a simple reductive-elimination reaction.

The reaction of NaH with $Ga(CH_3)_3$ was investigated in order to study the effects of the apparent reducing agent. Results that were different from those observed for KH were obtained. When 1 mmol quantities of both $Ga(CH_3)_3$ and NaH were combined in dimethoxyethane at 25 °C, 0.385 mmol of CH_4 was formed in 4 days. After the solvent was removed, the resultant mixture was heated at 135 °C for 72 h and an additional 0.216 mmol of CH_4 was formed. Further heating produced more CH_4; 145 °C for 72 h gave 0.124 mmol of CH_4; 160 °C for 120 h led to another 0.269 mmol of CH_4. In all, 0.994 mmol of CH_4 was formed. The material remaining in the tube after pyrolysis consisted of a gray solid, a viscous liquid, which was soluble in dimethoxyethane, and a "silver"-colored mirror of gallium metal. These results suggest extensive decomposition and partial reduction of the sample to gallium metal. It is interesting that KH and NaH give slightly different results. However, there is no evidence for the formation of a characterizable product by a simple, well-defined reductive-elimination reaction.

The observed chemistry of $In(CH_3)_3$ with NaH and KH leads to the same conclusions as those proposed for $Al(CH_3)_3$ and $Ga(CH_3)_3$. When 1 mmol of $In(CH_3)_3$ was combined with excess KH in benzene at 25 °C, 0.159 mmol of CH_4 and a gray-black solid were formed after 12 h. The reaction of $In(CH_3)_3$ with NaH in dimethoxyethane at 130 °C for 12 h produced 0.120 mmol of CH_4 and a black insoluble solid. It is of interest to compare our results with those of Gavrilenko, Kolesov, and Zakharin.[15] They reported that $In(CH_3)_3$ reacted with NaH and KH to form $NaIn(CH_3)_3H$ and $KIn(CH_3)_3H$. Heating to 100 °C led to the formation of $NaIn(CH_3)_4$. It is difficult to reconcile our results but all data suggest that a simple, stoichiometric, reductive-elimination reaction is not the only reaction occurring.

All of the results from the investigations of the reactions of group 3 organometallic compounds with alkali-metal hydrides suggest that reductive-elimination reactions can occur. The facility of the reaction depends on the alkali-metal hydride, the organic substituent, and the group 3 element. However, low oxidation state compounds are not the only product. The high temperatures required to initiate the reductive-elimination reaction for the aluminum compounds and the methyl derivatives lead to apparent decomposition reactions, which occur prior to or after the reduction reaction.

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Registry No. $Al(CH_2SiMe_3)_3$, 41924-27-0; $KAl(CH_2SiMe_3)_3H$, 80594-56-5; $KGa(CH_3)_3H$, 41575-37-5; $KAl(CH_3)_3H$, 53108-65-9; $KIn(CH_3)_3H$, 63213-62-7; $Ga(CH_3)_3$, 1445-79-0; $Al(CH_3)_3$, 75-24-1; $In(CH_3)_3$, 3385-78-2; KH, 7693-26-7; NaH, 7646-69-7; $LiCH_2SiMe_3$, 1822-00-0; $AlBr_3$, 7727-15-3.

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Aqueous Nitrosyliron(II) Chemistry. 1. Reduction of Nitrite and Nitric Oxide by Iron(II) and (Trioxodinitrato)iron(II) in Acetate Buffer. Intermediacy of Nitrosyl Hydride[1]

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Nitrite is reduced by Fe(II) sequentially to NO and N_2O at pH 5 (acetate buffer), and N_2 is not a product under these conditions. The nitrosyl complex $FeNO^{2+}$ is stable against reduction to N_2O below pH ca. 4; the threshold for reduction to N_2 occurs at ca. pH 8. The decomposition of $HN_2O_3^-$ is retarded by coordination to Fe(II) at pH 5 and 6 but produces the same products as "free" trioxodinitrate, N_2O and NO_2^-. The latter species is reduced by Fe(II), and nitrogen mass balance shows that some $HN_2O_3^-$ remains undecomposed, probably in coordination to Fe(III). A ^{15}N tracer experiment at pH 6 shows that N_2O product arises initially from Fe(II)-coordinated $HN_2O_3^-$ with both N atoms contributing to a random distribution, i.e. scrambled but still derived from an HNO precursor as in the case of uncoordinated $HN_2O_3^-$. Reduction of $^{15}N^{18}O$ by Fe(II) at pH 6 in the presence of $HN_2O_3^-$ (natural abundance) gives rise to N_2O, whose isotopic composition shows both self-dimerization and comingling dimerization of HNO from two sources, demonstrating that HNO is a primary product of the Fe(II) reduction of NO.

