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REACTION MECHANISMS OF INORGANIC NITROGEN COMPOUNDS

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I. Introduction

Any reviewer of aspects of the chemistry of inorganic compounds of nitrogen faces a problem because of the amount and the variety of material available. Many common ligands contain nitrogen, and complexes containing such ligands could be held to fall within the scope of the title of this chapter. Attention has been focused upon the "simple" compounds of nitrogen, and upon a few reactions of coordinated ligands containing nitrogen, but the bulk of coordination chemistry has been deliberately excluded. The chemistry of nitrogen is one of those areas where the border between inorganic and organic chemistry is difficult to define, and some readers may feel that some of our excursions stray into the province of physical-organic chemistry. Such raiding parties may return with valuable plunder, and this type of foray into neighboring territory should be encouraged. Most of the papers cited deal with aspects of solution chemistry, and gas-phase reactions are only occasionally included. A new field of inorganic work, bioinorganic chemistry has also been mentioned only in passing. The last readily accessible and substantial review of the reaction mechanisms of nitrogen compounds was published in 1974 (*92*), and includes material up to late 1972. In this review particular attention has been paid to material published since that date, but many earlier papers have also been included. Literature coverage goes to about the end of 1977. Interested readers will find a great deal of information about recent work in the various sections of the Chemical Society Specialist Reports devoted to Inorganic Reaction Mechanisms. Developments in the inorganic chemistry of nitrogen have been reviewed in volumes edited by Colburn (*47*), and a good deal of kinetic material is to be found in volume 6 of the series on Comprehensive Chemical Kinetics edited by Bamford and Tipper (*13*). A recent book, "Mechanism of Oxidation by Metal Ions" by Benson, includes mention of many papers dealing with the oxidation of inorganic nitrogen compounds (*23*).

The types of reaction examined are so varied that it seems best to classify material by the compound studied, ordering the material in the sequence of the average formal oxidation state of nitrogen, and then dealing in turn with different types of mechanism. Many systems could be classified under more than one heading, and the arrangement of material has necessarily been somewhat arbitrary at times.

II. Sulfamic Acid

A. HYDROLYSIS REACTIONS

The kinetics of the acid-catalyzed hydrolysis of sulfamic acid have been followed in solutions containing up to 10 M perchloric acid (*93*), a much higher acidity than was used in previous studies. In earlier work the rate had been found to increase with acidity, leveling off around 2 M acid. The new measurements show that a rate maximum is observed, with a slow decrease in rate with increase of acidity beyond 2 M perchloric acid. Candlin and Wilkins (*41*) had previously proposed an A-1 mechanism for the hydrolysis of sulfamic acid ($NH_3{}^+SO_3{}^-$) at lower acidities, and the new results are interpreted as an additional A-2 pathway (in an A-1 mechanism a water molecule is not involved as a nucleophile in the transition state, whereas in an A-2 process it is involved).

$$\text{Rate} = k[H^+][NH_3{}^+SO_3{}^-]a_w \qquad (1)$$

An A-2 mechanism is also postulated for N-phenylsulfamic acid hydrolysis (*180*). The kinetics of hydrolysis of the sulfamate anion in aqueous alkali at high temperatures have also been measured (*156*).

B. OXIDATION BY NITRIC ACID

Sulfamic acid is commonly used as a scavenger for nitrous acid in solutions of nitric acid, but if the concentration of the latter is sufficiently great, another reaction is observed:

$$\overset{+}{N}H_3SO_3{}^- + HNO_3 \rightarrow N_2O + H_2SO_4 + H_2O \qquad (2)$$

At low temperatures nitramide can be isolated from the reaction mixture (*195*); as nitramide readily decomposes to nitrous oxide and water, this suggests that it might be an intermediate. A brief kinetic study gave a rate equation first order in sulfamic acid and in nitric acid, and this was interpreted (*9*) as an electrophilic displacement of SO_3H^+ by $NO_2{}^+$ to form nitramide. However, this mechanism apparently needs modification. A more extensive study (*94*, *107*) shows that reaction involves three consecutive stages, with relative rates $v_1 > v_2 \geqslant v_3$. The kinetics of the last of these stages, v_3, are identical with those reported in (*9*). However the details of the mechanism are not yet clear, and at this stage it is not possible to postulate equations for the three stages with any degree of confidence.

III. Nitrogen Trihalides

A. NITROGEN TRICHLORIDE

Nitrogen trichloride is best known as a notoriously explosive compound, but there is a great deal of interest in the chemistry of its reactions in aqueous solution. It can be formed during the treatment of water, by chlorination of traces of ammonia. It gives an unpleasant taste and odor to drinking water, and it irritates mucus membranes with which it has contact. Aspects of its chemistry in aqueous solution have been discussed by Saguinsin and Morris (*164*). The chlorination of ammonia by hypochlorous acid involves a slow formation of chloramine, which is followed by faster processes to give dichloramine and nitrogen trichloride. It has proved possible to examine the kinetics of the final stage, and rate equation (3) has been deduced.

$$(d[\mathrm{NCl_3}]/dt)_0 = (k_1 + k_2[\mathrm{H^+}][\mathrm{Cl^-}])[\mathrm{HOCl}][\mathrm{NH_2Cl}]_0 \qquad (3)$$

This corresponds to chlorination by hypochlorous acid and chlorine. The chlorination of ammonia by $\mathrm{Me_3CCOCl}$ in *cyclo*-hexane solution containing 0.2 *M* *t*-butanol has also been investigated. Chloramine, dichloramine, and nitrogen trichloride were found to be formed successively (*19*).

The decomposition reaction of nitrogen trichloride in aqueous media has also been studied. The rate increases in alkaline solution, and follows Eq. (4).

$$-(d[\mathrm{NCl_3}]/dt)_0 = (k_3 + k_4[\mathrm{OH^-}])[\mathrm{NCl_3}] \qquad (4)$$

Reaction is thought to involve formation of dichloramine, followed by a complex disproportionation of this species

$$\mathrm{2NHCl_2 + H_2O \rightarrow N_2 + HOCl + 3H^+ + 3Cl^-} \qquad (5)$$

There has been a study of the thermal decomposition of nitrogen trichloride in carbon tetrachloride solution (*158*). The presence of aromatic compounds such as benzene, toluene, etc., increases the rate of decomposition, due to π complex formation; thus in the presence of toluene the activation energy drops by ca. 10 kcal mol^{-1}. In the presence of mesitylene an autocatalytic reaction is observed.

The reactions of one of the above intermediates, chloramine, were investigated by Anbar and Yagil (*6*) some years ago. In sufficiently alkaline solution chloramine hydrolyzes to give hydroxylamine as a primary product, probably by a bimolecular nucleophilic substitution by hydroxide ion. The same authors examined the formation of hydrazine from chloramine and ammonia (*5*), and concluded that reaction involved nucleophilic attack by ammonia on chloramine or its conjugate base.

B. NITROGEN TRIBROMIDE

A detailed picture has emerged of the decomposition of a closely related compound, nitrogen tribromide, in aqueous media in the pH range 6 to 8 (*112*, *127*). The tribromide is generated by treating an aqueous solution of ammonia with hypobromous acid or bromine, the bromamines being formed much more rapidly than the corresponding chloramines. In the decomposition of nitrogen tribromide the ammonia is oxidized to dinitrogen, and a two-term rate law [Eq. (6)] is observed.

$$-d[\mathrm{NBr_3}]/dt = k_5[\mathrm{NBr_3}]^2[\mathrm{OH^-}][\mathrm{HOBr}]^{-1} + k_6[\mathrm{NBr_3}]^2 \qquad (6)$$

The pathway proposed to account for the first term is (7)–(10), with (9) as the slow step

$$\mathrm{NBr_3 + H_2O \rightleftharpoons NHBr_2 + HOBr} \qquad (7)$$

$$\mathrm{NHBr_2 + OH^- \rightleftharpoons NBr_2^- + H_2O} \qquad (8)$$

$$\mathrm{NHBr_2^- + NBr_3 \rightarrow N_2Br_4 + Br^-} \qquad (9)$$

$$\mathrm{N_2Br_4 + 2H_2O \rightarrow N_2 + 2HOBr + 2H^+ + 2Br^-} \qquad (10)$$

The rate-determining step corresponding to the second term in equation (6) is suggested to be reaction (11), followed by fast steps (12) and (10)

$$\mathrm{2NBr_3 \rightarrow N_2Br_5^+ + Br^-} \qquad (11)$$

$$\mathrm{N_2Br_5^+ + H_2O \rightarrow N_2Br_4 + H^+ + HOBr} \qquad (12)$$

A related species (NCl_2^-), a chloronitrene (NCl) and dichlorodiimide (ClN=NCl) have been postulated (*218*) as intermediates in the reaction of *N*,*N*-dichloroamides with alkoxides.

IV. Hydrazine

A. PROTONATION OF HYDRAZINE

Hydrazine normally exists in aqueous solution as the free base or the monoprotonated conjugate acid $N_2H_5^+$, and both of these species are frequently postulated as the active species in kinetic studies of reactions of hydrazine. The doubly protonated form $N_2H_6^{2+}$ is known in the solid state, and there are reports of its existence in aqueous solution. A pK_a of -0.88 has been reported (*166*). If this is correct, it would be expected that a significant proportion of hydrazine would exist in this form in solutions containing several moles per liter of strong mineral acids, and this should show up in the dependence of rate reaction upon acidity. Attempts to observe this effect in the nitrosation of hydrazine have been unsuccessful (*154*). A search for PMR evidence for a second protonation of methylhydrazine was also unsuccessful. Spectrophotometric studies of the arylhydrazines in concentrated mineral acids indicate pK_a values for the doubly protonated species in the range -5 to -6 (*116*). Mechanistic studies of the oxidation of hydrazine often use a comparison of the reactivity of the alkylhydrazines with hydrazine as a criterion of mechanism, and it has always been assumed that protonation is almost 100% on the alkylated nitrogen. A study has been made by Condon and co-workers of the basicity; thus for protonated methylhydrazine it is calculated that there is 70% $CH_3NH_2{}^+NH_2$ and 30% $CH_3NHNH_3^+$ (*50*). This result is in close agreement with proportions of products observed in the electrophilic nitrosation of methylhydrazine, which appear to be derived from the two tautomers (*152*). Thus it seems desirable to consider the two different conjugate acid species when interpreting the results of mechanistic studies of the reactions of alkylhydrazines in acid solution.

B. REACTION OF HYDRAZINE WITH OXIDIZING AGENTS

Hydrazine has long been a favorite substrate for mechanistic studies with oxidizing agents because of the relationship between stoichiometry and mechanism. One equivalent reagents produce nitrogen and ammonia as products and may involve N_2H_3 (and N_4H_6) as intermediates, whereas two equivalent reagents form diimide, N_2H_2, and this gives exclusively nitrogen. At high acidities, and with two equivalent reagents, hydrazoic acid may be a product (*89*). Earlier work has been summarized by Sykes (*192*) and by Bottomley (*29*). Evidence for these species has recently come from a number of sources. Diimide and tetrazene have been obtained as pure species, and their decomposition reactions were investigated (Section V). The species N_2H_3 has been observed in pulse-radiolysis studies of the oxidation of hydrazine by the hydroxyl radical (*88*), and the conjugate acid $N_2H_4^+$ has been observed as an intermediate in the oxidation of hydrazine by cerium(IV) using electron spin resonance (ESR) methods (*140*).

The system that has been most intensively studied recently is the oxidation by chromium(VI). Haight *et al.* (*86*) have extended kinetic measurements up to 2 *M* acid. At lower acidities, pH 1.6–3.0, they find evidence for general acid catalysis. The mechanism proposed involves $^+NH_3NH_2CrO_3^-$ and related conjugate acid and base species, and complex formation occurs to a sufficient extent to allow the estimation of a formation constant.

$$HCrO_4^- + {}^+NH_3NH_2 \rightleftharpoons {}^+NH_3NHCrO_3^- + H_2O \quad (13)$$

$$NH_3NHCrO_3 \rightleftharpoons {}^+NH_3NHCrO_3H \quad (14)$$

$$^+NH_3NHCrO_3H + B^- \rightleftharpoons NH_2NHCrO_3H + HB \quad (15)$$

$$NH_2NHCrO_3H \rightleftharpoons Cr(IV) + N_2H_2 \quad (16)$$

$$2N_2H_2 \rightleftharpoons N_2H_4 + N_2 \quad (17)$$

$$2Cr(IV) \rightarrow Cr(V) + Cr(III) \quad (18)$$

$$Cr(V) + N_2H_4 \rightarrow \tfrac{1}{2}N_2 + Cr(III) \quad (19)$$

It is concluded that chromium(V) is formed by reaction (18), not by trapping with chromium(VI). Three other studies of the reaction have been reported (*16*, *83*, *159*). In the third of these papers (*159*), the formation of chromium(V) is explained as due to a reaction between chromium(IV) and chromium(VI), and the authors also suggest a direct reduction of chromium(V) to chromium(III) by diimide.

A number of other oxidizing agents have been studied. Thallium(III) oxidizes hydrazine, forming thallium(I) and nitrogen. The rate law is given in Eq. (20), and it is suggested that the inverse dependence upon $[H^+]$ indicates complexing between N_2H_4 and thallium(III) (*198*).

$$-d[\mathrm{Tl(III)}]/dt = k[\mathrm{Tl(III)}][N_2H_5{}^+][H^+]^{-1} \tag{20}$$

The oxidation of hydrazine by thallium(III) acetate complexes has been reported (*84*).

In the oxidation of hydrazine by $[\mathrm{Co(nta)(OH_2)_2}]$, reaction is thought to occur between the conjugate base of the complex and $N_2H_5{}^+$ (nta = nitrilotriacetate) (*197*). Similarly the oxidation of hydrazine by cerium(IV) is thought (*144*) to involve the hydrazinium ion in the rate-determining stage

$$\mathrm{CeOH^{3+} + N_2H_5{}^+ \rightarrow Ce^{3+} + N_2H_4{}^{+\cdot} + H_2O} \tag{21}$$

The protonated hydrazyl radical has been identified by flow ESR techniques (*140*). The oxidation of methylhydrazine by cerium(IV) in acid solution has also been investigated (*118*). Another powerful one-equivalent oxidizing agent, manganese(III), also reacts with the hydrazinium ion by pathways involving Mn^{3+} and $MnOH^{2+}$ (*55*). Two studies of oxidation reactions of hydrazine involving copper(II) have been published. The copper(II)-catalyzed oxidation of hydrazine by hydrogen peroxide obeys a rate law that is interpreted as showing the formation of a substantial amount of a copper(II)–hydrazine complex (*213*).

$$d[N_2]/dt = k[N_2H_4][H_2O_2][\mathrm{Cu(II)}](1 + K[N_2H_4])^{-1} \tag{22}$$

The other study concerns the oxidation of 1,1-dimethylhydrazine by copper(II) chloride in hydrochloric acid (*25*). Outer sphere mechanisms have been proposed (*128*) for the oxidation of hydrazine by $\mathrm{Mo(CN)_8{}^{3-}}$ and $\mathrm{W(CN)_8{}^{3-}}$. A rather complex mechanism, again involving a molybdenum(V) species, has been proposed for the molybdenum(VI)-catalyzed oxidation of hydrazine by nitric acid (*122*).

$$\mathrm{4Mo(VI) + N_2H_4 \rightarrow 2Mo_2(V) + N_2} \tag{23}$$

$$\mathrm{Mo_2(V) + N_2H_4 \rightarrow 2Mo(IV) + N_2H_2} \tag{24}$$

$$\mathrm{Mo(IV) + HNO_3 \rightarrow Mo(V) + NO_2{}^{\cdot}} \tag{25}$$

The oxidation of hydrazine by vanadium(V) has been studied (*20*), and so has the oxidation by $\mathrm{PtCl_6{}^{2-}}$ (*173*). Finally, we note studies of the reaction of trans-$\mathrm{Coen_2Cl_2{}^+}$ with hydrazine, with methylhydrazine and with 1,1-dimethylhydrazine (*42*), and of the reaction of methylhydrazine with $PtCl_2(CNAr)_2$ in dichloromethane (*44*).

