) in a nitric acid medium.

The rapidity of these reactions in the organic phase may be demonstrated by the failure of uranium(IV) to reduce plutonium(IV) or even to prevent oxidation of plutonium(III) in the absence of stabilizers, even though nitrous acid is initially absent.

Polarographic Runs

Fig. 4 shows the current versus time curve obtained when plutonium(III) (in very weak perchloric acid in TBP) is added to a 30% TBP phase containing nitric acid and uranium(IV). Nitrous acid was initially absent, the solution having been recently removed from an aqueous phase containing hydrazine. Sections AB and EF of the curve may be explained as due to production of nitrous acid by attack of uranium(IV) on nitric acid. Woodhead[12] has shown spectrophotometrically that uranium(IV) reduces nitric acid in the aqueous phase, producing one molecule of nitrous acid for every molecule of uranium(IV) oxidized. The oxidation was 39% complete after 20 h in 0·5M nitric acid and 75% complete in 4M nitric acid. The uranium(IV) concentration was 1·0 × 10^{-2}M. We have shown independently that nitrous acid gives reduction currents at a platinum electrode. The reducing current is probably due to the reaction $NO_2 + e^- \rightarrow NO_2^-$. The current-voltage curves and the sensitivity are very similar to those for plutonium(IV)

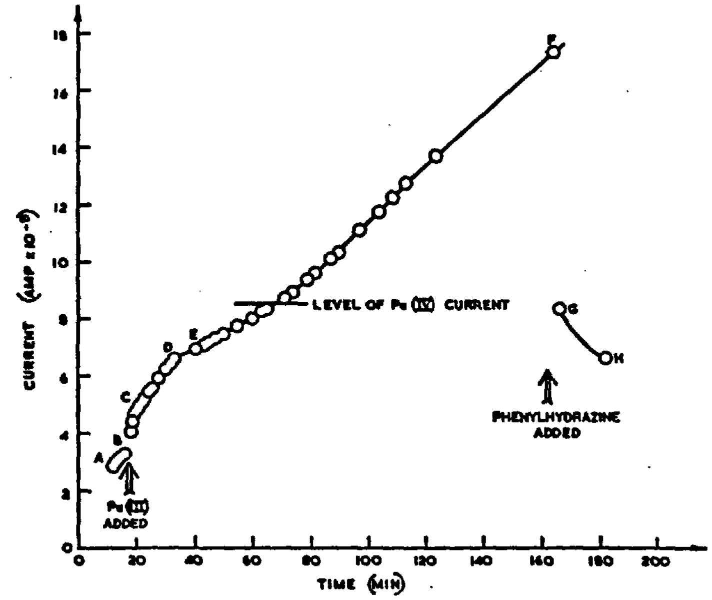

FIG. 4—Oxidation of Pu(III) in HNO_3 in 30% TBP in HPT in Presence of U(IV) at 20°C.

HNO_3	0·73M
U(IV)	7·0 × 10^{-5}M
Pu(IV)	9·4 × 10^{-5}M

but the current concentration curve is non-linear. The current at the point F on the curve corresponds to about 5×10^{-4}M nitrous acid (allowing for the current due to plutonium(IV)). The increase in current along BCD following addition of plutonium(III) at B is explained by production of plutonium(IV) and an equivalent quantity of nitrous acid. At F phenylhydrazine was added to make the solution 0·0185M in this reagent. The current falls to the value given by the point G (not zero) and does not approach zero over the section GH. The use of phenylhydrazine and the emergence of steady states is discussed below. Owing to the inability of the present method to distinguish between currents due to plutonium(IV) and those due to nitrous acid the experiment was repeated spectrophotometrically.

Spectrophotometric Runs

The following three solutions were shaken together in a conical flask:

(a) 15 ml of $1{\cdot}008 \times 10^{-2}$M plutonium(IV) in 30% TBP in presence of 0·07M HNO_3.
(b) 15 ml of $1{\cdot}005 \times 10^{-2}$M uranium(IV) solution in 0·73M HNO_3 in 30% TBP.
(c) 0·3 ml of 1M HNO_3, 0·1M $N_2H_4.HNO_3$ in water.

The very large phase volume ratio is necessary to ensure that sufficient plutonium(III) remains in the organic phase. The solution was centrifuged and separated and the organic layer placed in the spectrophotometer as quickly as possible (5 min). The spectrum showed a plutonium (IV) absorption band but no plutonium(III) bands.* The solution still gave a reducing reaction to ferroin indicator to which a little 0·01M ceric sulphate solution had been added. As a final test 0·3 ml of an aqueous solution 5M in hydrazine nitrate and 1·0M in nitric acid was placed in the bottom of the spectrophotometer cell. There was no reduction in the plutonium(IV) peak and no appearance of plutonium(III) peaks; the solution remained reducing to ferroin. This situation is deliberately analogous to that of a solution in the settling compartment of a mixer-settler.

Use of Phenylhydrazine as Stabilizer

At 20°C we found that hydrazine and sulphamic acid were precipitated from TBP-diluent solutions containing nitric acid and it is already known[12] that they do not extract appreciably from an aqueous to a TBP phase. Attempts to conduct reductions at 20°C in presence of these precipitated stabilizers failed; the current due to plutonium(IV) did not

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* In TBP solution the principal bands shift to 492 mμ for plutonium(IV) and 556, 592 mμ for plutonium(III). The latter are no longer of equal intensity.

decrease. Obviously the problem of stabilizer insolubility can be solved by the inclusion of an oleophilic organic substituent in the stabilizer molecule and phenylhydrazine is readily available for this purpose.

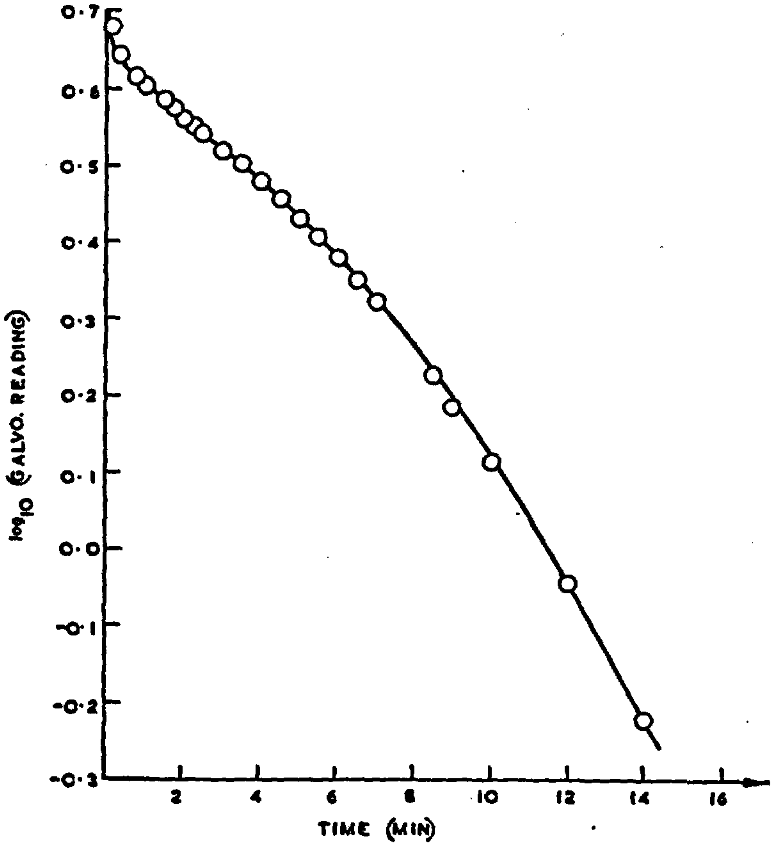

FIG. 5—Reduction of Pu(IV) by U(IV) at 11°C in 30% TBP in HPT.

HNO_3	0·73M
U(IV)	1·0 × 10^{-2}M
Initial Pu(IV)	1·17 × 10^{-4}M
Phenylhydrazine	0·0185M

In presence of 0·0185M phenylhydrazine at 0°C a rate plot was obtained in good agreement with that obtained in the presence of hydrazine (which was probably at least partly precipitated).

Fig. 5 shows a first order rate plot for reduction of plutonium(IV) (initially 1·17 × 10^{-4}M) by uranium(IV) (1·002 × 10^{-2}M) in 0·73M HNO_3 in 30% TBP at 11°C with 0·0185M phenylhydrazine as stabilizer. The graph shows fairly complete reduction and probably approximates to a true first order plot.

If the other conditions were kept the same but either the uranium(IV) concentration was increased to 0·1M, or 0·1M uranyl nitrate (as crystals) was added, no reduction occurred. This is attributed to an increased rate of production of nitrous acid under these conditions. An additional factor is the partial precipitation of phenylhydrazine nitrate.

Steady-state Behaviour at Temperatures near 25° C

If plutonium(IV) is added to a solution containing uranium(IV), nitric acid and phenylhydrazine in 30% TBP at temperatures near 25°C, a fairly steady current reading is obtained. The current is higher than would be expected for plutonium(IV) alone. Fig. 6 shows some of these graphs as a function of phenylhydrazine concentration. The solutions were initially free of nitrous acid.

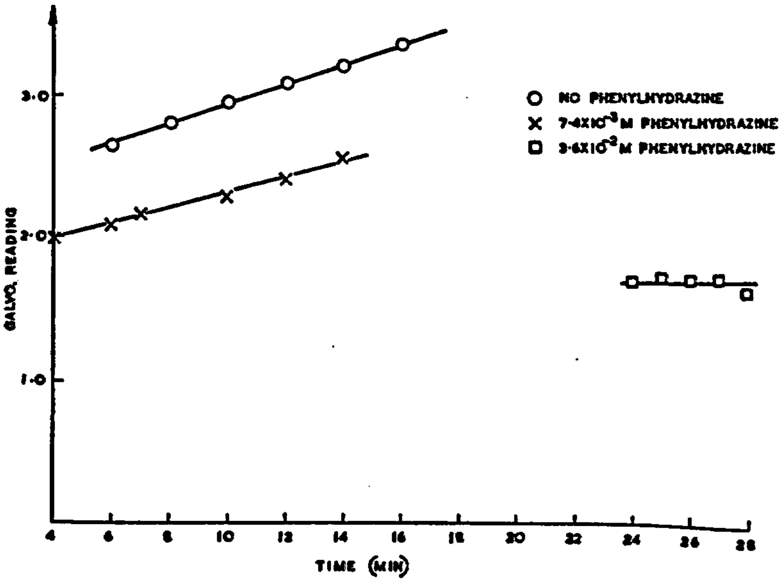

FIG. 6—Steady States in Pu(IV)–U(IV) Reaction with Stabilizer at 25·4° C in 30% TBP in HPT.

HNO_3	0·73M
U(IV)	$1·0 \times 10^{-2}$M
Pu(IV)	$1·17 \times 10^{-4}$M

The non-linear relation between current and concentration for nitrous acid makes it difficult to analyse the situation further, but it seems likely that the situation can be understood by regarding nitric acid, phenylhydrazine and uranium(IV) as the reactants and nitrosophenylhydrazine and uranium(VI) as the products. Plutonium(III), plutonium(IV) and nitrous acid may then be regarded as reactive intermediates whose concentration remains relatively static until one of the major reactants is used up. It is, however, clear from these results that while the distribution of phenylhydrazine between aqueous and organic phases is satisfactory (a rough iodometric determination gave a partition coefficient of 0·04 with 0·174M nitric acid in the organic phase) the rate of reaction with nitrous acid is not quite fast enough. We have therefore searched for a compound which will destroy nitrous acid more rapidly.

Rate of Reaction of Stabilizers with Nitrous Acid

The literature[13] on the kinetics of reaction of nitrous acid with organic amines shows that the mechanism involves attack by an electrophilic inorganic nitrosating agent (NO^+, $H_2NO_2^+$, N_2O_3) on the free amine. Either a first or a second order rate law may be expected according to the mechanism.

Since phenylhydrazine is so nearly successful it was hoped that *o*-methylphenylhydrazine might succeed, since substitution by methyl in the ortho position usually increases the rate towards an electrophilic reagent by a large factor.

Rates of Reaction of Phenylhydrazine and o-Methylphenylhydrazine with Nitrous Acid

At potentials between 0·7 and 1·0 V against silver/silver chloride in 0·1M hydrochloric acid in TBP, phenylhydrazine and *o*-methylphenylhydrazine are oxidized at the platinum electrode. The currents obtained were not reproducible. We have nevertheless carried out runs in which equimolar quantities of nitrous acid and substituted hydrazine were mixed (in HNO_3—TBP—HPT solution) and we followed the rate of loss of current i due to the aryl hydrazine. If $i = f \times$ stabilizer concentration (f is a constant), log i should be proportional to the time if the reaction is first order; the rate constant can then be obtained directly from the slope of the plot of log i. If the reaction is second order, $1/i$ should be proportional to the time; to obtain the rate from the slope it is then necessary also to determine f, which can be done by extrapolating the i against time curve to zero time.

The plots showed a certain amount of random curvature, probably due to variations in f. Nevertheless rough rate constants can be calculated, and Table 3 lists the values derived and also the rate of loss of traces of nitrous acid in the 0·01M stabilizer solution. Also included is the rate of production of nitrous acid by the autocatalytic oxidation of plutonium(III) when the latter is present at 2×10^{-6}M. (This level is

TABLE 3—*Rates of Reaction of Stabilizers with Nitrous Acid in* 30% *TBP/HPT at* 20°C *Stabilizer and Nitrous Acid both* 0·01M

$[HNO_3]_{org}$ (M)	First Order Rate Constant (min^{-1})	Second Order Rate Constant ($min^{-1}mole^{-1}l$)	Destruction of HNO_2 by 0·01M Stabilizer. Rate per unit HNO_2 conc.	Autocatalytic Production of HNO_2 by 2×10^{-5}M Pu(III). Rate per unit HNO_2 conc.
Phenylhydrazine				
0·174	0·092	20·0	−0·200*	—
0·399	0·337	58·2	−0·582*	0·076
0·738	4·81	—	−4·81†	0·585
o-Methylphenylhydrazine				
0·174	0·0599	44·1	−0·441*	—
0·399	0·399	101·5	−1·01*	0·076
0·738	0·971	—	−0·97†	0·585

* Derived from second order rate constant.
† Derived from first order rate constant.

appropriate to the organic phase of the feed stage of a mixer-settler contactor with plutonium fully reduced). The value is calculated from the k^* value (see p. 149). It is seen that *o*-methylphenylhydrazine reacts about twice as rapidly as phenylhydrazine itself; this is less than was

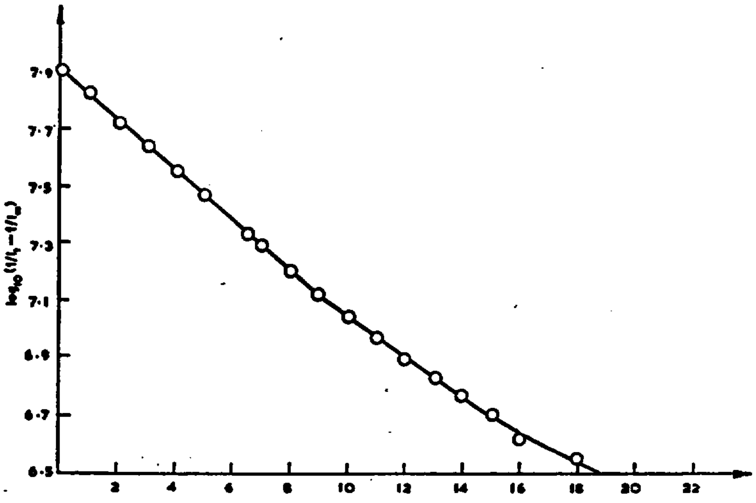

FIG. 7—Rate Plot for Autocatalytic Oxidation of Pu(III) at 20°C in 30% TBP in HPT.

HNO_3	0·286M
Initial Pu(III)	$5·76 \times 10^{-5}$M

hoped for, but is in line with results in the literature on nitrosation.[14] Table 3 also shows that the rate of removal of nitrous acid is about an order of magnitude greater than its rate of production in a mixer-settler. In our plutonium(IV)–uranium(IV) rate runs with 10^{-4}M plutonium(IV), at complete reduction the rate of formation and rate of loss must be almost exactly balanced.

Other Possible Stabilizers

Amines for use as stabilizers in a mixer-settler system must be of moderate base strength. A strong base will be entirely protonated in acid solutions and will therefore not extract into an organic phase. A weak base will not have sufficient electron density on the nitrogen atom to react rapidly with the electrophilic nitrosating agent. A large number of organic amines with pK_a in the range 0–5, listed in Appendix 2, were tested without success. They were nearly all insoluble in the HNO_3–TBP–HPT phase. Hydrazoic acid was studied in more detail since the azide ion is an extremely powerful nucleophile and the weak

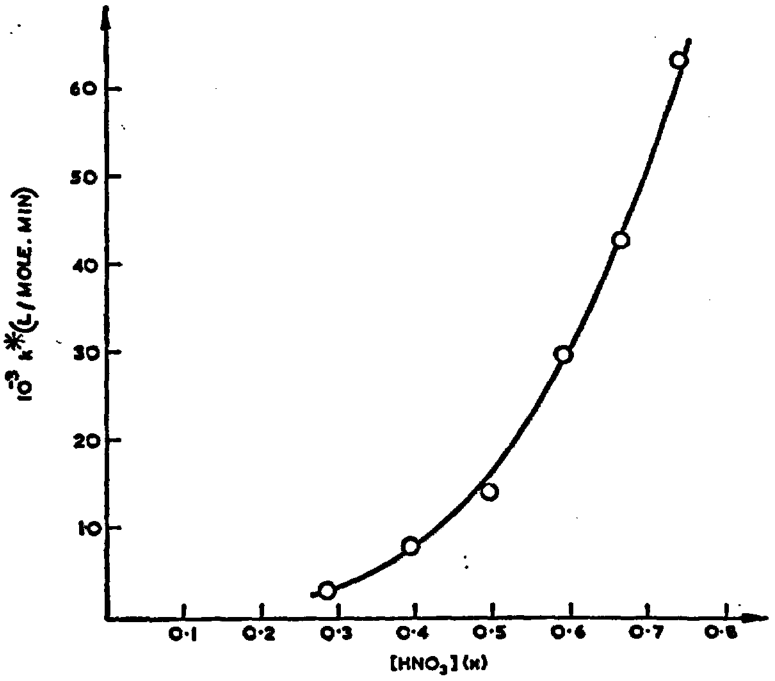

FIG. 8—Variation of Autocatalytic Pu(III) Oxidation Rate with HNO_3 Concentration in 30% TBP in HPT.

acid character of hydrazoic acid should lead to ready extraction into the organic phase. Its distribution coefficient was found to be 2·33, 1·50 and 1·08 when the aqueous phase concentration of HNO_3 was 0·25, 0·5 and 1·0M respectively. The experiments were at room temperature with 30% TBP. An attempted plutonium(IV)–uranium(IV) reaction with 0·73M nitric acid, 0·05M hydrazoic acid at 11·95°C in 30% TBP was however unsuccessful. The plutonium(IV) concentration was 1×10^{-4}M and the uranium(IV) 1×10^{-2}M.

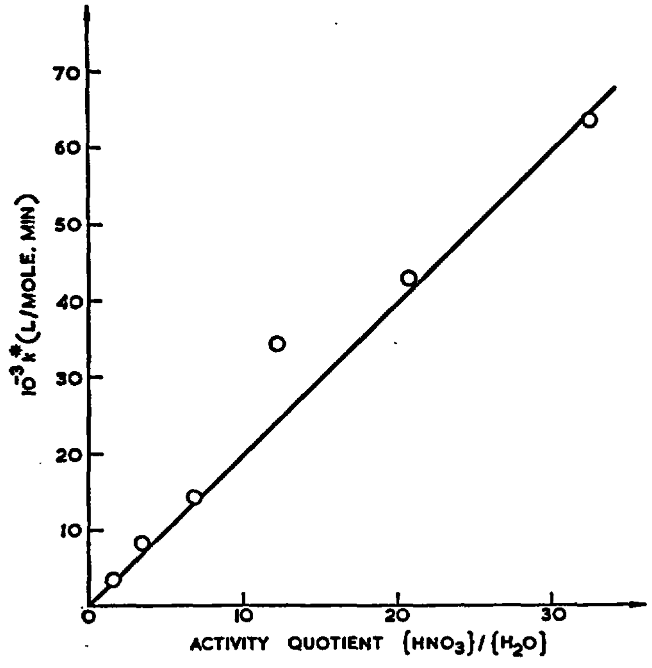

FIG. 9—Rate Constant against Activity Quotient for Oxidation of Pu(III) by HNO_3 in 30% TBP in HPT.

Rate of Autocatalytic Oxidation of Plutonium(III) in Nitric Acid in 30% TBP

We have examined the rate of oxidation of plutonium(III) when added to a nitrous acid-free solution of nitric acid in 30% TBP in the absence of stabilizer. Appendix 3 derives the rate law for the variation of current with time and the variation of this rate constant with nitric acid concentration. Fig. 7 shows a typical rate plot, based on the rate law, and Fig. 8 a plot of k^{*} (defined in Appendix 3) against nitric acid concentration. The curvature apparent in Fig. 7 shows that the rate law is not obeyed strictly, so not all the assumptions made in deriving it can be rigorously correct; nevertheless there is a fair period at the beginning of the reaction when the law constitutes a good approximation. As expected, a plot of k^* against $\{HNO_3\}/\{H_2O\}$ gave a straight line as shown in Fig. 9.

The steep fall in rate at the lower nitric acid concentrations is of doubtful advantage technologically since the rate of reaction of stabilizers with nitrous acid varies in the same direction. The evidence does suggest, however, that below 0·4M nitric acid, the stabilizer rate decreases less steeply with nitric acid concentration than the plutonium(III) rate. The dependence on acidity of the production rates of nitrous acid in presence of uranium(IV) and uranium(VI) must be determined before the technological significance of Fig. 8 can be assessed.

CONCLUSIONS

(a) The poor DF_{Pu} values which have been obtained on the uranium stream when using uranium(IV) as reductant are due to nitrous acid build up in the organic phase. This occurs mainly in the settlers and is due to the fact that existing stabilizers do not extract into the organic phase.

(b) Phenylhydrazine is a stabilizer which does dissolve to a limited extent in the organic phase, but the relative rates are such that it only functions at lowered temperatures. At this juncture, the only confident recommendation is for operation with phenylhydrazine at 0°C. Residence times in typical mixer-settler systems may then be only just sufficient for complete reduction of the plutonium(IV).

(c) If a stabilizer could be found which is more soluble in the organic phase than phenylhydrazine and reacts more rapidly with nitrous acid it would be possible to obtain good decontamination factors at ordinary temperatures.

(d) The indications are that choice of a flowsheet with low nitric acid concentrations favours nitrous acid destruction.

EXPERIMENTAL

Materials

Dicaesium Hexanitratouranate(IV). This salt was prepared by the method of Woodhead.[16] Titrations with ceric sulphate showed that oxidation to the extent of about 10% per annum was taking place. Fresh samples were prepared every three months and the compound was used as a standard substance.

TBP and Diluents. TBP was purified by the method of Alcock *et al.*[17] HPT and Odourless Kerosene (OK) were used without pretreatment. Except where stated otherwise, the diluent used was HPT.

Hydrazine. Pure hydrazine was prepared by distilling the hydrate from an excess of solid sodium hydroxide.

Phenylhydrazine. The commercial material was purified by distillation under reduced pressure. The distillate was sealed into glass ampoules under nitrogen atmosphere.

o-Methylphenylhydrazine. This was prepared by diazotization of *o*-toluidine and reduction of the diazonium salt with stannous chloride. The method followed exactly that of Bullock and Hand.[18] Fine white needles of m.p. 63°C (literature 59°C) were obtained and were stable when perfectly dry. Solutions of the material developed an orange-yellow colour very rapidly, presumably by oxidation.

Plutonium Nitrate Solution and Plutonium Metal. These were supplied by Windscale and Calder Works, U.K.A.E.A.

Other reagents. A.R. grade material was used.

Preparation of Stock Plutonium(III) and Plutonium(IV) Organic Solutions

Plutonium(IV) in Pure TBP. 100 μl of aqueous plutonium(IV) solution (260 g/l plutonium(IV), 8M HNO_3) was dissolved completely by 10 ml pure TBP.

Plutonium(IV) in 30% *TBP/HPT.* 1 ml of the aqueous solution (as above) was first saturated with sodium nitrate. 100 μl of this solution was then shaken with 10 ml 30% TBP and the organic phase removed.

Plutonium(III). Plutonium metal (0·225 g) was placed in a boiling tube with 1 ml water. 0·35 ml of 72% perchloric acid was then added dropwise, with cooling by immersing the tube in water. The product was then made up to 100 ml with pure TBP.

All these solutions were standardized by α-counting.

Equipment

Potentiometer. Conventional potentiometric equipment was used with the addition of a very sensitive Tinsley galvanometer (1800 mm/μA) for use with 10^{-5}M aqueous plutonium and 10^{-4}M organic plutonium solutions.

Rotating Platinum Microelectrode. The electrode consisted of a 0·010 in diameter platinum wire sealed at right angles to the axis of a 5 mm soda glass tube. About 2 mm of the wire projected. The glass tube was sealed with resin on to a brass tube mounted vertically in ball races and driven by bevel gears. The drive was taken horizontally from a synchronous motor (Honeywell recorder chart drive type 362481–1). Electrical contact was made through a column of mercury in the glass tube. The rotation speed was 150 r.p.m.

Examination of polarograms showed that, in the aqueous phase, a potential could always be found such that contributions from the acid, hydrazine and uranium(IV) species cancelled and the current was proportional to plutonium(IV) concentration. In the organic phase, it was necessary to assume that the background current due to uranium(IV) was constant.

Cell. A three compartment cell was used containing the reference electrode, isolating solution and working electrode respectively. The working electrode compartment contained a nitrogen inlet through a no. 4 glass sinter of 1 cm diameter in the base of the cell. A P.T.F.E. (Teflon) sleeve was used round the rotating electrode so as to reduce contact between the cell atmosphere and the exterior to a minimum. Two side arms on this compartment allowed a nitrogen supply to be brought in over the surface of the solution and the plutonium(IV) sample to be added.

Method of Determining Rate Constant

Rate determinations were carried out in a thermostat.

Aqueous Solutions. The uranium(IV) solution was prepared by weighing the dicaesium hexanitratouranate(IV) into previously standardized acid. Nitrogen gas was passed through the solution during a 20 min period of temperature adjustment. Rotation of the electrode was then commenced and the potentiometer adjusted to a position of zero current (usually about 0·2 V against S.C.E.). A small quantity (usually 10 μl) of the stock plutonium(IV) solution was then added. The nitrogen supply was then switched to flow over the surface of the solution. Since the plutonium(IV) concentration was always less than 1% of the uranium(IV) concentration the rate form is pseudo-first order and the rate constant is obtained by the slope of a plot of log (galvanometer reading) against time.

Organic Solutions. The organic phase was prepared for the run by shaking with aqueous nitric acid. Uranium(IV) and stabilizer were then added to this solution in the form of caesium hexanitratouranate(IV) and stock solution of stabilizer in TBP in HPT. Caesium nitrate was centrifuged off. The run was conducted in the same way as in aqueous phase experiments.

Preparation of Solutions for Spectrophotometric Experiment

Solution (a) (p. 143) was prepared by extracting 0·25 ml of aqueous plutonium(IV) solution (260 g/l in nitric acid) with 25 ml of 30% TBP, a few crystals of sodium nitrate being added to salt out the plutonium(IV). The mixture was centrifuged and separated.

Solution (b) was prepared by shaking 15 ml of 30% TBP with a stock aqueous nitric acid solution, centrifuging, separating and then shaking with a weighed quantity of caesium hexanitratouranate(IV) and decanting.

Reaction of Stabilizers with Nitrous Acid

The reaction of *o*-methylphenylhydrazine with nitrous acid was studied by mixing 250 μl of a 0·785M solution of the stabilizer with 25 ml of the nitrous acid solution. In the case of phenylhydrazine however, owing to the tendency to precipitate in 30% TBP containing nitric acid, a solution of 0·02M phenylhydrazine in this medium was prepared and mixed with an equal volume (10 ml) of 0·01M nitrous acid in the same organic nitric acid solution.

The nitrous acid solution was prepared by weighing out AnalaR sodium nitrite, dissolving it in the minimum quantity of water (3 drops) and extracting with the organic nitric acid solution.

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APPENDIX 1. RATE OF REACTION IN A TWO-PHASE SYSTEM

Notation: p	plutonium(IV) concentration (molar)
V	volume (litres)
k'	pseudo-first order rate constant (min^{-1})
Suffix o	organic phase
Suffix a	aqueous phase
P	total quantity (moles) of plutonium(IV) ($=p_oV_o + p_aV_a$)
R	phase volume ratio ($=V_o/V_a$)
D	distribution coefficient for plutonium(IV)

An amount $k_op_oV_odt$ of plutonium(IV) will be lost from an isolated organic phase by reduction in time dt, and an amount $k_ap_aV_adt$ from an isolated aqueous phase. The total loss is therefore

$$-dP = k_op_oV_odt + k_ap_aV_adt.$$

The total loss will be the same if the two phases are in contact, because any transfer between phases which may occur has no effect on the total quantity of plutonium(IV).