The reduction of nitrous acid by Fe(II) has been the subject of a number of previous investigations;[2-7] its products are known to include NO at low pH, with N_2O, N_2, and NH_3 appearing at successively higher pH levels whose thresholds have not been sharply established. Brown and Drury[6] have reported quantitative reduction of NO_2^- to NH_3 by excess $Fe(OH)_2$ in NaOH solution and proposed a sequential process involving the intermediate formation of HNO and NH_2OH at oxidation states +1 and −1, respectively. Chalamet[7] has reported NO, N_2O, and N_2 to be the reaction products at pH 5 in acetate buffer and proposed that NO and N_2O result from sequential single-electron-transfer reactions but that N_2 production is a separate, direct process.

If NO is produced in the presence of Fe(II), the well-known "brown ring" complex $Fe(H_2O)_5NO^{2+}$ forms, and reduction of NO by Fe(II) may therefore be influenced by the properties of this species. The composition of this complex has been known since early in this century.[8,9] Its UV spectrum is known to be independent of the anion present.[10] Oxidation of $FeNO^{2+}$ to Fe(III) by NO was reported in 1924[11] and NO

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oxidation of $FeSO_4$ in NaOH solution, with N_2O and N_2 as products, in 1929.[12] Contradictions in the earlier literature as to whether Fe(II) is[8,13] or is not[14,15] oxidized by NO in acid solution were addressed by Tarte,[16] who concluded that $FeNO^{2+}$ is stable against oxidation under (specified) acidic conditions and that prior claims to the contrary had resulted from NO_2 contamination.

The production of N_2O by Fe(II) reduction of NO raises interesting questions concerning the possible intermediacy of HNO (or NO^-) as either a ligand or a "free" species. Formation of this reactive species has been demonstrated in the cases of trioxodinitrate decomposition[17,18] and the hydroxylamine–nitric oxide reaction;[19] different electronic states of the intermediate appear to be involved in the two cases.[19,20] Transition-metal coordination of HNO has been demonstrated in the case of an octahedral Os complex.[21,22]

In this paper we report the results of studies of the Fe(II) reduction of nitrite and nitric oxide in weakly acidic and weakly alkaline solutions, establishing stability limits for $FeNO^{2+}$ against reduction to N_2O and beyond to N_2. We also report evidence that HNO is the primary product of reduction of NO by Fe(II), via a route that has caused us to explore the effects of Fe(II) coordination on the decomposition of trioxodinitrate.

Experimental Section

Reagents. Reagent grade chemicals were used without further purification, with the exception of iron(II) sulfate, gases, and trioxodinitrate. After initial preparation of $FeSO_4$ stock solutions, they were allowed to stand for 10 days and then filtered to remove all precipitate resulting from Fe(III) impurity. Purified solutions were stored under a continuous flow of O_2-free N_2; the maximum change in $KMnO_4$ titer observed was a 2% increase (i.e., due to solvent loss, not oxidation) over a 3-month period. Commercial CO_2 and N_2O were purified by successive passes through a helical trap at 195 K and then repeatedly frozen at 77 K and briefly pumped. Commercial CF_4 was deoxygenated by passage over BASF R3-11 catalyst at room temperature. Commercial NO and NO–CF_4 mixtures were purified by successive passes through a silica gel trap (later molecular sieve 5A) at 113 K and then repeatedly frozen and pumped at 77 K. Gas purity was assessed by gas chromatography and by mass spectrometry. Isotopically enriched NO (95.1% ^{15}N, 94.5% ^{18}O) was obtained from Los Alamos Scientific Laboratory. Sodium trioxodinitrate at natural isotopic abundance and $Na_2O^{15}NNO_2$ containing 19.6% ^{15}N at the indicated position were synthesized as described elsewhere.[17,23]

Reduction of Nitrite. Stoichiometric experiments were carried out by the method of Chalamet:[7] to a quantity of deaerated $FeSO_4$ solution held under helium in a boiling flask was added separately deaerated $NaNO_2$ solution through a septum. Agitation was provided by a magnetic stirring bar. Samples of the gas phase were withdrawn, first with a Hamilton gastight syringe and later with a Precision Sampling Pressure-Lok syringe with a locking tip and low-dead-volume needle, for injection into a gas chromatograph. Later experiments were conducted in a helium-filled glovebox interfaced directly to the GC injection port.

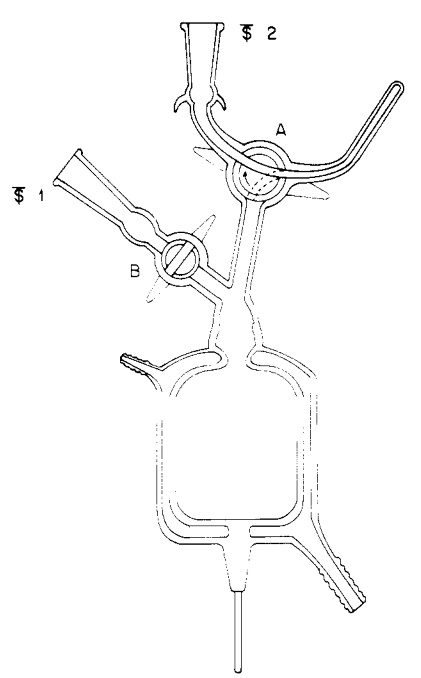

Figure 1. Reaction vessel.