V. Diimide and Tetrazene

A. DIIMIDE

Diimide (N_2H_2) also known as diimine or diazene, has long been proposed as an active intermediate, particularly in the oxidation of hydrazine. It can be made by passing hydrazine vapor through a microwave discharge and can be frozen out. Rapid warming of the frozen material enables diimide to be obtained in the gas phase (together with ammonia) (*225*). It can also be obtained by the thermal decomposition of alkali metal tosyl hydrazides (Li, Na, K) at very low pressures (*219*). Infrared spectra enable the cis and the trans isomers to be identified (*220*). With the cesium salt a different product is obtained: $NH_2{=}N$. Diimide is a moderately stable substance in the gas phase with a half-life typically of the order of minutes (*225*, *227*). The kinetics of decomposition are complex, and first-order, second-order, or mixed-order behavior may be observed. The decomposition in liquid ammonia ($-65°$ to $-38°C$) follows a somewhat complex path. In the early stages there is a rapid reaction with a kinetic order greater than one, while in the later stages a simple first-order decay is observed with $k_1 = 1.9 \times 10^3 \exp(-3300/T)\ \text{sec}^{-1}$. The authors speculate that the rapid initial process may involve the cis isomer while the slower first-order reaction may be a trans to cis isomerization (*225*). The activation energy is very much less than that calculated for the gas-phase isomerization (see below), and further work on this system would be of interest. Diimide is, of course, a good reagent for stereospecific hydrogenation, and the mechanism of reaction with a series of unsaturated compounds in the gas phase has been examined (*226*).

Diimide is a compound for which theoretical calculations can be useful in helping us to understand its properties. Winter and Pitzer (*230*) calculate that the trans- isomer is 6.6 kcal mol^{-1} more stable than the cis form, and the lowest energy pathway for isomerization should involve inversion at one nitrogen, with $E_a = 47$ kcal mol^{-1}. Calculations of the activation energy for cis- to trans-isomerization in XNNX by this mechanism are in the sequence F > H > Me > CN (*1931*).

B. TETRAZENE

Another frequently postulated intermediate is trans-2-tetrazene, NH_2NNNH_2, and this has now been isolated as a product of the reaction of tetrakis (trimethylsilyl) tetrazene with trifluoroacetic acid in methylene chloride at −78°C. It is unexpectedly stable; the solid begins to thermolyse at 0°C, and the gaseous substance is metastable at room temperature. On thermolysis of the pure compound a yield of 75% $N_2 + N_2H_4$ and 25% of $NH_4^+N_3^-$ was obtained. In methanol solution the corresponding yields were 40% and 60%, respectively (*221*). Other studies indicate that the thermal decomposition of tetrazene, which may be explosive, has a high activation energy (*123*, *149*).

VI. Hydroxylamine

A. Decomposition of Hydroxylamine in Alkaline Solution

Hydroxylamine is normally thought of as a moderately basic substance (in water NH_3OH^+ has a pK_a of 5.9), but it can also function as an acid. A value of 13.7 has been obtained for the pK_a of free hydroxylamine in aqueous solution at 25° (*97*).

$$NH_2OH \rightleftharpoons NH_2O^- + H^+ \tag{26}$$

In the absence of oxygen such solutions are stable, but in the presence of oxygen reaction occurs by attack upon the conjugate base, with the formation of the nitroxyl anion. This in turn reacts with oxygen to form the peroxonitrite anion (*95*).

$$NH_2O^- + O_2 \rightarrow H_2O_2 + NO^- \tag{27}$$

$$NO^- + O_2 \rightarrow ONOO^- \tag{28}$$

In the presence of copper(II) peroxonitrite then reacts with hydroxylamine, regenerating the nitroxyl anion, which in turn can form more peroxonitrite (*96*).

$$ONOO^- + NH_2OH + OH^- \rightarrow NO^- + NO_2^- + 2H_2O \tag{29}$$

Thus, in the presence of oxygen, alkaline solutions of hydroxylamine are effectively oxidized to nitrite.

Veprek-Siska and Lunak have examined the decomposition of hydroxylamine in the presence of $Ni(CN)_4^{2-}$, a complex that is known to act as a trap for NO^-. In alkaline media decomposition of hydroxylamine is reported to follow a rate law that is first order in hydroxylamine, and third order in hydroxide ion (*132*). Reaction is catalyzed by a range of cations, and when these are completely complexed decomposition does not occur. In the presence of $Ni(CN)_4^{2-}$ in an inert atmosphere, the pathway below is suggested. The absence of N_2O among the products is held to argue against nitroxyl as an intermediate (*209*).

$$Ni(CN)_4^{2-} + NH_2OH \rightleftharpoons Ni(CN)_3(NH_2OH)^- + CN^- \qquad (30)$$

$$Ni(CN)_3(NH_2OH)^- + NH_2OH + OH^- \rightarrow Ni(CN)_3NO^{2-} + NH_3 + 2H_2O \qquad (31)$$

$$Ni(CN)_3NO^{2-} + NH_2OH + CN^- \rightarrow Ni(CN)_4^{2-} + N_2 + OH^- + H_2O \qquad (32)$$

In the presence of oxygen, a different stoichiometry is found

$$Ni(CN)_4^{2-} + NH_2OH + \tfrac{1}{2}O_2 + OH^- \rightarrow Ni(CN)_3NO^{2-} + CN^- + 2H_2O \qquad (33)$$

The rate is increased by metal ions, and is decreased by added cyanide ion, and the mechanism (34) to (35) is postulated: (*210*).

$$Ni(CN)_4^{2-} + NH_2OH + 3OH^- \rightarrow Ni(CN)_3NO^{4-} + CN^- + 3H_2O \qquad (34)$$

$$Ni(CN)_3NO^{4-} + O_2 + H_2O \rightarrow Ni(CN)_3NO^{2-} + 2OH^- \qquad (35)$$

B. PHOTOLYSIS AND RADIOLYSIS OF HYDROXYLAMINE SOLUTIONS

Photolysis of hydroxylamine is thought to involve the formation of amino and hydroxyl radicals in the primary stage, and these may attack hydroxylamine with the abstraction of hydrogen to form $NHOH^\bullet$ (*18*), which can then disproportionate.

$$2NHOH^\bullet \rightarrow N_2 + 2H_2O \qquad (36)$$

Pulse radiolysis studies also lead to the conclusion that $NHOH^\bullet$ radicals are produced in the oxidation of hydroxylamine by hydroxyl (*178*). This radical can form a conjugate acid ($NH_2OH^{+\bullet}$), with a pK_a of 4.2. In more acidic media the radical $NH_2O^\bullet$ is often considered to be involved in the oxidation of hydroxylamine by metal ions, and this is a tautomer of $NHOH^\bullet$. The amino radical also acts as a base, and a pK_a of 6.7 has been suggested for $NH_3^{\bullet+}$.

C. REACTION OF HYDROXYLAMINE WITH OXIDIZING AGENTS

Hydroxylamine is oxidized by a wide variety of reagents and the stoichiometry is often a function of concentration. In many cases the postulated reaction mechanism involves oxidation to $NH_2O^{\cdot}$, which can decompose to nitrogen

$$NH_2OH \rightleftharpoons NH_2O^{\cdot} + H^+ \tag{37}$$

$$2NH_2O^{\cdot} \rightarrow N_2 + 2H_2O \tag{38}$$

In the presence of a suitable oxidizing agent, further oxidation to nitroxyl may occur, as in the oxidation of hydroxylamine by cerium(IV) (*211*)

$$NH_2O^{\cdot} \rightleftharpoons HNO + H^+ \tag{39}$$

$$2HNO \rightarrow N_2O + N_2O \tag{40}$$

In the oxidation of hydroxylamine by plutonium(IV), dinitrogen and nitrous oxide are products formed by this type of mechanism (*15*). The effect of ferric ion catalysis on the plutonium(IV)-hydroxylamine reaction has also been reported (*14*). In some cases further oxidation occurs to nitrous or nitric acids. This can sometimes be detected by changes in rate or stoichiometry when a nitrite trap, such as urea or sulfamic acid, is added to the reacting system as in the oxidation of hydroxylamine by thallium(III) (*199*). Here the stoichiometry varies with the ratio in which the reactants are used; with a sufficient excess of the oxidizing agent either nitrate or nitrate may be obtained; addition of urea (a nitrite scavenger) reduces the stoichiometry from Tl(III):NH_2OH::3:1 to 2:1. In many cases these later stages in the oxidation are rapid, and only the initial oxidation to $NH_2O^{\cdot}$ can be detected kinetically, as in the oxidation of hydroxylamine to nitric acid by manganese(III) (*54*) or silver(II) (*90*).

$$Ag^{2+} + NH_3OH^+ \rightarrow Ag^+ + NH_2O^{\cdot} + 2H^+ \tag{41}$$

$$AgOH^+ + NH_3OH^+ \rightarrow Ag^+ + NH_2O^{\cdot} + H_3O^+ \tag{42}$$

$$2H_2O + 5Ag^{2+} + NH_2O^{\cdot} \xrightarrow[\text{fast}]{} 5Ag^+ + NO_3^- + 6H^+ \tag{43}$$

The oxidation of hydroxylamine by cobalt(III) shows the complications that can arise. With a large enough excess of cobalt(III) the stoichiometry is given by (44), but when hydroxylamine is in large excess a different reaction (45) is observed.

$$6Co^{3+} + NH_3OH^+ + 2H_2O \rightarrow 6Co^{2+} + NO_3^- + 13H^+ \tag{44}$$

$$Co^{3+} + NH_3OH^+ \rightarrow Co^{2+} + N_2 + H_2O + 2H^+ \tag{45}$$

In the latter case the pathway is (31) to (33).

$$Co^{3+} + NH_3OH^+ \rightarrow Co^{2+} + NH_2O^{\cdot} + H^+ \tag{46}$$

$$CoOH^{2+} + NH_3OH^+ \rightarrow Co^{2+} + NH_2O^{\cdot} + H^+ \tag{47}$$

$$2NH_2O^{\cdot} \xrightarrow[\text{fast}]{} N_2 + 2H_2O \tag{48}$$

In excess oxidizing agent, the $NH_2O^{\cdot}$ is further oxidized, the active species being a cobalt(III)–cobalt(II) dimer (*181*).

$$Co^{2+} + Co^{3+} \rightleftharpoons Co^{3+}(H_2O)Co^{2+} \tag{49}$$

$$Co^{3+}(H_2O)Co^{2+} + NH_2O^{\cdot} \rightarrow 2Co^{2+} + HNO + H^+ \tag{50}$$

$$4Co^{3+} + HNO + 2H_2O \xrightarrow[\text{fast}]{} NO_3^- + 4Co^{2+} + 5H^+ \tag{51}$$

Many of the reactions in which hydroxylamine is oxidized by metal ions involve the formation of hydroxylamine complexes. The analytically useful reaction between hydroxylamine and ferric ion has been examined (*21*) kinetically by Bengtsson. In the absence of copper(II) as a catalyst, rate law (53) is observed in 0.1 *M* acid.

$$4Fe^{3+} + 2NH_3OH^+ \rightarrow 4Fe^{2+} + N_2O + 6H^+ + H_2O \tag{52}$$

$$\text{Rate} = \frac{k[\text{Fe(III)}]^2[NH_2OH]^2}{([NH_2OH] + k_2[\text{Fe(II)}])} \tag{53}$$

In the presence of copper(II) a more complex rate law is observed.

$$\text{Rate} = \frac{k_3[\text{Fe(II)}][\text{Cu(II)}][NH_2OH]}{([\text{Fe(II)}][NH_2OH] + k_4[\text{Cu(II)}][NH_2OH] + k_5[\text{Fe(II)}])} \tag{54}$$

[The concentration terms here refer to stoichiometric concentrations.] Bengtsson suggests that the mechanism involves binuclear intermediates containing two hydroxylamine bridges. He has also examined the oxidation of hydroxylamine by vanadium(V), and proposes a mechanism with two parallel pathways involving complexes of vanadium(V) with one or two hydroxylamine ligands, respectively (*22*).

The oxidation of hydroxylamine by hexacyanoferrate(III) is markedly affected by traces of iron(II) or copper(II) present in the reagents used. Addition of EDTA eliminates catalysis by copper(II), but introduces a new pathway involving the iron(III)–EDTA complex as a reactant, with a rate law first order in hydroxylamine and the total concentration of iron–EDTA complexes. The mechanism proposed (*31*) again involves formation of a hydroxylamine complex and is shown below, (55)–(58), where M^+ and M represent the oxidized and reduced forms of the catalytic species, i.e., $M^+ = Fe(III)\ EDTA^-$.

$$M^+ + NH_2OH \rightarrow M(NH_2OH)^+ \tag{55}$$

$$H_2O + M(NH_2OH)^+ + Fe(CN)_6{}^{3-} \rightarrow M(NH_2O)^+ + Fe(CN)_6{}^{4-} + H_3O^+ \tag{56}$$

$$M(NH_2O)^+ + NH_2OH \rightarrow M + N_2 + H_3O^+ + H_2O \tag{57}$$

$$M + Fe(CN)_6{}^{3-} \rightarrow M^+ + Fe(CN)_6{}^{4-} \tag{58}$$

If the forward reaction in (55) is rate limiting, the kinetics are accounted for satisfactorily. For the copper(II)-catalyzed reaction (in the absence of EDTA), the rate law is accounted for if (56) is rate determining ($M^+ = Cu^{2+}$). Copper(II) is also a catalyst in the oxidation of hydroxylamine by peroxodisulfate to nitrous oxide (*190*). The oxidation of hydroxylamine by copper(II) in the presence of a reagent to scavenge the copper(I) formed has also been examined (*111*).

Another oxidation of hydroxylamine in which complex formation with a metal ion is assumed, and that has aroused a good deal of interest, is the copper(II)-catalyzed reaction with hydrogen peroxide. The mechanism suggested (*69*) involves an active species in which both hydroxylamine and hydrogen peroxide are coordinated to the metal, and it has been proposed that this system models some features of the peroxidases. A study of oxidation of $[Coen_2Cl(NH_2OH)]^{2+}$ by hydrogen peroxide has recently been carried out, as in this case the hydroxylamine starts out coordinated to the metal ion. The dependence of rate upon acidity is not simple, but for solutions with a pH less than 3.9 the rate of reaction is first order with respect to the concentration of complex and hydrogen ion, and zero order with respect to that of hydrogen peroxide. A rate-determining loss of chloride ion, followed by a rapid entry of peroxide into the coordination sphere is postulated (*177*).