If the rate of transfer is fast compared with the rate of reduction, then at any instant

$$D = p_o/p_a,$$

and

$$p_o = DP/(DV_o + V_a)$$

$$p_a = P/(DV_o + V_a).$$

Hence

$$dP/dt = -(Dk_oV_o + k_aV_a)P/(DV_o + V_a)$$
$$= -(DRk_o + k_a)P/(DR + 1),$$

i.e. the two-phase pseudo-first order rate constant is

$$k' = (DRk_o + k_a)/(DR + 1).$$

APPENDIX 2: AMINES STUDIED AS POSSIBLE STABILIZERS

The following amines were insoluble in HNO_3—TBP—HPT:

Methyl anthranilate
1-Amino-2-naphthol-4-sulphonic acid
m-Aminobenzoic acid
Sulphanilic acid
2-Aminophenol-4-sulphonic acid
p-Aminobenzoic acid
sym-Diphenylguanidine
o-Phenylenediamine
1-Amino-8-naphthol-4-sulphonic acid
n-Octadecylamine
Guanidine

m-Aminophenol and diphenylamine were soluble, but neither of these materials was successful in a U(IV)–Pu(IV) reduction at 11·95°C, 0·73M HNO_3, 0·01M U(IV), 1×10^{-4}M Pu(IV).

APPENDIX 3. KINETICS OF THE AUTOCATALYTIC OXIDATION OF PLUTONIUM(III) IN NITRIC ACID

We assume the reaction scheme given on pp. 140–1, and for simplicity ignore any slight ionization of N_2O_4 and HNO_2.

For the rate of the Pu(III)–N_2O_4 reaction we have

$$d[\mathrm{Pu(III)}]/dt = -k[\mathrm{Pu(III)}][N_2O_4]$$

(*k* is the rate constant). For the equilibrium between HNO_2 and HNO_3 we have

$$\{HNO_2\}\{HNO_3\} = \text{constant} \times \{N_2O_4\}\{H_2O\},$$

which under the conditions of any one run (constant $[HNO_3]$ etc.) reduces to

$$[HNO_2] = \alpha[N_2O_4]$$

(α = constant). The extent of reaction x is given by

$$\begin{aligned} x &= [\mathrm{Pu(III)}]_0 - [\mathrm{Pu(III)}] \\ &= [\mathrm{Pu(IV)}] \\ &= 2([\mathrm{N_2O_4}] + [\mathrm{HNO_2}] - [\mathrm{N_2O_4}]_0 - [\mathrm{HNO_2}]_0) \end{aligned}$$

(suffix 0 denotes values at time $t = 0$; $[\mathrm{Pu(IV)}]_0$ is assumed to be zero). Writing

$$a = [\mathrm{Pu(III)}]_0$$

$$b = [\mathrm{N_2O_4}]_0 + [\mathrm{HNO_2}]_0$$

we therefore obtain

$$\begin{aligned} dx/dt &= k(a - x)(b + x/2)/(1 + \alpha) \\ &= k^*(a - x)(b + x/2), \end{aligned}$$

where $k^* = k/(1 + \alpha)$. On integration this gives

$$\ln [a(b + x/2)/b(a - x)] = (a/2 + b)k^*t.$$

Since b is very small, it can be neglected in comparison with a and, over all but the very early part of the reaction, in comparison with x. The equation therefore simplifies to

$$\ln [ax/2b(a - x)] = \tfrac{1}{2}ak^*t$$

or

$$\ln (1/x - 1/a) = -\tfrac{1}{2}ak^*t - \ln 2b.$$

Now the polarographic current i is given by

$$\begin{aligned} i &= \beta[\mathrm{Pu(IV)}] + \gamma[\mathrm{HNO_2}] \\ &= \beta x + \alpha\gamma x/2(\alpha + 1) \end{aligned}$$

(β and γ are constants; b has again been neglected). i is therefore proportional to x:

$$i = \theta x$$

(θ = constant). Noting that $x \to a$ as $t \to \infty$, we obtain finally

$$\ln (1/i - 1/i_\infty) = -\tfrac{1}{2}ak^*t - \ln 2\theta b$$

($i \to i_\infty$ as $t \to \infty$). The form of this equation would not be affected by assuming $\mathrm{NO^+}$ as the reactive intermediate, instead of $\mathrm{N_2O_4}$, nor by assuming that $\mathrm{NO^+}$ or $\mathrm{N_2O_4}$ rather than $\mathrm{HNO_2}$ contributes to the polarographic current, nor yet again by allowing for ionization of $\mathrm{N_2O_4}$ and $\mathrm{HNO_2}$ (though the meaning of the constants would then be different).

The rate constant k^* derived from the slope of plots of $\ln (1/i - 1/i_\infty)$ against t is related to the absolute rate constant k by the equation

$$\begin{aligned} k &= k^*(1 + \alpha) \\ &= k^*(1 + \text{constant} \times \{H_2O\}y_{N_2O_4}/\{HNO_3\}y_{HNO_2}) \end{aligned}$$

where the y's are activity coefficients. Since N_2O_4 and HNO_2 are dilute and essentially unionized, $y_{N_2O_4}/y_{HNO_2}$ probably does not vary greatly from unity. Moreover in the aqueous phase the known value of the equilibrium constant of the HNO_2–HNO_3 reaction to give N_2O_4 is such that $\alpha \gg 1$, and the same is probably true in the organic phase. We should therefore expect k^* to be approximately proportional to $\{HNO_3\}/\{H_2O\}$.

DISCUSSION ON PRECEDING THREE PAPERS

E. López-Menchero At Eurochemic we have done some work on the stability of uranium(IV) in aqueous nitric acid, in 30% TBP in Shellsol-T containing nitric acid, and in emulsions of both phases. This work will be described in a forthcoming Eurochemic report. I think that it is of interest to mention that we have observed complete stability of the uranium(IV) for 8 h either in an organic phase or in emulsions ($[HNO_3]_{aq}$, *ca.* 2M) in the absence of light and under a nitrogen atmosphere. We found a half-life of about 5 h for uranium(IV) when the solutions were air sparged and all the other parameters were kept the same. It is important to remember that the total nitrate concentration of the organic phase is rather low (about 0·5M) and the acidity is a few tenths molar. The partial hydrolysis of uranium(IV) in the organic phase leading to UOH^{3+} would favour an oxidation mechanism such as that proposed by Halpern, J. and Smith, J. G. (*Can. J. Chem.* 34, 1419 (1956)). Another fact which seems to call for the intervention of oxidants other than nitrous acid for uranium(IV) is that, as Streeton, R. J. W. and Jenkins, E. N. showed in AERE–R 3938 (1962), the hydrazine in solution in the aqueous phase destroys the nitrous acid present in the organic phase when the two phases are intimately mixed.

A. Naylor A half-life of 5 h for uranium(IV) is of a similar order to the values found at Windscale for solvent phases (20% TBP in kerosene) in equilibrium with *ca.* 2M nitric acid. The Eurochemic results further substantiate the conclusion that there was no loss of uranium(IV) in our preliminary counter-current trial (in which very little air was present) other than by plutonium(IV) oxidation.

J. H. Miles The stability of pure solutions of uranium(IV) does not indicate stability in the presence of plutonium. As our paper shows, the plutonium is in effect a catalyst.

X. L. R. Talmont We too have observed that the rate of oxidation of uranium(IV) in the solvent is faster at low acid concentrations, as would be expected from the reaction:

$$U^{4+} + 2H_2O + 2e^- \rightarrow UO_2^{2+} + 4H^+.$$

R. J. W. Streeton We have carried out experiments in which aqueous solutions of uranium(IV) and nitric acid were shaken with 30% TBP in kerosene in closed vessels under an atmosphere of air or oxygen. In the latter case there was little or no oxidation of the uranium(IV) while in the former case there was considerable oxidation which appeared to be proportional to the available oxygen. The rate of oxidation was greatest at low nitric acid concentrations.

H. A. C. McKay We found a catalytic effect in the oxidation of uranium(IV) by air in TBP phases. When the uranium(IV) was prepared electrolytically, oxidation at low acidities was quite rapid; but when $Cs_2U(NO_3)_6$ was used, oxidation was negligible. Addition of possible impurities failed to increase the rate in the latter case, so the catalyst has not been identified. We do not, however, believe that aerial oxidation plays any significant part under plant conditions.

C. S. Schlea It is interesting that the stage to stage decontamination factor quoted by Dr. Naylor in his mixer-settler experiments is about the same as we reported earlier (DP–809 (1963)) in the experiments with centrifugal contactors in which contact times are much smaller.

A. Naylor Our stage to stage decontamination factors do rise to about 10 in some instances, but fall off towards the 'top' of the box (stage 1).

J. H. Miles The centrifugal contactor was operated at 30–35°C instead of 20°C. This might counterbalance the shorter residence times.

C. S. Schlea When using hydrazine, hydrazoic acid will be present as a result of reaction between hydrazine and nitrous acid. We do not know if the hydrazoic acid and the nitrous acid react in the organic phase but we do have information (given in DP–808 (1963)) that hydrazoic acid reacts faster with nitrous acid than does hydrazine in the aqueous phase.

J. H. Miles We found that hydrazoic acid would not act as a stabilizer for an isolated organic phase. This does not mean that it does not react with nitrous acid in the organic phase but only that it does not react fast enough to beat the autocatalytic reaction with plutonium(III).

B. F. Warner It should not be assumed that hydrazine is absent in the organic phase of a settler. The finely dispersed aqueous phase can represent some 5% of the total aqueous phase, when averaged over the depth of the settler.

J. H. Miles Our case does not rest on the isolation of the organic from the aqueous phase in a settler. Unless the rate of reaction of nitrous acid with hydrazine is infinitely fast there must be a small standing concentration of nitrous acid in the mixer, since it is being produced by some or all of the reactions I mentioned. This will lead to a standing concentration of plutonium(IV) also, the rate of production by autocatalytic oxidation of plutonium(III) being balanced by the reduction of plutonium(IV) by uranium (IV).

J. Rydberg In a mixer-settler it may be possible to control the redox potential to some extent in the settler stages (e.g. concentration control of the uranium(IV) by electrolytic reduction or oxidation) at each stage. Could Dr. Naylor tell me if this possibility has been explored?

A. Naylor We have not investigated this type of system but practical difficulties may be encountered. If you were using electrolytic reduction you probably would not require uranium(IV) as a reductant.

D. J. Crouse Could Dr. Naylor tell me if back-mixing due to entrainment of aqueous phase in the solvent could be of importance in limiting the decontamination from plutonium?

A. Naylor Back-mixing can affect decontamination factors but we do not think it is the cause of the limiting DF_{Pu} values in our case. Our stage by stage data from the contactors show high efficiency in each stage.

W. Baxter Could M. Talmont tell me what percentage of the original plutonium is found in the solvent from the backwashing column in his flowsheet?

X. L. R. Talmont Less than 0·5%. It should decrease if the efficiency of the backwashing column is improved. In mixer-settler runs the loss of plutonium in the solvent was less than 0·1 mg/l.

B. Gaudernack I should like to make a comment on the paper presented by Dr. Naylor. I found the results most interesting as we have had similar experience in our reprocessing pilot plant at Kjeller. When we started using uranium(IV) as a reductant for plutonium a couple of years ago, we introduced the reductant close to the organic feed inlet in our partitioning column. The solution was 5M nitric acid containing the uranous nitrate and 0·1M hydrazine. We fed 0·5M nitric acid containing 0·1M hydrazine to the top of the column but we found that the plutonium losses to the uranium product stream became about twice as large as they had been previously when using ferrous sulphamate as reductant. In trying to improve this situation we found that by reducing the acidity of the upper reductant stream to 0·1–0·2M and at the same time including a small amount of uranium(IV), about 0·005M, in this stream, the plutonium losses were restored to the 'normal' level. We have not studied the problem systematically and consequently are unable to state how much of the beneficial effect should be attributed to the reduction of the acidity and how much to the presence of uranium(IV) in the upper aqueous stream.

H. A. C. McKay With reference to M. Talmont's paper, the incomplete reduction of the plutonium in Fig. 5 (p. 112) is not due to slow reaction and the amount left unreduced is too great to be explained by the presence of plutonium(VI) or by an impurity in the solvent. The only explanation left, of those so far put forward, is therefore the competing reactions involving nitrous acid, discussed in our paper.

Notes

Nitrogen Tracer Studies on the Decomposition of Hydroxylamine in Nitric Acid

Michael S. Garley, Kieran G. Phelan, and Geoffrey Stedman *
Chemistry Department, University College of Swansea, Singleton Park, Swansea SA2 8PP

The reaction of low concentrations of $[^{15}NH_3OH]^+$ with isotopically normal nitric acid produces singly labelled N_2O with equal amounts of ^{15}NNO and $N^{15}NO$ and very little $^{15}N_2O$, but as $[^{15}NH_3OH^+]$ increases there is an increasing amount of $^{15}N_2O$ formed, the highest observed yield being $[^{15}N_2O]/[N_2O]_{total} = 0.23$. This increase occurs as the system changes from one in which there is a net increase in nitrous acid due to oxidation of hydroxylamine to one in which hydroxylamine acts as a net scavenger of nitrous acid.

During a study of the oxidation of hydroxylamine by nitric acid to form dinitrogen monoxide + nitrous acid, tracer experiments were carried out[1] using $[^{15}NH_3OH]^+$ reacting with isotopically normal HNO_3. Mass-spectrometric analysis of the N_2O showed it to be singly labelled with ^{15}N, the tracer being distributed equally between the two nitrogens, with only a small percentage of doubly labelled N_2O. This distribution of tracer was very similar to that observed in the N_2O formed in the reaction between HNO_2 and $[^{15}NH_3OH]^+$ and clearly indicated that the N_2O was formed by reaction (1). The small proportion of $^{15}N_2O$ enabled us to reject mechanisms involving the dimerisation of nitroxyl (HNO) of the type often postulated as a pathway for the formation of N_2O such as those shown in equations (2) and (3). However in two experiments some 20% of $^{15}N_2O$ was observed, and this has now been investigated in more detail to see if it required the presence of a nitroxyl dimerisation pathway. Recent work[2] has placed emphasis on pathways of this type.

$$HNO_2 + [NH_3OH]^+ \longrightarrow N_2O + H_2O + [H_3O]^+ \quad (1)$$

$$[NH_3OH]^+ - 2e \longrightarrow HNO + 3H^+ \quad (2)$$

$$2HNO \longrightarrow N_2O + H_2O \quad (3)$$

Experimental

Hydroxylamine hydrochloride, labelled with ^{15}N to 97 atom % (Prochem), was used without further purification. The procedures used were identical to those described previously.[1] For some experiments at high $[^{15}NH_3OH^+]$ the amount of N_2O liberated was rather small, and this reduced the accuracy of the mass-spectrometric analyses. Experiments were carried out at ambient temperature, 20 ± 2 °C.

Computer simulations used a standard Runge–Kutta numerical integration program to integrate the differential equations corresponding to our published mechanism for this reaction. This program has already been used to simulate aspects of the kinetic behaviour of the hydroxylamine–nitric acid–nitrous acid system and the results have been published.[3] It was modified to distinguish between nitrogen atoms derived from $[^{15}NH_3OH]^+$, assumed 100% isotopic purity, and from the nitric acid and nitrous acid which were assumed to be 100% ^{14}N at the start of reaction. The calculations were made for the same system studied previously, 4.28 mol dm^{-3} nitric acid containing initially 8×10^{-4} mol dm^{-3} nitrous acid at 25 °C, with a range of different initial hydroxylamine concentrations. The rate constants used were the same as those used previously and gave the following expressions for the rate of reactions (4)—(6) and (9): $V(4) = 2.28\ [HNO_2]$ mol dm^{-3} s^{-1}; $V(9) = 20.6\ [HNO_2][NH_3OH^+]$ mol dm^{-3} s^{-1}; $V(6)/V(5) = 0.187\ [NH_3OH^+]^{-1}$.

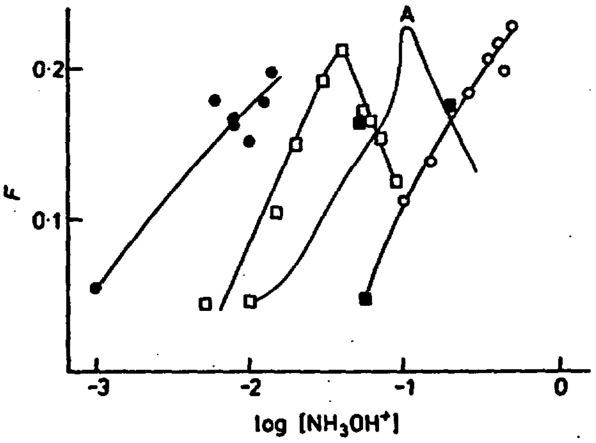

Figure. Plot of the fraction of doubly labelled dinitrogen monoxide, *F*, as a function of log $[NH_3OH^+]$. $[HNO_3]$/mol dm^{-3} = 2.5 (●), 3.5 (□), and 5.0 (○). ■, Earlier measurements described in ref. 1; A, curve calculated for reaction in 4.28 mol dm^{-3} nitric acid

Results and Discussion

The most complete set of experiments covered the range $[^{15}NH_3OH^+]$ = 0.005—0.5 mol dm^{-3} in 3.5 mol dm^{-3} nitric acid, and are shown in the Figure. At low $[^{15}NH_3OH^+]$ there is only a small amount of $^{15}N_2O$, but as the hydroxylamine concentration increased the ratio of the ion-current peaks $F = 46/(44 + 45 + 46)$ rises, reaches a maximum, and then decreases. Less extensive measurements in 5.0 mol dm^{-3} nitric acid showed a similar rise in *F* with $[^{15}NH_3OH^+]$, but over the more limited concentration range studied there was no evidence for a maximum. The results for 2.5 mol dm^{-3} nitric acid are clustered, and the line drawn through them is only justified by analogy with the results for the other two acidities. Included in the Figure are the earlier observations that stimul-

Table. Computer simulation of the decomposition of $[^{15}NH_3OH]^+$ in 4.28 mol dm^{-3} nitric acid at 25 °C

$10^2[^{15}NH_3OH^+]_0$/mol dm^{-3}	1	2	4	7	7.5	10	15	20	25	30
100 F	4.5	7.9	12.5	16.5	17.9	22.7	20.0	17.4	15.2	13.5
$10[HNO_2]_\infty/[^{15}NH_3OH^+]_0$	5.19	4.35	3.34	2.30	1.86	0	0	0	0	0
$10[N_2O]_\infty/[^{15}NH_3OH^+]_0$	6.39	6.51	6.70	6.95	7.06	0.65	0.17	0.093	0.062	0.046
$10^2[^{15}NH_3OH^+]_\infty$/mol dm^{-3}	0.0	0.0	0.0	0.0	0.0	9.2	14.7	19.8	24.8	29.8

ated the present work. The results show some scatter, and this may reflect problems in obtaining reproducible mixing. Solutions of nitric acid and of the hydroxylamine salt were in separate legs of a two-legged vessel. As reaction was sometimes very rapid, it is doubtful if reproducible mixing conditions were attained.

We base our discussion on the mechanism in equations (1) and (4)—(8), discussed in detail in previous papers.[1,3]

$$H^+ + HNO_2 + [NO_3]^- \longrightarrow N_2O_4 + H_2O \qquad (4)$$

$$N_2O_4 + H_2O \longrightarrow H^+ + HNO_2 + [NO_3]^- \qquad (5)$$

$$N_2O_4 + NH_2OH \longrightarrow N_2O_3 + HNO + H_2O \qquad (6)$$

$$N_2O_4 + HNO \longrightarrow N_2O_3 + HNO_2 \qquad (7)$$

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \qquad (8)$$

For low $[NH_3OH^+]$, $V(6) \gg V(5)$ and most of the N_2O_4 formed in (4) is hydrolysed back as shown in (5). The rapid formation and hydrolysis of N_2O_4 by (4) and (5) provides a pathway by which labelled nitrogen in HNO_2 is rapidly exchanged with the large excess of isotopically normal nitric acid. Thus although labelled HNO_2 is formed by oxidation of $^{15}NH_2OH$, the exchange reaction ensures that all the N_2O formed in (1) is derived from normal HNO_2 and $[^{15}NH_3OH]^+$, giving rise to equal amounts of ^{15}NNO and $N^{15}NO$.

As the concentration of hydroxylamine increases, an increasing proportion of the N_2O_4 is trapped by hydroxylamine, and $V(6) \gg V(5)$. Thus the route by which $H^{15}NO_2$ is exchanged with the large excess of nitric acid is removed, and the nitrous acid that reacts with $[^{15}NH_3OH]^+$ in (1) is a mixture of isotopically normal HNO_2 and $H^{15}NO_2$ derived from the route (6) and (7), $^{15}NH_2OH \longrightarrow H^{15}NO \longrightarrow H^{15}NO_2$. Thus the N_2O will be a mixture of $^{15}N^{15}NO$, ^{15}NNO, and $N^{15}NO$. If there were no exchange of nitrogen between HNO_2 and nitric acid, then a simple calculation shows that one should get 33.3% of doubly labelled N_2O and 66.6% of singly labelled N_2O. This will be an overestimate, because even if $[NH_3OH^+]$ was sufficiently high to ensure complete trapping of N_2O_4 at the start of the reaction, as the reaction proceeds hydroxylamine will be consumed and $V(6)/V(5)$ must fall. In the last stages of reaction the value of $[NH_2OH]$ will be low and the exchange reaction (4) + (5) will proceed.

Further insight can be obtained by use of a computer program to integrate numerically the differential equations corresponding to (1) and (4)—(8), distinguishing between nitrogen atoms derived from $[^{15}NH_3OH]^+$ and those from HNO_2 and HNO_3. The integration was initially carried out using a set of rate constants for 4.28 mol dm^{-3} nitric acid that were used in calculations previously reported. This gave curve A in the Figure. The maximum in the plot of F against log $[NH_3OH^+]$ is reproduced satisfactorily, and the curve falls almost midway between the points measured for 3.5 and 5.0 mol dm^{-3}. The calculations show that the maximum in F is associated with a change in chemistry. At low values of $[NH_3OH^+]$ the nitrite-generating reactions (6)—(8) dominate the nitrite-scavenging process (1) and reaction involves a net formation of the catalytic species HNO_2. All the hydroxylamine is destroyed, $[HNO_2]_\infty$ has a finite value, and $[NH_3OH^+]_\infty = 0$. At higher values of $[NH_3OH^+]_0$ the nitrite-scavenging process dominates, and all the HNO_2 is consumed before the $[NH_3OH]^+$ has completely reacted, *i.e.* $[HNO_2]_\infty = 0$ and $[NH_3OH^+]_\infty$ has a finite value. At these higher concentrations of $[^{15}NH_3OH]^+$ only a small amount of the hydroxylamine is oxidised to $H^{15}NO_2$ and the relative amounts of doubly and singly labelled N_2O depend on the amount of isotopically normal HNO_2 present initially and the amount of $H^{15}NO_2$ generated by the oxidation of $[^{15}NH_3OH]^+$. The yield of N_2O formed in the reaction with high concentrations of hydroxylamine is calculated to be quite low, and this probably accounts for the small amounts found in some of our experiments.

Although this approach enables us to understand the shape of the curve of F against log $[NH_3OH^+]$, and the occurrence of a maximum, its quantitative success depends upon the values assigned to the rate constants. The curve for 4.28 mol dm^{-3} nitric acid fits well into the pattern of experimental results, but attempts to extend the calculation to 2.5, 3.5, and 5.0 mol dm^{-3} were less successful. The shapes of the calculated curves were similar to that of A, and were in the expected sequence along the abscissa, but agreement with the experimental points was not good. Agreement can be improved by changing the values assigned to the rate constants, but we were not able to predict accurately the appropriate value on a chemical basis. The value for the rate constant for reaction (1) in nitric acid was predicted from measurements on this reaction in perchloric acid, and at a mineral acid concentration of several mol dm^{-3} there could well be substantial specific salt effects. It has been shown[4] that there are marked differences between perchloric and sulphuric acids. In predicting the variation of $V(5)/V(6)$ with $[HNO_3]$ we needed an acidity function to describe the protonation of NH_2OH. We used the H_0 acidity function, but recognise that it may not adequately describe the protonation of NH_2OH, as it uses indicator bases with a very different structure. With these uncertainties, and the limitations of the isotopic results, we do not think it worth pursuing these calculations further.

We conclude that the appearance of a substantial proportion of doubly labelled N_2O is a sign that the hydroxylamine–nitric acid–nitrous acid system is near the borderline where the chemical role of hydroxylamine changes from an autocatalytic decomposition that forms nitrous acid to a process whereby it scavenges nitrous acid. Although the dimerisation of nitroxyl is a well established route for the formation of N_2O in many reactions there is no compelling evidence to include it in the mechanism for the decomposition of hydroxylamine in nitric acid.

Acknowledgements

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Contribution from the Chemistry Division,
Oak Ridge National Laboratory,[1] Oak Ridge, Tennessee 37830

Oxidation of Hydroxylamine by Nitrous and Nitric Acids

M. R. BENNETT, GILBERT M. BROWN,* L. MAYA, and F. A. POSEY

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The kinetics of the reaction of hydroxylamine with nitrous acid and with nitric acid were studied in an acidic nitrate medium. The mechanism of the reaction with nitrous acid in an acidic perchlorate medium, proposed by previous workers, is O-nitrosation of the hydroxylammonium ion; our data are consistent with this mechanism at an ionic strength of 2 M. The data at higher ionic strength (3 and 4 M), when compared to an extended treatment of the proposed mechanism, indicate either a deviation from this mechanism at high acid concentration or a change in one of the principal species in solution. Raman and UV spectroscopies were unable to verify a change in the species. In the reaction of hydroxylamine with nitric acid, we identified HNO_2, N_2O, and N_2 as products. This reaction is autocatalytic in HNO_2, and the distribution of products is dependent on the initial concentrations of HNO_2, NH_3OH^+, and HNO_3. The product N_2O derives from the nitrosation of NH_3OH^+. The reaction of the intermediate N_2O_4 with NH_2OH produces HNO_2, and N_2 is postulated to arise from the reaction of HNO_2 with hyponitrous acid, which is an intermediate in the nitrosation of NH_3OH^+. A kinetic model is partially successful in rationalizing the distribution of products.

Introduction

The reaction of hydroxylamine with nitrous acid (eq 1) in

$$HNO_2 + NH_2OH \rightarrow N_2O + 2H_2O \qquad (1)$$

dilute concentrations of mineral acids has been extensively investigated. These studies include detailed kinetic measurements in $HClO_4$ solution[2] and product distributions by ^{15}N and ^{18}O isotopic labeling.[2b,3–5] At low pH and low concentrations of HNO_2, the reaction in perchlorate and sulfate media is postulated to proceed by O-nitrosation of the hydroxylammonium ion. This determination was made on the basis of the rate expression for reactions of the *N*-methyl and *O*-methyl derivatives of hydroxylamine;[2b] the latter reagent reacts considerably slower in acidic solution by the traditional diazotization path. Kinetics and stoichiometric studies of reaction 1 have been extended to nitric acid solutions in this report.

The oxidation of hydroxylamine by nitric acid becomes kinetically important at HNO_3 concentrations greater than ~2 M. A study of the reaction has been published by Pembridge and Stedman.[6] The reported reaction products were HNO_2 and N_2O, and HNO_2 was identified as an essential catalyst.[6] We find a difference in the yields of HNO_2 and N_2O from that observed by these workers, and we also find N_2 as a significant product at low initial concentrations of NH_3OH^+.

Experimental Section

A stock solution of hydroxylammonium nitrate was prepared by the following procedure. Reagent grade $(NH_3OH)_2SO_4$ was dissolved in water, and most of the SO_4^{2-} was precipitated by the addition of a slightly less than stoichiometric amount of $Ba(NO_3)_2$. The solution was filtered and the remaining SO_4^{2-} replaced with NO_3^- by passing the solution through an anion-exchange resin bed (Dowex 2-X8) in the NO_3^- form. The solution was analyzed for NH_3OH^+ content by the BrO_3^- titration method suggested by Vogel.[7] Analysis for SO_4^{2-} by the ORNL Analytical Chemistry Division indicated less than 2 × 10^{-2} M SO_4^{2-} in a 2 M NH_3OH^+ solution. This $(NH_3OH)NO_3$ solution was extremely stable; its titer changed by less than 5% over a period of 20 months. Solutions of HNO_2 were generated immediately before use by adding a weighed amount of $NaNO_2$ to the desired electrolyte or by adding an aliquot of a solution of $NaNO_2$ to the reaction mixture. Solutions of $NaNO_2$ and HNO_2 were protected from strong room light. Other chemicals (HNO_3 and $LiNO_3$) were of reagent grade and were used without further purification. Solutions of HNO_3 were initially sparged with an inert gas to remove NO_x.

The yields of gaseous products were determined by gas chromatography (Shimadzu GC5A) or by total gas volume with a 0–10 psia pressure transducer. Helium was used as a blanket gas and carrier gas for analysis of products by GC. Blank experiments indicated the procedure was satisfactory to eliminate atmospheric contamination. Samples for analysis were withdrawn with a pressure-lock syringe through rubber serum caps. The yield of HNO_2 produced by the reaction of hydroxylamine with nitric acid was determined spectrophotometrically on a Pye-Unicam Model SP8-100, Cary Model 15, or a Gilford updated Beckman DU spectrophotometer. Sample compartments of the spectrophotometers were maintained at 25 °C with circulating water baths. The majority of HNO_2 determinations were carried out with air-saturated solutions; several experiments with Ar- or He-saturated solutions indicated no change within experimental error. The presence of a gas space over the solutions was not a factor since the HNO_2 yields in the experiments described above and yields in the stopped-flow spectrophotometer were identical. (The latter instrument by its design does not leave a gas space above the solution.) GC experiments indicated NO was not a significant product of the reaction at ambient temperatures although evidence for NO was obtained at temperatures above 65 °C. The experiments were conducted under conditions such that ≥0.01 mol of NO/mol of NH_3OH^+ could be detected. We assume the origin of NO at higher temperatures (>65 °C) was decomposition of HNO_2.