Reduction of NO. Measurements were carried out in water-jacketed glass reaction vessels (Figure 1) attached to the vacuum system via a flexible glass coil, with mechanical vibration employed to maintain equilibrium between gas and solution phases, as described elsewhere.[24] A typical procedure begins with the introduction of buffer solution into the vessel through stopcock B. Standard taper 1 is then capped with a septum, and a long needle is inserted into the solution at the bottom of the vessel. Solution and vessel are deaerated by passage of inert gas into the solution, vented via a short fine-gauge needle at the septum. After an appropriate interval (ca. 1 h), a measured volume of previously deaerated $FeSO_4$ stock solution is introduced through the long needle. The needles are then removed from the septum, stopcock B is closed, and the vessel is attached to a vacuum line at standard taper 2. Solution and vessel are degassed by three successive periods of pumping with solution frozen at either 194 or 77 K. The vessel is then mounted on a Model E1 Vibromixer (Chemapec, Inc.) and reconnected to the vacuum system via a flexible glass coil. A previously prepared reactant gas–internal standard gas mixture is then introduced from a storage reservoir into the manifold connecting to standard taper 2. Stopcock A is opened for approximately 5 s to allow equilibration of total pressure in the vessel and manifold, which is then measured with a mercury manometer before removal of the gas mixture from the manifold by liquid-N_2 condensation. With stopcock A closed, the vibrator is started. Gas samples are withdrawn at intervals by momentary opening of three-way stopcock A to communicate with the sample volume. Liquid-N_2-condensable gas samples (NO, N_2O, CO_2, CF_4) were transferred by distillation to storage bulbs for subsequent GC analysis, via a helical trap at 194 K to remove H_2O; if N_2 was present or suspected, transfer was carried out by Toepler pump.

$Na_2N_2O_3$ Decomposition. For experiments in which $Na_2N_2O_3$ was employed, only the acid buffer component was initially added to the main reaction vessel along with $FeSO_4$. A solution of $Na_2N_2O_3$ in the basic buffer component (usually 1 M NaOH) was placed in a sidearm attached at the standard taper entry port. After both solutions had been rigorously degassed, reactant and reference gases were introduced, and reaction was then initiated by rotation of the sidearm to pour its contents into the main vessel. With mechanical vibration applied, kinetic measurements were obtained by periodic sampling and analysis of the gas phase.

Gas Chromatographic Analysis. Gas analyses other than isotopic were conducted initially in a Varian Model 920 gas chromatograph equipped with a 12 ft × $^1/_4$ in. Porapak Q column and later in a Hewlett-Packard Model 5712A instrument equipped with an 18 ft × 1/8 in. column (also Porapak Q), in both instances with thermal

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Table I. Apparent Products of the Fe(II) Reduction of Nitrite at pH 5 in Acetate Buffer[a]

	Hamilton syringe	Pressure-Lok syringe	glovebox	ref 7 (Hamilton syringe)
% N_2	12.2	2.8	0.6	28.1
% NO	12.8	14.7	15.1	37.2
% N_2O	75.0	82.5	84.3	34.7

[a] Conditions: $[Fe(II)]_0 = 0.050$ M; $[NaNO_2]_0 = 0.025$ M; reaction time = 24 h; t = 22 °C.

Table II. Products of Nitrite Reduction by Fe(II) as % N_2O (Remainder = NO)[a]

pH	$[Fe(II)]_0$, M	$[NaNO_2]_0$, M	% N_2O
2.8	0.05	0.025	0
5	0.02	0.01	64
5	0.05	0.025	85
5	0.16	0.08	88
6	0.05	0.025	84

[a] Conditions: reaction time = 24 h; t = 22 °C; acetate buffer.

conductivity detection and with digitally integrated output. Since N_2 was a potential gas product of interest and atmospheric background is difficult to eliminate when syringe injection methods are employed, a direct vacuum-line–GC interface was developed, as described elsewhere.[25] This method necessitates the use of an internal reference gas for which purpose initially CO_2 and later CF_4 were employed. The measured initial total pressure is taken to be equal to the sum $P^0_{NO} + P^0_{ref} + P_{H_2O}$. From the known partial pressure of reference gas, GC peak areas, detector/integrator sensitivity factors determined by calibration, and sample/reaction vessel volume ratio, total moles of each reactant and product gas were calculated for each sample. Corrections were made appropriately for gas solubilities and for losses due to prior sampling.