Another reaction of the same complex that has been studied involves nitrous acid, and has proved to be a complicated system. At sufficiently high acidities, the rate law has the form (59), while at low acidities Eq. (60) appears to hold.

$$\text{Rate} = k[\text{H}^+][\text{HNO}_2][\text{complex}] \tag{59}$$

$$\text{Rate} = k'[\text{H}^+]^{-1}[\text{HNO}_2][\text{complex}] \tag{60}$$

When the *O*-methylhydroxylamine complex is used, no reaction occurs. In acidic media, pH < 2, Eq. (59) is strictly analogous to the law observed (*98*) for reaction between hydroxylamine and nitrite, except that the coordinated hydroxylamine is roughly one-tenth as reactive as the free hydroxylammonium ion. An electrophilic nitrosation on the oxygen to form a species Co—NH$_2$—O—NO is proposed (*177*), and this seems very likely (the effect of O-methylation exactly parallels what is observed with the nitrosation of free hydroxylamine) (*99*). Interpretation of (60) is much more difficult. Reaction does not appear to involve substitution by nitrite ion at the complex because the direct displacement reaction leads to products different to those observed under the conditions where (60) holds. A reaction between nitrosonium ion and a doubly deprotonated complex would be consistent with the kinetic form, but one must ask whether the concentration of the doubly deprotonated complex could be great enough to account for the observed rate. This is an interesting but very difficult system.

The oxidation of hydroxylamine by chromium(VI) is also a complex system and has been studied in some detail by Haight *et al.* (*167*), and by Sen Gupta *et al.* (*174*). The stoichiometry varies with the pH, and with the initial composition of the reaction mixture. In acetate buffer the rate law reported is (61):

$$\begin{aligned} -d[\text{Cr(VI)}]/dt = {} & \{[\text{Cr(VI)}][\text{NH}_3\text{OH}^+](k_\text{A}[\text{H}^+] + k_\text{B}[\text{HOAc}] + k_\text{C} \\ & + k_\text{D}K_\text{f}K_\text{An}[\text{H}^+]^{-1} + k_\text{E}K_\text{f}K_\text{An}[\text{OAc}^-]K_\text{a}{}^{-1}\} \\ & \times \{1 + [\text{H}^+]K_\text{Ac}^{-1} + K_\text{f}[\text{HOAc}] \\ & + K_\text{f}K_\text{An}[\text{NH}_3\text{OH}^+][\text{H}^+]^{-1}\}^{-1} \end{aligned} \tag{61}$$

Reaction is thought to proceed through the formation of an O-bonded ester (in *O*-methylhydroxylamine reaction is greatly inhibited), and the ester NH$_3{}^+$OCrO$_3{}^-$ and its conjugate base are thought to undergo acid- and base-assisted internal redox reactions.

$$\text{B}\ \text{H}_3\overset{+}{\text{N}}\text{OCrO}_3{}^- + \text{H}^+ \rightarrow \text{BH}^+ + \text{NH}_2\text{OCrO}_3\text{H} \rightarrow \text{products} \tag{62}$$

$$B \curvearrowright H_2NOCrO_3^- \curvearrowright + H^+ \rightarrow BH^+ + H\bar{N}OCrO_3H \rightarrow \text{products} \qquad (63)$$

Sen Gupta and co-workers have also examined the oxidation of hydroxylamine by platinum(IV) in acetate buffers (*172*). The kinetics of oxidation of hydroxylamine by aqueous solutions of bromine have also been reported (*125*).

D. REACTION OF HYDROXYLAMINE WITH REDUCING AGENTS

Hydroxylamine also acts as an oxidizing agent. Tertiary phosphines are converted to phosphine oxides, with reduction of hydroxylamine to ammonia, and different pathways are proposed when the hydroxylamine is in the acidic and basic forms (*183*). The reduction of hydroxylamine by vanadium(III) (*204*) and by titanium(III) (*205*) has also been reported. It is postulated that $NH_2^\bullet$ radicals are intermediates, as suggested by earlier ESR measurements (*60*). The titanium(III) reaction has also been investigated by another group, who also propose an $NH_2^\bullet$ radical intermediate (*155*).

VII. The Sulfonic Acids of Hydroxylamine and Derived Species

A. HYDROXYLAMINE-*O*-SULFONIC ACID

The sulfonic acids derived from hydroxylamine, and some of the derivatives of these compounds, are treated as a group for the sake of convenience. Some earlier work has been summarized by Becke-Goehring and Flück (*17*). The reactions of hydroxylamine *O*-sulfonate with a variety of nucleophiles have led to the establishment of a reactivity sequence similar to that observed with substitution at methyl iodide, at *trans*-dipyridinedichloroplatinum(II) and at hydrogen peroxide.

$$\text{Nuc}^- + NH_2OSO_3^- \rightarrow \text{NucNH}_2 + SO_4^{2-} \qquad (64)$$

The polarizibility of the nucleophile seems to be important in determining the reactivity, and its basicity is of only minor importance (*124*). There seems to be a general similarity in the reactivity spread observed for nucleophilic substitution at sp^3 carbon and at sp^3 nitrogen. In some of these substitutions the rate law contains an acid-catalyzed term. Kinetic data are given in Table I.

The alkaline hydrolysis of hydroxylamine *O*-sulfonate is catalyzed by trace metal ions. This effect can be eliminated by the addition of

TABLE I

RELATIVE REACTIVITIES OF NUCLEOPHILES TOWARD $NH_2OSO_3^-$ AT 20° (*124*)

$C_2H_5S^-$	Ph_3P	$(NH_2)_2CS$	$S_2O_3^{2-}$	I^-	$(C_2H_5)_3N$	$HONH_2$	OH^-
460	>28	24	8	1.00	0.32	0.020	0.0003

EDTA as a complexing agent, although the advantages are somewhat offset by the introduction of a new reaction pathway involving EDTA (*189*). In the presence of hydrazine and hydroxylamine new pathways are observed involving N_2H_4 and NH_2O^- as nucleophiles. In the latter case diimide is postulated as a reaction intermediate.

$$NH_2OSO_3^- + NH_2O^- \rightarrow HNNH + SO_4^{2-} + 2H_2O \qquad (65)$$

A kinetic analysis of the variation of rate with pH leads to a pK_a of 13.7 for hydroxylamine, in agreement with other values (see Section VI,A). The disproportionation of diimide can yield hydrazine, and this can lead to kinetic complications. These can be minimized by scavenging the diimide with fumarate ions.

$$2HNNH \rightarrow N_2H_4 + N_2 \qquad (66)$$

$$N_2H_4 + NH_2OSO_3^- \rightarrow HNNH + NH_4^+ + SO_4^{2-} \qquad (67)$$

When thiourea is the nucleophile, the interesting new species $(NH_2)_2CSNH_2^+$ is formed.

B. HYDROXYLAMINE-*N*-MONOSULFONIC ACID

This species undergoes alkaline hydrolysis through the conjugate base $ONHSO_3^{2-}$, as the active form (*168*).

C. NITROSYLDISULFONIC ACID

The nitrosyldisulfonate radical anion, $^{\cdot}ON(SO_3)_2^{2-}$ (Fremy's salt) is a moderately stable substance. It has been used as an ESR standard, and as a selective oxidizing agent. It decomposes in aqueous solution by a first-order process, accompanied by a rapid chain reaction propagated by nitrous acid (a product of the first-order pathway). The stoichiometry of the chain process is probably given by (68).

$$4^{\cdot}ON(SO_3)_2^{2-} + 3H_2O \rightarrow 2HON(SO_3)_2^{2-} + N_2O + 4SO_4^{2-} + 4H^+ \qquad (68)$$

Nitrous acid has been found to be an intermediate, on the basis of spectrophotometric measurements (*228*). Addition of sulfamic acid as a nitrite trap eliminates the chain process and enables the first-order reaction to be studied in isolation. The stoichiometry is quite different in the presence of a nitrite scavenger.

$$4\dot{O}N(SO_3)_2{}^{2-} \rightarrow 2ON(SO_3)_3{}^{3-} + ON(SO_3)_2{}^{3-} + NO^+ \tag{69}$$

The likely mechanism is set out below, with (70) as the rate-determining stage:

$$O\dot{N}(SO_3)_2{}^{2-} \rightarrow O\dot{N}SO_3 + SO_3{}^{2-} \tag{70}$$

$$O\dot{N}SO_3 \rightarrow NO^+ + \dot{S}O_3{}^- \tag{71}$$

$$ON(SO_3)_2{}^{2-} + SO_3{}^{2-} \rightarrow {}^-ON(SO_3)_2{}^{2-} + \dot{S}O_3{}^- \tag{72}$$

$$O\dot{N}(SO_3)_2{}^{2-} + \dot{S}O_3{}^- \rightarrow ON(SO_3)_3{}^{3-} \tag{73}$$

Wilson has also examined the decomposition of the nitrosodisulfonate radical anion in strongly alkaline solutions (*229*) and concludes that nucleophilic attack by hydroxide ion results in displacement of the sulfite ion.

D. *N*-NITROSOHYDROXYLAMINE *N*-SULFONATE

The decomposition of *N*-nitrosohydroxylamine *N*-sulfonate, $ON(SO_3{}^-)(NO^-)$, can occur by an acid-catalyzed route, in which *cis*-hyponitrite has been suggested as an intermediate (*191*)

$$ON(SO_3{}^-)NO^- + H^+ \rightleftharpoons ON(SO_3{}^-)NOH \tag{74}$$

$$ON(SO_3{}^-)(NOH) + H_2O \rightarrow cis\text{-}HONNO^- + SO_4{}^{2-} + 2H^+ \tag{75}$$

$$cis\text{-}HONNO^- \rightarrow N_2O + OH^- \tag{76}$$

The intermediacy of *cis*-hyponitrite was postulated on the basis of nitrogen-15 labeling studies that showed that the two nitrogens became equivalent (*46*). No direct evidence for its formation was found. In the presence of boric acid another term appears in the rate law, and coordination of one of the oxygens of the SO_3^- group to boron is suggested

$$\text{Rate} = k[\mathrm{ON(SO_3^-)NO^-}][\mathrm{B(OH)_3}] \tag{77}$$

VIII. Hydrazoic Acid

Hydrazoic acid is a weak acid, $pK_a = 4.7$, but in sufficiently concentrated mineral acids it can act as a base, and a pK_a of -6.2 for $H_2N_3^+$ has been obtained (*12*) together with evidence that may indicate the formation of $H_3N_3^{2+}$. In aqueous solution hydrazoic acid is quite stable, though losses may occur because of its volatility. Values of the Henry's law constant are available (*196*). Photolysis results in the formation of a nitrene, and in the gas phase ΔH is 33 kcal mol^{-1} for forming NH in the lowest singlet state (*47*).

$$\mathrm{HN_3 \rightarrow HN + N_2} \tag{78}$$

In aqueous media photolysis of hydrazoic acid produces a quantitative yield of hydroxylamine, and a nitrene intermediate is involved (*175*).

$$\mathrm{HN_3 + H_2O \rightarrow NH_2OH + N_2} \tag{79}$$

A. Oxidation of Azide by Metal Ions or Metal Complexes

Many studies are available in which hydrazoic acid acts as a reducing agent. A common product is dinitrogen, but multiequivalent reagents often produce in addition nitrogen compounds in a higher oxidation state (*235*). Oxidation by cobalt(III) gives rate law (80), and this is consistent with either a rate-determining breakdown of $Co(H_2O)_5N_3^{2+}$ (or a species in tautomeric equilibrium, such as $Co(H_2O)_4(OH)(HN_3)^{2+}$) (*145*).

$$\text{Rate} = k[\mathrm{Co(III)}][\mathrm{HN_3}][\mathrm{H^+}]^{-1} \tag{80}$$

A different rate law has been reported by another group of workers (*214*), but this has been disputed (*203*). The likely mechanism involves oxidation to $N_3^{\bullet}$ radicals, which then react in a bimolecular step, possibly to form an adduct that breaks down to dinitrogen. Isotopic tracer experiments are consistent with this picture (a 6-membered ring would also fit the isotopic data).

$$2{*}NN{*}N^- \rightarrow 2{*}NN{*}N^{\cdot} \rightarrow 2{*}NN + 1{*}N{*}N \tag{81}$$

Manganese(III) also oxidizes azide to dinitrogen, and the mechanism set out in (82) to (85) has been proposed (*52*).

$$2MnN_3^{2+} \rightleftharpoons Mn^{2+} + Mn(N_3)_2^{2+} \tag{82}$$

$$Mn(N_3)_2^{2+} \rightarrow Mn^{2+} + 3N_2 \tag{83}$$

$$Mn(N_3)_2^{2+} \rightleftharpoons MnN_3^+ + N_3^+ \tag{84}$$

$$HN_3 + N_3^+ \rightarrow 3N_2 + H^+ \tag{85}$$

The same reaction has been studied by another group of workers, but with rather different results (*215*). It is claimed that the reaction is first order in [Mn(III)] rather than second order, and that there is no inhibition by Mn^{2+}. The oxidation of hydrazoic acid by cerium(IV) has also been studied (*216*), as has the oxidation by uranium(III) (*1*).

B. OXIDATION OF HYDRAZOIC ACID BY NONMETALLIC SPECIES

The oxidation of hydrazoic acid by bromate has been investigated by Thompson (*201*), who has shown that nitrous oxide is a product as well as dinitrogen. In the presence of an excess of azide the stoichiometry is given by (86).

$$H^+ + BrO_3^- + 2HN_3 \rightarrow 2N_2 + N_2O + HOBr + H_2O \tag{86}$$

In addition, some bromine is produced. Tracer experiments with azide ion labeled with nitrogen-15 in the terminal positions gave nitrogen containing 50% of the label, and nitrous oxide with *both* nitrogen atoms labeled. The rate law was first order in $[H^+]$, $[BrO_3^-]$, and $[HN_3]$, and the proposed mechanism is set out in reactions (87)–(91)

$$H^+ + BrO_3^- + HN_3 \rightarrow NNNBrO_2 + H_2O \tag{87}$$

$$H_2O + NNNBrO_2 \rightarrow N_2 + NOH + HBrO_2 \tag{88}$$

$$HBrO_2 + HN_3 \rightarrow HOBr + N_2 + NOH \tag{89}$$

$$2NOH \rightarrow N_2O + H_2O \tag{90}$$

$$HBrO_2 + 2HOBr \rightarrow BrO_3^- + Br_2 + H_3O^+ \tag{91}$$

This last reaction allows for the formation of bromine as a product. The rate equation can be rewritten in a form equivalent to $[H^+][HBrO_3][N_3^-]$, which fits attack by N_3^- upon BrO_2^+, the latter being a species often postulated in reactions of bromic acid. For reaction with an excess of bromate over azide, a complex stoichiometry is observed with higher oxidation states of nitrogen being formed, and these have been attributed to the oxidation of nitroxyl.

Another reaction that has been studied in detail is the oxidation of azide by nitrous acid. This work is relevant to some of the studies on coordinated azide mentioned below. Isotopic labeling experiments with nitrogen-15 indicate (*45*) that nitrosyl azide may be an intermediate, and this species can be isolated at low temperatures (*131*).

$$HNO_2 + H^*NN^*N \rightarrow [ON^*NN^*N] + H_2O \rightarrow O^*NN + N^*N \tag{92}$$

There are several kinetic investigations of the reaction of azide ion or hydrazoic acid with electrophilic nitrosating agents (*38*, *168*, *184*). The oxidation of hydrazoic acid by nitric acid has been briefly studied polarographically (*137*).