Slower kinetic experiments to determine the rate of appearance or disappearance of HNO_2 ($t_{1/2} > 20$ s) were carried out with one of the spectrophotometers mentioned above at the 372-nm adsorption maximum of HNO_2. Faster reactions were monitored in a kinetic stopped-flow spectrophotometer. This instrument consisted of a thermostated (25 °C) Aminco-Morrow stopped-flow mixing apparatus adapted to fit a Beckman DU monochromator. The tungsten lamp was powered by a Hewlett-Packard Model 6264B dc power supply. Changes in transmitted light were monitored with an RCA Model 6903 photomultiplier tube with standard operational amplifier current-to-voltage conversion circuitry; these changes were recorded on a storage oscilloscope or a conventional recorder. Changes in transmitted light were converted to changes in absorbance by the relationship $A_t - A_\infty = \log (I_\infty/I_t)$, where A is the solution absorbance, I is the intensity of the transmitted light, and the subscripts t and ∞ refer to any time t and time infinity, respectively. (The subscript 0 will be used to refer to time zero.) Although this spectrophotometer is an unreferenced single-beam instrument, the photomultiplier tube and lamp-power supplies are well regulated; signals were stable for more than 1 h after being warmed up.

The Raman spectra of solutions of hydroxylammonium nitrate were obtained with a Ramanor Model HG-27 spectrophotometer. An argon ion laser (Spectra Physics Model 164) operating at the 514.5-nm line was the excitation source.

Results and Discussion

Species Present in Solutions of Nitrous Acid and Hydroxylamine in Nitric Acid. In aqueous solution, NH_3OH^+ has a

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pK_a of 5.96.[8] There is no evidence in the literature for further protonation of NH_3OH^+ in strong acid. The species present in dilute HNO_3 solution is therefore the hydroxylammonium ion. As noted in a later section, the results of kinetic studies of the reaction of HNO_2 with NH_3OH^+ suggest another species of NH_3OH^+ may be generated at high HNO_3. Raman spectra of hydroxylammonium nitrate solutions were examined for evidence of association of NH_3OH^+ with NO_3^- or HNO_3. The solutions were 0.1 M in NH_3OH^+ in an electrolyte made of varying proportions of $LiNO_3$ and HNO_3, with a total ionic strength of 4.0 M. The solutions examined contained 0.2, 0.5, 2.0, and 3.0 M HNO_3. In addition, a solution with no added electrolyte was examined, as well as a 1.8 M $(NH_3OH)NO_3$ solution with no background electrolyte. The most prominent bands in all the spectra are those due to the symmetric stretching vibration of NO_3^- at 1047 cm^{-1} [9] and the NH and OH stretching frequencies which appear as a broad band in the 3500-cm^{-1} region.

It was hoped that a band due to a higher order complex such as $HNO_3 \cdot NH_3OH \cdot NO_3$ could be observed. The spectra in all cases showed a single symmetrical band for the $\nu_1(NO_3^-)$ vibration. Apparently if the postulated complex was present, the change in the $\nu_1(NO_3^-)$ vibration was not different enough from the free ion, which was present in a relatively large excess, to be detected. The OH and NH stretching bands are too broad to detect any change among the solutions examined. Higher order complexes such as ion pairs therefore cannot be ruled out. However, evidence for the association of molecular HNO_3 with neutral molecules in nonaqueous media is well-defined.[10]

The species present in dilute aqueous solutions of HNO_2 have been discussed in a recent review.[11] The pK_a of HNO_2 is 3.15,[8] and therefore no appreciable concentration of NO_2^- is present in the acid solutions employed in this study. The equilibria to be considered are given in eq 2–4. The equilibrium constant for reaction 2 is 3×10^{-3} M^{-1}.[12] The absorbance of HNO_2 solutions in perchloric acid is reported to obey Beer's law for concentrations of ≤0.05 M.[13] Similar results were found in this study for NO_3^- solutions.

$$2HNO_2 \rightleftarrows N_2O_3 + H_2O \qquad (2)$$

$$HNO_2 + H^+ \rightleftarrows NO^+ + H_2O \qquad (3)$$

$$HNO_2 + HNO_3 \rightleftarrows N_2O_4 + H_2O \qquad (4)$$

The UV spectrum of HNO_2 in $LiNO_3$–HNO_3 solutions (4.0 M ionic strength) shows the characteristic "four finger" pattern with well-defined maxima at 387, 372, and 359 nm, although the high energy maximum at ~347 nm is distorted in very dilute solutions by the NO_3^- background. At the 372-nm peak, there is no deviation from Beer's law in the HNO_2 concentration range 4×10^{-3}–3.2×10^{-2} M (3.0 M HNO_3) with ϵ_{372} 55.9 ± 0.7 M^{-1} cm^{-1}. Furthermore, a plot of A_{372} vs. A_{387} is linear with a zero intercept. At the concentrations of HNO_2 employed in this study, a negligible fraction of total nitrous acid existed as N_2O_3. In the concentration range in which the absorbance is directly proportional to $[HNO_2]_T$, we find no systematic variation of the extinction coefficient with an increase in $[HNO_3]$ at constant $[NO_3^-]_T$. The average value of ϵ_{372} in 1 M HNO_3 ($[HNO_2] = 1.2 \times 10^{-2}$ M) is 55.9 ± 1.1 M^{-1} cm^{-1}. In agreement with the results of Longstaff and Singer,[14] there is no evidence for any appreciable conversion of HNO_2 to NO^+ or N_2O_4 at $[HNO_3] \leq 4$ M. Therefore, the principal N(III) species present in the nitric acid solutions employed in this study is molecular nitrous acid. However, the species NO^+ and N_2O_4 will be postulated as reactive intermediates.

Table I. Observed First-Order Rate Coefficients for the Disappearance of HNO_2 as a Function of Hydroxylamine and Nitric Acid Concentrations at 25 °C

μ, M	$[H^+]$, M	$[NH_3OH^+]_0$, M	k_{obsd}, s^{-1}	a_{H^+}, M
2.0	0.20	0.10	0.255	
2.0	0.50	0.10	0.56	
2.0	1.50	0.10	1.12	
2.0	1.90	0.10	1.28	
2.0	1.00	0.10	1.06	
2.0	1.00	0.20	1.90	
2.0	1.00	0.25	2.49	
2.0	1.00	0.40	4.39	
2.0	1.00	0.65	5.98	
2.0	1.00	0.75	6.42	
4.0	0.20	0.10	1.65	0.255
4.0	0.30	0.10	2.22	0.381
4.0	0.50	0.10	2.91	0.633
4.0	1.00	0.10	2.80	1.254
4.0	2.00	0.10	1.88	2.469
4.0	2.00	0.20	3.96	2.469
4.0	3.00	0.10	1.01	3.634
4.0	3.90	0.10	0.64 ± 0.08	4.648

Reaction of Hydroxylamine with Nitrous Acid. The stoichiometry of reaction 1 was confirmed at 1 M HNO_3 by measurement of the N_2O produced in the reaction of excess NH_3OH^+ with HNO_2. The kinetics of reaction 1 were readily separated from other reactions at lower concentrations of HNO_3 (<2 M). At higher concentrations of HNO_3, the kinetics of the desired reaction were separable by using relatively high initial concentrations of NH_3OH^+.

The disappearance of HNO_2 was measured in the presence of a tenfold or greater excess of NH_3OH^+. In all cases plots of log $(A_t - A_\infty)$ vs. time were linear for 3.5–4 half-lives. These plots indicate the reaction is first order in $[HNO_2]_T$. Although the initial concentration of HNO_2 was not systematically varied, the observed rate constants are independent of $[HNO_2]_0$ in the range 4×10^{-3}–1.2×10^{-2} M. Rate measurements at a total ionic strength of 2.0 M (maintained by adding $LiNO_3$) and at a constant HNO_3 concentration of 1.0 M were determined as a function of the initial NH_3OH^+ concentration. These determinations indicate the reaction is also first order in $[NH_3OH^+]$. The reaction kinetics were also measured as a function of HNO_3 concentration at ionic strengths of 2.0 and 4.0 M. The observed first-order rate coefficients as a function of $[HNO_3]$, $[NH_3OH^+]$, and ionic strength are summarized in Table I.

A mechanism for reaction 1 in acidic solution has been proposed by Stedman and co-workers.[2] The reaction pathway involves O-nitrosation of the hydroxylammonium ion (eq 5–9).

$$HNO_2 + H^+ \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} NO^+ + H_2O \qquad (5)$$

$$NO^+ + NH_3OH^+ \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} \underset{\text{I}}{NH_3ONO^+} + H^+ \qquad (6)$$

$$NH_3ONO^+ \xrightarrow{k_7} ONNH_2OH^+ \qquad (7)$$

$$ONNH_2OH^+ \rightarrow \text{HONNOH (cis and trans)} + H^+ \qquad (8)$$

$$\text{HONNOH (cis)} \xrightarrow{\text{fast}} N_2O + H_2O \qquad (9a)$$

$$\text{HONNOH (trans)} \rightarrow N_2O + H_2O \qquad (9b)$$

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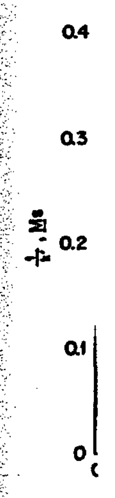

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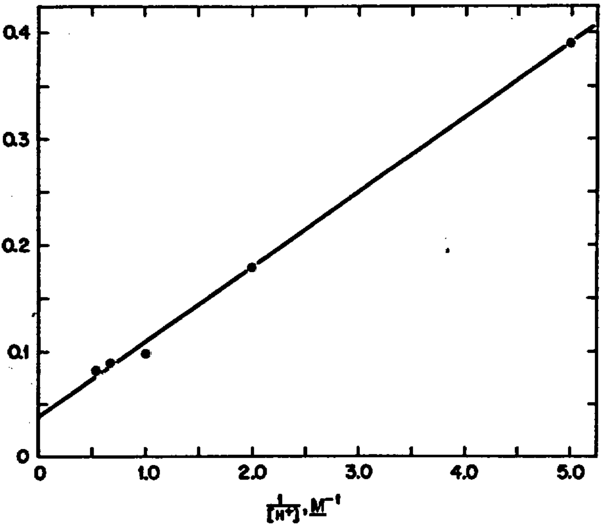

Figure 1. Plot of $1/k'$ vs. $1/[H^+]$ for the reaction of hydroxylammonium ion with nitrous acid at 2.0 M ionic strength (25 °C).

The isomerization of the intermediate (I) was proposed to become the rate-limiting step at high acid concentrations. A steady-state treatment of NO^+ and intermediate (I) leads to the rate equation (10). In deriving this equation, terms in

$$\frac{-d[HNO_2]}{dt} = \frac{d[N_2O]}{dt} = \frac{k_5k_6/k_{-5}[HNO_2][NH_3OH^+][H^+]}{1 + k_{-6}/k_7[H^+]} \quad (10)$$

the denominator containing $[NH_3OH^+]$ were neglected since the expermental results do not show rate saturation at high $[NH_3OH^+]_0$. The data obtained at 2.0 M ionic strength are in quantitative agreement with a rate expression of the form of eq 10. The observed second-order rate coefficient, k', is obtained by dividing the observed first-order rate coefficient by the concentration of NH_3OH^+. Figure 1 is a linear plot of $1/k'$ vs. $1/[H^+]$ as predicted by eq 10. The second-order rate coefficient was equated to the expression $a[H^+]/(1 + b[H^+])$ where a is k_5k_6/k_{-5} and b is k_{-6}/k_7. The calculated values of a and b are 14.2 ± 0.7 M^{-2} s^{-1} and 0.54 ± 0.08 M^{-1}, respectively. The interpretation of the parameter b changes if other approximations are used in deriving the rate expression. This will be discussed in more detail in a later section.

The experimental rate expression for reaction 1 is more complicated at 4.0 M ionic strength. The first-order dependence on $[HNO_2]$ and $[NH_3OH^+]$ is retained; however, the observed second-order rate coefficient, k', reaches a maximum between 0.5 and 1.0 M H^+ and decreases at higher nitric acid concentrations. This kinetic behavior was noted in earlier work for reaction 1 in a perchlorate medium at 3 M ionic strength ($NaClO_4$ and $HClO_4$).[2b] Equation 10 suggests that k' may become independent of $[H^+]$, but it does not predict a maximum. Previous workers[2b] suggested a maximum might be observed if k_7 decreased at higher ionic strength. The proposed mechanism (eq 5–9) involves the preequilibrium formation of NO^+. Therefore, the second-order rate coefficients were fitted to the calculated proton activities. Water and proton activity coefficients in the mixed $LiNO_3$–HNO_3 electrolyte were calculated by the method of Pitzer et al.[15-17] The appropriate equations were obtained from ref 16. The difference parameters θ and ψ were assumed to be 0; on the basis of results with

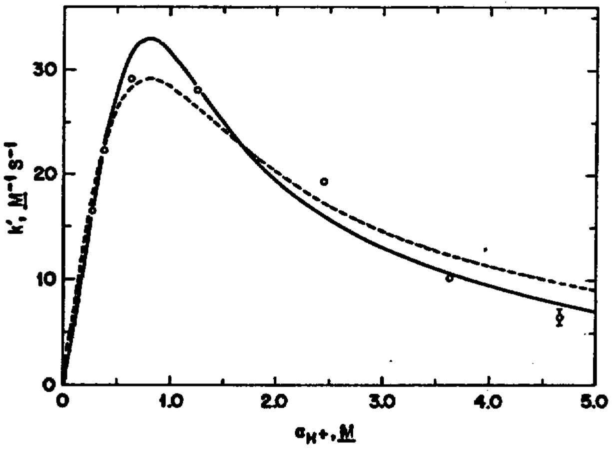

Figure 2. Plot of k' vs. a_{H^+}, the activity of protons, for the reaction of hydroxylammonium ion with nitrous acid at 4.0 M ionic strength (25 °C). Solid line is a nonlinear least-squares fit to eq 13. Dashed line is a fit by the procedure given in the Appendix.

(H^+, Li^+) mixed electrolytes of Cl^- and ClO_4^-, this is a valid approximation.[16] The appropriate constants for the $LiNO_3$ and HNO_3 system were those recommended by Pitzer and Mayorga.[17] The calculated activity of H_2O is virtually constant (1.232–1.235), and the proton activity is nearly directly proportional to concentration for $HNO_3 \leq 2$ M. The calculated proton activities are included in Table I.

A more exact treatment of the mechanism outlined in eq 5–9 can be used to generate a rate expression which predicts a maximum in k' as a function of proton activity or concentration. The approximations used in deriving the expression are outlined in detail in an appendix. The first-order rate of disappearance of $[HNO_2]$ is given by eq 11. The ratio

$$k_{obsd} \approx k_5k_6k_7[H^+][NH_3OH^+]/[(k_5[H^+] + k_{-5}) \times (k_{-6}[H^+] + k_7) + k_6[NH_3OH^+](k_5[H^+] + k_7)] \quad (11)$$

$k_{obsd}/[NH_3OH^+]$ is constant at constant $[H^+]$, and terms inverse in $[NH_3OH^+]$ will be neglected. The expression for the second-order rate coefficient, k', can be arranged in the form of eq 12. The important conclusions are that K_5 (=

$$k' \approx \frac{K_5k_6(a_{H^+})}{1 + (K_5 + (k_{-6}/k_7))(a_{H^+}) + K_5(k_{-6}/k_7)(a_{H^+})^2} \quad (12)$$

k_5/k_{-5}) is a rapidly established equilibrium and k_6 is the overall rate-limiting step. The form of this rate expression is a result of not requiring the species NO^+ and I to be at a steady state.

The second-order rate coefficients are shown as a function of proton activity in Figure 2. The solid line is a fit of the data to expression 13. A nonlinear least-squares fitting

$$k' = \frac{c(a_{H^+})}{1 + d(a_{H^+}) + f(a_{H^+})^2} \quad (13)$$

routine[18] was used to evaluate the constants c, d, and f which have best fit values of 52.4 ± 10.6 M^{-2} s^{-1}, -0.88 ± 0.35 M^{-1}, and 1.53 ± 0.21 M^{-2}, respectively. The negative value for the coefficient d indicates the expression in eq 12 is inadequate to describe the complete data set. The parameter d is extremely sensitive around the maximum. The data set is somewhat limited and may indicate the parameter d is near 0. The rate-determining step (eq 6) is expected to be highly dependent on ionic strength. Nitric acid is not completely dissociated at the higher concentrations employed in this study (the degree of dissociation of 4 M HNO_3 is 0.866).[19] The

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(15) Pitzer, K. S. *Acc. Chem. Res.* **1977**, *10*, 371–377.

(16) Pitzer, K. S.; Kim, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 5701–5707.

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constant ionic strength approximation will be less valid as the HNO_3 concentration increases. Therefore, the method of fitting the data outlined in the Appendix was used. This method heavily weights the data at low acid concentrations by using the initial slope, the maximum rate constant, and the proton activity at which the maximum occurs. The fitting parameters $c = 75$ M^{-2} s^{-1}, $k_{max} = 29$ M^{-1} s^{-1}, and $(a_{H^+})_{max} = 0.8$ M were employed; the calculated curve is shown as a dashed line in Figure 2.

The rate constants measured in this work can be compared to literature data by examining the initial slopes of plots of k' vs. $[H^+]$ at various ionic strengths and by identifying conditions in which a maximum is observed in plots of k' vs. $[H^+]$. The initial slope provides an estimate of K_5k_6 (eq A17). The second-order rate coefficients (k') measured in this work are in good agreement with values reported in other mineral acids at a similar acidity and ionic strength. Second-order rate coefficients have been reported[2b] as a function of $[H^+]$ at 0 °C in a mixed $HClO_4$–$NaClO_4$ electrolyte at a constant ionic strength of 3 M. These values were corrected to 25 °C with an activation energy of ~65 kJ mol^{-1},[6] the value measured in 4 M $HClO_4$. The corrected values for k' (at $[HClO_4] < [HClO_4]_{max}$) fall between those measured in this work at 2 and 4 M ionic strength. The second-order rate coefficient has also been reported in 1.0 M HNO_3 at variable ionic strength due to changes in $[NH_3OH^+]_0$.[20] Extrapolation to infinite dilution in $[NH_3OH^+]_0$ gives an estimated value for K_5k_6. The appropriate value in 0.1 M $HClO_4$ can be obtained from literature data[2a] after correction to 25 °C with an Arrhenius activation energy of ~61 kJ mol^{-1}. The variation in K_5k_6 with ionic strength is 2.5, 6, 14, 44, and 75 M^{-2} s^{-1} for 0.1,[2a] 1,[20] 2, 3,[2b] and 4 M ionic strength, respectively. If we ignore the ionic strength dependence of the activities of the species involved in equilibrium 5, then K_5k_6 should increase with increasing ionic strength because reaction 6 involves two positively charged reactants. This is the observed trend. The maximum rate constant, k'_{max}, in the 3 M perchlorate electrolyte occurs at an acid concentration of approximately 1.3 M.[6] The maximum in 4 M nitrate occurs at a proton activity of 0.8 M. Maxima were not observed at 2 M and lower ionic strengths. The approximate rate expression (eq 12) predicts the maxima should occur at lower proton activities at higher ionic strength due to the ionic strength dependence of k_{-6} (see eq A18). In a qualitative sense, the approximate expression (eq 12) for the second-order rate coefficient is in agreement with the data.

A comparison of the absolute values of the rate constants and the variation of the rate constants with ionic strength argues that the mechanism of this reaction is similar in perchlorate and nitrate media at lower acid concentrations. The trends are in agreement with the mechanism outlined in eq 5–9. Our data, obtained at constant ionic strength and correlated with the proton activity instead of a Hammett acidity function, and the literature data in 3 M perchlorate cannot be interpreted quantitatively within the framework of eq 12. The numerical values evaluated for K_5, k_6, and k_{-6}/k_7 are inconsistent. The value for K_5 is too large, and this results in a greater decrease in k' at higher acid concentration than would reasonably be expected. The basic reaction scheme is probably correct, but some changes appear necessary for quantitative agreement to high acid. Either one of the principal species in solution is changing or the acid dependence of the steps following nitrosation is incorrect. Spectroscopic measurements do not support a change of species. Previous workers[2b] have argued that the decrease in the second-order rate coefficient at higher acid concentrations is due to a decrease in k_7 with increasing ionic strength. The extended treatment of reactions 5–9 (eq 12) does not require this interpretation.

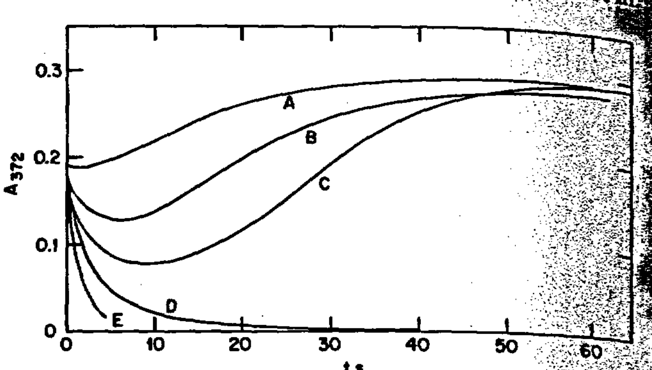

Figure 3. The absorbance of 372 nm vs. time for an initial HNO_2 concentration of ~4 × 10^{-3} M as a function of the initial hydroxylamine concentration (25 °C, 3 M HNO_3, 4 M ionic strength): A, 2 × 10^{-2} M; B, 3 × 10^{-2} M; C, 4 × 10^{-2} M; D, 5 × 10^{-2} M; E, 7 × 10^{-2} M (ϵ_{372} 50 ± 2 M^{-1} cm^{-1}).

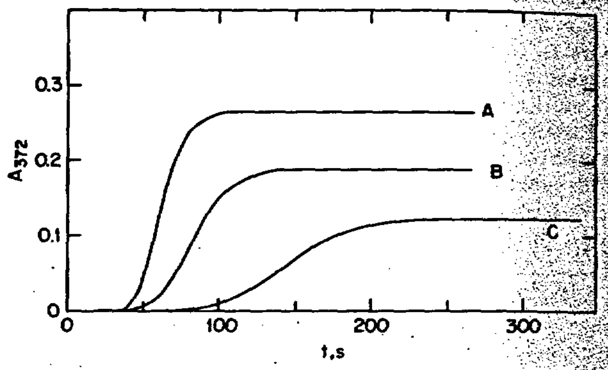

Figure 4. Time dependence of absorbance at 372 nm as a function of the initial hydroxylamine concentration with $[HNO_2]_0 < 4 \times 10^{-5}$ M (25 °C, 3 M HNO_3, 4 M ionic strength). Initial NH_3OH^+ concentration: A, 1.2 × 10^{-2} M; B, 6.0 × 10^{-3} M; C, 3.0 × 10^{-3} M.

Reaction of Hydroxylamine with Nitric Acid. At HNO_3 concentrations greater than 2 M, the reaction of HNO_3 with dilute solutions of hydroxylamine produces HNO_2 as a product. As noted by Pembridge and Stedman,[6] we find this reaction to be autocatalytic. The relative rate of this reaction should be put in perspective with the rate of the reaction of HNO_2 with NH_3OH^+, which was discussed in the previous section. Figure 3 shows the results of a series of experiments at constant acid with approximately the same initial concentration of HNO_2 and various initial concentrations of NH_3OH^+ (3.0 M H^+, $\mu = 4.0$ M). The time dependence of $[HNO_2]$ shown in Figure 3 illustrates the transition from the reaction described in eq 1 to more complex behavior. The decay of HNO_2 at the highest concentration of NH_3OH^+, 7 × 10^{-2} M, is exponential, and the ratio $k_{obsd}/[NH_3OH^+]_0$ is identical with that determined at higher concentration (Table I). At lower initial concentrations of NH_3OH^+, $[HNO_2]$ decreases at short times followed by an increase at longer times, resulting in a net increase in the concentration of HNO_2. At sufficiently low initial $[NH_3OH^+]$ (<2 × 10^{-2} M), the initial decrease in $[HNO_2]$ is not observed.

In the absence of deliberately added HNO_2, the appearance of HNO_2 is autocatalytic as shown in Figure 4 for $[H^+] = 3$ M. As previously indicated by Pembridge and Stedman,[6] HNO_2 is a necessary catalyst for the reaction of nitric acid with hydroxylamine. The induction period is highly dependent on the initial concentration of NH_3OH^+, and this is illustrated

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(19) Davis, W.; DeBruin, H. J. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1069–1083.

(20) Davis, W.; Maya, L.; Kelmers, A. D.; Valentine, K. Report ORNL-TM-7264; Oak Ridge National Laboratory: Oak Ridge, TN, 1980.

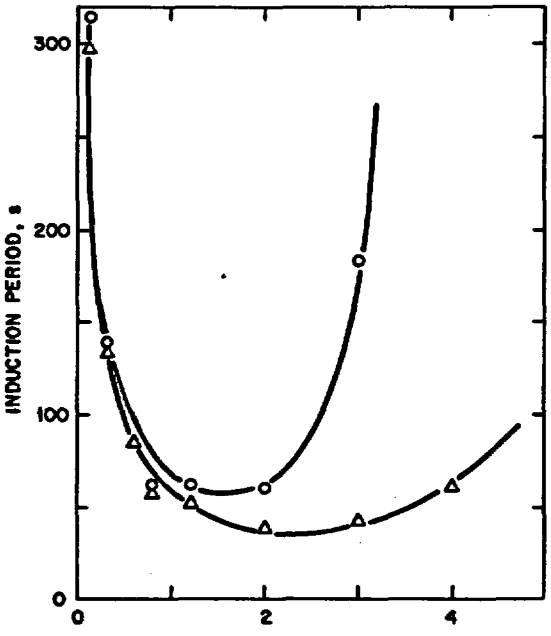

Figure 5. Plot of the induction period vs. the initial hydroxylamine concentration with an initial HNO_2 concentration of $<10^{-4}$ M (25 °C): circles, 3 M HNO_3; triangles, 4 M HNO_3.

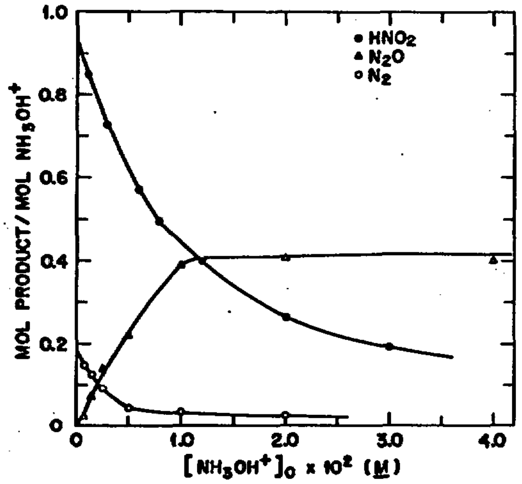

Figure 6. Plot of the yields of the products as a function of the initial concentration of hydroxylamine (25 °C, $[HNO_2]_0 < 10^{-4}$ M, 3 M H^+). Products: filled circles, HNO_2; triangles, N_2O; open circles, N_2.

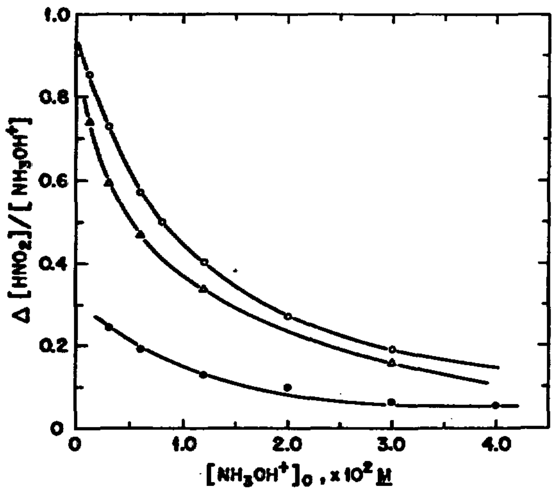

Figure 7. Plot of the net yield of HNO_2 vs. the initial NH_3OH^+ concentration for several initial HNO_2 concentrations (25 °C, 3 M H^+, 4 M ionic strength). $[HNO_2]_0$: open circles, $\leq 4 \times 10^{-5}$ M; triangles, 10^{-3} M; closed circles, 4×10^{-3} M.

Table II. Initial Rate of Net Formation of HNO_2 as a Function of $[HNO_2]_0$ and $[NH_3OH^+]_0$ at 25 °C (3.0 M H^+, 4.0 M Ionic Strength)

$10^3[NH_3OH^+]_0$, M	$10^3[HNO_2]_0$, M	$10^5 v_i$, M s^{-1}
1.20	0.36	0.71
1.20	0.82	1.14
1.20	1.65	1.45
3.00	0.39	2.00
3.00	0.79	3.41

in Figure 5. The induction period for this purpose is defined as the time when dA_{372}/dt is a maximum. Relatively concentrated solutions of hydroxylamine in nitric acid are stable for long periods of time. This behavior is explained by observations (Figure 5) that the induction period tends to increase at high hydroxylamine concentrations.

The observed products from the reaction of hydroxylamine with nitric acid are HNO_2, N_2O, and N_2. The yields of products are dependent on both the initial NH_3OH^+ and HNO_2 concentrations as well as the HNO_3 concentration. Figure 6 is a plot of the yields of these products as a function of the initial NH_3OH^+ concentration in the absence of deliberately added HNO_2 at a HNO_3 concentration of 3.0 M (μ = 4.0 M). The net yields of HNO_2 and N_2 reach a maximum as the NH_3OH^+ concentration approaches 0. The N_2O yield increases rapidly as the NH_3OH^+ concentration increases. Analogous results were observed at 4.0 M HNO_3. The extrapolated maximum HNO_2 yields are not particularly dependent on HNO_3 concentration although the range of $[HNO_3]$ investigated is limited. The dependence of the HNO_2 yield on the initial HNO_2 concentration was investigated in some detail at 3.0 M HNO_3. The results are shown in Figure 7 as a function of the initial NH_3OH^+ concentration. The maximum HNO_2 yield (net production of HNO_2) is obtained at low initial HNO_2 concentration. As previously observed by Pembridge and Stedman,[5] the maximum yield of HNO_2 for a fixed concentration of NH_3OH^+ occurs at an HNO_3 concentration of ~5.3 M. It is obvious from these data that the yields of the various products are controlled by the kinetics of competing reactions. Therefore, it seems inappropriate to ascribe a stoichiometry to this process.