Tracer Experiments. Experiments employing $^{15}N^{18}O$ and $Na_2O^{15}NNO_2$ were carried out by the procedure described above. Isotopic analyses were performed in part on a Consolidated Nier isotope ratio mass spectrometer[26] and later on an AEI MS-30 instrument with an appropriate gas inlet at the reference side.[27]

Results and Discussion

Products of Fe(II) Reduction of Nitrite. In our initial efforts to reproduce the experimental conditions of Chalamet[7] (pH 5, acetate buffer), we observed NO, N_2O, and measurable but variable proportions of N_2 as products. As shown in Table I, changing from the syringe type employed by Chalamet to a syringe with locking tip and low-dead-volume needle gave the illusion of a dramatic reduction in N_2 product level. Upon repeating the experiment using Hamilton syringe injection inside a He-filled glovebox in which N_2 background was a few parts per thousand, we found N_2 to be reduced to background level. We conclude that N_2 is not a product of nitrite reduction by Fe(II) at pH 5, that the N_2 observed by Chalamet was of atmospheric origin, and that his postulated separate process for its production is incorrect. In later experiments we have shown that the threshold for production of N_2 by Fe(II) reduction of NO occurs at about pH 8; we assume that it would appear as a product of nitrite reduction only as a result of a third step in a sequential process.

Additional product distribution measurements were made by the method of Chalamet, with use of Pressure-Lok syringe injection corrected for N_2 background (Table II). These data show the predominance of N_2O over NO expected for sequential appearance of the two products when the reactant ratio is 2:1. Results reported in ref 7 under the conditions $[Fe(II)]_0$:$[NaNO_2]_0$ = 1:1 and 1:2, and in which reported N_2 contents are much lower than shown in Table I, are also consistent with sequential reduction.

Table III. Yields of N_2O from the Reduction of NO by Fe(II)[a]

pH	buffer	I, M	$[Fe(II)]_0$, M	$(n_{NO}/n_{Fe(II)})_0$	yield of N_2O, %
1.0	sulfate	1.0	0.10	0.2	0.0
2.0	sulfate	1.0	0.10	0.2	0.0
3.0	perchlorate	0.30	0.050	1.49	0.0
3.8	acetate	0.29	0.050	1.57	0.3
4.0	acetate	0.30	0.050	1.44	0.3
5.0	acetate	0.50	0.050	0.51	45.3
6.0	acetate	3.0	0.050	2.0	99.0
6.0	acetate	3.0	0.050	1.09	100.8
6.0	acetate	3.0	0.050	0.51	99.8
6.0	acetate	3.0	0.050	0.23	99.3

[a] Conditions: reaction time = 24 h; t = 25.0 °C. Percent yields of N_2O are based on the initial moles of Fe(II) or of NO, whichever is limiting.

Products of Fe(II) Reduction of NO. Experiments were carried out to determine the yields of N_2O produced upon addition of NO to Fe(II) (Table III). With efficient phase mixing maintained by mechanical vibration, formation of the nitrosyl complex was indicated in each instance by rapid development of a dark green to dark brown color in the solution. The data indicate a threshold for N_2O production at ca. pH 4 and a very high degree of stability of $FeNO^{2+}$ at pH 3 and below, a stability that appears to be a property of $Fe(NO)^{2+}$ rather than of the combination Fe(II) plus NO. Far from being inhibited by acidity, NO reduction is reported to be first order in $[H^+]$ in several other instances, e.g., in both the Cu(I)-catalyzed[28] and the uncatalyzed[29] reaction with Sn(II) and in the reaction between NO and Eu(II).[30]

In addition to the experiments reported in Table III, NO gas has been brought into contact with saturated aqueous Fe(II) in the presence of its hydrous oxide precipitate. The predominant gas remained N_2O, but N_2 was also observed, first appearing at ca. pH 8 (borate buffer, I = 0.10 M). Yields were not measured, but the molar ratio N_2:N_2O at 24 h increased from 0.012 at pH 8.4 to 0.11 at pH 10 and then decreased to 0.06 at pH 14 (NaOH), perhaps due to further reduction to NH_3.[6,12] It is not clear whether reduction to oxidation states below +1 is due to pH increase alone or to the presence of hydroxide gel, as has been suggested by Brown and Drury.[6]

No oxidation of Fe(II) in $FeNO^{2+}$ was observed by Tarte[16] during extended periods at pH 1, 2, and 3 in H_2SO_4 and also in a solution reported to contain $FeSO_4$ alone. A solution prepared in the same way in our laboratory employing commercial $FeSO_4 \cdot 7H_2O$ gave a measured pH of 3.2. Tarte also reported no oxidation in a KH_2PO_4 solution; as specified, we calculate that the pH of this solution would have been slightly greater than 4 in the absence of $FeSO_4$. With $FeSO_4$ added, the pH may well have been less than 4. The one condition for which Tarte reported Fe(II) oxidation (KH_2PO_4–Na_2HPO_4) is difficult to characterize due to heterogeneity. Our results are thus concordant with Tarte's but provide a clearer idea of the pH thresholds for N_2O and N_2 production.