C. Reactions of the Coordinated Azide Ion

Some of the most interesting aspects of azide chemistry investigated in recent years deal with the reactions of coordinated azide ion. In acidic solution hydrolysis may occur by an acid-catalyzed mechanism, as is common for basic ligands. In other cases, however, a coordinated nitrene may be produced, as in the case of ruthenium(III) complexes (*115*), and iridium(III) complexes (*126*). These species can also be produced photochemically (*160, 161*). The reactions of the nitrene complex $Ir(NH_3)_5N^{2+}$ illustrate the interesting variety of behavior that can be observed (*71*, *212*).

$$Ir(NH_3)_5N^{2+} + 2H^+ + 2Cl^- \rightarrow Ir(NH_3)_5(NH_2Cl)^{3+} \tag{93}$$

$$Ir(NH_3)_5N^{2+} + H^+ + ClO_4^- \rightarrow Ir(NH_4)_5(NHOClO_3)^{2+} \tag{94}$$

$$Ir(NH_3)_5(NHOClO_3)^{2+} + H_2O \rightarrow Ir(NH_3)_5(NH_2OH)^{3+} + ClO_4^- \tag{95}$$

$$Ir(NH_3)_5N^{2+} + HSO_3^- + H^+ \rightarrow Ir(NH_3)_5(NH_2SO_3)^{2+} \tag{96}$$

Another interesting class of reactions of coordinated azide are these occurring with nitrous acid. Haim and Taube used the reaction with $Co(NH_3)_5N_3{}^{2+}$ to generate the five-coordinate species $Co(NH_3)_5{}^{3+}$, taking advantage of the instability of nitrosyl azide (*87*).

$$Co(NH_3)_5N_3{}^{2+} + H^+ + HNO_2 \rightarrow Co(NH_3)_5NNNNO^{3+} \qquad (97)$$

$$Co(NH_3)_5NNNNO^{3+} \rightarrow Co(NH_3)_5{}^{3+} + N_2 + N_2O \qquad (98)$$

The same five coordinate intermediate has been generated again, using reactions of a coordinated cyanate ion (*34*).

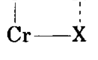
$$(NH_3)_5CoNCO^{2+} \xrightarrow{H^+, H_2O} (NH_3)_5CoNH_2COOH^{3+} \qquad (99)$$

$$(NH_3)_5CoNH_2COOH^+ \begin{array}{l} \nearrow (NH_3)_5Co(OH_2)^{3+} \\ \rightarrow (NH_3)_5CoOOCNH_2{}^{2+} \\ \searrow (NH_3)_6Co^{3+} \end{array} \qquad (100)$$

In the presence of nitrous acid the deprotonated complex $(NH_3)_5$-$CoNHCOOH^{2+}$ is nitrosated, and the product decomposes to liberate $(NH_3)_5Co^{3+}$

$$(NH_3)_5CoNHCOOH^{2+} + HNO_2 + H^+ \rightarrow (NH_3)_5Co^{3+} + N_2 + CO_2 + H_2O \qquad (101)$$

A number of other systems in which coordinated azide reacts with nitrous acid have been studied. However, in examining reactions of this sort it is important to consider other possibilities, apart from the obvious mechanism. Thus Moore and his co-workers (*138, 139*) have shown that nitrous acid can accelerate the aquation of $Cr(H_2O)_5X^{2+}$, but not that of $Cr(NH_3)_5X^{2+}$, where $X^- = Cl^-$ or Br^-. The same acceleration is observed with *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, but not with *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. The effect is due to O-nitrosation in a position cis to the leaving group, with the possibility of neighboring group assistance because of an interaction between NO^+ and X^-. A similar effect can be seen in the hydrolysis of *cis*-$Cr(NH_3)_4(ONO)(NCS)^+$.



A distinction can be drawn upon kinetic grounds. In the reaction between $Cr(H_2O)_5N_3{}^{2+}$ and nitrous acid, the rate law characteristic of electrophilic nitrosations was observed (*202*), [Eq (102)], whereas in the systems studied by Moore a different dependence upon acidity is found:

$$\text{Rate} = k[\text{complex}][\text{HNO}_2](1 + K[\text{H}^+])^{-1} \qquad (102)$$

In addition to studying the attack of nitrite on coordinated azide, one can examine the attack of azide upon coordinated nitrosyl, nitrito, or nitro groups. Seel and Meyer have examined (*171*) the reaction of *cis*- and *trans*-$\text{Coen}_2(\text{NO}_2)_2{}^+$ with hydrazoic acid.

$$\text{Coen}_2(\text{NO}_2)_2{}^+ + 2\text{HN}_3 + 2\text{H}^+ \rightarrow \text{Coen}_2(\text{OH}_2)_2{}^{3+} + 2\text{N}_2 + 2\text{N}_2\text{O} \qquad (103)$$

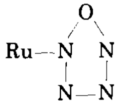
The rate law, (104), is consistent with the attack of azide ion upon a protonated $\text{NO}_2{}^-$ ligand.

$$\text{Rate} = k[\text{Coen}_2(\text{NO}_2)_2{}^+][\text{HN}_3] \qquad (104)$$

Swinehart *et al*, (*231*) have examined the reaction of nitroprusside with azide ion at pH 6 by a tracer method, and the results are consistent with intermediacy of a nitrosyl azide species.

$$\text{Fe(CN)}_5(^*\text{NO})^{2-} + \text{NNN}^- + \text{H}_2\text{O} \rightarrow \text{Fe(CN)}_5(\text{H}_2\text{O})^{3-} + \text{NN} + \text{N}^*\text{NO} \qquad (105)$$

Not all systems react in this fashion. Feltham and Douglas (*61*) have examined the reaction of *trans*-RuCl $(\text{NO})(\text{das})_2{}^{2+}$ with azide [das = o-phenylenebis(dimethylarsine)] using a nitrosyl group labeled with ^{15}N. Approximately equal amounts of $^{14}\text{N}^{14}\text{NO}$ and $^{14}\text{N}^{15}\text{NO}$ were found, suggesting a cyclic intermediate:



It is suggested that the N_4O unit is lost into the solution before it breaks down to $\text{N}_2 + \text{N}_2\text{O}$. This structure is reminiscent of the cyclic pentazoles observed in the reaction of azide ions with diazonium ions (236).

IX. Hyponitrous Acid and Nitroxyl

A. HYPONITROUS ACID

A detailed account of the chemistry of the hyponitrites can be found in a review by Hughes (*101*). Although there is evidence that the cis isomer of sodium hyponitrite can exist as a solid, instantaneous decomposition occurs on addition to water.

$$2Na_2N_2O_2 + H_2O \rightarrow 2NaOH + N_2O \tag{106}$$

Tracer experiments on the distribution of ^{15}N between the two nitrogen atoms of nitrous oxide indicate that a symmetrical intermediate may be formed in the decomposition of $ON(SO_3^-)(NO^-)$ (see Section VII,C), and in the reaction between sodium nitrite and hydroxylamine hydrochloride at pH 7 *cis*-hyponitrous acid may be involved. The only stable species known in aqueous solution are derived from the trans isomer. The three conjugate acid-base species $H_2N_2O_2$, $HN_2O_2^-$, and $N_2O_2^{2-}$, are all known, the pK_a values of hyponitrous acid being 7.2 and 11.5. Under normal conditions, pH 1–12, 25°C, decomposition occurs almost exclusively by the breakdown of the mono-anion.

$$HONNO^- \rightarrow HO^- + N_2O \tag{107}$$

A plot of the rate of decomposition against pH shows a typical bell-shaped profile, with a flat maximum from pH 8 to 10, the variation of rate with pH being controlled by the acid-base equilibria between the three hyponitrite species (*7, 32, 102, 157*). In acidic solutions, pH 1, and at sufficiently high temperatures, two other pathways can be distinguished involving the dehydration of $H_2N_2O_2$ (*32, 103*).

$$-d[H_2N_2O_2]/dt = (k + k'h_0)[H_2N_2O_2] \tag{108}$$

Under some conditions erratic kinetics can be observed, due to the incursion of free-radical processes, which can be suppressed by the addition of ethanol. A variety of metal cations can cause oxidation of $H_2N_2O_2$ to $HN_2O_2^{\cdot}$ which cleaves to $N_2O + OH^{\cdot}$. A possible series of reactions that has been suggested is set out below:

$$X^+ + HONNOH \rightarrow X + HONNO^{\cdot} + H^+ \tag{109}$$

$$HONNO^{\cdot} \rightarrow N_2O + OH^{\cdot} \tag{110}$$

$$HONNO^{\cdot} + HONNOH \rightarrow HNO_2 + N_2 + OH^{\cdot} \tag{111}$$

One of the products of the above scheme, nitrous acid, itself reacts further with hyponitrous acid, and shows a number of interesting features.

$$HNO_2 + H_2N_2O_2 \rightarrow HNO_3 + N_2 + N_2 + H_2O \tag{112}$$

The reaction obeys a simple second-order rate law, which can readily be rearranged into the form characteristic of electrophilic attack by NO^+ upon the mono-anion $HN_2O_2^-$.

$$\text{Rate} = k_2[HNO_2][H_2N_2O_2] = (k_2/K_1)[H^+][HNO_2][HN_2O_2^-] \quad (113)$$

K_1 is the first dissociation constant of hyponitrous acid. This interpretation would suggest that nitrosyl hyponitrite, O=N—O—N=N—OH, is an intermediate from which the breakdown to $NO_2^+ + N_2 + OH^-$ could readily be envisaged. However, the value of k_2/K_1 is about 400 times greater than the expected rate of encounter between NO^+ and a singly charged anion (see Section XIII,B). It has been suggested (*33*) that a radical chain process is involved. The addition of 1.4% ethanol, a known hydroxyl radical trap, produces a decrease rate of a factor of 4.5. The likely mechanism is set out below, following Buchholz and Powell's original suggestion:

$$H^+ + HNO_2 + ONNOH^- \rightarrow ONONNOH + H_2O \quad (114)$$

$$ONONNOH \rightarrow NO_2^{\cdot} + N_2 + OH^{\cdot} \quad (115)$$

$$NO_2^{\cdot} + HONNOH \rightarrow H^+ + NO_3^- + N_2 + OH^{\cdot} \quad (116)$$

$$OH^{\cdot} + HNO_2 \rightarrow H_2O + NO_2^{\cdot} \quad (117)$$

$$OH^{\cdot} + NO_2^{\cdot} \rightarrow HNO_3 \quad (118)$$

Powell and Buchholz suggest a minimum chain length of ca. 8, but in view of the factor of 400 mentioned above it seems likely that the chain length is much longer.

Measurements on this reaction have been extended to higher acidities, with interesting results. The rate increases with increasing perchloric acid concentration, reaches a maximum in 7 *M* acid, and then decreases sharply in those solutions where there is substantial conversion of molecular nitrous acid to the nitrosonium ion. When a correction for this last factor is introduced, the results fit Eq. (119).

$$-d[H_2N_2O_2]/dt = (k_2 + k_3h_0a_w)[HNO_2][H_2N_2O_2] \quad (119)$$

It thus appears that the nitrosonium ion is not the active species. Hughes and Wimbledon (*104*) suggest that the mechanism may involve nitric oxide in a radical pathway, and Buchholz and Powell earlier noted that nitric oxide is rapidly absorbed by a solution of hyponitrous acid in 1 *M* mineral acid.

B. NITROXYL

Nitroxyl is a species that is quite often postulated as an intermediate in reactions in which nitrous oxide is formed. It is sometimes written as the O-protonated species, and sometimes as the N-protonated form.

$$2HNO \rightarrow N_2O + H_2O \tag{120}$$

Sometimes hyponitrous acid is postulated as an additional intermediate (presumably the cis species). Angeli's Salt, $Na_2N_2O_3$ (see Section XIII), is a good source of nitroxyl, the kinetics of decomposition being well understood (*28, 106*).

$$HN_2O_3^- \rightarrow HNO + NO_2^- \tag{121}$$

Nitroxyl has been directly observed in pulse-radiolysis studies (*79*), when nitric oxide reacts with the solvated electron to produce NO^-, or with the hydrogen atom to form HNO; a pK_a of 4.7 for HNO was reported. A variety of other species have been identified, resulting from further reactions of NO^-, and pK_a values, equilibrium constants and rate constants have been evaluated.

$$NO^- + NO \rightleftharpoons N_2O_2^- \overset{H^+}{\rightleftharpoons} HN_2O_2 \tag{122}$$

$$N_2O_2^- + NO \rightleftharpoons N_3O_3^- \overset{H^+}{\rightleftharpoons} HN_3O_3 \tag{123}$$

In the presence of oxygen, the anion NO^- reacts readily to form peroxonitrite, which in acidic solution isomerizes to nitric acid (*96, 143, 234*).

$$NO^- + O_2 \rightarrow ONOO^- \tag{124}$$

$$HOONO \rightarrow HNO_3 \tag{125}$$

A characteristic reaction, which can be used to show the formation of nitroxyl in solution, is the reaction with $Ni(CN)_4{}^{2-}$ to form the violet complex $Ni(CN)_3NO^{2-}$. Electrochemical studies of the cathodic reduction of nitrous acid in moderately concentrated perchloric acid indicate a rapid reaction between nitroxyl and nitrous acid to form nitric oxide and water (*88a*).

X. Nitramide

Nitramide, NH_2NO_2, also known as nitroamine, is an isomer of hyponitrous acid, and it can also decompose to give nitrous oxide.

This reaction is one of the classic examples of general base catalysis, and there has been a recent investigation of the solvent isotope effect for the phenolate anion catalyzed decomposition (*113*). The isotope effect shows a maximum in the region $\Delta pK = 0$. The decomposition in acid media has not been studied so intensively, but previous work has now been extended up to 8.27 *M* perchloric acid. The results show a mild degree of acid catalysis.

$$\text{Rate} = k[\mathrm{NH_2NO_2}] + k'[\mathrm{NH_2NO_2}]\,\mathrm{h}_0^{0.34} \tag{126}$$

This somewhat low dependence upon H_0 is interesting, and on the basis of Bunnett's w and w^* values it would appear that water may act as a nucleophile, though this does not fit in well with the value of $\Delta S^{\ddagger}$. At this stage the details of the mechanism are not at all clear (*133*).

It is convenient at this point to consider another reaction of nitramide, that occurring with nitrous acid. The stoichiometry is similar to that of the analogous reaction (112) with isomeric hyponitrous acid.

$$\mathrm{NH_2NO_2 + HNO_2 \rightarrow HNO_3 + N_2 + H_2O} \tag{127}$$

The rate law is shown in Eq. (128).

$$\text{Rate} = (k_3 + k_4[\mathrm{H^+}]))\mathrm{NH_2NO_2}][\mathrm{HNO_2}] \tag{128}$$

This is interpreted (*108*) as being due to parallel reaction pathways involving electrophilic nitrosation of nitramide (k_4) and its conjugate base (k_3).

$$\mathrm{NO^+ + NHNO_2^- \rightarrow ONNHNO_2 \rightarrow HON{=}NNO_2} \tag{129}$$

Further fast steps are postulated to lead to the final products. It is interesting to note that the conjugate base species $\mathrm{NHNO_2^-}$ is a much stronger nucleophile toward the nitrosonium ion than is the isoelectronic nitrate ion, presumably because of the more nucleophilic nitrogen of the imide group. Evidence for reaction between nitrosyl thiocyanate and the conjugate base of nitramide has recently been obtained (*104*).