Many of the results obtained in this work are in agreement with those previously reported.[6] However, one observation is in sharp contrast. We observe N_2 as a significant reaction product at low initial $[NH_3OH^+]_0$. This product was apparently missed because gas analyses were made at an initial concentration of NH_3OH^+ where N_2 is not a significant product. Second, we find no evidence for simple first-order dependencies on the concentration of HNO_2 and NH_3OH^+ in kinetic experiments measuring the rate of appearance of HNO_2 with low initial NH_3OH^+. At a constant NH_3OH^+ concentration, an increase in the initial HNO_2 concentration does shorten the induction period. Although the previous approach[6] is valuable as a first approximation, we observe that an initial concentration of HNO_2 approximately equal to the initial NH_3OH^+ concentration is required to completely remove the induction period. Under these latter conditions, a first-order rate of appearance of HNO_2 is not expected. Typical data are shown in Figure 8 for reaction in 3.0 M HNO_3 (μ = 4.0 M). An analogous effect was also observed in 4.0 M HNO_3. The data in Figure 8 and other data at 3.0 M H^+ were treated by the method of initial rates. The experimental results are summarized in Table II. The initial rate divided by the product of the initial HNO_2 and NH_3OH^+

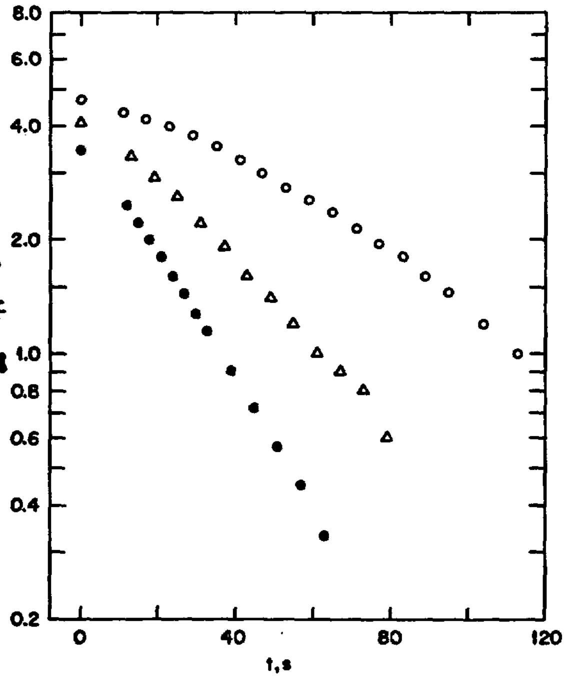

Figure 8. First-order plot for the net appearance of nitrous acid at 372 nm and an initial NH_3OH^+ concentration of 1.2×10^{-3} M (25 °C, 3 M H^+, 4 M ionic strength). Initial HNO_2 concentration: open circles, 3.8×10^{-4} M; triangles, 8.2×10^{-4} M; closed circles, 1.67×10^{-3} M.

concentrations provides a reasonable estimate of the second-order rate coefficient for the net appearance of HNO_2. The average value for the entries in Table II is 13 M^{-1} s^{-1}. Although the data show scatter, this analysis indicates the rate of net appearance of HNO_2 is competitive with the rate of disappearance of HNO_2 expected from reaction 1. The second-order rate coefficient for reaction 1 at 3 M H^+ is 10 M^{-1} s^{-1} (see Table I). The isotopic composition[6] of N_2O from the reaction of ^{15}N-labeled hydroxylamine and isotopically normal nitric acid supports reaction 1 as the origin of N_2O.

Pembridge and Stedman[6] suggested the reaction given by eq 14 is occurring in competition with eq 1 for the reaction

$$2HNO_3 + NH_2OH \rightarrow 3HNO_2 + H_2O \qquad (14)$$

of hydroxylamine. These workers suggested the reaction sequence in eq 15–19 to account for the observed autocatalytic

$$HNO_2 + H^+ + NO_3^- \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} N_2O_4 + H_2O \qquad (15)$$

$$N_2O_4 + NH_2OH \xrightarrow{k_{16}} HNO + N_2O_3 + H_2O \qquad (16)$$

$$N_2O_4 + HNO \rightarrow HNO_2 + N_2O_3 \qquad (17)$$

$$N_2O_3 + H_2O \rightarrow 2HNO_2 \qquad (18)$$

$$NH_3OH^+ \rightleftharpoons NH_2OH + H^+ \qquad (19)$$

appearance of HNO_2. On the basis of a steady-state treatment of N_2O_4 (the equilibrium described by eq 15 lies far to the left) and reaction 16 as the rate-determining step, the theoretical rate of appearance of HNO_2 by reaction 14 is given by eq 20.

$$\text{rate} = \frac{(k_{15}/k_{-15})k_{16}K_{19}[HNO_2][NH_3OH^+][NO_3^-]}{1 + (k_{16}/k_{-15})K_{19}([NH_3OH^+]/[H^+])} \qquad (20)$$

This mechanism appears reasonable since the inverse dependence on $[NH_3OH^+]$ is consistent with the relative stability of more concentrated solutions of hydroxylamine. At constant acid and nitrate concentrations, the general form of the rate expression is eq 21.

$$\text{rate} = \frac{g[HNO_2][NH_3OH^+]}{1 + h[NH_3OH^+]} \qquad (21)$$

We suggest that an additional reaction is occurring between HNO_2 and hyponitrous acid, $H_2N_2O_2$ (eq 8), to account for the observation of N_2 as a product. Hyponitrous acid is an intermediate in the nitrosation of NH_3OH^+ (eq 1 and eq 5–9). The reaction of HNO_2 with $H_2N_2O_2$ (eq 22) has been studied

$$HNO_2 + H_2N_2O_2 \rightarrow N_2 + HNO_3 + H_2O \qquad (22)$$

in some detail in aqueous perchloric acid by Buchholz and Powell[21] and by Hughes and Stedman.[22] The mechanism suggested by these workers is given by eq 23–26, where eq 24

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O \qquad (23)$$

$$NO^+ + H_2N_2O_2 \rightarrow HONNONO + H^+ \qquad (24)$$

$$HONNONO \rightarrow NO_2 + N_2 + \cdot OH \qquad (25)$$

$$NO_2 + \cdot OH \rightarrow HNO_3 \qquad (26)$$

is the rate-determining step. The experimentally observed rate law is eq 27, where h_0 is the Hammett acidity function (h_0 is

$$\frac{-d[HNO_2]}{dt} = \frac{d[N_2]}{dt} = (k + k_a h_0)[H_2N_2O_2][HNO_2] \qquad (27)$$

~25 for 3 M HNO_3). At 25 °C in perchloric acid, the experimentally determined values[21] of k and k_a are 0.4 M^{-1} s^{-1} and 0.08 M^{-2} s^{-1}; thus, the expected second-order rate constant under our conditions is given by eq 28. The importance of

$$k_{22} = (k + k_a h_0) \approx 2.4\ M^{-1}\ s^{-1} \qquad (28)$$

this reaction depends on the relative stability of $H_2N_2O_2$ in this medium. Literature reports suggest that *cis*-$H_2N_2O_2$ is short-lived in solution whereas *trans*-$H_2N_2O_2$ is relatively stable. Spectroscopic detection of $H_2N_2O_2$ is impossible due to the interference of the electrolyte medium.

The observed product yields can be accounted for, at least in a qualitative sense, by the competition of the four reactions eq 29–32. A quantitative treatment will be attempted for two

$$HNO_2 + NH_3OH^+ \rightarrow H_2N_2O_2 + H_2O + H^+ \qquad (29)$$

$$2HNO_3 + NH_3OH^+ \rightarrow 3HNO_2 + H^+ + H_2O \qquad (30)$$

$$HNO_2 + H_2N_2O_2 \rightarrow HNO_3 + N_2 + H_2O \qquad (31)$$

$$H_2N_2O_2 \rightarrow N_2O + H_2O \qquad (32)$$

limiting cases; in both a constant excess of HNO_3 and a low initial concentration of HNO_2 are present. (1) The yields of HNO_2 and N_2 are maximized and the yield of N_2O approaches 0 as the initial concentration of NH_3OH^+ approaches 0. (2) At higher initial concentration of NH_3OH^+, the yield of N_2O is relatively constant, N_2 is a minor product, and the yield of HNO_2 is approaching an asymptotic limit.

In the first case, the rate of reaction 31 appears to be fast compared to the other reactions. The net reactions to be considered are reactions 30 and 33. Reaction 33 is obtained

$$2HNO_2 + NH_3OH^+ \rightarrow HNO_3 + N_2 + 2H_2O + H^+ \qquad (33)$$

by combining reactions 29 and 31. Extrapolating the yields of HNO_2 and N_2 to an initial NH_3OH^+ concentration of 0 allows the ratio of rate constants to be interpreted at constant HNO_3 concentration. With reference to eq 10 and 21 and the appropriate stoichiometric factors, the rate of net appearance of HNO_2 is given by eq 34. An analogous treatment leads

$$\frac{d[HNO_2]}{dt} = 3g[HNO_2][NH_3OH^+] - 2k'[HNO_2][NH_3OH^+] \qquad (34)$$

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(21) Buchholz, J. R.; Powell, R. E. *J. Am. Chem. Soc.* 1965, *87*, 2350–2353.

(22) Hughes, M. N.; Stedman, G. *J. Chem. Soc.* 1963, 4230–4234.

to an expression for the disappearance of NH_3OH^+ (eq 35).

$$-\frac{d[NH_3OH^+]}{dt} = g[HNO_2][NH_3OH^+] + k''[HNO_2][NH_3OH^+] \quad (35)$$

The elimination of time from eq 34 and 35 gives eq 36, and

$$-\frac{d[HNO_2]}{d[NH_3OH^+]} = \frac{3g - 2k'}{g + k'} \quad (36)$$

integrations from the limits $[HNO_2]_{t=0}$ to $[HNO_2]_{t=\infty}$ and $[NH_3OH^+]_0$ to $[NH_3OH^+]_\infty$, the latter quantity being 0, give an expression for the yield (eq 37). The data in Figure 6 (3.0 M H^+, 4.0 M ionic strength) show the limiting yield of HNO_2 is 0.93; the calculated value of the ratio g/k' is 1.44. A treatment of the rate of appearance of N_2 (eq 38) leads to expression 39 for the yield.

$$\frac{[HNO_2]_\infty - [HNO_2]_0}{[NH_3OH^+]_0} = \frac{3g/k' - 2}{g/k' + 1} \quad (37)$$

$$\frac{d[N_2]}{dt} = k''[HNO_2][NH_3OH^+] \quad (38)$$

$$\frac{[N_2]_\infty}{[NH_3OH^+]_0} = \frac{k'}{g + k'} = \frac{1}{g/k' + 1} \quad (39)$$

The ratio g/k' calculated from the yield of N_2 in Figure 6 and eq 39 is 3.5, a value in poor agreement with that calculated above. The initial rate of the net appearance of HNO_2 at low $[NH_3OH^+]$ can be used to estimate the parameter g by using eq 34. The value of k' measured in 3 M H^+ is 10 $M^{-1}\ s^{-1}$. Thus the initial rate divided by the product of the initial concentrations of HNO_2 and NH_3OH^+ is $3g - 2k'$. Although there is some scatter in these data, the calculated ratio g/k' is 1.2 in reasonable agreement with the value estimated from the net yield of HNO_2.

In the second limiting region, reactions 29 and 32 are rapid compared to reaction 31. Reaction 31 is ineffective in scavenging the HNO_2 produced by reaction 30. We will, to a first approximation, ignore the small yield of N_2. The reactions to be considered are thus (1) and (30). In reaction 30, the higher concentration of NH_3OH^+ shifts the rate-determining step to the production of the reactive intermediate, N_2O_4 (see eq 15). The equations describing the time dependence of the concentrations of HNO_2, NH_3OH^+, and N_2 at constant $[H^+]$ are eq 40–42. The yields of HNO_2 and N_2 are calculated by integrating the ratios of eq 40 and 41 and eq 42 and 41, respectively (eq 43 and 44). The ratio g/h is equal to $k_{15}[H^+][NO_3^-]$, the first-order rate coefficient for formation of N_2O_4. The rate constant k_{15} was measured by Abel, Schmid, and co-workers[23] in a series of papers in which the kinetics and equilibrium of HNO_2 formation and decomposition were studied (eq 45). The rate of formation of HNO_2 was demonstrated to involve the intermediate formation of N_2O_4 (eq 15). The third-order rate constant, k^0_{15}, has the value $2.7 \times 10^{-2}\ M^{-2}\ s^{-1}$ at 25 °C and extrapolated to infinite dilution. A numerical rate constant appropriate to the conditions of this study is obtained from the relationship $k_{15} = k^0_{15}/(\gamma_{HNO_3})^2$,[24] where γ_{HNO_3} is the activity coefficient of nitric acid (see Table I). The calculated ratio g/h is thus $3.2 \times 10^{-1}\ s^{-1}$ at 3 M H^+. This value, combined with the measured value of 10 $M^{-1}\ s^{-1}$ for k' in this medium, can be used to calculate the yields of HNO_2 and N_2O as a function of the initial NH_3OH^+ concentration (eq 43 and 44). The value of g/h required to approximate the experimentally observed yields of HNO_2 and N_2O in Figure 6 is $\sim 5 \times 10^{-2}$–$10^{-1}\ s^{-1}$. These values are about a factor of 3–6 smaller than the value measured by Abel and Schmid.[24] The data of the latter authors were obtained in a dilute ionic medium, and the small amount of data available suggests the rate constant k_{15} decreases with increasing ionic strength. The detailed mechanism for the reaction 15 may be the reaction of the equilibrium concentration of NO^+ with NO_3^-. The rate of the reaction of oppositely charged ions is expected to decrease with increasing ionic strength. An absolute comparison of the experimental and calculated yields in this second limiting region does not appear feasible. A single value of the parameter $g/k''h$ will not simultaneously fit both the HNO_2 and N_2O yields, although the shapes of the curves are in reasonable agreement with eq 43 and 44.

$$\frac{d[HNO_2]}{dt} = 3g/h[HNO_2] - k''[HNO_2][NH_3OH^+] \quad (40)$$

$$-\frac{d[NH_3OH^+]}{dt} = g/h[HNO_2] + k''[HNO_2][NH_3OH^+] \quad (41)$$

$$\frac{d[N_2O]}{dt} = k''[HNO_2][NH_3OH^+] \quad (42)$$

$$\frac{[HNO_2]_\infty - [HNO_2]_0}{[NH_3OH^+]_0} = \frac{4g}{k''h[NH_3OH^+]_0} \ln\left[1 + \frac{k''h}{g}[NH_3OH^+]_0\right] - 1 \quad (43)$$

$$\frac{[N_2O]_\infty}{[NH_3OH^+]_0} = 1 - \frac{g}{k''h[NH_3OH^+]_0} \ln\left[1 + \frac{k''h}{g}[NH_3OH^+]_0\right] \quad (44)$$

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \quad (45)$$

Conclusions

The reaction of nitrous acid with hydroxylamine in acidic nitrate solutions follows the reaction scheme outlined by earlier workers. The second-order rate coefficients in HNO_3 solutions are in good agreement with those reported in $HClO_4$ solutions. A more exact treatment of the rate expression, based on the proposed mechanism, is in better agreement with the experimental data than correlations based on the Hammett acidity function. However, a deviation of the experimental results from those predicted by the model at high acid suggests some modification in the steps following the nitrosation of NH_3OH^+ may be appropriate.

The reaction of hydroxylamine with nitric acid is more ambiguous. Nitrogen is observed as a significant product at low initial concentrations of hydroxylamine. This previously unidentified product may result from the reaction of hyponitrous acid with nitrous acid. It is clear that several reactions are occurring simultaneously. A kinetic model is partially successful in rationalizing the distribution of products as a function of the initial hydroxylammonium ion concentration. The treatment presented in this work is not completely satisfactory, and other reactions may also be occurring. It seems clear that a determination of the rates and equilibrium constants of reactions 2–4 at relatively high nitric acid concentrations is essential for a better understanding of this complex system.

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Appendix

The mechanism for reaction of hydroxylammonium ion with nitrous acid (eq 5–9) can be expressed as the generalized reaction scheme of eq A1–A3 since both protons and hydroxylammonium ion are used in swamping excess. The differential equations describing the time dependence of the concentrations of species A, B, C, and D are eq A4–A7. At time zero and under the conditions of our experiments, the species A and B are initially present in the equilibrium concentrations $[A]_0$ and $[B]_0$ ($[B]_0 = k_{ab}[A]_0/k_{ba} = K_{ab}[A]_0$) and the species C and D are initially absent. The Laplace transform is taken of eq A4–A7, resulting in a series of four equations in four unknowns (eq A8–A11), where s is the Laplace variable and dependence of a species on s indicates the concentration of the species in the Laplace plane. Solution of eq A8–A11 for the variable $[A(s)]$ yields eq A12. The observed disappearance of $[HNO_2]_T$ is clearly exponential for greater than 90% of the reaction. Thus we are searching for a solution of the form of eq A13 which implies a Laplace transform of the form of eq A14. We recognize that higher powers of s refer to the time dependence of the concentration of species A at very short times. Therefore terms in s^2 and s in the numerator and terms in s^3 and s^2 in the denominator will be dropped. The resulting equation for the concentration of species A in the Laplace plane is then eq A15. Inverse Laplace transformation gives an expression for $[A(t)]$ which can be differentiated with respect to time (eq A16). We will use the definitions

$$A \underset{k_{ba}}{\overset{k_{ab}}{\rightleftharpoons}} B \tag{A1}$$

$$B \underset{k_{cb}}{\overset{k_{bc}}{\rightleftharpoons}} C \tag{A2}$$

$$C \xrightarrow{k_{cd}} D \tag{A3}$$

$$d[A(t)]/dt = -k_{ab}[A(t)] + k_{ba}[B(t)] \tag{A4}$$

$$d[B(t)]/dt = k_{ab}[A(t)] - (k_{ba} + k_{bc})[B(t)] + k_{cb}[C(t)] \tag{A5}$$

$$d[C(t)]/dt = k_{bc}[B(t)] - (k_{cb} + k_{cd})[C(t)] \tag{A6}$$

$$d[D(t)]/dt = k_{cd}[C(t)] \tag{A7}$$

$$(k_{ab} + s)[A(s)] - k_{ba}[B(s)] = [A]_0 \tag{A8}$$

$$k_{ab}[A(s)] - (s + k_{ba} + k_{bc})[B(s)] + k_{cb}[C(s)] = -K_{ab}[A]_0 \tag{A9}$$

$$k_{bc}[B(s)] - (s + k_{cb} + k_{cd})[C(s)] = 0 \tag{A10}$$

$$k_{cd}[C(s)] - s[D(s)] = 0 \tag{A11}$$

$$[A(s)] = [A]_0\{[s^2 + s(k_{ab} + k_{ba} + k_{bc} + k_{cb} + k_{cd}) + k_{ab}k_{cb} + k_{ab}k_{cd} + k_{ba}k_{cb} + k_{ba}k_{cd} + k_{bc}k_{cd}]/[s^3 + s^2(k_{ab} + k_{ba} + k_{bc} + k_{cb} + k_{cd}) + s(k_{ab}k_{bc} + k_{ab}k_{cb} + k_{ab}k_{cd} + k_{ba}k_{cb} + k_{ba}k_{cd} + k_{bc}k_{cd}) + k_{ab}k_{bc}k_{cd}]\} \tag{A12}$$

$$[A(t)] = (\text{constant}) \exp[-k_{obsd}t] \tag{A13}$$

$$[A(s)] = (\text{constant})\left[\frac{1}{s + k_{obsd}}\right] \tag{A14}$$

$$[A(s)] = [A]_0[(k_{ab}k_{cb} + k_{ab}k_{cd} + k_{ba}k_{cb} + k_{ba}k_{cd} + k_{bc}k_{cd})/(k_{ab}k_{bc} + k_{ab}k_{cb} + k_{ab}k_{cb} + k_{ba}k_{cb} + k_{ba}k_{cd} + k_{bc}k_{cd})]/[s + [k_{ab}k_{bc}k_{cd}/(k_{ab}k_{bc} + k_{ab}k_{cb} + k_{ab}k_{cd} + k_{ba}k_{cb} + k_{bc}k_{cd}k_{bc}k_{cd})]] \tag{A15}$$

$$-\frac{d[A(t)]}{dt} = k_{obsd}[A(t)] \tag{A16}$$

$$k_{obsd} = k_{ab}k_{bc}k_{cd}/(k_{ab}k_{bc} + k_{ab}k_{cb} + k_{ab}k_{cd} + k_{ba}k_{cb} + k_{ba}k_{cd} + k_{bc}k_{cd})$$

$$k_{ab} = k_5[H^+] \qquad k_{ba} = k_5[H_2O] \qquad k_{bc} = k_6[NH_3OH^+]$$
$$k_{cb} = k_{-6}[H^+] \qquad k_{cd} = k_7$$

and note the observed first-order rate coefficient divided by the initial NH_3OH^+ concentration is a constant at constant HNO_3 concentration. The resulting expression for the second-order rate coefficient as a function of acid concentration is eq A17. (In deriving this expression, terms inverse in $[NH_3OH^+]$ were neglected). This equation predicts k' as a function of acid should have a maximum. Experimental observation of the initial slope (S_{in}) in a plot of k' vs. $[H^+]$, the value of $[H^+]$ at which the maximum occurs, and the maximum rate constant are required to evaluate the parameters K_5, k_6, and k_{-6}/k_7. The value of $[H^+]$ at which the maximum occurs is obtained by differentiating eq A17 with respect to $[H^+]$, setting the derivative equal to 0, and solving for $[H^+]_{max}$.

$$k' = \frac{K_5k_6[H^+]}{1 + (K_5 + k_{-6}/k_7)[H^+] + K_5k_{-6}[H^{2+}]^2/k_7} \tag{A17}$$

$$([H^+]_{max})^2 = k_7/K_5k_{-6} \tag{A18}$$

Substitution of eq A18 in eq A17 gives the value of the maximum rate constant, k'_{max}:

$$k'_{max} = \frac{K_5k_6}{2(K_5k_{-6})^{1/2}/k_7 + K_5 + k_{-6}/k_7}$$

$$k'_{max} = \frac{S_{in}[H^+]_{max}}{2 + [H^+]_{max}(K_5 + k_{-6}/k_7)}$$

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KINETIC AND PRODUCT STUDIES ON THE DECOMPOSITION OF HYDROXYLAMINE IN NITRIC ACID

RORY J. GOWLAND and GEOFFREY STEDMAN*
Chemistry Department, University College of Swansea, Singleton Park, Swansea SA2 8PP, Wales

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Abstract—The kinetics and stoicheiometry of the decomposition of hydroxylamine in nitric acid have been investigated for the range of conditions where there is a change in function of hydroxylamine from acting as a nitrite scavenger to acting as a generator of nitrous acid. Borderline conditions for this change in function have been identified. Formation of nitrous acid is favoured by increase in [HNO_3], decrease in [NH_3OH^+] and increase in temperature. Some unusual kinetic phenomena have been observed in the borderline region; the nitrous acid concentration can decrease in the initial stages of reaction, pass through a minimum and then autocatalytically increase to a value greater than the initial value. The results are discussed in terms of the mechanism of reaction.

INTRODUCTION

Hydroxylamine has been proposed[1] as a possible reagent in nuclear fuel reprocessing for the reduction of Pu(IV) to Pu(III) in nitric acid solution. Such solutions may contain nitrous acid, which is a powerful catalyst in the re-oxidation of Pu(III) to Pu(IV)[2], and so the general chemistry of hydroxylamine in solutions containing nitric acid and nitrous acid is of interest. The most familiar reaction between nitrous acid and hydroxylamine is that involving the formation of dinitrogenmonoxide(1), and the mechanism has been studied in some detail[3]. However in a recent study

$$NH_3OH^+ + HNO_2 \rightarrow N_2O + H_3O^+ + H_2O \quad (1)$$

it was shown[4] that in sufficiently concentrated nitric acid medium another reaction could occur in which nitrous acid was generated rather than consumed (2). This reaction only occurs in the presence of nitrous acid,

$$NH_3OH^+ + 2HNO_3 \rightarrow 3HNO_2 + H_3O^+ \quad (2)$$

and is an autocatalytic process. It therefore seemed of interest to examine the conditions which determined the relative importance of reactions (1) and (2), and see if it was possible to define conditions for which (1) dominates (2) and vice-versa). In our previous study we found[4] that at low hydroxylamine concentrations, <0.01 M, the initial rate of formation of nitrous acid followed a simple second order equation at a fixed nitric acid concentration.

$$(d[HNO_2]/dt)_0 = k[HNO_2][NH_3OH^+].$$

Over the range 3–8 M nitric acid k varied only slightly, but when [HNO_3] was decreased below 3 M a critical concentration was reached, below which k decreased very sharply to zero. This "critical" concentration of nitric acid seemed to vary slightly with [NH_3OH^+], lower hydroxylamine concentrations corresponding to slightly lower critical nitric acid concentrations. These observations served as a guide in the choice of what concentrations of hydroxylamine and nitric acid to investigate in a search for borderline conditions.

EXPERIMENTAL

Materials. All the materials used were AnalaR grade chemicals, and were used without further purification. Hydroxylamine solutions were made up from the sulphate, in order to avoid any possible complications due to chloride ion in nitric acid.

Kinetic methods. Reaction was followed by monitoring the nitrous acid concentration spectrophotometrically at 370 nm in a Unicam SP700 with a thermostatted cell holder. Previous work[4] had shown that at this wavelength the only species with significant absorbance is nitrous acid. Reaction was started by adding a solution of hydroxylamine sulphate to a solution of nitrous acid in nitric acid. Nitric acid normally contains small (and variable) concentrations of nitrous acid, and we found it desirable to standardise our work by starting with a known nitrous acid concentration (generated from a solution of sodium nitrite). We found the mixing technique used to start the reaction to be a very important factor. Our early experiments involved injecting the hydroxylamine solution with a hypodermic syringe and needle into the nitric and nitrous acids contained in a spectrophotometer cell in the Unicam SP700, but this did not give sufficient reproducibility. Most experiments used a simple *T* piece mixing device made by drilling out a block of perspex: two syringes could be fitted into the block, and when the plungers were pressed simultaneously the solutions were mixed at a *T* junction and injected directly into the spectrophotometer cell. Although this gave satisfactory mixing it was not possible to obtain good initial rates of reaction over the first 10 sec or so, which partly reflects the limitations of our spectrophotometer.

Attempts to follow reaction by the stopped-flow technique using a Canterbury SF-3A apparatus, where the efficiency of mixing is known to be good were unsuccessful. Because of the autocatalytic nature of the reaction it was found that decomposition would spread from the mixing chamber back through the coils in which the hydroxylamine solution was thermostatted into the reservoir vessels, and decomposition would go to completion. One complication in all the present work was that it was essential to keep the hydroxylamine separate from the nitric acid until the reaction solutions were mixed. In practice this meant that it was necessary to start reaction by mixing aqueous hydroxylamine sulphate with nitric acid + nitrous acid, and that there was a temperature rise on mixing due to the heat of dilution of nitric acid. This temperature rise was measured in independent experiments, and has been allowed for in the results.

Computer calculations. Numerical integrations were carried out with a standard Runge–Kutta programme, using an ICL 1904 computer.

RESULTS

We have examined the transition between the reactions (1) and (2) by carrying out groups of experiments in

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*Author to whom correspondence should be addressed.

which one parameter (either [HNO_3] or [NH_3OH^+]) was systematically varied by small amounts. The change in the nitrous acid concentration was monitored spectrophotometrically, and a typical set of experimental curves of % transmission vs time is shown in Fig. 1. The change in kinetic behaviour with [HNO_3] is very striking, and the switch in behaviour from consumption to formation of nitrous acid can be seen very clearly. A small change in conditions can produce a drastic effect on the reaction-time curve.

In order to study this system we need a criterion for determining the "boundary conditions" separating the regions in which reactions (1) and (2) dominate as a function of [HNO_3], [NH_3OH^+], temperature etc. (It is important to remember that both (1) and (2) proceed in parallel, and that when we write about a change from (1) to (2) we refer to a change from (1) as the *dominant* reaction to (2) and the *dominant* reaction; we do not mean that reaction (2) replaces reaction (1).) Several possible criteria have been considered. We could use (*a*) the initial rate condition $(d[HNO_2]/dt)_0 = 0$ for a fixed value of [HNO_2], or (*b*) the minima in the plots of [HNO_2] vs time, or (*c*) the conditions for which there is no overall change in nitrous acid concentration at the end of the run, $([HNO_2]_\infty - [HNO_2]_0) = 0$. The advantage of (*a*) is that it refers to known initial conditions, defined by quantities of reagents added, but it suffers from the experimental difficulty in measuring good initial rates. Furthermore for this condition as reaction proceeds invariably (2) dominates (1) and [HNO_2] increases. If one is concerned with preventing an increase in [HNO_2], then (*a*) does not seem to be a useful, practical definition. The same objection applies to (*b*), though in this case there are other problems as well. For some runs the minimum is very broad and flat and it is not easy to locate its exact postion. Furthermore even when this is known, further analysis are needed to obtain the value of [NH_3OH^+]. Criterion (*c*) is fairly straightforward to apply, and as in practical systems it is usually desirable to prevent the formation of nitrous acid it seems a useful definition with which to work. In the early stages of a reaction meeting criterion (*c*) (1) will dominate (2) but in the later stages (2) will dominate (1). Boundary conditions were found by plotting the yield of nitrous acid, Y, $([HNO_2]_\infty - [HNO_2]_0)/[NH_3OH^+]_0$ against $[NH_3OH^+]_0$ and extrapolating to $Y = 0$. Such a group of experiments provided a combination of values of [NH_3OH^+], [HNO_3] and T corresponding to a transition from (1) to (2). Other groups of runs for varying initial concentrations and temperatures enabled the boundary conditions to be mapped out. Some extrapolations were obtained by plotting Y vs T for constant [NH_3OH^+] and [HNO_3]; such plots were often more linear than graphs of Y vs [NH_3OH^+], and the extrapolation to $Y = 0$ was more straightforward. Figure 2 shows a plot of the boundary conditions fo a range of conditions; the area of high [HNO_3] and high T corresponds to reaction (2) dominating reaction (1).