Decomposition of Fe(II)-Coordinated Trioxodinitrate. As a next step in exploration of the $FeNO^{2+}$ reaction system, we wished to establish whether N–N bonds are formed as an integral part of the reaction process or whether there is a monomeric N(I) precursor to N_2O product (i.e., HNO or NO^-). As will be described, this involved the introduction of

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Table IV. Decomposition of $Na_2N_2O_3$ in the Presence of Fe(II) in Acetate Buffer at 25.0 °C[a]

t, min	$10^4 n_{N_2O}$	$10^4 n_{NO}$	*t*, min	$10^4 n_{N_2O}$	$10^4 n_{NO}$
(a) pH 5.0, $I = 0.71$, $[Fe(II)]_0 = 0.014$, $[Na_2N_2O_3]_0 = 0.050$					
10	0.28	0.35	80	2.11	8.83
20	0.61	1.80	1440	2.78	9.35
40	1.38	7.25			
(b) pH 5.0, $I = 0.71$, $[Fe(II)]_0 = 0.010$, $[Na_2N_2O_3]_0 = 0.053$					
10	0.39	0.16	80	3.26	7.10
20	0.88	0.75	3780	4.22	8.60
40	1.75	2.96			
(c) pH 6.0, $I = 3.0$, $[Fe(II)]_0 = 0.010$, $[Na_2N_2O_3]_0 = 0.050$					
10	0.19	0.03	120	1.11	0.73
20	0.31	0.10	210	1.82	1.49
40	0.57	0.24	1440	4.08	1.91
80	0.86	0.50			

[a] Solution volume = 20.0 mL. All concentrations in molar units.

Table V. Mass Spectra of N_2O Produced by Decomposition of $Na_2O{*}NNO_2$ in the Presence of Fe(II) at pH 6.0 in Acetate Buffer Solution ($I = 3.0$ M) and 25 °C[a]

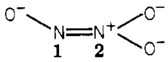
		obsd		calcd	
				19.6% ^{15}N	9.8% ^{15}N
t, min	15	30	60		
% *m/e* 46	1.01	1.40	1.96	3.84	0.96
% *m/e* 45	15.9	18.2	21.0	31.5	17.7
% *m/e* 44	83.1	80.4	77.0	64.6	81.4
% ^{15}N in *m/e* 44–46	8.95	10.5	12.5		
% ^{15}N in *m/e* 30–31	9.36	10.9	12.5		
n_{NO}/n_{N_2O} (GC)	0.006	0.2	0.32		

[a] $[Na_2N_2O_3]_0 = 0.0533$ M, $[Fe(II)]_0 = 0.0203$ M, N = 19.6% ^{15}N. The "calculated" spectra are for random distribution at the levels given.

$HN_2O_3^-$ as a known HNO source, and it was first necessary to examine the effects of Fe(II) on the source reaction

$$HN_2O_3^- = HNO + NO_2^- \qquad (1)$$

The anion $N_2O_3^{2-}$ has the known planar structure[31]



In reaction 1 it is N(1) that becomes HNO,[17] and in the usual case both nitrogen atoms in the N_2O product arise from N(1) via the reaction

$$HNO + HNO = N_2O + H_2O \qquad (2)$$

Bidentate coordination of $N_2O_3^{2-}$ has been observed in Ni^{2+} and Pb^{2+} solutions,[32] and crystalline tris(trioxodinitrate) complexes of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} have been isolated with $Co(NH_3)_6^{3+}$ as the counterion.[33] The unstable monobasic anion $HN_2O_3^-$ is predominant in aqueous solution in the pH range ca. 4–8, and we assume this to be the species that coordinates to Fe(II) in the pH range employed in this study. Since first protonation of $N_2O_3^{2-}$ is now known to occur at N(1),[34] the availability of cis oxygen atoms for coordination is left unimpaired.