XI. Nitric Oxide

Nitric oxide is normally described as a neutral oxide, and it shows no exchange of oxygen atoms with ^{18}O-enriched water under acid or alkaline conditions. Angeli's salt, $Na_2N_2O_3$, decomposes in acidic solution to liberate nitric oxide, and has been described (*148*) sometimes as the salt of an oxyacid of nitric oxide (see Section XII). Pulse radiolysis studies have shown that the nitrite ion reacts with the solvated electron to form NO_2^{2-} (*79*). In acid solutions HNO_2^- and H_2NO_2 are formed with pK_a values of 7.7 and 5.7, respectively, and these species can decompose to liberate nitric oxide.

$$HNO_2^- \rightarrow OH^- + NO \qquad (130)$$

If one is to regard nitric oxide as an acid anhydride, H_2NO_2 rather than $H_2N_2O_3$ is to be looked on as the corresponding oxyacid.

In the presence of nitrous acid, oxygen exchange between nitric oxide and water does occur. Bonner and Jordan have studied the isotope exchange reactions between ^{15}NO and potassium nitrite in $H_2{}^{18}O$, following the isotopic composition of the nitric oxide (*26*). Nitrogen exchange seems to occur by a single mechanism with rate law (131).

$$\text{Rate} = k[HNO_2][NO] \qquad (131)$$

Thus in a solution of sodium nitrite the small amount of nitrous acid produced by hydrolysis is essential for exchange to occur. Although mechanisms that can be postulated to account for nitrogen exchange should also lead to oxygen exchange, the rate of oxygen exchange is *less* than that of nitrogen exchange at the higher pH values studied. This is a complex system because oxygen exchange between nitrite and water is very dependent upon pH; however, Bonner *et al.* find that the rates of oxygen exchange that they observe are much *greater* than is predicted from experiments on the exchange between nitrous acid and water. The authors tentatively propose a rate law (132) for oxygen exchange, but further work on this most interesting system seems desirable, in particular experiments using a nitrite–water system labeled with ^{18}O, and in isotopic equilibrium.

$$\text{Rate} = k[H^+][HNO_2][NO] \qquad (132)$$

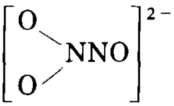
Bonner and Jordan (*27*) have also examined the exchange of ^{15}N and ^{18}O tracer between nitric oxide and dilute nitric acid (0.05–0.94 *M*). Nitrogen exchange appears to be controlled by the formation and hydrolysis of dinitrogentetroxide.

$$H^+ + HNO_2 + NO_3^- \rightleftharpoons N_2O_4 + H_2O \qquad (133)$$

The exchange processes between NO, NO_2, N_2O_3, and N_2O_4 are known to be quite rapid (Section XIV). Other studies of related systems have been reported (*10, 11*).

XII. Trioxodinitrate(II)

Sodium trioxodinitrate(II), $Na_2N_2O_3$, also known as sodium oxyhyponitrite, sodium nitrohydroxylamate, sodium hyponitrate, or Angeli's salt is something of a chemical curiosity. It has the structure



with a nitrogen to nitrogen bond length of 0.1264 nm, suggesting a fair degree of double-bond character. In alkaline solution its decomposition yields the products shown in (134), whereas in acid media it decomposes to nitric oxide.

$$H_2O + Na_2N_2O_3 \rightarrow N_2O + NaNO_2 + NaOH \qquad (134)$$

$$H_2N_2O_3 \rightarrow 2NO + H_2O \qquad (135)$$

The changeover from one stoichiometry to the other seems to occur about pH 5. The pK_a values for H_2NO_3 have been measured by potentiometric titration and are ca. 2.4 and 9.4. It is of interest as a source of nitroxyl and has been postulated as an intermediate in the nitrogen cycle. It is an awkward compound to work with, and it can be difficult to prepare really pure samples. In the presence of oxygen, oxidation to nitrite occurs, and samples can easily be contaminated with nitrite.

The chemistry has been much clarified by two independent kinetic studies by Bonner and Ravid (*28*) and by Hughes and Wimbledon (*106*). At pH values greater than 5, the two sets of results are in agreement, the reaction involving the monoanion as reactant, with fission of the nitrogen to nitrogen bond.

$$N_2O_3^{2-} + H^+ \rightleftharpoons HN_2O_3^- \xrightarrow[\text{slow}]{} NOH + NO_2^- \qquad (136)$$

$$2NOH \rightarrow N_2O + H_2O \qquad (137)$$

The doubly charged anion seems to be quite stable. In more acid media the behavior is complex, and there is some disagreement between the two investigations. The account below follows the work of Hughes and Wimbledon, which appears to be more extensive than that of Bonner and Ravid. Individual kinetic runs still give good first-order kinetics in Angeli's salt (k_1), and the rate increases sharply with increasing acidity below pH 3. However, the pseudo first-order rate constant increases markedly with increase in the initial concentration of Angeli's salt. This is attributed to the presence of an impurity that catalyzes the decomposition, and the most likely culprit is sodium nitrite. Added sodium nitrite certainly causes a marked acceleration in the rate of decomposition at low pH values. By extrapolating plots of k_1 against initial concentration of Angeli's salt to $[Na_2N_2O_3]_0 = 0$ it is possible to obtain limiting values of k_1, free from the effects of the impurity. These limiting rate constants actually *decrease* with increasing acidity, in marked contrast to the raw k_1 values. Analysis of the data shows that the decrease in rate is due to protonation of $HN_2O_3^-$ to H_2NO_3, and yields a first pK_a value of 3.0 for the latter species. This may be more accurate than values obtained by the more direct method of carrying out a pH titration of a solution of Angeli's salt with standard acid.

Experiments on the effect of added nitrite (the suspected catalytic impurity) reveal a complex pattern of behavior. At higher pH values, around 5, added nitrite stabilises Angeli's salt, and k_1 *decreases* to a limiting value at around $[NO_2^-] = 0.005$–0.01 *M*. This is presumably due to the reversal of the breakdown of $HN_2O_3^-$ to NOH and NO_2^-. The fact that the kinetics remain first order with respect to Angeli's salt implies either that the formation of nitrous oxide is first order in nitroxyl concentration (possibly involving some reaction with water?) or that there is some molecular mechanism for the breakdown of $HN_2O_3^-$ to $\frac{1}{2}\,N_2O + NO_2^-$. Further work is needed on this point (*105*).

In sufficiently acidic media, where the decomposition products are 100% nitric oxide, the rate law is given by (138).

$$\text{Rate} = k[H^+][HNO_2][H_2N_2O_3] \tag{138}$$

Although this equation has the characteristic kinetic form for an electrophilic nitrosation reaction, the magnitude of the rate constant is much greater than the normal limiting value for such processes (the encounter limit). Reaction is inhibited by added ethanol, a known trap for hydroxyl radicals, and Hughes and Wimbledon suggest a chain mechanism for the decomposition.

$$H^+ + HNO_2 + H_2N_2O_3 \rightarrow ONON{=}NO(OH) + H^+ + H_2O \tag{139}$$

$$ONON{=}NO(OH) \rightarrow NO_2^{\cdot} + N_2O + OH^{\cdot} \tag{140}$$

$$NO_2^{\cdot} + H_2N_2O_3 \rightarrow HNO_2 + OH^{\cdot} + 2NO^{\cdot} \tag{141}$$

$$OH^{\cdot} + HNO_2 \rightarrow H_2O + NO_2^{\cdot} \quad (142)$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \rightarrow H_2O + O_2 \quad (143)$$

A different mechanism for the decomposition to nitric oxide in acidic media has been proposed by Bonner (*28*). He suggests that there may be a rapid decomposition reaction of $H_2N_2O_3$, followed by another rapid redox reaction such as (144), where H_2NO^+ is protonated nitroxyl.

$$H_2NO^+ + NO_2^- \rightarrow 2NO + H_2O \quad (144)$$

Attempts to distinguish between this proposal, and that of Hughes and Wimbledon by using ^{15}N enriched nitrite have not yielded any firm conclusion, partly because of complications due to the formation of nitric oxide by the spontaneous decomposition of nitrous acid. It is clear, however, that although the decomposition of Angeli's salt in acidic solutions yields nitric oxide, the reaction is *not* a dehydration of $H_2N_2O_3$.

XIII. Nitrous Acid

The chemistry of nitrous acid is one of those areas where there has been a particularly fruitful interaction between physical-organic and physical-inorganic chemistry. Most of the common electrophilic nitrosating agents are inorganic species, and the mechanisms by which they are formed in aqueous solutions were largely worked out from studies of diazotization and deamination. Ideas from these studies have proved applicable to many inorganic systems, and a few of the main features are outlined below. Diazotization and deamination have been reviewed by Ridd (*162*), and Turney and Wright (*207*) have reviewed nitrosation reactions.

A. Species Present in Solutions of Nitrous Acid

It is useful to consider first the species present in aqueous solutions of "nitrous acid". It is a weak acid, $pK_a = 3.3$ at 25°, and in sufficiently concentrated solutions (ca. 0.05–0.1 *M*) in moderately concentrated mineral acid (4 *M*) will dehydrate to the anhydride dinitrogen trioxide.

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \quad (145)$$

This is a blue species with a maximum at 625 nm, and from measurements of the absorbance at this wavelength an approximate equilibrium constant $[N_2O_3]/[HNO_2]^2 = 0.2\ M^{-1}$ at 20° has been estimated (*37*). Other spectrophotometric and distribution measurements lead to similar results, and Turney (*206*) has proposed a mean value of $0.2\ M^{-1}$. Schmid and Krenmayr (*165*) propose a slightly lower value of $0.16\ M^{-1}$. Another approach to estimating this equilibrium constant is to combine a value of 530 $\sec^{-1}$ for the first-order rate constant for the hydrolysis of N_2O_3 at 20° (*80*) with a value for the rate of formation of N_2O_3 from $2HNO_2$ of 4 $M^{-1}\ \sec^{-1}$ at 20°, giving $[N_2O_3]/[HNO_2]^2 = 7.5 \times 10^{-3}\ M^{-1}$. The source of the somewhat large discrepancy between these two values is not clear. The extinction coefficient for N_2O_3 used in the original publication (*37*) is some 5 to 10 times lower than values measured recently for solutions of dinitrogen trioxide in a range of organic solvents (*176*), but the distribution experiments also gave results close to 0.2. Calculations based on a thermodynamic cycle gave a value $0.0089\ M^{-1}$ for 25° (*208*).

At higher concentrations of mineral acid, ionization to the nitrosonium ion occurs, and this can be quantitative in sufficiently acidic solutions.

$$H^+ + HNO_2 \rightleftharpoons NO^+ + H_2O \tag{146}$$

The equilibrium has been studied spectrophotometrically and has been shown to follow the H_R acidity function (*59*) over at least a limited range of acidity. A range of values for the pK_a have been reported from -6.5 to -8.5 (*182*). A great deal of effort has been devoted to looking for evidence for the nitrous-acidium ion, $H_2NO_2{}^+$, but so far no firm evidence for the existence of sizable concentrations of this species has been found. In the presence of other anions the corresponding nitrosyl compounds may be formed

$$H^+ + HNO_2 + X^- \rightleftharpoons ONX + H_2O \tag{147}$$

These often have characteristic colors, and the equilibrium constants have been measured spectrophotometrically.

B. ELECTROPHILIC NITROSATIONS

Many reactions of nitrous acid involve an electrophilic nitrosation in the initial stages, and the common nitrosating agents in order of reactivity are (*163*) $NO^+ > (H_2NO_2{}^+) > ONCl > ONBr > ONSCN > ONNO_2 > ONOAc \gg ONOH$, the most reactive species being the least discriminating. The nitrous acidium ion, $H_2NO_2{}^+$, is included in parentheses, as its role as a nitrosating agent must now be in some doubt (see below). The presence of nitrosyl acetate in this list emphasizes the fact that the kinetics of nitrous acid reactions can be powerfully affected by the presence of buffers; a nucleophilic buffer anion may introduce a new nitrosating species into the system, and in any kinetic study it is essential to investigate the dependence of rate upon buffer concentration. The formation of these inorganic nitrosyl compounds has been investigated kinetically, and it follows rate law (148).

$$d[\mathrm{ONX}]/dt = k[\mathrm{H}^+][\mathrm{HNO_2}][\mathrm{X}^-] \qquad (148)$$

Values of k are shown in Table II, and are remarkably independent of the nature of X^-. A similar pattern of behavior is found for the nitrosation of a range of neutral nucleophiles. The clearest examples have come from physical organic chemistry, where the nitrosation of *o*-chloroaniline *p*-nitroaniline, and *o*-nitroaniline follow a similar rate law and give rate constants of 175, 161, and 145 M^{-1} sec^{-1} at 0°; these are very similar despite the wide variation in basicity of the free amines. For comparison it may be noted that *O*-methylhydroxylamine and *O*,*N*-dimethylhydroxylamine and thiourea nitrosate at 0° with rate constants are 184, 225, and 638 M^{-2} sec^{-1}. Here again the reactivities seem to be encompassed within a rather small range of values. The most revealing piece of information is the value of the bimolecular rate constants for the nitrosation of reactive free aromatic amines by nitrosyl chloride or nitrosyl bromide. These can be calculated from the experimentally determined rate constant, the equilibrium constants for the formation of the nitrosyl halide and the pK_a of the protonated amine.

$$\mathrm{ONX} + \mathrm{ArNH_2} \rightarrow \mathrm{ArNH_2NO^+} + \mathrm{X^-} \qquad (149)$$

TABLE II

RATE CONSTANTS FOR FORMATION OF NITROSYL COMPOUNDS AT 0° (*163*)

X^- =	Cl^-	Br^-	I^-	SCN^-	$NO_2{}^-$	CH_3COO^-	$N_3{}^-$	$NO_3{}^-$	$NH_2SO_3{}^-$
k	975	1170	1370	1460	1893	2000	2340	0.0018	170
$10^4 K$	5.5	220	—	46000	570	—	—	0.000026	—

$d[\mathrm{XNO}]/dt = k[\mathrm{H}^+][\mathrm{HNO_2}][\mathrm{X}^-]$; $K = [\mathrm{ONX}]\alpha_w/[\mathrm{H}^+][\mathrm{HNO_2}][\mathrm{X}^-]$

These bimolecular rate constants are found to be greater than 10^9 M^{-1} $\sec^{-1}$, indicating an encounter-controlled process. It seems certain that the reason for the narrow spread in reactivities among the anions, and among the neutral nucleophiles, is that in each case we are observing an encounter-controlled reaction. The somewhat greater reactivity of the anions than the neutral species reflects the effect of coulombic attraction on the encounter rate. Less reactive nitrosating agents, such as ONSCN, $ONNO_2$, do not in general react at the encounter rate.

For many years there was a dispute in the literature as to whether the active nitrosating species in dilute aqueous solutions of nitrous acid, and responsible for Eq. (150), was the nitrous-acidium ion or an equilibrium concentration of the nitrosonium ion NO^+.

$$\text{Rate} = k_1[H^+][HNO_2][\text{substrate}] \tag{150}$$

$$H^+ + HNO_2 \rightleftharpoons H_2NO_2^+ \rightleftharpoons NO^+ + H_2O \tag{151}$$

Provided that the equilibria were established rapidly, either reagent could give rise to Eq. (150). Anbar and Taube (*3*) produced evidence that the nitrosonium ion was the active species by a kinetic and isotopic study of the reaction with hydrogen peroxide.

$$HNO_2 + H_2O_2 \rightarrow H_2O + HOONO \rightarrow HNO_3 \tag{152}$$

At high concentrations of hydrogen peroxide they claimed to observe a rate law of form (153), corresponding to a rate-determining formation of the nitrosonium ion.

$$\text{Rate} = k_2[H^+][HNO_2] \tag{153}$$

Similar rate laws have been observed in the reaction of azide with nitrite (*169*) and sulfite with nitrite (*170*). Their case was strengthened by an ^{18}O tracer study, which indicated that at high concentrations of hydrogen peroxide exchange of the tracer into nitrous acid was inhibited, presumably because of competition between hydrogen peroxide and water for the same electrophile. This view was vigorously disputed (*91*), but a recent study of the reaction by the stopped-flow method by Moore and Benton (*143*) provides strong support for Anbar and Taube's original interpretation.