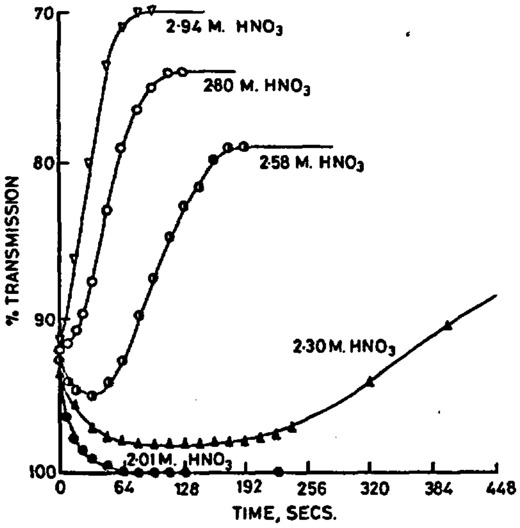

Fig. 1. Effect of nitric acid concentration on the decomposition of hydroxylamine. Per cent transmission (370 nm, 1 cm cells)/time curves; light abosrption due only to HNO_2.

DISCUSSION

We can discuss these results in terms of the mechanism proposed for the reaction of our previous paper[4].

$$H^+ + HNO_2 + NO_3^- \rightarrow N_2O_4 + H_2O \qquad k_1 \qquad (3)$$

$$N_2O_4 + H_2O \rightarrow H^+ + HNO_2 + NO_3^- \qquad k_{-1} \qquad (4)$$

$$N_2O_4 + NH_2OH \rightarrow HNO + N_2O_3 \qquad k_2 \qquad (5)$$

$$N_2O_4 + HNO \rightarrow HNO_2 + N_2O_3 \qquad k_3 \qquad (6)$$

$$N_2O_3 + H_2O \rightarrow 2HNO_2 \qquad \text{fast} \qquad (7)$$

$$HNO_2 + NH_3OH^+ \rightarrow N_2O + H_2O + H_3O^+. \qquad (8)$$

The basic reason why the nitrous acid scavenging reaction (1) dominates at high values of [NH_3OH^+] is that the rate of the nitrous acid generating mechanism (3)–(7) can be limited by a slow initiation step (3). The nitrate ion is a weak nucleophile, and the rate of formation of N_2O_4 by (3) is many orders of magnitude less than the rates of formation of other nitrosyl compounds NOX by reaction of H^+, HNO_2 and X^-. When hydroxylamine is present in sufficiently great concentration, then essentially every molecule of N_2O_4 formed is captured by reactions (5) + (6). The rate of nitrous acid generation is then controlled by the rate of formation of N_2O_4, and is given by $3k_1[H^+][NO_3^-][HNO_2]$, which is independent of

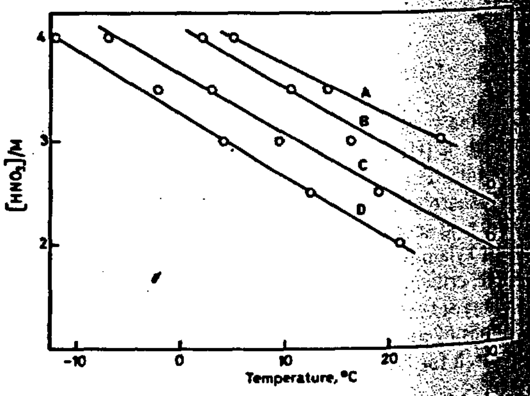

Fig. 2. Boundary conditions for the decomposition of hydroxylamine in nitric acid; (a) [NH_3OH^+]/M = 0.05. (b) 0.02. (c) 0.01 (d) 0.005.

$[NH_3OH^+]$. However the kinetics of the nitrous acid scavenging reaction are given by $k_4[HNO_2][NH_3OH^+]$ and this will continue to increase with increase in $[NH_3OH^+]$, so that (1) dominates (2). The interesting kinetic curves where $[HNO_2]$ decreases, reaches a minimum and then increases arise close to the border line conditions. At the start of the run $[NH_3OH^+]$ is sufficiently large for (1) to dominate (2), but as reaction proceeds the hydroxylamine concentration falls, and the rate of scavenging falls off more than the rate of nitrite formation. This causes the system to cross the borderline so that now(2) dominates (1) and $[HNO_2]$ increases. The effect of increasing the nitric acid concentration is clearly to increase the concentration of the oxidising species N_2O_4, while increased acidity is known[3] to slightly decrease the rate of the scavenging reaction (8). Thus the increased dominance of (2) over (1) at higher nitric acid concentrations is readily understood. The activation energy for the generation of nitrous acid was found to be 105 kJ mol^{-1},[5], while for nitrous acid scavenging it is reported to be *ca.* 65 kJ mol^{-1}. Thus increase in temperature is expected to favour reaction (2) over (1).

We can make this discussion more quantitative by treating the system by the steady state approximation assuming $\partial[N_2O_4]\partial t = \partial[HNO]/\delta t = 0$. The differential eqns (9) and (10) may readily be deduced.

$$d[HNO_2]/dt = [HNO_2][NH_3OH^+]((3k_1[H^+][NO_3^-] \quad ((k_{-1}/k_2) + 2[NH_3OH^+])^{-1}) - k_4) \qquad (9)$$

$$-d[NH_3OH^+]/dt = [HNO_2][NH_3OH^+]((k_1[H^+][NO_3^-] \quad ((k_{-1}/k_2) + 2[NH_3OH^+])^{-1}) + k_4). \qquad (10)$$

As hydroxylamine exists essentially completely as NH_3OH^+ in the solutions we are discussing, the rate equation has been expressed in terms of $[NH_3OH^+]$, and the rate constant k_2 is calculated in terms of the stoichiometric concentration of this species.

In order to be able to use these equations it is necessary to assign values for the various rate constants. Values of $k_1[H^+][NO_3^-]$ have been reported by Schmid and Bähr[6] for a range of nitric acid concentrations (1.5–5.0 M) at 0, 10 and 20°C. It is more difficult to assign a value for k_4. The kinetics of reaction (8) have been measured in perchloric acid[3], and we have assumed that k_4 will gave the same numerical values for solutions in perchloric and nitric acids with the same value of H_0. Using the measured rates of formation of nitrous acid reported in our previous paper[4], we can substitute for $k_1[H^+][NO_3^-]$ and k_4 in (9) to yield a value for k_{-1}/k_2. The differential eqns (9) and (10) can then be integrated for known initial conditions using the Runge–Kutta method. Figure 3 shows the results of such a set of calculations, and it is clear that the treatment reproduces the main kinetic features that we observe experimentally. The calculations show that it is possible under some conditions for the nitrous acid concentration to fall very close to zero, and for a very broad minimum in $[HNO_2]$ to be observed, which is followed by a relatively sudden increase in $[HNO_2]$.

Another approach is to integrate eqns (9) and (10) analytically by eliminating time as an independent variable.

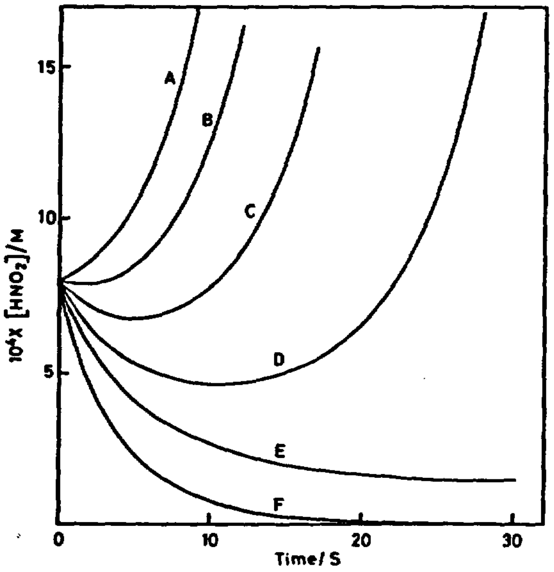

Fig. 3. Calculated curves for the formation of nitrous acid at different hydroxylamine concentrations, at 25°C. (a) $[NH_3OH^+]/M = 0.070$. (b) 0.075. (c)0.080. (d) 0.085. (e) 0.090. (f) 0.100.

$$\frac{-d[HNO_2]}{d[NH_3OH^+]} = \frac{3k_1[H^+][NO_3^-] - k_4(k_{-1}/k_2) - 2k_4[NH_3OH^+]}{k_1[H^+][NO_3^-] + k_4(k_1/k_2) + 2k_4[NH_3OH^+]}.$$

Standard substitution procedures enable this to be integrated to yield (11)

$$\frac{[HNO_2]_\infty - [HNO_2]_0}{[NH_3OH^+]_0 - [NH_3OH^+]_\infty} = \frac{2k_1[H^+][NO_3^-]\ln[(N + [NH_3OH^+]_\infty)/(N + [NH_3OH^+]_0)]}{k_4([NH_3OH^+]_0 - [NH_3OH^+]_\infty)} + 1 \qquad (11)$$

where $N = (0.5k_1[H^+][NO_3^-]/k_4) + 0.5k_{-1}/k_2$. Substitution of the conditions for the complete destruction of hydroxylamine, $[NH_3OH^+]_\infty = 0$, allows the yield of nitrous acid to be calculated. Calculations of $([HNO_2]_\infty - [HNO_2]_0)$ for various values of $[NH_3OH^+]_0$ enables one to obtain the hydroxylamine concentration corresponding to our "borderline" condition $[HNO_2]_\infty - [HNO_2]_0 = 0$. The main difficulty with all theoretical approaches is in assigning values for k_4. An error in the assigned value of k_4 also results in an error in k_{-1}/k_2, because k_4 is used in calculating k_{-1}/k_2 from the measured rates of generation of nitrous acid. Our procedure of taking values from measurements in perchloric acid solution should give values of the correct order of magnitude, but there may be errors due to differences in medium effects between perchloric and nitric acids. In our previous paper[4] we combined product analysis data with kinetic results to deduce values of k_4 for nitric acid solutions. These values were somewhat lower (50–80%) than the corresponding numbers for k_4 deduced by comparison with the perchloric acid data, and it seems likely that there are

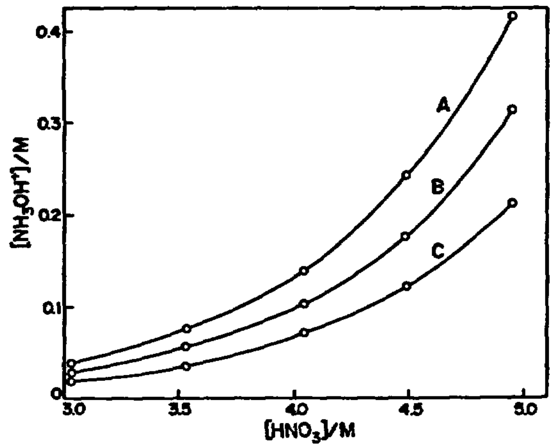

Fig. 4. Effect of changes in the value assumed for k_4 in calculation of borderline conditions at 25°C *B* is calculated from our best values for k_4; for *A* values of k_4 are 20% less, and for *c* 20% greater than for *B*.

medium effects. In Fig. 4 we show plots of the "boundary conditions" for reaction at 25°C for our assumed values of k_4, and for sets of values that are 20% higher and 20% lower, calculated from (11). The general shape of the "borderline" remains the same, but its calculated position shifts with changes in the values assumed for k_4.

In addition to this problem we must note a limitation to the above treatment, the fact that it can only be applied satisfactorily for fairly dilute solutions of hydroxylamine, say $[NH_3OH^+]_0 < 0.01$ M. The difficulty is that both reactions (1) and (2) are substantially exothermic, and as the decomposition reactions are so rapid it is not possible for the heat of reaction to be dissipated to the thermostat sufficiently rapidly to maintain a constant temperature. For 0.1 M hydroxylamine the temperature rise during reaction is *ca.* 4°C, which will cause significant changes in all of the rate constants. In view of the uncertainties about the value of k_4 we do not think it worth trying to refine out treatment to take account of this factor, and all rate constants used refer to one temperature only, 25°C.

We conclude that our mechanism gives a satisfactory semi-quantitative account of the behaviour of solutions of hydroxylamine in nitric acid. If the system contains other species that can generate or scavenge nitrous acid then additional equations will be required in the mechanism, and the position of the boundary will be modified.

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Comparison of the Reactivity of Nine Nitrous Acid Scavengers

James Fitzpatrick, Thomas A. Meyer, Marion E. O'Neill, and D. Lyn H. Williams *
Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE

Rate constants have been measured for the reaction of nitrous acid in aqueous solution at 25 °C with urea, 2,4-dinitroaniline, hydroxylamine, sulphanilic acid, hydrazoic acid, sulphanilamide, hydrazine, sulphamic acid, and 4-nitroaniline, as a function of acidity up to *ca.* 1.5M. The acid–rate profiles, which are all consistent with mechanisms involving electrophilic nitrosation and various protonation equilibria, give the order of reactivity at each acidity of these potential nitrous acid scavengers. The order of reactivity varies with the acidity because of the different acidity dependences, *e.g.* the 'best' scavenger at 0.05M-acid is 4-nitroaniline followed by sulphamic acid, whilst at 1.3M-acid the most reactive is the hydrazinium ion followed by hydrazoic acid. The effect of added halide ion, thiocyanate ion, and thiourea was also examined. Nitrosation of urea, 2,4-dinitroaniline, hydrazinium ion, and sulphamic acid was not catalysed by any added nucleophile, probably because of the importance, for these substrates containing electron-withdrawing groups, of the reversibility of the initial nitrosation. For the remaining five substrates normal nucleophilic catalysis was observed; analysis of the kinetic data enables the second-order rate constant for attack by the nitrosyl halide, *etc.* to be evaluated. The reactivity sequence NOCl > NOBr > NOSCN > $NO\overset{+}{S}C(NH_2)_2$ was found in each case.

Nitrous acid can readily be decomposed, often yielding gaseous products, by reaction with a number of species, mainly amines and related compounds, where the rate-limiting step is usually one of *N*-nitrosation. These reactions are of some interest from a mechanistic point of view where it is instructive to correlate the reactivity with structure, but also are of practical interest in cases where it is important to remove traces of nitrous acid from reaction solutions, *e.g.* for some nitration reactions in concentrated nitric acid,[1] and also in some nuclear fuel reprocessing reactions where reoxidation of plutonium(III) to plutonium(IV) can occur.[2] Further, decomposition of nitrous acid is important in the prevention of nitrosamine formation possibly *in vivo*, and in the analysis of nitrosamine yields it is sometimes necessary to remove quantitatively, rapidly, and irreversibly excess of nitrous acid from solution. A number of species such as urea, sulphamic acid, ascorbic acid *etc.* have been used for this purpose and some have been examined kinetically from a mechanistic point of view, *e.g.* sulphamic acid,[3] hydrazine,[4,5] hydroxylamine,[6] and hydrazoic acid.[5,7] However, the reactions are dependent on the acidity of the medium, in different ways, depending on various protonation equilibria, and so extrapolation of data from one acidity to another is difficult. In this paper we have set out to examine the reactivity of nine potential nitrous acid scavengers, urea, hydroxylamine, sulphanilic acid, hydrazoic acid, hydrazine, sulphanilamide, sulphamic acid, 4-nitroaniline, and 2,4-dinitroaniline, over a range of acidity, typically 0—1.5M-HClO$_4$. In addition we have noted the effect of added nucleophiles such as halide ion and thiocyanate ion for each substrate since catalysis occurs in some cases and not in others. In this way it was hoped to present data which enable the correct choice of scavenger to be made under given experimental conditions. An indirect method of establishing a relative reactivity scale has been presented,[8] based on the rates of denitrosation of nitrosamines in the presence of such scavengers, but suffers from the disadvantage that it is useful only in the high acid region necessary to bring about such denitrosations at convenient rates. Clearly a series of direct measurements of the rate constants over a wide acid range is the more desirable procedure.

$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+$$
$$H_2NO_2^+ + S \longrightarrow \text{Product}$$
$$S + H^+ \rightleftharpoons SH^+$$

Scheme 1.

Results and Discussion

Acid-catalysed Reactions.—Reaction rate constants were determined for many of the substrates in the acid range 0—1.5M-HClO$_4$. Under these conditions and with $[\text{substrate}]_{\text{Total}} \gg [HNO_2]$ all the reactions were first order in $[HNO_2]$, indicating that the pathway involving N_2O_3 is not important here. Reaction is believed to occur by the attack of the nitrous acidium ion $H_2NO_2^+$, present in very low equilibrium concentration, or possibly by the free nitrosonium ion NO^+. These two possibilities, which are indistinguishable kinetically have been discussed fully recently[9,10] and this is not a point which is at issue in this work. We shall assume the pathway set out in Scheme 1 involving $H_2NO_2^+$. Under these acid conditions we can neglect the ionisation of nitrous acid to give nitrite ion, but need to consider the protonation equilibria of many of the substrates S. The general rate equation derived from Scheme 1 is that given by equation (1), where K_a is the acid dissociation constant of $[SH^+]$, $[S]_T$ is the total

$$\text{Rate} = \frac{kK_a[H^+][S]_T[HNO_2]}{K_a + [H^+]} \qquad (1)$$

stoicheiometric concentration of the substrate ($=[S] + [SH^+]$) and k is the product of the rate constant for reaction of $H_2NO_2^+$ the equilibrium constant for its formation. Clearly two limiting forms are to be expected, (a) when $K_a \gg [H^+]$ and (b) when $K_a \ll [H^+]$; these are given by equations (2) and (3) respectively in the form of the first-order observed

$$k_0 = k[H^+][S]_T \qquad (2)$$

$$k_0 = kK_a[S]_T \qquad (3)$$

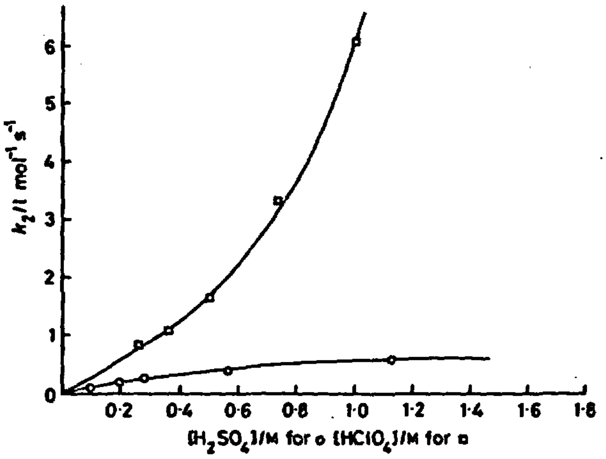

Figure 1. Acid-rate profiles for the nitrosation of urea (○) and the diazotisation of 2,4-dinitroaniline (□)

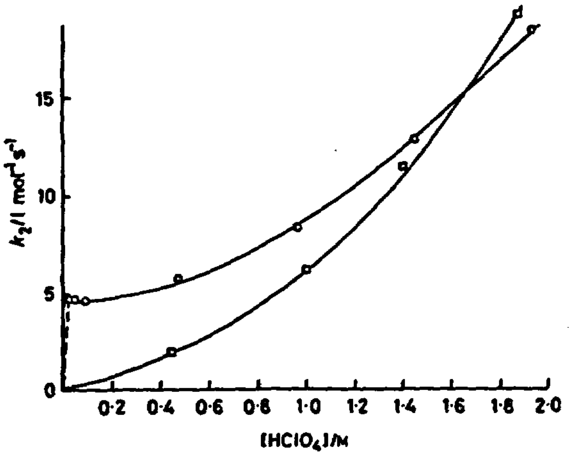

Figure 2. Acid-rate profiles for the diazotisation of sulphanilic acid (○) and for the nitrosation of the hydroxylammonium ion (□)

rate constant k_0 defined by $-d[HNO_2]/dt = k_0[HNO_2]$. Acid-catalysis is thus to be expected only when $K_a \gg [H^+]$. We have used in this treatment $[H^+]$ as the measure of the acidity, and at low $[H^+]$ this is in order, but at higher acidities, typically >0.5M, this should be replaced by an appropriate acidity function.

Throughout this paper we represent the reactivity of any substrate towards nitrosation by the second-order rate constant k_2 defined by $k_0/[S]_T$ at each and every acidity. For two substrates, 4-nitroaniline and 2,4-dinitroaniline, the experimental conditions were different, because of solubility difficulties. Again the reactions were carried out under first-order conditions but with $[HNO_2] \gg [S]_T$ and so k_2 is given by $k_0/[HNO_2]$. In both cases reactions were so rapid that the spontaneous decomposition of nitrous acid was not a problem.

Urea.—This has been extensively used as a nitrous acid trap, particularly to cut out the pathway in nitration involving nitrosation, usually in concentrated nitric acid solutions. Previous work [8] has indicated that urea is the least effective trap, but has the advantage of a high solubility in water. The reaction yields gaseous products, as shown by equation (4),

$$CO(NH_2)_2 + 2HNO_2 \longrightarrow CO_2 + 2N_2 + 3H_2O \quad (4)$$

but has never been studied kinetically, as far as we are aware. We found the reaction to be first order both in $[HNO_2]$ and in [urea] and to be acid-catalysed at low acidities, but this effect levelled off at higher acidities as expected from equation (1) if K_a and $[H^+]$ are comparable. The acidity dependence of k_2 is shown in Figure 1. The reciprocal form of equation (1) allows K_a to be determined from a plot of $(k_0)^{-1}$ *versus* $(h_0)^{-1}$. We find a pK_a value of 0.14 compared with the literature value of 0.18.[11] We have used the Hammett acidity function h_0 here to represent the protonation equilibrium, which is indistinguishable from h_A, the function appropriate to amide protonation, under these acidities. It is clear from Figures 1—4 that urea is by far the least effective trap for nitrous acid at all acidities considered here. The k value [equation (1)] was deduced as 0.89 l^2 mol^{-2} s^{-1}.

2,4-*Dinitroaniline*. Again reaction was first order in [substrate] and $[HNO_2]$, k_2 is shown as a function of acidity in Figure 1. Acid catalysis over the whole acid range is found and is expected when $[H^+] \ll K_a$ applies. The plot is not linear in $[H^+]$ because of the necessity to use an appropriate acidity function for the protonation of HNO_2. So even though 2,4-dinitroaniline is rather unreactive at low acidity, the form of acid catalysis suggests that at very high acidities diazotisation should proceed rapidly, since no significant protonation is likely to occur until very high acid concentrations are used (pK_a −4.5). A limiting value for k at low acidities (assuming a linear H^+ dependence in that region) is 2.5 l^2 mol^{-2} s^{-1}. This compares with a value[*] of 0.37 l^2 mol^{-2} s^{-1} reported by Larkworthy [12] for reaction at 0°, where a similar acid dependence was found.

Hydroxylammonium Ion.—The nitrosation of hydroxylamine has been extensively studied kinetically at 0°.[6,13] We have obtained k_2 values at 25° for comparison purposes with the other substrates. The results, shown in Figure 2, are of the same form as those reported for reaction at 0°, including a levelling-off of k_2 and subsequent reduction in k_2 at even higher acidities (not shown in the Figure). The rate profile up to 1.8M-$HClO_4$ is of the same form as that of 2,4-dinitroaniline, which is consistent with a mechanism proposed by Stedman *et al.*,[6,13] involving nitrosation of the hydroxylammonium ion $\overset{+}{N}H_3OH$. The limiting value of k [equation (1)] at low acidities is 3.6 l^2 mol^{-2} s^{-1} compared with the reported value at 0° of 0.24 l^2 mol^{-2} s^{-1}.[13]

Sulphanilic Acid.—This has been much used as a nitrous acid trap and also synthetically in the production of azo dyes. The kinetics do not appear to have been examined previously. Our results are shown in Figure 2. Here the amine is significantly more basic than either 4-nitroaniline or 2,4-dinitroaniline, with a pK_a value of 3.2. It is thus difficult to pick up acid catalysis since $[H^+] \gg K_a$ except at very low acidity. Initially the graph shows the expected constancy of k_0 with $[H^+]$ as expected from equation (3), but above *ca.* 0.2M-$HClO_4$ there is a further acid catalysis. This has been interpreted [14] for aniline derivatives of basicity greater than pK_a *ca.* 3, in terms of another mechanistic pathway involving the nitrosation of the *protonated* form of the amine, possible *via* some complex where NO^+ is bound initially to the aromatic ring. The limiting k value at low acidities (ignoring this additional catalysis) is calculated as 7.3 × 10^3 l^2 mol^{-2} s^{-1} [from equation (3)]. This is one of the largest values reported at 25° and is quite close to the values reported for thiourea and some alkylthioureas for *S*-nitrosation,[15] and it is believed [9]

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[*] The value usually quoted is 3.7 l^2 mol^{-2} s^{-1}, but there is an error in the original paper and the correct value should be 0.37 l^2 mol^{-2} s^{-1}

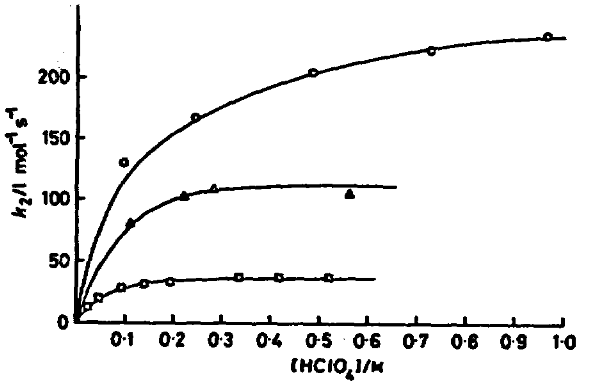


Figure 3. Acid–rate profiles for the diazotisation of 4-nitroaniline (O), sulphanilamide (□), and the nitrosation of sulphamic acid (△)

that k values in this region represent the diffusion-controlled limit.

Sulphanilamide.—This aniline derivative has also been much used in diazotisation and coupling reactions but there appears to be no data on the kinetics of diazotisation other than a comparison between diazotisation by nitrous acid and by an alkyl nitrite.[16] Our results are presented graphically in Figure 3, and show the expected behaviour predicted by equation (1) with $K_a \sim [H^+]$. The double reciprocal plot yields a value of 1.3 for the pK_a which does not agree very well with the literature values [11] of 2.3, 2.06, 2.02, and 2.10. However this procedure yields good agreement for the pK_a values of urea, 4-nitroaniline, and sulphamic acid (see later) so we have some confidence in the value of 1.3. The value of k, also deduced from the double reciprocal plot is 900 l^2 mol^{-2} s^{-1}, significantly below the value for sulphanilic acid as expected for the less basic and less nucleophilic sulphanilamide.

Sulphamic Acid.—This is probably the most widely used trap for nitrous acid, reacting according to equation (5). The

$$NH_2SO_3H + HNO_2 = N_2 + HSO_4^- + H_2O + H^+ \quad (5)$$

reaction was studied at 0° by Hughes,[3] who showed that at low acidity reaction occurred *via* the sulphamate ion. We find a similar acid dependence at 25° as shown in Figure 3, the levelling off of k_2 being entirely consistent with the protonation of the sulphamate ion to the less reactive sulphamic acid. We find from these data a pK_a value of 1.1, in reasonable agreement with the value 0.98 of Hughes at 0°. Sulphamic acid thus behaves in a similar fashion to sulphanilamide showing the intermediate behaviour of equation (1) when $K_A \sim [H^+]$ generally, but tending to a zero order H^+ dependence at higher acidity.

4-Nitroaniline.—The acid–rate profile is also included in Figure 3 and shows again the same pattern as for sulphanilamide and sulphamic acid. Again rate constants have not previously been reported at 25° but the rate law has been established [12] at 0°. Analysis of the data by a double reciprocal plot yields a value of 1.0 for the pK_a (literature value 1.0 [11]) and a value of k [equation (1)] of 2.7×10^3 l^2 mol^{-2} s^{-1} (below that expected for diffusion controlled reactions).

Hydrazoic Acid.—Since the reactive species in acid solution HN_3 is not expected to undergo further protonation in the acid range studied here, it is to be expected therefore that the limiting rate equation (2) will apply. Figure 4 shows the expected acid catalysis, which is not linear in $[H^+]$ as for 2,4-dinitroaniline and hydroxylamine (and hydrazinium ion later) because of the activity effects which are not allowed for. Hydrazoic acid is significantly more reactive than either 2,4-dinitroaniline or hydroxylamine with a k value [equation (2)] of 160 l^2 mol^{-2} s^{-1} (assuming a linear $[H^+]$ dependence as $[H^+] \longrightarrow 0$), which is compatible with the reported value [7] of 33.7 l^2 mol^{-2} s^{-1} at 0°.