As a preliminary, our kinetics method was tested on the decomposition of 0.051 M $Na_2N_2O_3$ at 25 °C and pH 5 in acetate buffer, without addition of Fe(II). Measured values of $[Na_2N_2O_3]$ calculated from $[Na_2N_2O_3]_0$ and accumulated moles of N_2O product displayed rigorously first-order behavior over 5 half-lives and a rate constant of 6.17 × 10^{-4} s^{-1}, in close agreement with spectrophotometrically measured values.[18,19] Some NO product was observed during later stages of the reaction, due to accumulation of nitrite.[17,18]

Upon addition of $Na_2N_2O_3$ to Fe(II) in acetate buffer at pH 5 and 6, the solution acquires a pale yellow color within seconds; this intensifies quickly and shifts through orange to red, and after 3 min the solution has an intense, deep red color. The iron(III) trioxodinitrate complex is known to exhibit an intense charge-transfer band at 420 nm,[33] and the deep red color clearly indicates the presence of Fe(III). Over a period of several hours the color intensity declines, showing decomposition of the trioxodinitrate, but a characteristic orange color persists at "infinite" time.

Results of kinetics experiments on $HN_2O_3^-$ decomposition in the presence of Fe(II) are shown in Table IV. If these data are plotted as ln $[Na_2N_2O_3]$ vs. *t*, with $[Na_2N_2O_3]$ being based on the stoichiometry of eq 1 and 2, nonlinear plots are obtained whose initial slopes correspond to $k_1 = 1.2 \times 10^{-4}$ and 0.48 × 10^{-4} s^{-1} at pH 5 and 6, respectively. These values are substantially lower than those for "free" $HN_2O_3^-$, indicating stabilization of trioxodinitrate by coordination. The nonlinearity is more pronounced in the pH 5 case, and greater quantities of NO are evolved at pH 5 than at pH 6.

The NO product in these experiments must arise from NO_2^- (eq 1), through its reduction by Fe(II), its attack on undecomposed $HN_2O_3^-$,[17b] or both. In the two pH 5 experiments, the molar quantity of NO observed at "infinite" time is greater than the number of moles of Fe(II) initially present; attack of NO_2^- on $HN_2O_3^-$ must therefore be involved in this case. At pH 6, NO production from this source does not occur to an appreciable extent.[17b] In this case, the number of moles of Fe(II) initially present (2.0 × 10^{-4}) is nearly equal to the moles of NO produced (1.9 × 10^{-4}).

The number of moles of N_2O produced at pH 6 ("infinite" time) corresponds to 8.2 × 10^{-4} mol of $HN_2O_3^-$ decomposed. Of the equal quantity of NO_2^- produced, 1.9 × 10^{-4} mol has been reduced by Fe(II), leaving 6.3 × 10^{-4} mol in solution. A total of 16.4 × 10^{-4} mol of N atoms is accounted for, out of 20.0 × 10^{-4} mol initially added as $HN_2O_3^-$. The remaining 3.6 × 10^{-4} mol is approximately twice the number of moles of Fe(III) present, suggesting that undecomposed $HN_2O_3^-$ is stabilized and held in the Fe(III) coordination sphere. A similar relation between moles of N remaining in solution and moles of Fe present can also be seen in the more complicated case of the two pH 5 experiments. The persistence of an orange color at "infinite" time also suggests the continuing presence of ligands other than H_2O in the coordination sphere of Fe(III), and we conclude that it is most probably due to the species $Fe(HN_2O_3)(H_2O)_4^{2+}$.

Two experiments were carried out in phosphate buffer at pH 8.0 and $I = 0.60$ M; in contrast to our experience with the reaction of Fe(II) with NO at this pH, the system remained homogeneous during most of the course of reaction. Hydrous oxide precipitate did not appear until after about 24 h. Traces of N_2 were detected, and the quantity of NO produced was extremely small and nearly constant with time. Both runs gave linear first-order plots over 2 half-lives, with an initial rate constant (6.05 × 10^{-4} s^{-1}) corresponding closely to the value for "free" $HN_2O_3^-$. After the initial period of linearity, however, the reaction exhibited gradual deceleration. It is not clear why these results are so different from those observed at pH 5 and 6.

Decomposition of Fe(II)-Coordinated $HN_2O_3^-$ with ^{15}N Label. From the results reported above we conclude that $HN_2O_3^-$ decomposition yields the same products, N_2O and NO_2^-, with and without coordination to Fe(II). When $HN_2O_3^-$ with a ^{15}N label at N(1) undergoes decay as a "free" anion,

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Table VI. Mass Spectra of N_2O Produced by Fe(II) Reduction of $^{15}N^{18}O$ in the Presence of $HN_2O_3^-$ [a]

(a) Percent Values for $(n_{NO})_0 = 2(n_{Fe(II)})_0$

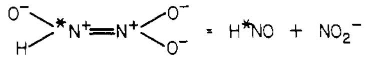
	t, min					*t*, min			
m/e	6	12	20	40	*m/e*	6	12	20	40
48	48.2	47.6	49.5	45.3	33	44.3	53.8	54.3	53.8
47	17.6	19.8	20.2	21.9	32		5.6	4.6	5.6
46	2.5	1.8	2.2	5.0	31	1.6	3.6	1.9	4.0
45	15.8	17.5	17.0	17.7	30	38.2	37.0	39.2	36.7
44	15.9	13.3	11.0	10.1					