Benton and Moore worked in perchloric acid solution, and so avoided possible complications due to nucleophilic buffer anions, and they followed the formation of the initial product, pernitrous acid, over the concentration range in which a switch in rate-determining stage took place from (155) to the forward reaction of (154)

$$H^+ + HNO_2 \rightleftharpoons NO^+ + H_2O \tag{154}$$

$$NO^+ + H_2O_2 \rightarrow HOONO + H^+ \tag{155}$$

$$H^+ + HOONO \rightarrow HNO_3 + H^+ \tag{156}$$

Their rate law is shown in (157), and has the required kinetic form.

$$d[HOONO]/dt = k_3[H^+][HNO_2][H_2O_2](1 + k_4[H_2O_2])^{-1} \tag{157}$$

The limiting rate for high concentrations of hydrogen peroxide agreed with Anbar and Taube's value. At 0°C it is given in (158).

$$\text{Rate} = 637[H^+][HNO_2]\ M\,\text{sec}^{-1} \tag{158}$$

One problem with this result is that the rate is about 3-fold faster than the measured rate of oxygen exchange between nitrous acid and water at 0°, which has the same kinetic dependence (*37*) upon $[H^+]$ and $[HNO_2]$. Ridd has pointed out (*163*) that the average lifetime of a nitrosonium ion in water must be very short, ($t_{1/2} \approx 3 \times 10^{-10}$ sec) and that such a short-lived species might stand a good chance of reacting with the same water molecule on rehydration that it lost in the dehydration stage. This is an interesting idea, because it has been always assumed that the water exchange rate gives a good value for the rate of dehydration of the oxyacid. In aromatic nitration it has been shown that the rate of oxygen exchange between nitric acid and water is equal to the rate of the zero-order nitration of reactive aromatic substrates in aqueous nitric acid, and this has been used as evidence that the nitrating agent in such media is NO_2^+, not $H_2NO_3^+$. However, the average half-lifetime for the nitronium ion in 68% w/w H_2SO_4 is ca 10^{-6} sec, so long that the water molecule lost from $H_2NO_3^+$ upon dehydration will be "lost" in the solvent. Hence the oxygen exchange rate should be a good measure of the rate of formation and rehydration of the nitronium ion. However, for much shorter-lived electrophiles such as NO^+, it appears that this may not be true. To round off this argument, we may note that if the pK_a for (154) is taken to be -6.5, then taking the experimentally determined rate constants for (148), it is found (*163*) that the bimolecular rate constant for (159) are ca. $7 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ at 0°, very close to the encounter rate.

$$NO^+ + X^- \rightarrow ONX \tag{159}$$

This topic has been discussed at some length partly because of its intrinsic interest, partly because it represents an interesting interface between physical organic and physical inorganic chemistry, and also partly because reactions of nitrous acid with a variety of other nitrogen-containing substrates involve similar processes.

We may also note that if the nitrosyl compounds ONX are formed by a reaction between NO^+ and X^-, then the principle of microscopic reversibility requires that the hydrolysis should proceed by dissociation to $NO^+ + X^-$, followed by reaction with water. Because in many cases the anion X^- will be a much better nucleophile than a water molecule, it is likely that the hydrolysis of nitrosyl halides involve the formation of an encounter pair, $(NO^+X^-)_{ep}$, in a solvent cage, which usually recombines to form ONX, but undergoes hydrolysis following the diffusion apart of its constituents.

$$ONX \rightleftharpoons (NO^+X^-)_{ep} \rightleftharpoons NO^+ + X^- \tag{160}$$

We will now consider the reactions of nitrous acid with a variety of inorganic species. These all appear to involve the initial formation of a nitrosyl compound, although the fate that this species undergoes varies widely. Starting with simple nucleophiles, we will consider the oxidation of iodide to iodine.

$$HNO_2 + H^+ + I^- \rightarrow \tfrac{1}{2}I_2 + NO + H_2O \tag{161}$$

The rate equation has been established by Indelli and his co-workers (*72*) to be (162), and the interpretation is set out in reactions (163) and (164):

$$\text{Rate} = k_5[H^+]^2[HNO_2]^2[I^-]^2 \tag{162}$$

$$H^+ + HNO_2 + I^- \rightleftharpoons ONI + H_2O \tag{163}$$

$$2ONI \rightarrow 2NO + I_2 \tag{164}$$

This is the reverse of the familiar mechanism for the termolecular reaction in the gas phase between nitric oxide and chlorine or bromine to form the nitrosyl halide. Beck and his co-workers report in the rate law an additional term which is ascribed to reaction (165), followed by a rapid oxidation of I_2^- (*62*).

$$\mathrm{ONI + I^- \rightarrow NO + I_2^-} \tag{165}$$

The oxidation of thiocyanate by nitrous acid to nitric oxide, sulfuric acid, and hydrogen cyanide probably involves nitrosyl thiocyanate as an intermediate. This is readily detected in solutions by its red color, and decomposition to nitric oxide and thiocyanogen could occur by a mechanism(s) similar to that for nitrosyl iodide. The hydrolysis of thiocyanogen is known to form sulfuric acid and hydrogen cyanide. However, a mechanistic study has not been reported yet. The reaction between azide ion and nitrous acid, which fits the same general pattern, was discussed in Section VIII,B. A preliminary account of the thermal decomposition of nitrosyl cyanide has appeared (*110*).

Some work that has analogies to the nitrous acid–iodide system is a recent kinetic study of the reaction between nitrous acid and thiourea. This system was originally examined by Werner (*217*), who showed that there were two reactions (166) and (167), the former favored by low acidities, and the latter by high acidities.

$$\mathrm{CS(NH_2)_2 + HNO_2 \rightarrow HNCS + N_2 + 2H_2O} \tag{166}$$

$$\mathrm{2H^+ + 2CS(NH_2)_2 + 2HNO_2 \rightarrow (NH_2)_2CSSC(NH_2)_2{}^{2+} + 2NO + 2H_2O} \tag{167}$$

Werner also reported a transient red color in his reaction mixtures, and this has recently been identified (*2*) as due to $(NH_2)_2CSNO^+$. This is formed by an encounter-controlled electrophilic nitrosation of the type described above, with the usual rate law. Values for the equilibrium constant, and the rate constants for the forward and back reactions have been obtained, together with extinction coefficients for the visible and UV maxima for the S-nitroso compound.

$$\mathrm{H^+ + HNO_2 + CS(NH_2)_2 \rightleftharpoons (NH_2)_2CSNO^+ + H_2O} \tag{168}$$

A kinetic study of (166) shows the rate law to be given by (169).

$$d[\mathrm{HNCS}]/dt = k_6[\mathrm{HNO_2}][\mathrm{CS(NH_2)_2}] \tag{169}$$

This is interpreted as a rate-determining nitrosyl migration from sulfur to nitrogen in the conjugate base of the *S*-nitroso compound.

$$(NH_2)_2CSNO^+ \rightleftharpoons NH_2(NH)CSNO + H^+ \quad (170)$$

$$NH_2(NH)CSNO \rightarrow NH_2C(S)NHNO \quad (171)$$

$$NH_2C(S)NHNO \rightarrow NH_2C(S)N{=}NOH \quad (172)$$

$$NH_2C(S)N{=}NOH \rightarrow H^+ + HNCS + N_2 + OH^- \quad (173)$$

Steps (172) and (173) are very similar to those postulated in the deamination of organic primary amino compounds.

The other reaction that Werner observed has been examined in oxygen free solutions, with a large excess of thiourea over nitrite, under conditions such that virtually all the nitrite is converted to $(NH_2)_2CSNO^+$. Reaction was followed by the fading of the yellow color, and individual runs gave reasonable pseudo-second-order plots, suggesting a mechanism analogous to (164). However, a comparison of initial rates of reaction yielded a quite different rate law, and a radical cation mechanism may be operative (*48*)

$$\text{Rate} = [(NH_2)_2CSNO^+](k + k'[CS(NH_2)_2]) \quad (174)$$

$$(NH_2)_2CSNO^+ \rightleftharpoons (NH_2)_2CS^{+\cdot} + NO^{\cdot} \quad (175)$$

$$2(NH_2)_2CS^{+\cdot} \rightarrow (NH_2)_2CSSC(NH_2)_2{}^{2+} \quad (176)$$

$$(NH_2)_2CS^{+\cdot} + (NH_2)_2CSNO^+ \rightarrow (NH_2)_2CSSC(NH_2)_2{}^{+\cdot} + NO \quad (177)$$

$$(NH_2)_2CSSC(NH_2)_2{}^{+\cdot} + \text{oxid} \rightarrow (NH_2)_2CSSC(NH_2)_2{}^{2+} + \text{red} \quad (178)$$

Similar studies on the formation of sulfur S-nitroso compounds of the alkylthioureas have appeared (*49*). Further work on these compounds is desirable in view of the possible biological significance of sulfur-nitroso compounds (*141*). Werner's intermediate, $(NH_2)_2CSNO^+$, can also act as an electrophilic nitrosating agent, and Williams has shown (*222*) that its behavior is very similar to that of another sulfur-nitroso compound, ONSCN.

Another sulfur nucleophile, the thiosulfate anion, reacts with nitrous acid to form a yellow species, which appears to be O_3SSNO^-. A preliminary study of the thiosulfate–nitrite reaction was published many years ago by Edwards, who reported (*68*) a rate equation that was almost zero order in thiosulfate (179):

$$\text{Rate} = k[H^+]^2[NO_2^-][S_2O_3^{2-}]^{0.2} \quad (179)$$

a form that is very similar to that observed by Anbar and Taube, and by Moore and Benton. A stopped-flow study of the formation of the yellow species also shows (*74*) the existence of a term that is second order in nitrite and zero order in thiosulfate, indicating that the yellow species may also be formed from $S_2O_3^{2-}$ and N_2O_3.

Interest in the chemistry of nitrous acid often arises from the need to remove the last traces from a particular system because it catalyzes some undesirable process [e.g., in nuclear fuel reprocessing where there can be autocatalytic reoxidation of plutonium(III) to plutonium(IV) in the presence of traces of nitrite (*65*)]. There have been studies of the efficiency of various inorganic scavengers of nitrous acid in moderately concentrated solutions of mineral acid (*24, 154*).

Williams has determined (*224*) the relative reactivities of sulfamic acid, hydrazine, hydroxylamine, hydrazoic acid, and urea by a kinetic and product study of the Fischer–Hepp rearrangement of *N*-nitroso-*N*-alkylanilines in the presence of nitrite traps (*224*). The interpretation of such experiments requires caution, because the dependence of rate upon acidity varies widely from one scavenging agent to another, and unless comparisons are made at the same acidity erroneous conclusions may be drawn (*154*). Another complication is the possible catalytic effect of nucleophilic anions. When allowance is made for these factors there is good agreement between the relative reactivities determined from the Fischer–Hepp studies and those determined directly. Williams has also used his method to determine the reactivities of nitrosyl chloride and nitrosyl thiocyanate as electrophilic nitrosating agents (*223*).

A detailed study of the reaction of the scavenger hydrazine with nitrous acid has been published (*153*). This again involves an initial encounter-controlled nitrosation of the hydrazinium ion, and parallel pathways to form hydrazoic acid + water, or ammonia + nitrous oxide are proposed, which are represented in a simplified form in (180).

$$NH_2NHNO \rightarrow NH_2N{=}NOH \begin{array}{l} \nearrow NH_3 + N_2O \\ \searrow HN_3 + H_2O \end{array} \qquad (180)$$

At high acidities the products are 100% hydrazoic acid, while at low acidities a limiting yield of 40% of azide is obtained. This mechanism has many analogies to the processes thought to occur in the reactions of nitrosating agents with organic amino compounds. It is very different to the mechanisms usually put forward for oxidation of hydrazine by inorganic reagents, in which diimide and tetrazene intermediates feature. One such mechanism has been proposed, largely on the basis of a reported stoichiometry (*12*) shown in equation (181).

$$7N_2H_4 + 12HNO_2 + H^+ \rightarrow HN_4^+ + HN_3 + 5N_2 + 6N_2O + 18H_2O \tag{181}$$

However, it has been argued that reaction is so fast that mixing effects and complications due to secondary reactions of the primary product (*153*), were responsible for the unusual stoichiometries reported. Application of a new fast reaction method indicates the formation of a transient species absorbing at 370 nm under some conditions, but no structure or mechanism has yet been proposed (*117*). Measurements have also been made of the kinetics of nitrosation of some alkyl and arylhydrazines (*152, 186*).

C. OXIDATION OF NITRITE BY METAL IONS AND METAL COMPLEXES

The reactions discussed above all appear to involve an electrophilic nitrosation as the first stage. Other pathways are also possible. Thus the oxidation of nitrous acid by manganese(III) involves the oxidation to nitrogen dioxide (*54*)

$$Mn^{3+} + HNO_2 \rightarrow Mn^{2+} + H^+ + NO_2^{\cdot} \tag{182}$$

$$MnOH^{2+} + HNO_2 \rightarrow Mn^{2+} + H_2O + NO_2^{\cdot} \tag{183}$$

$$H_2O + Mn(III) + NO_2^{\cdot} \xrightarrow[\text{fast}]{} Mn^{2+} + NO_3^- + 2H^+ \tag{184}$$

Similar behavior was found for the oxidation of nitrous acid by cobalt(III) (*53*). Hexacyanoferrate(III) reacts in a similar way to (182) (*187*). Interest in the redox reactions of the actinides with nitric and nitrous acids continues. The rate law observed for neptunium(VI) and americium(VI) is shown in (185), where An = Actinide.

$$\text{Rate} = [AnO_2^+][HNO_2](k_1 + k_2[H^+]^{-1}) \tag{185}$$

Again a rate law with a term containing a dependence upon $[H^+]^{-1}$ is observed, as for manganese(III) and cobalt(III). This is interpreted as a pathway involving the nitrite ion as a reducing agent (*232*).

$$AnO_2^{2+} + HNO_2 \rightarrow AnO_2^+ + H^+ + NO_2^{\cdot} \quad k_1 \tag{186}$$

$$AnO_2^{2+} + NO_2^- \rightarrow AnO_2^+ + NO_2^{\cdot} \quad k_2 \tag{187}$$

$$H_2O + AnO_2^{2+} + NO_2^{\cdot} \rightarrow AnO_2^+ + NO_3^- + 2H^+ \text{ fast} \tag{188}$$

The oxidation of nitrite ion by 1,2 diaminocyclohexanetetraacetatomanganate(III), $[\mathrm{Mn(III)(cydta)}]^-$, gives a rate law with a second-order dependence upon nitrite concentration in the pH range where nitrite ion is the bulk component (pH 4.5–7.5). The mechanism proposed (*114*) is set out in (189)–(193).

$$-d[\mathrm{Mn^{III}(cydta)^-}]/dt = k_3[\mathrm{Mn^{III}(cydta)^-}]^2[\mathrm{NO_2}^-]^2(k_4[\mathrm{Mn^{II}(cydta)^{2-}}]^2 + [\mathrm{Mn^{III}(cydta)^{2-}}])^{-1} \tag{189}$$

$$\mathrm{Mn^{III}(cydta)(H_2O)^-} + \mathrm{NO_2}^- \rightleftharpoons \mathrm{Mn^{III}(cydta)(NO_2)^{2-}} + \mathrm{H_2O} \tag{190}$$

$$\mathrm{H_2O} + 2\mathrm{Mn^{III}(cydta)\,NO_2}^{2-} \rightleftharpoons \mathrm{Mn^{II}(cydta)H_2O^{2-}} + \mathrm{Mn^{III}(cydta)(N_2O_4)^{2-}} \tag{191}$$

$$\mathrm{Mn^{III}(cydta)(N_2O_4)^{2-}} + \mathrm{H_2O} \rightleftharpoons \mathrm{Mn^{II}(cydta)\,H_2O^{2-}} + \mathrm{N_2O_4} \tag{192}$$

$$\mathrm{N_2O_4} + \mathrm{H_2O} \rightarrow \mathrm{NO_2} + \mathrm{NO_3}^- + 2\mathrm{H}^+ \tag{193}$$

Oxidation of nitrite by another powerful oxidizing agent, thallium(III), has been studied by Gupta (*200*). He suggests the formation of complexes of the form $\mathrm{TlNO_2}^{2+}$, $\mathrm{Tl(NO_2)_2}^+$, and $\mathrm{Tl(NO_2)_3}$, and reaction occurring by an internal redox reaction in the dinitro species.