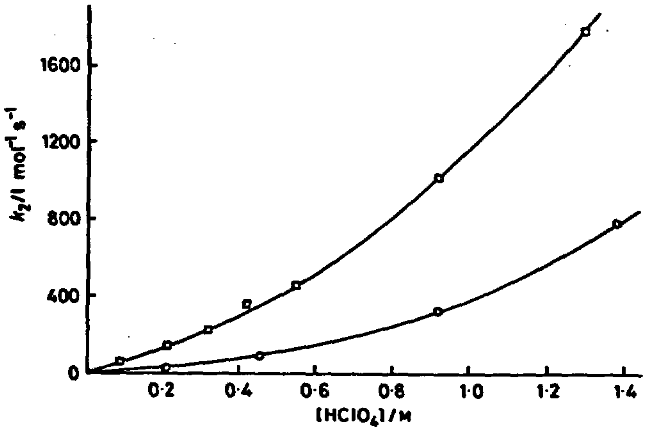


Figure 4. Acid–rate profiles for the nitrosation of hydrazoic acid (O) and the hydrazinium ion (□)

Hydrazinium Ion.—The observed rate profile (Figure 4) is consistent with the reaction of the protonated form $NH_2NH_3^+$ as has been established by Stedman *et al.*[4,5] The limiting value of k as $[H^+] \longrightarrow 0$ is 620 l^2 mol^{-2} s^{-1} which agrees well with that reported by Stedman *et al.* (611 l^2 mol^{-2} s^{-1}).

The overall efficiency of a nitrous acid trap thus depends crucially on the acidity of the medium. Table 1 collects the data (expressed as the second-order rate constant k_2 defined by rate $= k_2[HNO_2][S]_T$) for all of the substrates studied here at three different acidities (0.05, 0.5, and 1.3M-H^+) so that easy direct comparison can be made at each of three acidities.

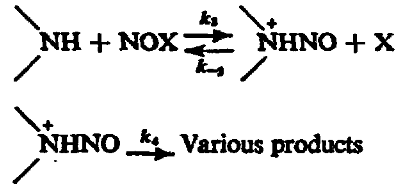
At low acidities (0.05M) the increasing order of overall reactivity of the substrates examined is given by the order in the first column, *i.e.* urea is the least reactive and 4-nitroaniline the most. At higher acidities however, the order changes significantly as various protonation equilibria come into play so that at 1.3M-H^+ the hydrazinium ion and hydrazoic acid become the most efficient traps. The results are included (in Table 1) also for three thiol-carboxylic acids examined in a parallel study.[17] The k_2 values clearly show that these substrates are indeed the most efficient of nitrous acid traps, and although the acid catalysis was not extended to very high acid concentrations, it is likely that protonation of the sulphur atom (and consequent reduction in efficiency in nitrosation) is not an important factor contrasting with many basic nitrogen containing species.

If reaction occurs in these systems *via* $H_2NO_2^+$ then it is not possible to evaluate the actual second-order rate constants for the process $H_2NO_2^+ + S \longrightarrow S^+\text{-}NO$, since the dissociation constant of $H_2NO_2^+$ is not known. However, other arguments, notably the relative insensitivity of the third-order rate constant k [equation (1)] to substrate structure for some reactive species, have been used to put the case for diffusion controlled processes here. A value of k of *ca.* 7×10^3 l^2 mol^{-2} s^{-1} has been regarded [9] as this limiting value at 25°. The only substrate studied in the present work with a value of k in this region is sulphanilic acid (7.3×10^3 l^2 mol^{-2} s^{-1})

Table 1. Data (expressed as second-order rate constants) for all substrates studied, at three different acidities

Substrate	k_2/l mol^{-1} s^{-1} at 25°		
	0.05M-H$^+$	0.5M-H$^+$	1.3M-H$^+$
Urea	0.03	0.36	0.59
2,4-Dinitroaniline	0.12	1.7	~14 *
Hydroxylammonium ion	0.15	2.1	9.6
Sulphanilic acid	4.6	5.5	11
Hydrazoic acid	8.0	105	680
Sulphanilamide	20	37	37 *
Hydrazinium ion	31	390	1 820
Sulphamic acid	47	112	112 *
4-Nitroaniline	72	207	250 *
Cysteine †	26	~200 *	
Mercaptosuccinic acid †	64	~600 *	
Mercaptopropanoic acid †	233	~2 000 *	

* Not measured directly at these acidities, but are extrapolated values. † Measured in a parallel study.[17]



Scheme 2.

which suggests that diffusion control operates. As expected 4-nitroaniline has a smaller k value (2.3×10^3 l^2 mol^{-2} s^{-1}). The modest overall reactivity of sulphanilic acid (Table 1) is of course attributable to its relatively high basicity.

Nucleophile Catalysed Reactions.—A further complication arises when comparing reactivities of various nitrite traps, if non-basic nucleophiles such as halide ion or thiocyanate ion (X^-) are present, since these produce equilibrium concentrations of NOX species which can themselves effect nitrosation. Thus many cases of catalysis of nitrosation and diazotisation by added halide ion and thiocyanate ion have been noted. However this seems to be confined to amine substrates and attention has been drawn [18] to the fact that amide nitrosation shows no such catalysis. This question has been further examined and a pattern has emerged [19] in which substrates containing a powerful electron-withdrawing group (such as the carbonyl group) show no catalysis. An explanation has been put forward [20] in terms of the reversibility of the initial *N*-nitrosation (see Scheme 2); if $k_{-3}[X^-] \gg k_4$ no X^- catalysis should result. Scheme 2 should also include a mechanism for reaction *via* $H_2NO_2^+$, which could either be a dominating or insignificant term. The same argument can be (and has been) applied to the reverse reaction in the denitrosation of nitrosamines,[21] nitrosamides,[20,22] and nitrososulphonamides [23] and leads to the same conclusion that when $k_{-3}[X^-] \gg k_4$ no catalysis by X^- of the denitrosation reaction occurs.

We have in this paper examined each substrate given in Table 1 for catalysis by added Cl^-, Br^-, I^-, SCN^-, and $SC(NH_2)_2$, and find catalysis for hydroxylammonium ion, hydrazoic acid, sulphanilamide, sulphanilic acid, and 4-nitroaniline, and no catalysis for urea, hydrazinium ion, sulphamic acid, and 2,4-dinitroaniline. The results fit into the general pattern that when there are powerful electron-withdrawing groups present, $>C{=}O$, $\overset{+}{N}H_3$, SO_3H, and two nitro-substituents, no catalysis occurs. These substrates should have a much larger value of k_{-3} and so allow $k_{-3}[X^-] \gg k_4$ to be achieved more readily. The only apparent exception is the reaction of the hydroxylammonium ion $\overset{+}{N}H_3OH$ where it is believed that *O*-nitrosation is followed by rearrangement.

Table 2. Nucleophilic catalysis in the diazotisation of sulphanilic acid. [H$^+$] 4.8×10^{-2}M, [NaNO$_2$] 5.0×10^{-5}M, [sulphanilic acid] 1.22×10^{-2}M, 25°

[Cl$^-$]/M	k_0/s^{-1}	[Br$^-$]/M	k_0/s^{-1}
0.025	0.382	0.025	7.2
0.050	0.708	0.050	11.5
0.075	0.963	0.075	14.6
0.100	1.26	0.100	16.9
10^3[SCN$^-$]/M	k_0/s^{-1}	10^3[I$^-$]/M	k_0/s^{-1}
1.74	1.30	1.01	0.69
3.49	2.55	2.02	1.36
6.97	4.65	3.03	1.94
10.5	6.58	4.04	2.57

Table 3. Absence of catalysis in the nitrosation of hydrazinium ion (1.0×10^{-2}M). [H$^+$] 0.21M, [NaNO$_2$] 1.0×10^{-3}M, 25°

[Cl$^-$]/M	k_0/s^{-1}	[Br$^-$]/M	k_0/s^{-1}
0.01	1.46	0.01	1.47
0.03	1.55	0.03	1.59
0.05	1.53	0.05	1.80
0.10	1.81	0.10	2.05
[SCN$^-$]/M	k_0*/s^{-1}		
0.01	0.38		
0.05	0.37		
0.10	0.41		
0.20	0.40		

* At 0°.

Thus the reactivity order is affected not only by the acidity of the medium but also by the presence of nucleophilic species. This explains why hydrazoic acid appears to be a better trap than hydrazinium ion (as measured by the indirect method earlier [8]) when the reaction medium was hydrochloric acid or contained added bromide ion.

Typical sets of data are included in Tables 2 and 3 showing respectively catalysis of nitrosation of sulphanilic acid and the absence of catalysis in the nitrosation of hydrazine. Nucleophilic catalysis has previously been reported for hydroxylamine ion, hydrazoic acid,[5,7] and 4-nitroaniline [12,24] whereas the absence of catalysis for the sulphamic acid reaction has also been noted; [3] the data for the other substrates are new. Contrary to a report in the literature [4] we find no catalysis in the nitrosation of the hydrazinium ion (see Table 3) either at 25 or 0°, other than a very small effect attributable to a salt effect. It is interesting to note the difference in behaviour between 4-nitroaniline and 2,4-dinitroaniline, where the introduction of the second nitro-group is sufficient to remove catalysis completely. Presumably the increased nucleophilicity is sufficient to ensure that $k_{-3}[X^-] \gg k_4$. Even for 4-nitroaniline the reversibility is important as shown [24] by the curved plots of k_0 *versus* $[X^-]$. The full expression for the rate from Scheme 2 is given in equation (6), with an

$$\text{Rate} = \frac{k_3k_4[S]_T[HNO_2][X^-][H^+]K_{NOX}K_a}{(K_a + H^+)(k_{-3}[X^-] + k_4)} \quad (6)$$

Table 4. Values of k_3 (from Scheme 2) at 25°

	k_3/l mol^{-1} s^{-1}			
	NOCl	NOBr	NOSCN	$NO\overset{+}{S}C(NH_2)_2$
NH_2OH	5.9×10^8	1.7×10^8	1.2×10^7	
HN_3	1.9×10^6	$\left\{\begin{matrix} 1.3 \times 10^6 \\ 2.0 \times 10^6 \end{matrix}\right\}$ †		
Sulphanilic acid	1.4×10^9	0.99×10^9	2.0×10^6	5.9×10^3
Sulphanilamide	1.8×10^8	4.4×10^7	7.3×10^4	2.0×10^2
4-Nitroaniline *	2.1×10^8	4.3×10^7		

* From ref. 24. † Two values were obtained, one at constant [HN_3] and varying [Br^-] and the other at constant [Br^-] and varying [HN_3].

Table 5. Values of k_7 [equation (7)]/l^2 mol^{-2} s^{-1} at 25°

SCN^-	11 740	From measurements at different [SCN^-]
	11 700	From measurements at different [HN_3]
	1 460	Literature value at 0° (ref. 7)
$SC(NH_2)_2$	7 091	From measurements at different [$SC(NH_2)_2$]
	7 200	From measurements at different [HN_3]
	6 960	Direct measurement (ref. 26)

additional term due to the uncatalysed reaction. Thus k_0 *versus* [X^-] is linear if $k_{-3}[X^-] \ll k_4$ and k_0 is independent of [X^-] if $k_{-3}[X^-] \gg k_4$. The intermediate situation can readily be analysed by taking the reciprocal form of equation (6) and plotting $(k_0)^{-1}$ *versus* $[X^-]^{-1}$. Values of k_3 are collected in Table 4 for the five substrates for which we have found nucleophilic catalysis. For most of the reactions k_0 *versus* [X^-] was linear over the concentration range studied but for some, curved plots were found and analysis was carried out by the double reciprocal plot. The results show clearly the now established trend [19] of reactivity NOCl > NOBr > NOSCN > $NO\overset{+}{S}C(NH_2)_2$ with the values for both NOBr and NOCl approaching the diffusion controlled limit for the sulphanilic acid case. The values for both sulphanilic acid and sulphanilamide (again for NOBr and NOCl) fit reasonably well on the log k_3 *versus* pK_a plot (from ref. 24), illustrating that the nucleophilicities of aniline derivatives towards electrophilic nitrosation by a variety of reagents, show the same trend as their basicities.

One further point of mechanistic interest emerges regarding the nucleophile catalysed reactions of hydrazoic acid. Whilst for [X^-] = bromide the reaction was first order in [HN_3], for both thiocyanate and thiourea the reaction became zero order in the substrate. This has previously been noted for diazotisation at low acidities of aniline [25] and nitrosation of HN_3 [7] at 0° for halide ion catalysed reactions. This has now been extended to thiocyanate ion and thiourea catalysed reactions at 25°. Zero-order dependence on HN_3 is to be

$$H_2\overset{+}{N}O_2 + SCN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NOSCN + H_2O$$

$$NOSCN + HN_3 \xrightarrow{k_4} \text{Products}$$

Scheme 3.

expected when (Scheme 3) $k_4[HN_3] \gg k_{-3}$ and attack by SCN^- (or thiourea) is rate limiting. The rate equation is then given by equation (7). Values of k_7 are included in Table 5

$$\text{Rate} = k_7[HNO_2][H^+][SCN^-] \text{ (or } [SC(NH_2)_2]) \quad (7)$$

and were obtained in two ways, (a) from the variation of k_0 with [SCN^-] (or [$SC(NH_2)_2$]) and (b) from measurements at different [HN_3]. There is good agreement between the two methods. No rate constant for the reaction of an anion with nitrous acid has been reported at 25°, but it has been argued [9] on the basis of the similarity of values for different anions at 0°, that the reaction rate is close to diffusion limit. Our value of 11 700 l^2 mol^{-2} s^{-1} is perhaps rather larger than expected, given the reported value at 0° of 1 460 l^2 mol^{-2} s^{-1}, and corresponds to an activation energy of *ca.* 56 kJ mol^{-1} which is significantly larger than that expected for a diffusion-controlled reaction. For the thiourea reaction there is excellent agreement between our k_7 values and that reported [26] for the direct reaction between thiourea and nitrous acid in acid solution. If both reactions are at the diffusion controlled limit then the difference between 11 700 l^2 mol^{-2} s^{-1} for SCN^- and 7 000 l^2 mol^{-2} s^{-1} for $SC(NH_2)_2$ may be due to the different charge type of the reactants.

Experimental

All materials were of the highest purity grade available and were used as such. Fresh sodium nitrite solutions were used daily. All the kinetic experiments were carried out under first-order conditions with [substrate] $\gg$ [HNO_2] except for 4-nitroaniline and 2,4-dinitroaniline where the nitrous acid was in large excess. Most of the reactions were followed by stopped-flow spectrophotometry noting the disappearance of the absorbance at 360 nm due to HNO_2 or for the aniline derivatives, the appearance of the absorption due to the diazonium ion or the disappearance of the amine absorption. The spectrophotometer was interfaced with an Apple II Europlus microcomputer using Hitech stopped-flow data acquisition software. The mean value of at least five separate kinetic runs was taken. For the less reactive substrates, *e.g.* urea and 2,4-dinitroaniline, reaction was followed in a conventional spectrophotometer.

Acknowledgements

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Contribution from the Savannah River Laboratory,
E. I. du Pont de Nemours and Company, Aiken, South Carolina 29808

Oxidation of Hydrazine by Nitric Acid[†]

David G. Karraker

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Hydrazine is oxidized by hot nitric acid in a first-order reaction to produce N_2, N_2O, HN_3, and NH_4^+. The rate law for the reaction is $-d \ln (N_2H_4)/dt = k(NO_3^-)(H^+)^2$ where $k = 5.8 \times 10^{-5}\ M^{-3}\ min^{-1}$ at 100 °C in 5.44 M HNO_3 and $\mu = 6$. The data are consistent with a reaction mechanism that involves HN_3, HNO_2, and the N_2H_2 free radical as intermediates and N_2, N_2O, and NH_4^+ as products. The Arrhenius equation constants over the temperature range 70–100 °C were $A = 1.2 \times 10^{11}\ M^{-3}\ min^{-1}$ and $E = 26$ kcal/mol. The reaction is catalyzed by Fe^{3+}, and the rate data are correlated by the semiempirical expression $\ln [(N_2H_4)/(N_2H_4)_0] = -[a'(Fe^{3+}) + b'(Fe^{2+})](H^+)t$ where $a' = 0.114\ M^{-2}\ min^{-1}$ and $b' = 0.065\ M^{-2}\ min^{-1}$. A reaction mechanism is proposed for the ferric-catalyzed reaction whose major reactions involve the reduction of Fe^{3+} to Fe^{2+} by hydrazine and the oxidation of Fe^{2+} to Fe^{3+} by nitric acid.

Introduction

Hydrazine is used in nuclear fuel reprocessing as both a reducing agent and a nitrous acid scavenger.[1,2] As a reducing agent, hydrazine normally reacts slowly at room temperature but has reaction rates at higher temperatures rapid enough to be useful for the reduction of Pu(IV) and Np(V).[3] The rapid reaction of hydrazine with HNO_2 is applied to the stabilization of U(IV) nitrate, ferrous sulfamate, and hydroxylamine solutions in solvent-extraction and ion-exchange processes for the separation of uranium, actinides, and fission products. A recent application is the use of hydrazinium nitrate–HNO_3–KF solutions for dissolving plutonium metal.[4] Hydrazine prevents the precipitation of plutonium(IV) oxides during the dissolving of plutonium metal.

Many of these applications involve temperature and acid concentrations where the stability of hydrazine is unknown and where the maintenance of a hydrazine concentration is critical to the success of the process. This study was begun to provide more detailed information on the reaction rates and products of the hydrazine–nitric acid reaction. Since Fe(II) is used as a reagent in the chemical processing, the effect of Fe(II) and Fe(III) on hydrazine oxidation was also investigated.

Experimental Section

Reagents. Hydrazinium nitrate solution was purchased by the Savannah River Plant (SRP) from Fairmont Chemical Co., Newark, NJ, as a 3.6 M solution. The solution for the study was obtained from the plant stock. Nitric acid, sodium azide, sodium hydroxide, and ferric nitrate were CP grade reagents. Ferrous nitrate solution was prepared by dissolving iron metal in 3 M HNO_3–0.5 M $N_2H_4 \cdot HNO_3$ at a temperature below 50 °C.

Analyses. Hydrazine was determined by the indirect iodate method. The sample was added to a measured excess of standard KIO_3 solution, acidified with 2 M H_2SO_4, and mixed for 1 min or more. Unreacted KIO_3 was reduced to I_2 with an excess of 0.1 M KI solution, and liberated I_2 was titrated with standard $Na_2S_2O_3$ solution.

Hydrazoic acid was determined by two methods. For small samples, the solution was mixed with HNO_3–$Fe(NO_3)_3$ solution and the concentration of the FeN_3^{2+} complex determined spectrophotometrically.[5] When large amounts of sample (~5 mL) were available, HN_3 was nitrogen-sparged from an acid solution and collected by absorbing the vapor in a measured volume of standard NaOH solution. A few drops of $Fe(NO_3)_3$ solution were added to the sample before sparging; the disappearance of the red-brown FeN_3^{2+} color indicated complete removal of HN_3. Hydrazoic acid was then determined by titration with standard Ce^{4+}.[6]

Nitric acid was determined by titration with standard base with a methyl red indicator. Ammonium ion was determined with an ammonia electrode (Orion Associates, Cambridge, MA).

Gas samples were analyzed by a Hewlett-Packard Model 5750 gas chromatograph with a Carbosieve column. Results were corrected for air leakage from oxygen analyses.

Ferrous ion was determined by titration with standard ceric sulfate solution in 2 M H_2SO_4. Tests found that interference from HN_3 or N_2H_4 was negligible under these conditions.

Procedure. The reaction vessel was a two-necked 100-mL flask immersed in a thermostated oil bath. One neck of the flask was used for reagent addition and liquid sampling; the other neck was fitted with a reflux condenser that was connected at its upper end to a gas sample bulb. The gas sample bulb was in turn connected to a water-filled flask. Evolution of gas during the reaction displaced water into a graduated cylinder for measurement. The reaction mixture was magnetically stirred. Gas volumes were determined in parallel experiments that were not disturbed by solution sampling.

The initial solution volume in all experiments was 52 mL. Eighteen milliliters of concentrated nitric acid (15.7 M) and a combined volume of 26 mL of water, 10 M NaOH, and 1.3 M $Fe(NO_3)_3$ solution were mixed and brought to the selected temperature in the oil bath; the reaction was initiated by adding 8 mL of 3.6 M $N_2H_4 \cdot HNO_3$ solution. NaN_3 and $Fe(NO_3)_2$ were added after the hydrazine addition in experiments where their effects on the reaction were explored. The initial ionic strength (HNO_3 + $NaNO_3$ + $N_2H_4 \cdot HNO_3$) was 6.0 M; the final ionic strength (HNO_3 + $NaNO_3$ + HN_3 + NH_4NO_3) was ~5.6–5.8 M.

The concentration of $NaNO_3$ in this study is always the difference between 5.44 M and the acid concentration. For example, a reaction in 4.41 M HNO_3 in this paper is a reaction in 4.41 M HNO_3–1.03 M $NaNO_3$.

Results

A. Nitric Acid Oxidation of Hydrazine. Acid Dependence. Experiments in 6.0 M NO_3^- at 100 °C established initially that the reaction was first order in hydrazine. Figure 1 shows a typical first-order plot for the concentration of hydrazine with time for the initial conditions 4.38 M HNO_3–0.55 M $N_2H_4 \cdot HNO_3$. The reaction rate was also found to depend on the square of the acidity (Table I).

Reaction Products. The products of the hydrazine–HNO_3 reaction are N_2, N_2O, HN_3, and NH_4^+; no NO or NO_2 was detected in any of the gas samples. Figure 2 shows the concentrations of N_2H_4, NH_4^+, and HN_3 during the reaction and the rate of gas evolution during the reaction in 5.44 M HNO_3 at 100 °C. The decrease in HN_3 concentration near the end of the reaction indicates that HN_3 is being destroyed as well as produced in the system. A 1-h test in 6 M HNO_3 at 100 °C found that there was no change in the concentration of NH_4^+ within the limits of error of the experiment, ±3%. Ammonium ion is therefore considered to be a final product. Data for the solution products of the reaction are presented in Table I.

HN_3 Volatility. Pure HN_3 is quite volatile (bp 37 °C) and is easily removed from acid solutions by a sparging gas stream.

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Table I. Reaction Data for N_2H_4 Oxidation at 100 °C[a]

	final concn, M					
(HNO_3), M	N_2H_4	HN_3	NH_4^+	reacn half-time, h	half-time × $(HNO_3)^2$	10^5k,[b] M^{-3} min^{-1}
5.44	0.083	0.077	0.061	1.08	32.0	6.00
5.20	0.035	0.078	*c*	1.2	32.4	5.96
5.05	0.041	0.030	0.085	1.4	35.7	5.41
4.41	0.12	0.096	0.067	1.6	31.1	6.21
3.90	0.074	0.072	0.063	2.1	31.9	6.05
3.41	0.22	0.13	0.062	3.0	34.9	5.53
3.04	0.18	0.090	0.070	3.3	29.7	6.49
2.98	0.19	0.095	*c*	3.9	34.6	5.58
2.56	0.33	0.077	0.055	5.5	36.0	5.36
					33.2 ± 1.9 (av)	5.83 ± 0.33 (av)

[a] Initial conditions: 0.55 M $N_2H_4 \cdot HNO_3$, $\mu = 6.0$. [b] k for $d \ln (N_2H_4)/dt = k(NO_3^-)(H^+)^2$. [c] Not determined.

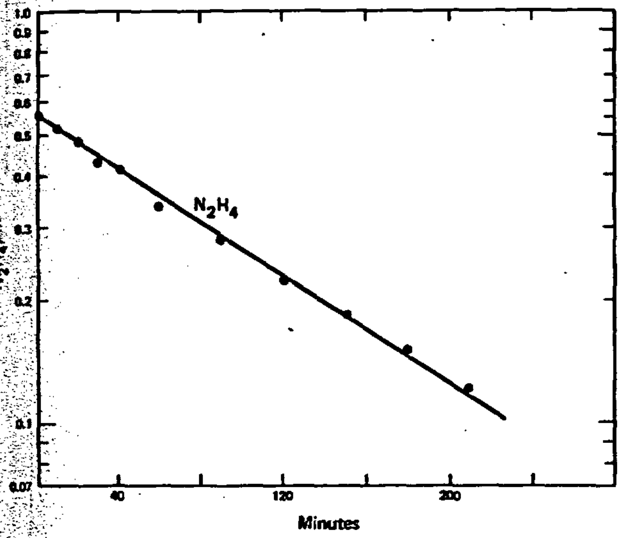

Figure 1. Typical rate data. Reaction conditions: 4.38 M HNO_3, 1.24 M $NaNO_3$, 100 °C.

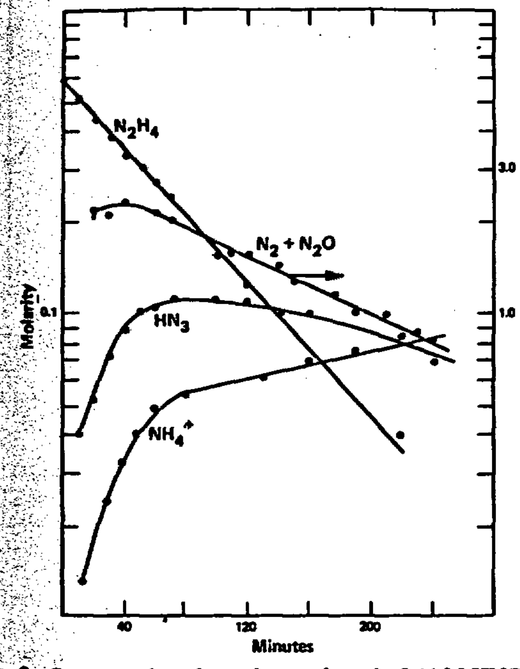

Figure 2. Concentration of reaction products in 5.44 M HNO_3 at 100 °C.

However, no HN_3 could be detected escaping the condenser in these experiments. Tests of the stability of HN_3 in 5.4 M HNO_3 found a 2.4% loss in 1 h at 80 °C and a 20% loss in 1 h at 100 °C. The loss at 100 °C is believed due to the oxidation of HN_3 by HNO_3, and a calculated first-order rate constant for this loss is ca. 4×10^{-3} min^{-1}. Other workers have reported a first-order rate constant of 5.1×10^{-3} min^{-1} at 97 °C for the oxidation of HN_3 by 6.1 M HNO_3.[8] The HN_3–HNO_3 reaction rate is strongly acid-dependent,[8] so the agreement between values is quite good and supports the assumption that oxidation by HNO_3 is responsible for HN_3 loss at 100 °C.

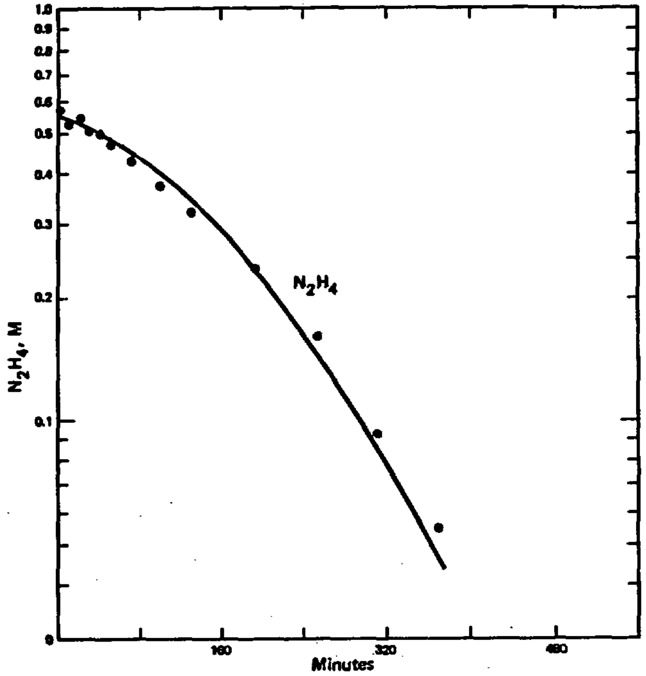

Figure 3. Data for the N_2-sparged reaction for 4.35 M HNO_3–1.22 M $NaNO_3$ at 100 °C and 70 mL of N_2/min.

In several experiments, HN_3 was continuously removed from solution by a sparging nitrogen stream and collected from the N_2 stream by scrubbing with 0.1 M NaOH. The effect of HN_3 removal on the oxidation of N_2H_4 is shown in Figure 3; the continuous removal of HN_3 causes a deviation from a first-order reaction. The HN_3 recovered in the NaOH-filled scrubber corresponded to a 90% yield for HN_3 from N_2H_4–nitrogen. Sparging the solution is a simple preparation for HN_3 or NaN_3.

The oxidation of hydrazine can be expected to have a free-radical mechanism.[11-13] Several attempts were made to scavenge free radicals by sparging the reacting solution with ethylene or acetylene at flow rates up to 70 mL/min. The rate data were indistinguishable from data obtained by N_2 sparging, so it was concluded that the experiments were unsuccessful. Neither C_2H_4 or C_2H_2 is a particularly good radical scavenger, but normal radical scavengers are too unstable for use in this system.

Gaseous Products. After a brief induction period, N_2 and N_2O are evolved at a rate that decreases more slowly than the decrease

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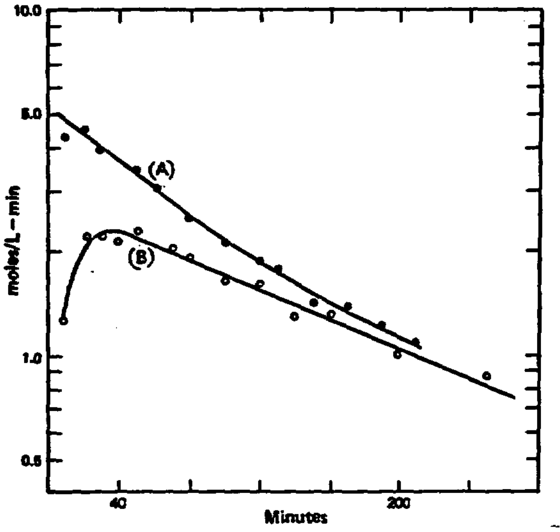

Figure 4. Gas evolution rates at 100 °C for (A) 5.44 M HNO_3–0.55 M N_2H_4·HNO_3–0.15 M NaN_3 and (B) 5.44 M HNO_3–0.55 M N_2H_4·HNO_3.