(b) Percent Values for $(n_{NO})_0 = (n_{Fe(II)})_0$

	t, min							*t*, min					
m/e	6	12	20	30	50	90	*m/e*	6	12	20	30	50	90
48	29.7	34.7	38.3	39.1	37.4	29.1	45	13.2	13.2	13.8	14.9	16.8	19.9
47	14.5	15.2	16.5	17.6	19.5	20.4	44	38.7	34.5	29.1	25.6	23.0	27.1
46	4.0	2.4	2.3	2.8	3.2	3.5							

[a] $^{15}N^{18}O$ = 95.1% ^{15}N, 94.5% ^{18}O; $HN_2O_3^-$ is at natural abundance. Conditions: acetate buffer; pH 6.0; I = 3.0 M; $[Na_2N_2O_3]_0$ = 0.050 M; $[Fe(II)]_0$ = 0.020 M; volume of solution = 20.0 mL. Masses 44–48 are reported as a percent of total N_2O^+ (parent); masses 30–33 are reported as a percent of total NO^+ (electron-impact product).

the ^{15}N label is found entirely and randomly distributed in the N_2O product:[17]


(3)

$$H^*NO + H^*NO = {}^*N^*NO + H_2O \qquad (4)$$

Results of a tracer experiment designed to examine this point in the presence of Fe(II) at pH 6.0 are reported in Table V. As seen in the table, the first N_2O withdrawn in this experiment contains ^{15}N at 100% isotopic dilution, with an isotopic composition closely resembling a random distribution of N atoms drawn from both sides of the $HN_2O_3^-$ ion. The presence of $^{15}N^{15}NO$ (*m/e* 46) shows that the N_2O precursor is monomeric (HNO or NO^-), and the correspondence of the ^{15}N content of parent N_2O (*m/e* 44–46) with that of electron-impact NO^+ (*m/e* 30–31) indicates that $^{14}N^{15}NO$ and $^{15}N^{14}NO$ are present in equal proportions. The increases observed with time (30 and 60 min) at *m/e* 45 and 46, and hence in total ^{15}N content, indicate that unscrambled $HN_2O_3^-$ remains in solution and that it decomposes via the "normal" route (eq 3 and 4) during later stages of the reaction.

N atom scrambling in $HN_2O_3^-$ is known to occur in the presence of acetate, but only to a small extent at pH 6.[17b] While a rapid N to N tautomerism within the Fe(II) coordination sphere could account for the scrambling observed here, such a mechanism should affect all of the $HN_2O_3^-$ ions present and result in an N_2O product whose isotopic composition is constant with time. The scrambling and N_2O-producing processes may therefore be identical or rapidly sequential. We note that very little NO has appeared in the gas phase at t = 15 min (Table V). A possible explanation of the apparent scrambling of N atoms, shown in eq 5–8, is that a

$$Fe(H^*NONO_2)^+ \rightarrow H^*NO + NO_2^- + Fe^{II} \qquad (5)$$

$$NO_2^- + Fe^{II} + H^+ \rightarrow Fe^{III} + NO + {}^1/_2H_2O \qquad (6)$$

$$NO + Fe^{II} + H^+ \rightarrow Fe^{III} + HNO \qquad (7)$$

$$HNO + H^*NO \rightarrow \{{}^*N^*NO + {}^*NNO + N^*NO + NNO\} \qquad (8)$$

two-step reduction of NO_2^- to HNO follows N–N bond rupture rapidly enough, during early stages of the reaction, to account for the observed isotopic dilution. In this interpretation, the coincidental appearance of NO as product and increase in ^{15}N content of N_2O (30 and 60 min, Table V) simply reflect depletion in the Fe(II) concentration. There is no evidence bearing on the question whether assumed processes 5–8 involve HNO and NO_2^- as ligands or as "free" species.

Reaction of $^{15}N^{18}O$ with Fe(II) in the Presence of $HN_2O_3^-$. The results of the tracer experiment described above suggest but do not prove that HNO is produced in a two-stage reduction of NO_2^- by Fe(II) and that it is in turn capable of dimerizing with HNO from another source to produce N_2O. The results of two experiments designed to examine this point are shown in Table VI; $^{15}N^{18}O$ was caused to react with Fe(II) in the presence of isotopically normal $HN_2O_3^-$, and N_2O product was withdrawn at intervals for mass spectrometry. Conditions were chosen to provide approximate equality of rates and incomplete coordination by trioxodinitrate in order to have Fe(II) sites available for NO. Visual observations were similar to those in the absence of NO, i.e., a shift of solution color and intensity from pale yellow, through orange, to deep red, over ca. 3 min.