The mechanism of oxidation of nitrous acid by another familiar reagent, potassium permanganate, has been studied by two groups of workers. Beck and Dòzsa originally postulated (*63*) a rate law containing terms that were first order, second order, and third order in nitrous acid, but a reinvestigation with the aid of stopped-flow techniques has led to a modified rate equation (*64*).

$$-d[\mathrm{MnO_4}^-]/dt = k_5[\mathrm{HNO_2}] + k_6k_7[\mathrm{HNO_2}]^2[\mathrm{Mn(VII)}](k_7[\mathrm{Mn(VII)}] + k_6K[\mathrm{H}^+][\mathrm{HNO_2}])^{-1} \tag{194}$$

Beck suggests that there is a sizable amount of nitrosyl permanganate species formed, $\mathrm{O_3MnONO}$, and he obtains a value for the equilibrium constant $K = [\mathrm{O_3MnONO}]/[\mathrm{H}^+][\mathrm{HNO_2}][\mathrm{MnO_4}^-]$ by means of an analysis of his kinetic data. This species is thought to be *inert* to redox reaction, and thus reduces the active concentration of nitrous acid and permanganate. It would be desirable to obtain direct spectrophotometric evidence for this species.

An independent investigation by Hughes and Shrimanker (*177*) also using stopped-flow spectrophotometry is generally consistent with (194) although the kinetics are expressed in a less explicit form (195):

$$-d[\mathrm{MnO_4}^-]/dt = k_8[\mathrm{HNO_2}]^{1.6} \tag{195}$$

On decreasing the permanganate concentration the order in $[MnO_4^-]$ *increases* from 0 to ca. 0.5. Both groups of authors propose a mechanism that involves a rate-determining formation of dinitrogen trioxide, which is rapidly trapped by some permanganate species. This seems very plausible, but unfortunately does not give information about the details of the mechanism. We have, in fact, returned to a mechanism where the initial stage is an electrophilic nitrosation process. These studies have been made by following the decrease in absorbance due to the permanganate ion. Although the normal reduction product of the oxidizing agent is manganese(II), Beck states that manganese(IV) accumulates in the reaction solution. However, the stoichiometry for reaction in acetate buffers at pH 3.5 (*177*) is definitely the expected value $NaNO_2:KMnO_4::5:2$. A complex rate law is also found for the oxidation of nitrous acid by chromium(VI). Nitrite esters of chromic acid are proposed as intermediates (*66*).

D. Oxidation of Nitrous Acid by the Halogens

The kinetics of oxidation of nitrite to nitrate by halogens or related species follow reasonably simple kinetics in alkaline media. In a study of hypochlorite oxidation, the results fit Eq. (196), and a mechanism involving nitryl chloride is proposed (*40*).

$$-d[ClO^-]/dt = (k_1 + k_2[NO_2^-])[ClO^-][NO_2^-][OH^-] \qquad (196)$$

In more acid media some very complex rate laws can be obtained, as is shown below (*151*).

$$-d[Cl_2]/dt = (k_3 + k_4[HNO_2])[Cl_2][NO_2^-][Cl^-]^{-2} \quad \text{pH } 0\text{–}1 \qquad (197)$$

$$-d[Br_2]/dt = (k_5 + k_6[Br^-]^{-1})[Br_2][NO_2^-]^2 \quad \text{pH } 4.2\text{–}5.8 \qquad (198)$$

$$\begin{aligned}-d[Br_2]/dt = {} & [Br_2][HNO_2]^2(k_7 + k_8[Br^-]^{-1}) \\ & \times (1 + k_9[H^+][Br_2])^{-1} \quad \text{pH } 0.8\text{–}2.5\end{aligned} \qquad (199)$$

Several unusual intermediates have been postulated. For the reaction with bromine, pH 4.2–5.8, (200)–(202) is proposed as a mechanism for the first term (k_5) while (203)–(205) is suggested for the second (k_6).

$$NO_2^- + NO_2^- \rightleftharpoons N_2O_4^{2-} \qquad (200)$$

$$N_2O_4^{2-} + Br_2 \rightarrow N_2O_4Br_2^{2-} \qquad (201)$$

$$N_2O_4Br_2^{2-} + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+ + 2Br^- \quad (202)$$

$$NO_2^- + Br_2 \rightleftharpoons NO_2Br + Br^- \quad (203)$$

$$NO_2Br + NO_2^- \rightleftharpoons N_2O_4 + Br^- \quad (204)$$

$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+ \quad (205)$$

An alternative explanation of the k_5 term in (198) is an attack by NO_2^- on a species $NO_2Br_2^-$.

$$NO_2^- + Br_2 \rightleftharpoons NO_2Br_2^- \rightleftharpoons NO_2Br + Br^- \quad (206)$$

$$NO_2Br_2^- + NO_2^- \rightarrow N_2O_4 + 2Br^- \quad (207)$$

This is rejected on the grounds that at lower pH values a mechanism involving a double nitrite species, possibly N_2O_3, is involved. This does not seem a conclusive argument; to the writer, (206)–(207) seems preferable to (200)–(202). The authors also discuss earlier studies on the oxidation of nitrite by iodine (*67*).

E. REDUCTION OF NITROUS ACID BY METAL IONS AND METAL COMPLEXES

Only a few of these reactions have been studied. The reduction by hexacyanoferrate(II) gives simple second-order kinetics, independent of acidity.

$$Fe(CN)_6H_2^{2-} + HNO_2 \rightarrow Fe(CN)_6^{3-} + NO^{\cdot} + 2H^+ \quad (208)$$

$$\text{Rate} = k[Fe(CN)_6H_2^{2-}][HNO_2] \quad (209)$$

Such a rate law can be rearranged to a form consistent with nucleophilic attack upon the nitrosonium ion, substituting from the ionization constant $K_a = [H^+][Fe(CN)_6H^{3-}]/[Fe(CN)_6H_2^{2-}]$.

$$\text{Rate} = k \cdot K_a^{-1}[Fe(CN)_6H^{3-}][H^+][HNO_2] \quad (210)$$

The value of $k \cdot K_a^{-1}$ at 25° and 1 M ionic strength is 55,000 M^{-2} sec^{-1}, close to the figure expected for an encounter-controlled reaction between NO^+ and $Fe(CN)_6H^{3-}$ (*187*). Two other systems of interest, the reduction of nitrous acid by chromium(II) and by molybdenum(V), are discussed in Section XV together with the corresponding reactions of nitric acid. The cathodic reduction of HNO_2 has been studied (*88a*).

XIV. Dinitrogen Tetroxide and Nitrogen Dioxide

Dinitrogen tetroxide is the mixed anhydride of nitric and nitrous acid, and it plays a vital role in a range of reactions in which nitric acid acts as an oxidizing agent. It is convenient at this point to summarize the main facts in its aqueous chemistry. The foundation for a great deal of the chemistry of the nitric acid/nitrous acid system is to be found in the classic studies of the formation and decomposition reactions of nitrous acid carried out by Abel and his co-workers. These have been summarized by Bray (*30*).

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \tag{211}$$

$$N_2O_3 \rightleftharpoons NO^{\cdot} + NO_2^{\cdot} \tag{212}$$

$$2NO_2^{\cdot} \rightleftharpoons N_2O_4 \tag{213}$$

$$H_2O + N_2O_4 \rightleftharpoons H^+ + NO_3^- + HNO_2 \tag{214}$$

The rate-determining step is stage (214), and Abel obtained rate constants for the formation of dinitrogen tetroxide.

$$d[N_2O_4]/dt = k[H^+][HNO_2][NO_3^-] \tag{215}$$

Although this is the same form of rate law as that observed for the formation of other nitrosyl compounds, the reactivity of the nitrate ion is many orders of magnitude *less* than that of azide, nitrite, chloride ion, etc. Abel's value for k is consistent with other values for the same reaction, such as that obtained from the nitrite-catalyzed exchange of oxygen atoms between nitric acid and water (*35*), and of the nitrite-catalyzed oxidation of thiocyanic acid by nitric acid (*100*). Both these studies involve a rate-determining formation of dinitrogen tetroxide, as in (214). More recently rate constants have become available for the forward and back reactions of all stages; the data are set out in Table III. Many of these data are due to pulse-radiolysis studies (*80, 81*). It should be noted that there are quite different values in the literature for some of these quantities, e.g., for the recombination of nitrogen

TABLE III

RATE CONSTANTS FOR THE STEPS IN DECOMPOSITION OF NITROUS ACID AT 20°

Reaction	Rate/M sec^{-1}	References
$2HNO_2 \rightarrow N_2O_3 + H_2O$	$4\ [HNO_2]^{2a}$	(*36*, *163*)
$H_2O + N_2O_3 \rightarrow 2HNO_2$	$5.3 \times 10^2[N_2O_3]^a$	(*80*)
$N_2O_3 \rightarrow NO + NO_2$	$8 \times 10^4[N_2O_3]^a$	(*80*)
$NO + NO_2 \rightarrow N_2O_3$	$1.1 \times 10^9\ [NO][NO_2]^a$	(*80*)
$N_2O_4 \rightarrow 2NO_2$	$6.9 \times 10^3\ [N_2O_4]^a$	(*81*)
$NO_2 + NO_2 \rightarrow N_2O_4$	$9 \times 10^8\ [NO_2]^{2a}$	(*81*)
$H^+ + HNO_2 + NO_3^- \rightarrow N_2O_4 + H_2O$	$1.7 \times 10^{-2}[H^+][HNO_2][NO_3^-]^b$	(*30*)
$H_2O + N_2O_4 \rightarrow H^+ + HNO_2 + NO_3^-$	$1 \times 10^3[N_2O_4]^b$	(*81*)

[a] Using E_a of 13 kcal mol^{-1}.

[b] Using E_a of 17.2 kcal mol^{-1}.

dioxide to dinitrogen tetroxide (*51*, *147*). The equilibrium constant for reaction (4), $[N_2O_4]/[H^+][HNO_2][NO_3^-]$, can be calculated from the rate constant for the back reaction obtained by Abel, and that for the forward reaction obtained by Henglein (*81*). At 20° this is 1.66×10^{-5} M^{-2}, in good agreement with a figure of $2.6 \times 10^{-5}\ M^{-2}$ obtained by Maschka (*136*) by spectrophotometric methods. Other spectrophotometric measurements of the percentage conversion of nitrite to dinitrogen tetroxide in concentrated nitric acid solution have been reported (*130*), and are consistent with this picture. It is of interest to calculate what degree of dissociation one might expect under typical conditions. If one takes a solution of 0.001 *M* total nitrite in 8.6 *M* nitric acid (for which spectrophotometric results suggest a lower limit of about 10% conversion of nitrite to $N_2O_4 + 2NO_2^{\cdot}$), then a simple calculation suggests that it might contain 8.2×10^{-5} *M* of N_2O_4 and 3.54×10^{-5} *M* of $NO_2^{\cdot}$. Clearly the dissociation may be greater at lower concentrations of nitrite and nitric acid, and vice versa. It might have been thought that with degrees of dissociation as large as these, deviations might be observed in the Beer–Lambert law plots of absorbance against [nitrite] at wavelengths in the range 350–400 nm (where HNO_2, $NO_2^{\cdot}$, and N_2O_4 all absorb). However, such plots have been found to be linear (*37*).

The discussion so far has ignored the problem of the mechanism of the hydrolysis reaction. Dinitrogen tetroxide has the symmetrical structure O_2NNO_2 (*82*), the rate law for its formation (*215*) leads one to expect that $ONONO_2$ will be formed from NO^+ and NO_3^- and the principle of microscopic reversibility requires that the hydrolysis reactions involve the same species. It has long been recognized that liquid dinitrogen tetroxide reacts as $NO^+NO_3^-$. The symmetrical form might be obtained from the unsymmetrical species by homolytic dissociation and recombination.

$$ONONO_2 \rightleftharpoons 2\,NO_2^{\cdot} \rightleftharpoons O_2NNO_2 \tag{216}$$

The low rate of formation of dinitrogen tetroxide may be due to low nucleophilic reactivity of the nitrate ion, or to the fact that $ONONO_2$ dissociates heterolytically much more readily than it does homolytically.

Anbar and Taube (*4*) attempted to examine the problem directly by allowing dinitrogen tetroxide + nitrogen dioxide vapor to bubble through alkaline ^{18}O enriched water. This sort of experiment is very difficult, because of the possibility of adventitious exchange due to high local concentrations of acid, nitrite, etc. At low nitrogen oxide concentrations the results indicated that all three oxygens in the nitrite were derived from the dinitrogen tetroxide as required for reaction of NO^+ with NO_3^-. However, in many other experiments they obtained results indicating that only two of the oxygens were so derived; this would appear to suggest a reaction of $NO_2^{\delta +}NO_2^{\delta -}$.

A distinction between mechanisms involving N_2O_4 as active species, and those involving NO_2 is readily made upon kinetic grounds. For a rate-determining attack by N_2O_4 on a substrate the rate law should take the form of (217), whereas for attack by NO_2 Eq. (218) would be expected.

$$\text{Rate} = k[H^+][HNO_2][NO_3^-][\text{substrate}] \tag{217}$$

$$\text{Rate} = k[H^+]^{1/2}[HNO_2]^{1/2}[NO_3^-]^{1/2}[\text{substrate}] \tag{218}$$

The distinction between the two cases when there is a rate-determining formation of dinitrogen tetroxide is not so clear cut, because the possibility of rapid dissociation to $NO_2^{\cdot}$ and capture by the substrate (i.e., $\nu_a \gg \nu_b$) would also yield (215)

$$H^+ + HNO_2 + NO_3^- \xrightarrow[\text{slow}]{} N_2O_4 \tag{219}$$

$$N_2O_4 \underset{\nu_b}{\rightleftharpoons} 2NO_2 \xrightarrow[\nu_a]{\text{substrate}} \text{products} \tag{220}$$

Thus in the oxidation of thiocyanic acid by nitric and nitrous acids, the active species is established (*100*) as N_2O_4 by observing (221) at high values of $[H^+][SCN^-]$, and (222) at low $[H^+][SCN^-]$.

$$\text{Rate} = k[\mathrm{H}^+][\mathrm{HNO_2}][\mathrm{NO_3}^-] \tag{221}$$

$$\text{Rate} = k[\mathrm{H}^+]^2[\mathrm{HNO_2}][\mathrm{NO_3}^-][\mathrm{SCN}^-] \tag{222}$$

Sometimes conflicting evidence is obtained, as in the technologically important oxidation of plutonium(III) to plutonium(IV). Dukes has produced (*65*) a rate law implicating N_2O_4 as the species reacting with plutonium(III), whereas Koltunov and Marchenko find nitrogen dioxide as the active species (*119*). Koltunov has also suggested a similar interpretation for the kinetics of oxidation of uranium(IV) and neptunium(V) by nitric and nitrous acids. The existence of good values for the rate constants for the forward and back reactions of (213) should be valuable when considering the mechanism of the process involving nitrogen(IV) oxides as catalysts.