Table II. Gas Evolution Data[a] at 100 °C

(HNO_3), M	(NaN_3), M	gas yield, mmol	vol % N_2	vol % N_2O
5.5		22.3	76	24
4.0		17.3	77	23
3.0		10.6	79	21
5.5	0.15	30.6	72	28
3.0	0.15	11.1	73	27

[a] Initial (N_2H_4·HNO_3) was 0.55 M.

in N_2H_4 concentration (Figure 4). The gas evolved is 21–24% N_2O, and the N_2O content does not appear to be significantly affected by acidity (Table II). The initial addition of HN_3 leads to a rapid initial evolution of gas that is richer in N_2O than normal and to an increase in the total gas evolved (Table II, Figure 4). A simple calculation indicates that about 40% of the gas evolved from the HN_3 addition is N_2O, suggesting that the reaction

$$HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O$$

is a major contributor to the production of N_2O.

Temperature Effects. The oxidation of hydrazine by nitric acid has a strong temperature dependence. Reaction half-times in 5.44 M HNO_3 at lower temperatures (h, °C): 2.7, 90; 8, 80; 33, 70. The corresponding values for k are shown graphically vs. $1/K$ in Figure 5. The constants for the Arrhenius equation

$$k = A \exp(-E/RT)$$

are $A = 1.2 \times 10^{11}\ M^{-3}\ min^{-1}$ and $E = 26$ kcal/mol.

Net Reaction. The net reaction depends on the time allowed for the reaction. For a reaction in 5.44 M HNO_3 at 100 °C that was 75% complete, the net reaction is approximately

$$N_2H_4 + 0.8HNO_3 \rightarrow 0.19HN_3 + 0.17NH_4NO_3 + 0.7N_2 + 0.2N_2O + 1.8H_2O$$

B. Iron-Catalyzed Oxidation of Hydrazine. Nature of the Reaction. The catalytic effect of iron ions was studied primarily at 80 °C and with an initial iron concentration of 0.1 M. These conditions were chosen to keep the reaction rate in a measurable range for the sampling techniques used, to have iron concentrations in a measurable range by titration techniques, and to ensure that the main route of the hydrazine oxidation would be by the iron-catalyzed reaction, rather than nitric acid oxidation. Preliminary experiments found reaction half-times of 0.33, 2.7, and 8 h for 0.1 M, 10^{-2} M, and zero ferric nitrate, respectively, added initially to the reaction mixture. From these data, it can be calculated that 97% of the hydrazine oxidation occurs by the iron-catalyzed route at 80 °C with 0.1 M $Fe(NO_3)_3$ initially present, but only 55% of the oxidation proceeds through a catalytic path when the initial $Fe(NO_3)_3$ concentration is 10^{-2} M.

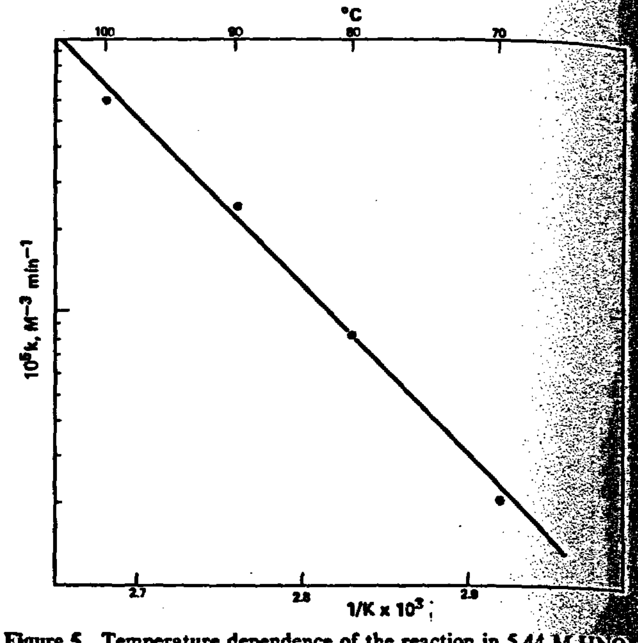

Figure 5. Temperature dependence of the reaction in 5.44 M HNO_3.

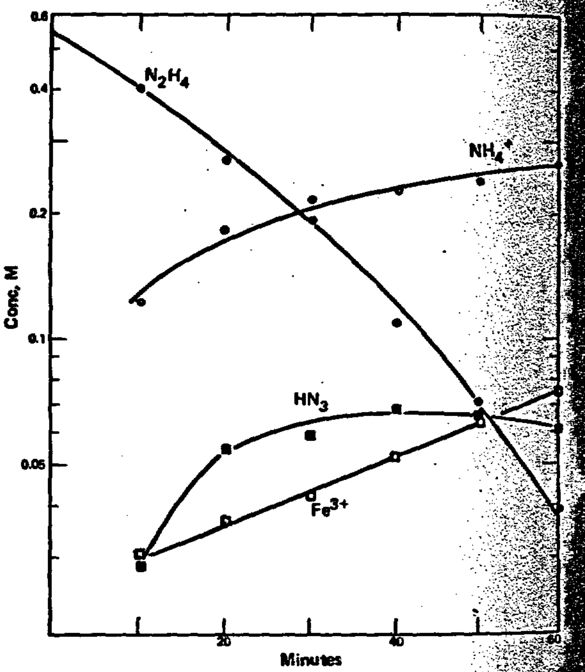

Figure 6. Reactant concentrations. Initial conditions: 4.67 M HNO_3, 0.1 M $Fe(NO_3)_3$, 0.55 M N_2H_4·HNO_3, 80 °C.

Preliminary experiments found that not only were the iron ions oxidized and reduced during the reaction but also the first-order oxidation of hydrazine accelerated as the ferric concentration increased (Figure 6). Iron ions were added both as $Fe(NO_3)_3$ and as hydrazine-stabilized $Fe(NO_3)_2$. When 0.1 M Fe^{3+} was added initially, there was a rapid evolution of gas during the first 10 min of the reaction at 80 °C in 2.93 M HNO_3, but when the initial iron addition was 0.1 M Fe^{2+}, there was only a minor gas evolution (Figure 7). The measured difference between initial additions of Fe^{3+} and Fe^{2+} was 2.3 mmol of gas. This initial reaction was expected from the results of earlier investigators[13] and is due to

$$N_2H_5^+ + Fe^{3+} \rightarrow N_2H_3 + Fe^{2+} + 2H^+$$

followed by

$$2N_2H_3 + 2H^+ \rightarrow 2NH_4^+ + N_2$$

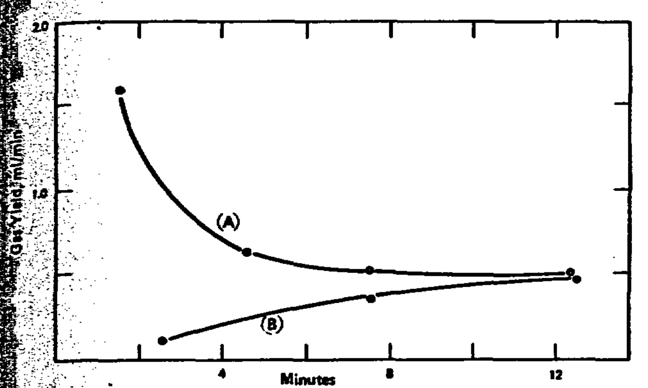

Figure 7. Gas evolution from 2.93 M HNO_3–0.55 M N_2H_4·HNO_3 at 80 °C with an initial addition of (A) 0.1 M $Fe(NO_3)_3$ or (B) 0.1 M $Fe(NO_3)_2$.

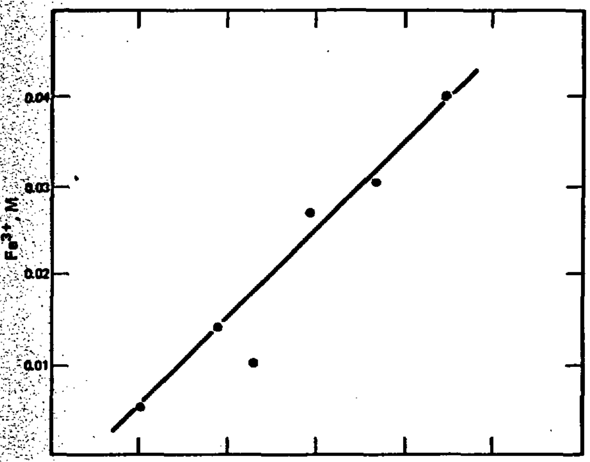

Figure 8. Fe^{3+} concentration 10 min after reaction initiation.

Table III. Initial Fe^{3+} Concentration[a] and Reaction Half-Times

(HNO_3), M	T, °C	(Fe^{3+}), M	reacn half-time, min
5.44	80	0.040	16
4.67	80	0.030	18
3.90	80	0.027	22
3.30	80	0.010	26
2.93	80	0.014	28
1.99	80	0.005	48
5.44	70	0.038	60
3.90	70	0.039	62
3.90	90	0.039	14
2.93	90	0.01	9
5.44[b]	90	c	33
3.90[b]	90	c	84

[a] Initial concentrations: 0.55 M N_2H_4·HNO_3, $(Fe^{3+}) + (Fe^{2+}) = 0.1$ M. [b] $(Fe^{3+}) + (Fe^{2+}) = 0.013$ M. [c] Not determined.

The reduction of the 5.2 mmol of Fe^{3+} initially added could produce 2.6 mmol of N_2. As the reduction of Fe^{3+} in the first 10 min is 87% complete, the expected yield of N_2 is 2.26 mmol. The 2.3-mmol experimental value agrees well with the calculated value.

The initial reduction of Fe^{3+} depends on both the acid concentration and the temperature. Higher acidities and higher temperatures result in a higher Fe^{3+} concentration in the initial stage of the reaction. The concentration of Fe^{3+} 10 min after reaction initiation at varying acidities is shown in Figure 8; data on Fe^{3+} concentration and initial reaction half-times are shown in Table III.

The Fe^{3+} concentration measured 10 min after the start of the reaction is normally the minimum concentration and increases during the hydrazine oxidation. The Fe^{3+}/Fe^{2+} ratio maintains a steady state between the reduction of Fe^{3+} by hydrazine and reducing intermediates and the oxidation of Fe^{2+} by HNO_3. When the hydrazine concentration becomes small, the Fe^{3+} concentration increases and the reaction rate increases, as in Figure 6.

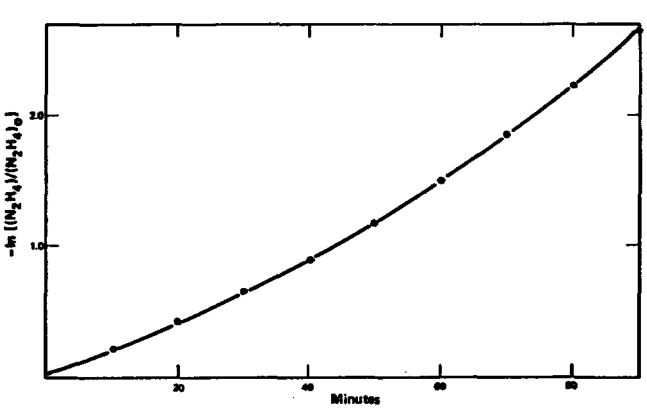

Figure 9. Data fit for 2.93 M HNO_3–0.1 M $Fe(NO_3)_3$–0.55 M N_2H_4·HNO_3 at 80 °C. Points are experimental; line is a computer fit.

Table IV. Least-Squares Constants from Data Fit[a]

(HNO_3), M	T, °C	a, M^{-1} min^{-1}	$a/(H^+)$	b, M^{-1} min^{-1}	$b/(H^+)$
5.44	80	0.656 ± 0.029	0.121	0.348 ± 0.055	0.064
4.67	80	0.448 ± 0.012	0.096	0.311 ± 0.026	0.066
3.90	80	0.414 ± 0.008	0.106	0.239 ± 0.010	0.061
3.30	80	0.416 ± 0.017	0.125	0.243 ± 0.017	0.073
2.93	80	0.364 ± 0.004	0.124	0.184 ± 0.004	0.063
1.99	80	0.402 ± 0.015	0.201	0.176 ± 0.003	0.086
5.44	70	0.180 ± 0.005	0.033	0.098 ± 0.008	0.018
3.90	90	1.02 ± 0.05	0.262	0.98 ± 0.14	0.025
3.90	70	0.147 ± 0.002	0.038	0.073 ± 0.003	0.019

[a] Initial conditions: 0.55 M N_2H_4·HNO_3, 0.10 M Fe^{3+}, $\mu = 6.3$. Constants for $-\ln [(N_2H_4)/(N_2H_4)_0] = [a(Fe^{3+}) + b(Fe^{2+})]t$.

Reaction Rates. Table III shows the reaction half-times as measured by the initial slope of a graph like Figure 6. Between 5.44 and 2.93 M HNO_3 at 80 °C, the reaction has a first-power dependence on acidity. The reaction rate increases about a factor of 3 for each 10 °C increase in the temperature.

A more detailed analysis of the data involved a computer fit of the data to a two-path model. Of the several fits attempted, the best fit was achieved for the model

$$-\ln [(N_2H_4)/(N_2H_4)_0] = [a(Fe^{3+}) + b(Fe^{2+})]t$$

where $(N_2H_4)_0$ is the initial concentration of hydrazine and the values for (N_2H_4), (Fe^{3+}), and (Fe^{2+}) are the experimental values measured at time t (min).

The run data were fit with a nonlinear least-squares program (PROC NLIN) in the SAS[14] system on an IBM 3081 computer to determine values for the coefficients a and b. A sample of the computer fit for one data set (2.93 M HNO_3, 0.1 M $Fe(NO_3)_3$, 0.55 M N_2H_4·HNO_3, 80 °C, initial conditions) is shown in Figure 9. The average deviation for this data set between the experimental data and the computer fit was 1.4%. Values for a and b for all data are shown in Table IV.

The values for both a and b show a linear dependence on acidity for the data at 80 °C at 2.93 M HNO_3 and higher acidities. (See the first five entries in columns 4 and 6, Table IV.) At 80 °C, $a = 0.114(H^+)$ and $b = 0.065(H^+)$; the computer-fitted data can be represented empirically by

$$-\ln [(N_2H_4)/(N_2H_4)_0] = [0.114(H^+)(Fe^{3+}) + 0.065(H^+)(Fe^{2+})]t$$

where t is in minutes.

Temperature Dependence. The temperature dependence of $a' = a/(H^+)$ and $b' = b/(H^+)$ was determined from a graph of the appropriate values from Table IV vs. $1/T$ (Figure 10). The

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[14] SAS Institute, Inc., P.O. Box 8000, Cary, NC 25711.

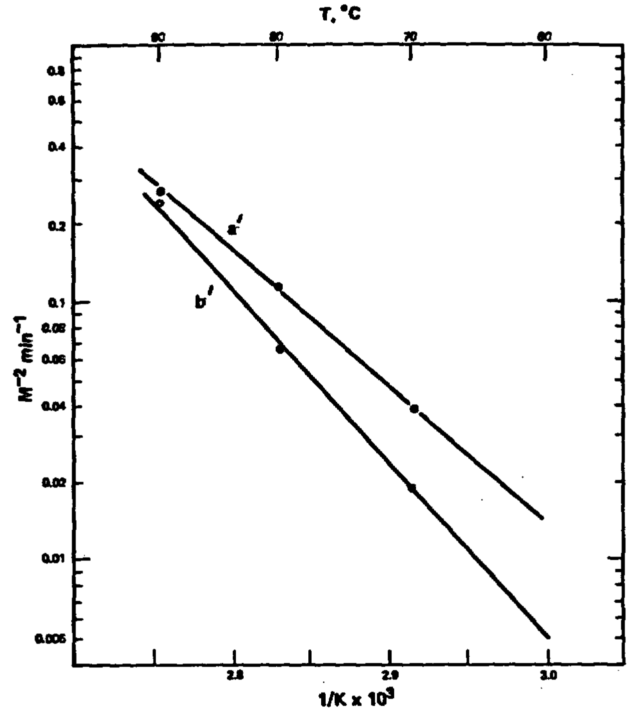

Figure 10. Temperature dependence of constants *a'* and *b'*.

Table V. Reaction Products for Fe^{3+}/Fe^{2+}-Catalyzed Hydrazine Oxidation

initial			final				
			mmol			%	
(HNO_3), M	(Fe^{3+}), M	*T*, °C	NH_4^+	HN_3	$N_2 + N_2O$	N_2	N_2O
5.44	0.1	90	16.1	2.6	20.9	76	23
	0.1	80	16.6	2.5	19.0	79	21
		90	4.7	4.9		74	26
	0.013[a]	90	13.0	3.2	20.4		
	0.076[a]	65	14.0	3.6	13.7[b]	82	18
	0.013	90	13.5	3.2	18.5	69	31
4.67	0.1	80	15.1	2.9	19.3	72	28
3.90	0.1	90	14.0	2.0		80	20
	0.1	80	16.6		19.9	72	28
	0.01	90	16.6	3.1			
	0.1	70					
2.93	0.1	80	12.5	3.6		71	29
1.99	0.1	80	15.1	3.1	19.3	68	32

[a] Fe^{2+}. [b] Reaction incomplete.

temperature dependence of *b'* is about 30% greater than the temperature dependence of *a'*.

Reaction Products. The reaction products (Table V) show remarkably little variation with temperature and acidity. There is a slight increase in the N_2O yield at lower acidity that may be real. However, the percentages of N_2 and N_2O change enough during a reaction that the composition of the gas sample can be affected by the time of sampling. In a reaction at 90 °C, 5.44 M HNO_3, and 0.10 M $Fe(NO_3)_3$, gas samples showed 89%, 74%, and 65% N_2 at the beginning, middle, and end of the reaction, respectively. Large gas samples were taken to obtain an average value, but the gas samples did not include all the gas produced during a reaction.

The major difference between the Fe^{3+}-catalyzed and the uncatalyzed reaction is the large increase in NH_4^+ produced in the catalyzed reaction. The uncatalyzed reaction (Figure 2) produces roughly equal amounts of NH_4^+ and HN_3; the Fe^{3+}-catalyzed reaction produces about 5 times as much NH_4^+ as HN_3.

Net Reaction. The net reaction at 80 °C in 2.93 M HNO_3 with 0.1 M Fe^{3+} catalyst can be calculated from the data of Table V to be

$$N_2H_4 + 1.4HNO_3 \rightarrow$$
$$0.56N_2 + 0.24N_2O + 0.15HN_3 + 0.70NH_4NO_3 + 1.5H_2O$$

Discussion

A. Hydrazine Oxidation by Nitric Acid. Reaction Mechanism. The mechanisms for the oxidation of hydrazine have been the subject of kinetic investigation for over 60 years, but no study of the oxidation of hydrazine by nitric acid has been reported. (Stedman and co-workers[8] indicate that they have a study in progress.) Hydrazine can react with one-electron-oxidizing agents (Fe^{3+}) to produce the hydrazyl radical, N_2H_3, or with two-electron-oxidizing agents (HNO_3) to produce the diazene radical N_2H_2.[11-13] If one accepts the proposal[11] that the initial step is the formation of HNO_2 and the diazene radical, the initial reaction is

$$N_2H_5^+ + HNO_3 \xrightarrow{k_1} N_2H_2 + H^+ + HNO_2 + H_2O \quad (1)$$

followed by the very rapid[1,2] reaction between $N_2H_5^+$ and HNO_2

$$N_2H_5^+ + HNO_2 \xrightarrow{k_2} HN_3 + 2H_2O + H^+ \quad (2)$$

The reactions with initial additions of NaN_3 showed both increased N_2–N_2O yields and an increase in the N_2O/N_2 ratio. This suggests the secondary reaction[15]

$$HN_3 + HNO_2 \xrightarrow{k_3} N_2 + N_2O + H_2O \quad (3)$$

The N_2H_2 radical reaches a steady state between its formation in reaction 1 and its destruction by

$$N_2H_2 + HN_3 + H^+ \xrightarrow{k_4} 2N_2 + NH_4^+ \quad (4)$$

$$N_2H_2 + HNO_3 \xrightarrow{k_5} N_2 + HNO_2 + H_2O \quad (5)$$

HN_3 also reaches a steady state among reactions 2–4. These reactions were found sufficient to derive rate laws for each of the reaction products that were consistent with the experimental data.

Other reactions were considered but ruled out as inconsistent with the experimental data or unlikely from reactant concentrations. The reaction[8] between HN_3 and HNO_3 yields a mixture of N_2, N_2O, and NO as gaseous products and was not considered, since no NO was found in analyses of the product gases. The radical–radical dis- and reapportionation reactions of N_2H_2 have been suggested[11]

$$H^+ + 2N_2H_2 \rightarrow N_2 + N_2H_5^+$$

$$H^+ + 2N_2H_2 \rightarrow HN_3 + NH_4^+$$

but require reactions between two N_2H_2 radicals, which must be present in very low concentration. A reaction between two N_2H_2 radicals is therefore unlikely to be a major reaction in this system. The reaction

$$N_2H_2 + HNO_3 \rightarrow {}^3/_2N_2O + {}^3/_2H_2O$$

appears plausible, but on detailed analysis leads to N_2O/N_2 ratios greater than 1, in disagreement with the experimental data.

To describe the system conceptually, as hydrazine is oxidized, the reactive species HNO_2, N_2H_2, and HN_3 are produced and achieve a steady state between their production and destruction. When steady-state conditions are established, the oxidation proceeds by a first-order rate law.

Rate Laws. From the equilibria described by

$$K_1 = \frac{(N_2H_5^+)}{(N_2H_4)(H^+)} = 8.5 \times 10^7 \text{ at } 25\ ^\circ\mathrm{C}^7 \quad (6)$$

$$K_2 = \frac{(HNO_3)}{(NO_3^-)(H^+)} \approx 22 \text{ at } 25\ ^\circ\mathrm{C}^{14} \quad (7)$$

and reaction 1, the experimental rate law is derived as

$$d(N_2H_4)/dt = -k_1(N_2H_5^+)(HNO_3) \quad (8)$$

$$d(N_2H_4)/dt = -k_1K_1K_2(N_2H_4)(NO_3^-)(H^+)^2 \quad (9)$$

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(15) Phelan, K. G.; Stedman, G. *J. Chem. Soc., Dalton Trans.* 1982, 160

or

$$d\ln(N_2H_4)/dt = -k'(NO_3^-)(H^+)^2 = -F \qquad (10)$$

$$k' = k_1K_1K_2 \qquad F = k'(NO_3^-)(H^+)^2$$

This corresponds to the experimental rate law.

Rate laws for the concentration with time of N_2H_4, NH_4^+, and HN_3 are derived in the Appendix from reactions 1–5. The derivations assume steady-state concentrations for N_2H_2 and HNO_2, omit terms of lesser magnitude, and treat some slowly varying terms as constants. The derived rate laws will be compared with the data sets for the acid range 3–5.44 M and illustrated for data at 5.44 M (Figure 2 and Table VI).

$$\ln\frac{(N_2H_4)}{(N_2H_4)_0} = -nFt \qquad (11)$$

$$n = \frac{2k_4(HN_3) + 3k_5'(NO_3^-)}{k_4(HN_3) + k_5'(NO_3)}$$

The value of n, considering HN_3 as a constant, was obtained by comparing rate data for NH_4^+ with the rate law for NH_4^+ derived in the Appendix. The rate law for NH_4^+ is

$$(NH_4^+) = \frac{k_4(HN_3)[(N_2H_4)_0 - (N_2H_4)_t]}{2k_4(HN_3) + 3k_5'(NO_3^-)} \qquad (12)$$

A graph (Figure 11) of (NH_4^+) vs. $[(N_2H_4)_0 - (N_2H_4)_t]$ for the data of Figure 2 (tabulated in Table VI) shows a linear fit to the experimental data.

The slope of the straight line (Figure 11) had an average value of 0.155 ± 0.010 for four sets of data over the acid range 3–5.44 M. Then

$$0.155 = \frac{k_4(HN_3)}{2k_4(HN_3) + 3k_5'(NO_3^-)} \qquad (13)$$

from which $k_4(HN_3)/k_5'(NO_3^-) = 0.67$ and $n = 2.60$. The experimental first-order rate constant $k = nk' = 5.83 \times 10^{-5}$ M^{-3} min^{-1}; hence, $k' = k_1K_1K_2 = 2.24 \times 10^{-5}$ M^{-3} min^{-1}.

The rate law for HN_3 as derived in the Appendix is

$$(HN_3) = \frac{[1 - k_4(HN_3)][(N_2H_4)_0 - (N_2H_4)_t]}{2k_4(HN_3) + 3k_5'(NO_3^-)} - \frac{Fk_3(HN_3)[1 + k_4(HN_3)]}{k_2'(H^+)[k_4(HN_3) + k_5'(NO_3^-)]}t \qquad (14)$$

Figure 12 shows data from Table VI graphed against $[(N_2H_4)_0 - (N_2H_4)_t]$. The initial slope of the graph is due to the first term in eq 14, and the curvature at high values is approximated by the second term. Three other sets of data over the acid range 3–5.5 M HNO_3 had an initial slope of 0.48 ± 0.01, with no apparent trend with acid concentration. A least-squares program fitted the data of Table VI to eq 14 (Figure 12), yielding

$$\frac{1 - k_4(HN_3)}{2k_4(HN_3) + 3k_5'(NO_3^-)} = 0.482 \pm 0.015 \qquad (15)$$

and

$$\frac{Fk_3(HN_3)[1 + k_4(HN_3)]}{k_2'(H^+)[k_4(HN_3) + k_5'(NO_3^-)]} = 8.4\ (\pm 0.5) \times 10^{-4} \qquad (16)$$

Equation 15 combined with the ratio $k_4(HN_3)/k_5'(NO_3^-) = 0.67$ from eq 13 yields $k_4(HN_3) = 0.25$ and $k_5'(NO_3^-) = 0.37$. From these values and eq 16, $k_2'(H^+)/k_3(HN_3) \simeq 8$, which supports the assumption used for this approximation in the Appendix, eq A14.

An estimate of the concentration of the N_2H_2 free radical can be made from the rate law for nitrogen. This rate law

$$d(N_2)/dt = d(N_2O)/dt + [2k_4(HN_3) + k_5'(NO_3^-)](H^+)(N_2H_2) \qquad (17)$$

can be solved for the N_2H_2 concentration from the values for $k_4(HN_3)$ and $k_5'(NO_3^-)$ and the data (Table VI) for the rate of N_2 and N_2O evolution (Appendix). When these values are substituted, N_2H_2 concentration is calculated to be ~2×10^{-4} M during the first reaction half-time. When average values for HN_3 and NO_3^- are substituted, $k_4 = 3.1$ M^{-3} min^{-1} and $k_5' = k_5K_2 = 0.062$ M^{-2} min^{-1}. As K_2 is of the order of 10, reaction 4 must be at least 100 times faster than reaction 5.

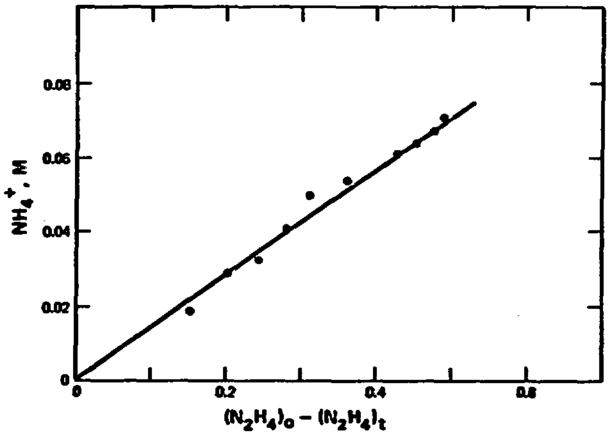

Figure 11. Test of eq 12 (data from Table VI for 5.44 M HNO_3 and 100 °C).

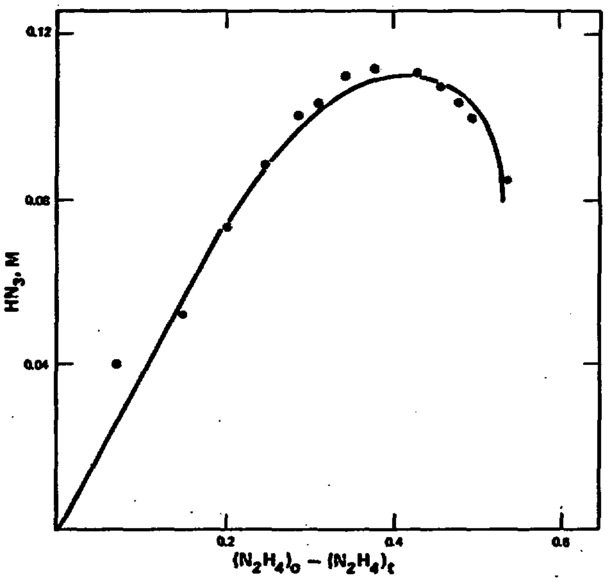

Figure 12. HN_3 data at 5.44 M HNO_3 and 100 °C. Points are data; line is calculated from (14).

B. Ferric Catalysis. Reaction Mechanism. The proposed mechanism for the Fe^{3+}-catalyzed oxidation of hydrazine proceeds through the oxidation of hydrazine by Fe^{3+} and the oxidation of Fe^{2+} to Fe^{3+} by HNO_3. These reactions compete to create a steady-state concentration of Fe^{3+}, the primary oxidant for hydrazine. However, the detailed mechanism is considerably more complex. Hydrazine normally reacts with one-electron oxidants to form hydrazyl (N_2H_3) free radicals.[11,13,16] Reduction of HNO_3 can lead to NO_2, HNO_2, and NO as intermediates.[17-20] The reactions of the intermediates lead to the final products N_2, N_2O, NH_4^+, and HN_3.

A plausible reaction mechanism begins with the primary reaction between Fe^{3+} and $N_2H_5^+$:

$$Fe^{3+} + N_2H_5^+ \rightarrow Fe^{2+} + 2H^+ + N_2H_3 \qquad (18)$$

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(16) Higginson, W. C. E.; Sutton, D.; Wright, P. *J. Chem. Soc.* **1953**, 1380.
(17) Stedman, G. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 113.
(18) Epstein, I. R.; Kustin, K.; Warshaw, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 3751.
(19) Orban, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 5918.
(20) Kummer, J. T. *Inorg. Chim. Acta* **1983**, *76*, L291.

Fe^{2+} is oxidized by HNO_3, and under conditions where HNO_3 is in large excess, the most probable reaction is

$$Fe^{2+} + HNO_3 + H^+ \rightarrow Fe^{3+} + NO_2 + H_2O \quad (19)$$

NO_2 must reduce rapidly to HNO_2, since no NO_2 or NO was found in any gas sample. Two paths are possible, reduction by Fe^{2+} or by $N_2H_5^+$, as

$$Fe^{2+} + NO_2 + H^+ \rightarrow Fe^{3+} + HNO_2 \quad (20)$$

$$N_2H_5^+ + NO_2 \rightarrow HNO_2 + N_2H_3 + H^+ \quad (21)$$

HNO_2 is rapidly scavenged by $N_2H_5^+$ and HN_3:[1,15,21]

$$HNO_2 + N_2H_5^+ \rightarrow HN_3 + H^+ + 2H_2O \quad (22)$$

$$HN_3 + HNO_2 \rightarrow N_2O + N_2 + H_2O \quad (23)$$

The hydrazyl free radical reacts[11] by

$$2N_2H_3 + 2H^+ \rightarrow 2NH_4^+ + N_2 \quad (24)$$

$$N_2H_3 + 2H^+ + Fe^{2+} \rightarrow N_2H_5^+ + Fe^{3+} \quad (25)$$

$$N_2H_3 + Fe^{3+} \rightarrow N_2H_2 + Fe^{2+} + H^+ \quad (26)$$

The diazene free radical also reacts[11] by

$$N_2H_2 + HN_3 + H^+ \rightarrow 2N_2 + NH_4^+ \quad (27)$$

$$N_2H_2 + 2Fe^{3+} \rightarrow 2Fe^{2+} + 2H^+ + N_2 \quad (28)$$

The relative importance of reactions 18–28 can be estimated from the data of Tables III and IV. These reactions are largely responsible for maintaining the Fe^{3+}–Fe^{2+} steady state and oxidizing N_2H_4. Reaction 23 is the only reaction that produces N_2O and thus accounts for about 55% of the gaseous products. Reaction 24 is most important in the early part of the reaction. As the N_2H_4 concentration is depleted, the concentration of N_2H_3 radicals decreases and the bimolecular reaction becomes less probable. Reactions 26–28 become more important as the reaction nears completion.

Rate Law. Ideally, a rate law for the concentration of the reactants and the products as a function of time could be derived from a steady-state treatment of reactions 18–28. However, the system is quite complicated and a number of approximations and assumptions were necessary to solve the equations. The derived rate law should have a form similar to the experimental rate law

$$\ln [(N_2H_4)/(N_2H_4)_0] = -[a'(Fe^{3+}) + b'(Fe^{2+})](H^+)t \quad (29)$$

where $a' = a/(H^+)$ and $b' = b/(H^+)$.

With different approximations, three different rate laws for hydrazine were derived. All three had the same leading term as the experimental rate law, $-k_1'(Fe^{3+})(H^+)t$ ($k_1' = a' = 0.114$ M^{-2} min^{-1} at 80 °C), but none agreed with the acid dependence of the second term. Attempts to computer-fit data to the derived rate laws were unsuccessful.

Conclusion

The experimental data for the oxidation of hydrazine by nitric acid are remarkably consistent with the rate laws derived from a relatively simple set of reactions, a circumstance that may be fortuitous. A change in experimental conditions that increases the reaction rate (higher temperatures, higher acid concentrations) could make some of the reactions that were not considered in this analysis significant and render the approximations of the treatment presented here inadequate. At lower acid concentrations and lower acidities, this study is considered satisfactory and should provide a useful basis for more elaborate studies, such as ^{15}N experiments.

The rationalization of the data for the ferric-catalyzed hydrazine oxidation is considered only partially successful. There is probably some competition with the uncatalyzed reaction at low acidities, and the relative importance of the reactions proposed for this system changes during the course of an experiment. Under such circumstances, it is difficult to estimate whether the inadequacy of the derived rate to be consistent even with the oxidation of hydrazine is due to the complexity of the system, the inadequacy of the proposed mechanism, or the approximations applied to obtain a solution. However, the experimental data fit can be used to predict the behavior of hydrazine in plant operations and this work could be a useful starting point toward further studies.

Table VI. Run Data for 5.5 M HNO_3 at 100 °C

time, min	(N_2H_4), M	(HN_3), M	(NH_4^+), M	amt of gas evolved, mmol/(L min)
0	0.586			
10	0.514	0.040		1.3
20	0.432	0.052	0.018	2.2
30	0.381	0.073	0.024	2.1
40	0.337	0.088	0.032	2.15
50	0.302	0.101	0.040	2.3
60	0.270	0.104	0.049	
70	0.243	0.111		2.05
80	0.218	0.110	0.053	1.9
100	0.154	0.111	0.060	1.65
120	0.124	0.108	0.063	1.6
140	0.104	0.101	0.067	1.3
160	0.091	0.100	0.070	1.3
220	0.040	0.085	0.077	0.95
280	0.017	0.063	0.084	0.7

Acknowledgment. The author is grateful to W. L. Frazier for gas analyses, to R. L. Postles for the versatile and useful PROC NLIN program, and to J. C. Shaw for his experimental assistance.

Appendix. Derivation of the Rate Laws for the N_2H_4–HNO_3 Reaction

The rate law for N_2H_4 from reactions 1 and 2 is given by

$$d(N_2H_4)/dt = -F(N_2H_4) - k_2K_1(N_2H_4)(H^+)(NO_3^-) \quad (A1)$$

where $F = k'(NO_3^-)(H^+)^2$.

The rate law for HNO_2 from reactions 1, 2, and 5 is

$$d(HNO_2)/dt = F(N_2H_4) - k_2'(N_2H_4)(H^+)(HNO_2) - k_3(HN_3)(HNO_2) + k_5'(NO_3^-)(H^+)(N_2H_2) \quad (A2)$$

where $k_2' = k_2K_1$ and $k_5' = k_5K_2$.

The rate law for N_2H_2 is

$$d(N_2H_2)/dt = F(N_2H_4) - [k_4(HN_3) + k_5'(NO_3^-)](H^+)(N_2H_2) \quad (A3)$$

Equations A2 and A3 can be solved for (HNO_2) and (N_2H_2) by assuming steady-state conditions, i.e., $d(HNO_2)/dt$ and $d(N_2H_2)/dt$ both equal to zero. Then

$$(N_2H_2) = \frac{F(N_2H_4)}{(H^+)[k_4(HN_3) + k_5'(NO_3^-)]} \quad (A4)$$

and

$$(HNO_2) = \left(\frac{k_4(HN_3) + 2k_5'(NO_3^-)}{k_4(HN_3) + k_5'(NO_3^-)}\right)\frac{F(N_2H_4)}{k_2'(N_2H_4)(H^+) + k_3(HN_3)} \quad (A5)$$

Substituting eq A4 and A5 into eq A1 and rearranging yields

$$d \ln (N_2H_4)/dt = -F\{1 + k_2'(N_2H_4)(H^+)[k_4(HN_3) + 2k_5'(NO_3^-)]/[k_2'(N_2H_4)(H^+) + k_3(HN_3)][k_4(HN_3) + k_5'(NO_3^-)]\} \quad (A6)$$

If it is assumed that $k_2'(N_2H_4)(H^+) >> k_3(HN_3)$ (an assumption defended in the Discussion), then

$$k_2'(N_2H_4)(H^+) + k_3(HN_3) \simeq k_2'(N_2H_4)(H^+)$$

$$d \ln (N_2H_4)/dt = -F\left(\frac{2k_4(HN_3) + 3k_5'(NO_3^-)}{k_4(HN_3) + k_5'(NO_3^-)}\right) \quad (A7)$$

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Equation A7 can be integrated by considering the HN_3 concentration constant. The result is

$$\ln \frac{(N_2H_4)}{(N_2H_4)_0} = -nFt \qquad (A8)$$

where

$$n = \frac{2k_4(HN_3) + 3k_5'(NO_3^-)}{k_4(HN_3) + k_5'(NO_3^-)}$$

The rate law for NH_4^+ from reaction 4 is

$$d(NH_4^+)/dt = k_4(HN_3)(H^+)(N_2H_2) \qquad (A9)$$

Substituting from eq A4 for (N_2H_2) gives

$$d(NH_4^+)/dt = \frac{k_4(HN_3)(N_2H_4)F}{k_4(HN_3) + k_5'(NO_3^-)} \qquad (A10)$$

(N_2H_4) is replaced by $(N_2H_4)_0 \exp(-nFt)$, and the resulting expression is integrated. After evaluation of the integration constant, the result is

$$(NH_4^+) = \left(\frac{k_4(HN_3)}{2k_4(HN_3) + 3k_5'(NO_3^-)}\right)(N_2H_4)_0[1 - \exp(-nFt)] \qquad (A11)$$

A more useful form is the equivalent expression

$$(NH_4^+) = \frac{k_4(NH_3)}{2k_4(HN_3) + 3k_5'(NO_3^-)}[(N_2H_4)_0 - (N_2H_4)_t] \qquad (A12)$$

where $(N_2H_4)_t$ is the N_2H_4 concentration at time t.

The rate law for HN_3, derived from reactions 2–4, is

$$d(HN_3)/dt = [k_2'(N_2H_4)(H^+) - k_3(HN_3)](HNO_2) - k_4(HN_3)(H^+)(N_2H_2) \qquad (A13)$$

After equivalent expressions are substituted for HNO_2 and N_2H_2, eq A15 becomes

$$d(HN_3)/dt = F(N_2H_4)\{([k_2'(N_2H_4)(H^+)][1 - k_4(HN_3)] - k_3(HN_3)[1 + k_4(HN_3)])/[k_2'(N_2H_4)(H^+) + k_3(HN_3)] \times [k_4(HN_3) + k_5'(NO_3^-)]\} \qquad (A14)$$

The fraction enclosed in braces will be represented below as m. The fraction m includes terms depending on HN_3 and N_2H_4, which are mixed to the extent that the separation of variables does not appear possible. The approach taken was to assume

$$k_2'(N_2H_4)(H^+) >> k_3(HN_3)$$

in the denominator of m. This leads, after substitution of $(N_2H_4)_0[1 - \exp(-nFt)]$ for N_2H_4 and integration, to the expression

$$(HN_3) = \frac{[1 - k_4(HN_3)][(N_2H_4)_0 - (N_2H_4)_t]}{2k_4(HN_3) + 3k_5'(NO_3^-)} - \frac{Fk_3(HN_3)[1 + k_4(HN_3)]t}{k_2'(H^+)[k_4(HN_3) + k_5'(NO_3^-)]} \qquad (A15)$$

In form, eq A15 is an exponential growth combined with a linear decay, although the data would be expected to have an exponential decay. However, eq A15 does fit the data fairly well.

The rate law for N_2 from reactions 3–5 is

$$d(N_2)/dt = k_3(HN_3)(HNO_2) + [2k_4(HN_3) + k_5'(NO_3^-)](H^+)(N_2H_2) \qquad (A16)$$

Since the rate law for N_2O from reaction 3 is

$$d(N_2O)/dt = k_3(HN_3)(HNO_2) \qquad (A17)$$

then

$$d(N_2)/dt = d(N_2O)/dt + [2k_4(HN_3) + k_5'(NO_3^-)](H^+)(N_2H_2) \qquad (A18)$$

Registry No. N_2H_4, 302-01-2; HNO_3, 7697-37-2; Fe, 7439-89-6.

Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Characterization of *o*-Phenanthroline and 2,2′-Bipyridine Complexes by Laser Mass Spectrometry

K. Balasanmugam, Robert J. Day,[†] and David M. Hercules*

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A series of *o*-phenanthroline (*o*-phen) and 2,2′-bipyridine (bpy) metal complexes has been studied by using laser mass spectrometry (LMS). The molecular cation is observed in the positive ion spectra for the tetracoordinated complexes $[Ag(L)_2]NO_3$, $[Cu(L)_2]_2SO_4\cdot 5H_2O$, $[Cu(L)_2]SO_4$, and $[Tl(L)_2](ClO_4)$, where L = bpy or *o*-phen. Structurally significant fragment ions (ML_2^+, ML^+, M^+, LH^+) are also observed. The hexacoordinate complexes $[M(L)_3]Cl_2$ and $[Fe(L)_3](ClO_4)_2$, where L = bpy or *o*-phen and M = Ni, Co, or Ru, show molecular cations in the positive ion spectra; $[Mn(bpy)_3]Br_2$ does not. Generally, fragment ions such as ML_3^+, ML_2X^+, ML_2^+, MLX^+, ML^+, and $(L + H)^+$ are observed, where X = halogen. Complexes such as $[M(o\text{-phen})_2(H_2O)_4](ClO_4)_2\cdot 2o\text{-phen}$, where M = Ba or Pb, show ions having four ligands, e.g. $ML_4ClO_4^+$. The effect of anion on the fragmentation pattern of transition-metal complexes was studied with $[Ni(bpy)_3]X_2$ where X = Cl^-, Br^-, I^-, ClO_4^-, or SCN^-. Molecular cations were observed for all nickel complexes. The fragmentation patterns were similar for halide analogues. Ions arising from ion–molecule reactions from the dissociated products of ClO_4^- and CNS^- are observed. The negative ion LMS spectra of all complexes provide information about the anion and the formal oxidation state of the central metal atom.

Introduction

The mass spectrometry of coordination compounds is of interest because of their use in catalysis and chemical analysis.[1-3] Because many coordination compounds are involatile and thermally labile, analysis by mass spectrometry has been limited. Conventional mass spectrometry[4,5] has been used with limited success; field desorption (FD) has been applied to some inorganic complexes.[6-9] Though fast atom bombardment (FAB) is widely used for the

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[†] Present address: IBM System Products Division, Endicott, NY 13760.

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Decomposition of Hydrazoic Acid in Nitric Acid

Brian M. Maya and Geoffrey Stedman *
Chemistry Department, University College of Swansea, Singleton Park, Swansea SA2 8PP

Hydrazoic acid in solution in nitric acid at 97 °C decomposes to form a mixture of N_2, N_2O, and NO. The reaction is strongly acid catalysed and the kinetics of decomposition are first order with respect to hydrazoic acid concentration. The mechanism proposed involves electrophilic attack by NO_2^+ on hydrazoic acid to form N_3ONO, which can then fragment to $N_2 + 2NO^{\cdot}$ or dissociate to $N_3^{\cdot} + NO_2^{\cdot}$. Dinitrogen monoxide is thought to arise from the reaction sequence: $2NO_2^{\cdot} \longrightarrow N_2O_4$; $N_2O_4 + HN_3 \longrightarrow N_3NO + HNO_3$; $N_3NO \longrightarrow N_2 + N_2O$.

During the course of an investigation of the reaction of hydrazine with hot, moderately concentrated nitric acid, it became necessary to consider possible side reactions of one of the products, hydrazoic acid. Very little work has been done on this reaction. Caronna and Sansone[1] studied the oxidation by concentrated, fuming nitric acid, and found that a mixture of dinitrogen, dinitrogen monoxide, and nitrogen monoxide was formed. As however there would probably have been some nitrous acid or related species in concentrated fuming nitric acid, these results may have been complicated by the presence of products formed by the well known nitrous acid–hydrazoic acid reaction. Masek[2] has reported a very brief study of the reaction of hydrazoic acid and nitric acid in sulphuric acid solution, and proposed the stoicheiometry (1). He postulated the mechanism in equations (2)—(4).

$$4HN_3 + 2[NO_2]^+ \longrightarrow 4N_2 + 3N_2O + H_2O + 2H^+ \quad (1)$$

$$HN_3 + [NO_2]^+ \longrightarrow 2NO^{\cdot} + N_2 + H^+ \quad (2)$$

$$2NO^{\cdot} + [NO_2]^+ + 2H^+ \longrightarrow 3[NO]^+ + H_2O \quad (3)$$

$$[NO]^+ + HN_3 \longrightarrow N_2O + N_2 + H^+ \quad (4)$$

This paper describes an investigation of the kinetics and stoicheiometry of the decomposition.

Experimental

It was necessary to investigate the decomposition of hydrazoic acid in nitric acid at the same temperature as had been used in a study of the reaction between hydrazine and nitric acid. CAUTION: At this temperature, 97 °C, hydrazoic acid is volatile and as it is both explosive and toxic special care was needed. Reaction vessels were thermostatted in an oil-bath, which was placed in a fume cupboard. Reactions were carried out using closed reaction vessels; in most cases there was an alkali trap connected between the reaction vessel and the atmosphere. The explosive properties of hydrazoic acid are known[3] to be significant at concentrations above *ca.* 4 mol dm^{-3}, but the present experiments involved solutions approximately two orders of magnitude lower in concentration.

Measurements of the vapour pressure of hydrazoic acid in solutions of NH_3 in nitric acid were made by the technique of King and Templeton,[4] passing a stream of fine bubbles of dinitrogen carrier gas through an aqueous solution, and analysing for the amount of hydrazoic acid carried away in the gas stream by absorbing it in sodium hydroxide solution. Azide concentrations were determined by the standard cerium(IV) sulphate method of analysis.[5]

Product analyses were carried out by allowing degassed solutions of sodium azide and nitric acid to mix in an evacuated vessel, with a large vapour:solution volume ratio. A sample of the evolved gas was transferred to another vessel, and its pressure was measured with the vessel immersed to a fixed mark in (*a*) liquid N_2, (*b*) in a solid–liquid n-pentane slush-bath, and (*c*) at ambient temperatures. The analysis basically assumed a mixture of N_2, $NO^{\cdot}$, and N_2O, and at these temperatures the gas phase should be (*a*) N_2, (*b*) $N_2 + NO^{\cdot}$, and (*c*) $N_2 + NO^{\cdot} + N_2O$ respectively. We checked our calibration by analysing the equimolar mixture of N_2 and N_2O obtained from the azide–nitrite reaction, and found that 1 mol of HNO_2 produced on average 0.96 mol N_2 and 1.02 mol N_2O. Thus, although this is a very simple method of analysis, it seems to produce reasonable results; the analysis for $NO^{\cdot}$ is probably[6] not as good as that for N_2 and N_2O.

Kinetic measurements were made by removing aliquots and quenching them in a solution containing a known excess of cerium(IV) sulphate. The excess of cerium(IV) was back-titrated with ammonium iron(II) sulphate solution using an iron(II) phenanthroline indicator.

Results and Discussion

The results of our measurements of the gaseous products of the reaction between hydrazoic acid and 9.18 mol dm^{-3} nitric acid are summarised in Table 1. We find close to 2 mol of gas formed per mol of azide consumed, although no significance is attached to this integral number. The only other familiar compound of nitrogen that might be stable under our reaction conditions of hot, moderately concentrated nitric acid is the ammonium ion. We treated samples of the infinity solutions with excess of sodium hydroxide, and distilled the alkaline solution into a known amount of standard acid. We could find no evidence for the presence of ammonia. Any nitrous acid or dinitrogen tetroxide would be destroyed

Table 1. Gas analysis measurements of the decomposition of HN_3 in 9.18 mol dm^{-3} HNO_3 at 97 °C: number of moles of product per mol of HN_3 reacted

					x	
HN_3	N_2	NO	N_2O	Total	*a*	*b*
−1	1.22	0.22	0.45	1.89	0.424	0.56
−1	1.15	0.25	0.45	1.85	0.48	0.45
−1	1.23	0.27	0.50	2.00	0.508	0.73
−1	1.46	0.30	0.47	2.23	0.508	1.16
−1	1.20	0.13	0.58	1.91	0.484	0.69
−1	1.23	0.20	0.47	1.90	0.468	0.60
−1	1.29	0.34	0.46	2.09	0.52	0.84
−1	1.32	0.29	0.42	2.03	0.484	0.77

[a] Calculated from redox balance. [b] Calculated from mass balance.

Table 2. First-order rate constants for the decomposition of hydrazoic acid at 97 °C

$[HNO_3]$/mol dm^{-3}	6.12	7.65	9.18	10.7
10^3k_1/min^{-1}	5.1	24.5	84	249

by reaction with hydrazoic acid; hydrazine and hydroxylamine decompose much more readily in nitric acid than does hydrazoic acid. Thus we think the stoicheiometric equation is given by (5). If our assumption that there are no other

$$x\,HNO_3 + HN_3 \longrightarrow 1.27\,N_2 + 0.27\,NO + 0.46\,N_2O + y\,H_2O \quad (5)$$

nitrogenous products is correct, then values of x and y can be obtained either from the material balance or the redox balance of equation (5).

Calculation of x by redox balance gives $x = 0.49$, while mass balance yields $x = 0.73$. When we examine the calculations based upon the individual experiments it is apparent that the redox-balance calculation (in which the N_2 formed disappears from the equation, as it has a formal oxidation number of zero) is much more self-consistent than the mass-balance calculation as can be seen from the sixth and seventh columns of Table 1. If we take the x value from the redox balance as correct, then the analysis for dinitrogen would have to yield a factor of 1.15 instead of 1.27 in equation (5) to give a mass balance. There are certainly much better analytical systems for N_2/NO/N_2O than our method which could probably improve on our results. For the present we will use equation (6), assuming our analysis for dinitrogen to have been high.

$$0.486\,HNO_3 + HN_3 \longrightarrow 1.15\,N_2 + 0.27\,NO + 0.46\,N_2O + 0.73\,H_2O \quad (6)$$

The kinetics of reaction, followed by the disappearance of hydrazoic acid, obeyed a simple first-order rate law with respect to hydrazoic acid concentration. The first-order rate constant increased markedly with increase in $[HNO_3]$ as can be seen from Table 2. A plot of log k_1 against H_0 was linear over the range 6.1—10.7 mol dm^{-3} nitric acid at 97 °C with a slope of 1.71. Measurements over the temperature range 50—70 °C in 12.2 mol dm^{-3} nitric acid gave an Arrhenius activation energy of 89 kJ mol^{-1}.

Measurements of the interaction of hydrazoic acid with the solvent aqueous nitric acid were made by measuring the Henry's law constant. The results are shown in Table 3. The results for solutions in water are in good agreement with the earlier studies of Feitknecht and Sahli,[7] of D'Orazio and Wood,[8] and of King and Templeton,[4] and do not require further comment. Salt effects on the solubility of non-electrolytes have been reviewed by Long and McDevitt.[9] They are usually rather small, and those observed for nitric acid are commonly unusually small, when compared with other 1 : 1 electrolytes. Thus, the small decrease in the Henry's law constant for HN_3 with increase in $[HNO_3]$ is reasonable. It might be argued that the results in Table 3 refer only to relatively low nitric acid concentrations, and that the effects might be different in more concentrated solutions. However, other volatilisation experiments over the range 4.65—7.75 mol dm^{-3} nitric acid at 97 °C showed no detectable variation in rate of volatilisation with acidity. Hydrazoic acid can interact with strong mineral acids and protonate to form $H_2N_3^+$ in relatively concentrated sulphuric acid, and a pK_a of −6.2 for this species has been proposed.[10] There would be no significant amount of protonation in our solutions for which the highest acidity corresponds to $H_0 = -3.3$.

Table 3. Henry's law constants for hydrazoic acid in aqueous solution

θ_c/°C	25	25	25	45	45
$[HNO_3]$/mol dm^{-3}	0	1.58	3.16	0	1.58
10^2K/atm dm^3 mol^{-1}	8.5	8.0	7.0	20.0	17.3
θ_c/°C	45	60	60	60	
$[HNO_3]$/mol dm^{-3}	3.16	0	1.58	3.16	
10^2K/atm dm^3 mol^{-1}	17.5	30	27	26	

Turning to the interpretation in terms of mechanism, the most striking features of the kinetics is the rapid increase in rate with acidity. This does not seem to involve any interaction of the medium with hydrazoic acid. The effect of acidity on the rate of reaction must be due to an increase in the concentration of the active nitrogen(V) species. The only likely candidates are the nitronium ion, the nitrate-acidium ion, and covalent nitric acid. The slope of a plot of log k_1 *versus* H_0 is very similar to the value of 1.80 observed[11] for reaction between nitric acid and sulphamic acid at 70 °C, and in this reaction the nitronium ion was considered to be the active species.

Certainly the increase in rate with stoicheiometric concentration of nitric acid is far too great for the active species to be covalent nitric acid. The nitrate acidium ion, $[H_2NO_3]^+$, is a possible electrophile, but has never been identified as an active species. We assume that our active species is $[NO_2]^+$.

The most likely reaction would appear to be an electrophilic substitution to form N_3NO_2 [equation (7)]. Two isomeric

$$[NO_2]^+ + HN_3 \longrightarrow N_3NO_2 + H^+ \quad (7)$$

species may be envisaged, $\mathrm{NNNN}\!<\!\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$ and NNNONO. The latter offers an obvious route to the nitrogen monoxide product by a fragmentation reaction (8), the same overall process as postulated by Masek.[2] The formation of N_2O is less easily

$$\mathrm{NNNONO} \longrightarrow N_2 + 2NO^{\cdot} \quad (8)$$

accounted for without postulating a rather complex rearrangement. Masek's suggestion, equations (3) and (4), appears plausible. However, the reaction between NO and HNO_3 to form HNO_2 is normally considered[12] to occur as in equations (9)—(12). The reaction of NO· basically requires

$$H^+ + HNO_2 + [NO_3]^- \rightleftharpoons N_2O_4 + H_2O \quad (9)$$

$$N_2O_4 \rightleftharpoons 2NO_2^{\cdot} \quad (10)$$

$$NO_2^{\cdot} + NO^{\cdot} \rightleftharpoons N_2O_3 \quad (11)$$

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2 \quad (12)$$

$NO_2^{\cdot}$, which is derived from N_2O_4 and its precursor HNO_2. It seems doubtful whether in the presence of a powerful nitrite scavenger such as hydrazoic acid there would be a sufficient concentration of HNO_2 for reaction by this route. Exchange of ^{15}N between NO· (g) and dilute nitric acid certainly requires the presence of traces of HNO_2 as a catalyst.[13]

An alternative pathway whereby NO_2 can be generated without HNO_2 as a precursor is set out in equations (13)—(16). This mechanism leads to a stoicheiometry (17). A

$$N_3ONO \longrightarrow N_3^{\bullet} + NO_2^{\bullet} \qquad (13)$$

$$2N_3^{\bullet} \longrightarrow 3N_2 \qquad (14)$$

$$2NO_2^{\bullet} \longrightarrow N_2O_4 \qquad (15)$$

$$N_2O_4 + HN_3 \longrightarrow [N_3NO] + HNO_3 \longrightarrow N_2 + N_2O + HNO_3 \qquad (16)$$

$$\tfrac{1}{3}\,HNO_3 + HN_3 \longrightarrow \tfrac{4}{3}\,N_2 + \tfrac{1}{3}\,N_2O + \tfrac{2}{3}\,H_2O \qquad (17)$$

combination of (8) and (17) cannot, however, account for the observed stoicheiometry. If we had 77.8% reaction by (8) and 22.2% by (17) we could account for the ratio of HNO_3 : HN_3 of 0.486 : 1; this would, however, predict 0.259 mol of N_2O and 0.444 mol of NO per mol of HN_3, almost the opposite of what is observed.[1] However, we have not allowed for interaction between these two mechanisms, and one possibility that must be considered is shown in equations (18) and

$$NO^{\bullet} + NO_2^{\bullet} \longrightarrow N_2O_3 \qquad (18)$$

$$N_2O_3 + 2HN_3 \longrightarrow 2N_2 + 2N_2O + H_2O \qquad (19)$$

(19). If this reaction occurred to some extent, then it would increase the proportion of N_2O, and decrease that of $NO^{\bullet}$. It is possible to attempt a more quantitative treatment by assuming that an amount α reacts by equation (8), an amount γ by equation (17), and that an amount β of the NO formed in (8) reacts with NO_2 formed as an intermediate in (13) as shown in (18) and (19). Our stoicheiometric equations can then be written as in (20) and (22).

$$\alpha\, HNO_3 + \alpha\, HN_3 \longrightarrow \alpha\, N_2 + 2\alpha\, NO + \alpha\, H_2O \qquad (20)$$

$$\gamma\, HNO_3 + 3\gamma\, HN_3 \longrightarrow 4\gamma\, N_2 + \gamma\, N_2O + 2\gamma\, H_2O \qquad (21)$$

$$\beta\, HNO_3 + 3\beta\, HN_3 + \beta\, NO \longrightarrow 3.5\,\beta\, N_2 + 2\beta\, N_2O + 2\beta\, H_2O \qquad (22)$$

By fitting (20)—(22) to the numbers in (6) one can show that $\alpha/T = 0.229$, $\beta/T = 0.118$, and $\gamma/T = 0.084$ gives a fair fit to (6) ($T = \alpha + 3\beta + 3\gamma$). We do not lay any emphasis on these numbers, other than noting that a combination of these two mechanisms can account for the product distribution. Other explanations are possible; clearly equation (23) would account for an increase in N_2O and a decrease in NO

$$NO^{\bullet} + N_3^{\bullet} \longrightarrow N_3NO \longrightarrow N_2 + N_2O \qquad (23)$$

and N_2. A similar mathematical treatment shows that the interactive pathway could also account for the results. Clearly both paths (18) + (19) and (23) might occur, and there may be other alternative explanations also.

There is no evidence at the moment to distinguish between these possibilities.

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