The usual role of nitrogen dioxide involves the reduction to nitrite ion, as postulated above by Koltunov. A more unusual mode of action has been observed in the reaction of hexacyanoferrate(III) with nitric and nitrous acids. The product appears to be a dimer $[(NC)_5Fe(II)\mu(NO)Fe(II)(CN)_4NO]^{3-}$, and the nitrogen dioxide reduces iron(III) to iron(II), oxidizes a cyanide ligand to cyanate (which in aqueous solution gives carbon dioxide and water), and introduces the NO^+ ligand (*56*). This is not a reaction peculiar to ferricyanide; similar behavior has been observed for $Fe_2(CN)_{10}^{4-}$, $Fe(bipy)(CN)_4^-$, and $Fe(phen)(CN)_4^-$ (*48*), and there is evidence that a similar reaction occurs with $Ru(CN)_6^{3-}$ (*57*).

Nitrogen dioxide is also thought to be the active species in the nitrous acid-catalyzed oxidation of hydrobromic acid to bromine. The rate law is shown in (223).

$$\text{Rate} = k[\mathrm{HNO_2}]^{1.5}[\mathrm{Br}^-]^x[\mathrm{H}^+]^y \tag{223}$$

At low acidities, $[H^+] \leqslant 0.5$ *M*, x and y are close to 2, but at high acidities y rises to ca. 6 and x can fall to ca. 1. The results (*70*) are generally consistent with an earlier study (*129*), in which a similar intermediate $N_2O_3BrH^+$ was postulated

$$\mathrm{H^+ + HNO_2 + NO_3^- \rightleftharpoons H_2O + N_2O_4 \rightleftharpoons 2NO_2^{\cdot}} \tag{224}$$

$$\mathrm{H^+ + HNO_2 + Br^- \rightleftharpoons H_2O + ONBr} \tag{225}$$

$$\mathrm{NO_2^{\cdot} + ONBr \rightleftharpoons N_2O_3Br^{\cdot}} \tag{226}$$

$$H^+ + N_2O_3Br^{\cdot} \rightarrow HNO_2 + NO^{\cdot} + Br^+ \tag{227}$$

$$Br^- + N_2O_3Br^{\cdot} \rightarrow Br_2 + NO^{\cdot} + NO_2^- \tag{228}$$

$$Br^- + N_2O_3Br^{\cdot} \rightleftharpoons Br_2 \tag{229}$$

XV. Nitric Acid

Nitric acid is only a moderately strong mineral acid, and solutions containing several moles per liter contain an appreciable amount of the nonionized HNO_3. A very useful paper by Davis and de Bruin (*58*) tabulates the degree of dissociation, the activity coefficients of the species involved, and the activity of water over a wide concentration range. This information can be valuable when interpreting kinetic data obtained for moderately concentrated solutions of nitric acid. Measurements of the acidity of nitric acid solutions, expressed as H_0 values, have been reported by Wyatt and Dawber (*233*). In sufficiently concentrated solutions of nitric acid, the nitronium ion is detectable by Raman spectroscopy. Measurements of the kinetics of ^{18}O exchange between nitric acid and water at 0° have established the nitronium ion as an active species down to 40 mol % HNO_3 in both isotope exchange and aromatic nitration (*35*). Stopped-flow methods have been used to measure the rate of nitronium ion formation in solutions of nitric acid in 74–82% w/w sulfuric acid (*43*). Other workers have somewhat different values for the rate of nitronium ion formation (*142*). Many reactions of nitric acid in solutions of high acidity are catalyzed by traces of nitrous acid, and in order to eliminate such effects it is often necessary to add a scavenger to remove the last traces of nitrite. When this is done, the residual rate, due to nitrogen(V) species alone, may be observed. A study of the oxidation of thiocyanic acid in the presence of nitrite scavengers has been reported (*188*). In some cases the substrate itself may be a nitrite trap, as is the case in the nitric acid oxidation of hydrazine. Here it has been suggested that the active oxidizing agent is the nitronium ion itself (*120*).

A. RADIOLYSIS AND PHOTOLYSIS

There have been many studies of the radiolysis of nitric acid and of nitrate solutions, partly because of the use of nitric acid as a medium in the processing of nuclear fuels. One pulse radiolytic study that is of interest is that by Gratzel, Henglein, and Taniguchi, in which it was shown that NO_3^{2-}, HNO_3^-, and H_2NO_3 could be formed. The last of these three is the oxyacid of which the familiar nitrogen dioxide is the anhydride. pK_a values were reported to be 4.8 and 7.5, and the decomposition reactions to form nitrogen dioxide were observed at 20° (*78*).

$$NO_3^{2-} + H_2O \rightarrow NO_2 + 2OH^- \qquad (230)$$

$$HNO_3^- \rightarrow NO_2 + OH^- \qquad (231)$$

Under other conditions, pulse radiolysis of concentrated sodium nitrate solutions is reported to form NO_3, and these combine in a bimolecular step to form N_2O_6, with $k = 6.8 \times 10^7$ (*51*). The photolysis of nitrate solutions has been suggested (*11*) to involve the formation of excited pyramidal NO_3^- in the $^3\pi\pi$ state, followed by intramolecular rearrangement to the peroxonitrite, i.e., $ONOO^-$. In acid media peroxonitrite isomerizes to nitric acid, and the kinetics of this reaction have been reported (*78*, *143*).

B. REACTIONS OF NITRIC ACID AS AN OXIDIZING AGENT

A feature of the nitrous acid-catalyzed oxidation reactions of nitric acid is that they commonly involve reduction of nitrate to nitrous acid or some equivalent species. The reaction is thus autocatalytic, and there are many examples in the literature (*65*, *100*, *130*). An example of this effect under current investigation (*150*) can be observed in the oxidation of hydroxylamine by nitric acid; the stoichiometry varies with the reactant concentrations, but at higher hydroxylamine concentrations approximates to (232)

$$4NH_3OH^+ + 2NO_3^- \rightarrow 3N_2O + 7H_2O + 2H^+ \qquad (232)$$

Hydroxylamine is only a relatively poor scavenger for nitrite, and thus the reaction shows autocatalytic behavior as nitrous acid (an intermediate species) builds up. This is in contrast to the oxidation of hydrazine by nitric acid [see Koltunov *et al.* (*120*)].

An oxidation reaction of some technological interest is that in which iodine reacts with concentrated nitric acid (16–21 *M*). Reaction occurs by a two-stage process.

$$I_2 + 3HNO_3 \rightleftharpoons 2I^+ + 2NO_3^- + HNO_2 + H_2O \qquad (233)$$

$$I^+ + 6HNO_3 \rightleftharpoons I^{5+} + 4NO_3^- + 2HNO_2 + 2H_2O \qquad (234)$$

(The charges on the cationic iodine species merely represent formal oxidation states.) The kinetics of the forward process are first order with respect to I_2 and I^+, respectively. Equilibrium constants have been obtained, but no detailed mechanism has been postulated (*134*, *135*). It would be surprising if the mechanism did not involve $NO_2^{\cdot}$ or N_2O_4. Indeed although the stoichiometric equations quote HNO_2 as the product, in 16–21 *M* nitric acid, this would be almost completely converted to $N_2O_4 + NO_2^{\cdot}$. An unusual species postulated (*39*) for reactions of aromatic iodo compounds with concentrated nitric acid is HNO_2I^+.

Turning now to the reduction of nitrate by metal complexes, there is a complicated reaction with chromium(II). The products depend upon the initial proportions of the reactants, but with an excess of nitric acid three main species are formed, $Cr(H_2O)_5NO^{2+}$, $Cr(H_2O)_6{}^{3+}$, and $(H_2O)_4Cr\mu(OH)_2Cr(H_2O)_4{}^{4+}$. The rate law takes the form (235), and parallel reaction pathways involving the nitrate ion and nitric acid are postulated (*146*)

$$\text{Rate} = (k + k^1[H^+])(1 + K[H^+])^{-1}[Cr^{2+}][NO_3{}^-] \qquad (235)$$

The proposed mechanism is summarized below.

$$Cr^{2+} + NO_3{}^- + 2H^+ \rightarrow Cr(IV) + NO_2{}^- + H_2O \qquad (236)$$

$$Cr(IV) + Cr^{2+} \rightarrow (H_2O)_4Cr\mu(OH)_2Cr(H_2O)_4{}^{4+} \qquad (237)$$

$$Cr^{2+} + NO_2{}^- + H^+ \rightarrow Cr(H_2O)_6{}^{3+} + NO^{\cdot} + H_2O \qquad (238)$$

$$Cr^{2+} + NO^{\cdot} \rightarrow Cr(H_2O)_5NO^{2+} \qquad (239)$$

The authors have also examined the reaction of nitrous acid with Cr^{2+}, and found a rate law with a simple first-order dependence upon each component. As, under these conditions, nitrous acid was only slightly ionized, the result does not exclude a reaction between nitrite ion and Cr^{2+}. Armour and Buchbinder (*8*) have found that, when there is an excess of nitric acid over Cr^{2+}, complications ensue because of reactions between Cr^{2+} and $Cr(H_2O)_5NO^{2+}$.

A very interesting study on the reduction of nitrate ion by a molybdenum(V) complex, $[MoOCl_3(OPPh_3)_2]$, in dichloromethane solution has been reported (*76*), together with an associated paper on the reduction of nitrite (*109*). The interest in this system is stimulated by the fact that interaction between a molybdenum(V) center and a nitrate ion has been proposed to be involved in the reduction path of *nitrate reductase* enzymes.

It is convenient to consider the paper on nitrite reduction first. The overall stoichiometry appears to be of type (240):

$$NO_2^- + Mo(V) \rightarrow NO^\cdot + Mo(VI) \tag{240}$$

but the nature of the Mo(VI) product depends upon the initial proportions of the reactants. With a 1:1 ratio the products consist of of equimolar amounts of $MoO_2Cl_4^{2-}$ and $MoO_2Cl_2(OPPh_3)_2$, but as the amount of nitrite (used as the tetraethylammonium salt) is increased above that of Mo(V) there is a reduction in the amount of $MoO_2Cl_4^{2-}$ formed (and possibly also of $MoO_2Cl_2(OPPh_3)_2$). In the presence of at least a 6-fold excess of nitrite a solid product $[Et_4N]_4[Mo_8O_{26}]$ can be isolated in essentially quantitative yield. Kinetic studies showed the presence of three consecutive reactions:

$$MoOCl_3(OPPh_3)_2 \rightarrow MoOCl_3(OPPh_3)(NO_2)^- \tag{241}$$

$$MoOCl_3(OPPh_3)(NO_2)^- \rightarrow MoOCl_3(NO_2)^*(OPPh_3)^- \tag{242}$$

$$MoOCl_3(NO_2)^*(OPPh_3)^- \rightarrow MoO_2Cl_3(OPPh_3)^- + NO \tag{243}$$

$$MoO_2Cl_3(OPPh_3) \xrightarrow{NO_2^-} \text{Products} \tag{244}$$

Stage (242) may be an isomerization from an *N*-bonded to an *O*-bonded nitrite group, and stage (243) is postulated as a rapid process. The details of the final stages are not fully worked out, rate law (245) being postulated:

$$\begin{aligned} \text{Rate} &= [MoO_2Cl_3(OPPh_3)^-](a + b[OPPh_3]^{-1}) \\ &\quad \times [(Et)_4NNO_2](1 + c[Et_4NNO_2])^{-1} \end{aligned} \tag{245}$$

A rather similar pattern of behavior is found when the oxidant is the nitrate ion (*76*). Once again the products depend upon the initial ratio of the reactants, and the mechanism proposed involves an initial dissociation of a triphenylphosphineoxide ligand, complexation with a nitrate ion, and nitrogen–oxygen bond fission in a redox step to form an oxo complex and nitrogen dioxide.

For reactions with at least a 2-fold initial excess of Mo(V) over nitrate, a slower reaction may occur in which the nitrogen dioxide in turn oxidizes Mo(V) to Mo(VI). This process has been separately studied, using $MoOCl_3(OPPh_3)_2$ and nitrogen(IV) oxide in methylene chloride as initial reactants. Parallel pathways involving $NO_2^{\bullet}$ and N_2O_4 are found to occur (*75*).

$$-d[\mathrm{Mo(V)}]/dt = k[\mathrm{NO_2^{\bullet}}][\mathrm{Mo(VO)}] + k'[\mathrm{NO_2^{\bullet}}]^2[\mathrm{Mo(V)}] \qquad (246)$$

The mechanism proposed is shown in (247) to (249).

$$2\mathrm{NO_2^{\bullet}} \rightleftharpoons \mathrm{N_2O_4} \; K_1 \text{ fast} \qquad (247)$$

$$\mathrm{NO_2^{\bullet}} + \mathrm{Mo(V)} \rightarrow \mathrm{Mo(VI)} + \mathrm{NO^+} \qquad (248)$$

$$\mathrm{N_2O_4} + \mathrm{Mo(V)} \rightarrow \mathrm{Mo(VI)} + \mathrm{NO^+} + \mathrm{NO_2^{\bullet}} \qquad (249)$$

One problem with reactions involving the nitrogen dioxide–dinitrogen tetraoxide system is that the kinetic order depends upon the position of equilibrium (247). A reaction involving $NO_2^{\bullet}$ as active species is first order with respect to [N(IV)] if the equilibrium lies largely in favor of $NO_2^{\bullet}$, whereas it is half order if the equilibrium strongly favors N_2O_4. With the concentrations quoted in this investigation, $1.2–27.5 \times 10^{-3}$ *M*, one would expect the bulk component of the N(IV) species to be N_2O_4 based upon reported (*82*) values for K_1 in solvents similar to CH_2Cl_2. Thus a term that is first order in [N(IV)] should correspond to N_2O_4 as reactant, and a term that is second order would appear to require *two* molecules of N_2O_4. Many of the data for K_1 are rather old, but even so it seems unlikely that, at concentrations of around 10^{-3} *M* nitrogen(IV) oxide should be largely dissociated to $NO_2^{\bullet}$. Another investigation of the reduction of nitrate by molybdenum(V) complexes involves the reaction of $(NH_4)_2MoOCl_5$ in DMF (*194*). The mechanistic interpretation of the results has been the subject of some discussion (*77, 179*).

These results are in marked contrast to earlier studies (*85*) on the reduction of nitrate by molybdenum(V) in aqueous media, where the main reduction product was nitric oxide, and kinetics that were half-order with respect to molybdenum were ascribed to a monomer–dimer equilibrium in the reducing agent. The reduction of nitrite to nitric oxide by molybdenum(V) also follows a quite different path in aqueous media (*73*).

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