The major constituents of N_2O in these experiments are observed at masses 48, 47, 45, and 44. The N_2O of mass 48, $^{15}N^{15}N^{18}O$, must derive nearly entirely from $^{15}N^{18}O$ and mass 44 ($^{14}N^{14}N^{16}O$) from atoms initially present in $HN_2O_3^-$. Masses 47 and 45 could be mixtures of $^{14}N^{15}N^{18}O$ plus $^{15}N^{14}N^{18}O$ and $^{14}N^{15}N^{16}O$ plus $^{15}N^{14}N^{16}O$, respectively, but the small proportions of electron-impact NO^+ observed at masses 32 ($^{14}N^{18}O$) and 31 ($^{15}N^{16}O$) indicate that these masses consist overwhelmingly of $^{14}N^{15}N^{18}O$ and $^{15}N^{14}N^{16}O$. Since the $^{15}N^{18}O$ reactant gas contains significant ^{14}N and ^{16}O, some contribution to all other possible N_2O species is anticipated and found, e.g., in the small concentrations of $^{15}N^{15}N^{16}O$ and $^{14}N^{14}N^{18}O$ at mass 46.

It is clear in the results of Table VI that both the Fe(II)–NO redox reaction and the $HN_2O_3^-$ decomposition yield HNO as an intermediate in this multiple-reaction setting, that HNO from each source undergoes self-dimerization, and that HNO molecules from the two sources also comingle to form N_2O containing atoms from both (eq 9–11). Calculations show

$$H^{15}N^{18}O + H^{15}N^{18}O \rightarrow {}^{15}N^{15}N^{18}O\ (m/e\ 48) + H_2{}^{18}O \qquad (9)$$

$$H^{14}N^{16}O + H^{14}N^{16}O \rightarrow {}^{14}N^{14}N^{16}O\ (m/e\ 44) + H_2{}^{16}O \qquad (10)$$

$$H^{15}N^{18}O + H^{14}N^{16}O \left[\begin{array}{l} \rightarrow {}^{14}N^{15}N^{18}O\ (m/e\ 47) + H_2{}^{16}O \\ \rightarrow {}^{15}N^{14}N^{16}O\ (m/e\ 45) + H_2{}^{18}O \end{array}\right. \qquad (11)$$

that relative proportions of N_2O at masses 47 and 45 are about

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right for production of the two species in eq 11 at equal probability, i.e., from a symmetric intermediate or transition state. The fact that mass 48 product is more prominent when initial Fe(II):NO is 1:2 rather than 1:1 reflects the expected greater rate of $H^{15}N^{18}O$ production. The shifting proportions of the three kinds with time is caused by changing relative production rates of the two kinds of HNO. If the intermediate produced by Fe(II) reduction of NO is identical with the species produced in pulse radiolysis, as we believe to be the case for the product of $HN_2O_3^-$ decomposition, it would occur predominantly as NO^- under the conditions of these experiments, since its pK_a is reported to be 4.7.[35]

Registry No. Fe, 7439-89-6; NO_2^-, 14797-65-0; NO, 10102-43-9; $Na_2N_2O_3$, 13826-64-7; N_2O, 10024-97-2; $HN_2O_3^-$, 67180-31-8; HNO, 14332-28-6.

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Aqueous Nitrosyliron(II) Chemistry. 2. Kinetics and Mechanism of Nitric Oxide Reduction. The Dinitrosyl Complex[1,2]

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The formation constant for $Fe(NO)^{2+}$ is independent of pH in aqueous sulfate (pH 0.5–3.3) and has the value of 0.634 ± 0.023 atm^{-1} at 25.0 °C (I = 2.20 M). At pH 4.6 in the presence of 2.0 M acetate, the constant is 29.0 ± 1.5 atm^{-1} and increases to 70 atm^{-1} at $[OAc^-]$ = 3 M. Acetate ligation is involved in this enhancement, probably one ion per Fe(II) center. With decreasing Fe(II)/NO ratio and above pH 4 the presence of dinitrosyl complex is detected stoichiometrically, with a constant of formation (from $Fe(NO)^{2+}$ + NO) of 0.98 ± 0.15 atm^{-1} (pH 4.6, $[OAc^-]$ = 2.0 M, I = 2.20 M). From kinetic data the value of this constant at pH 6.0 in acetate buffer at I = 3.0 M is inferred to be 15 atm^{-1}, and the probable presence of one OH^- in the Fe(II) coordination sphere is indicated. The reduction of NO by Fe(II) in concentrated acetate buffer at pH 6 is shown to conform to the rate law $-d[Fe(II)]/dt = k_1[Fe(NO)_2^{2+}] + k_2[Fe(NO)_2^{2+}]^2$, where $k_1 = (1.6 \pm 0.4) \times 10^{-4}$ s^{-1} and $k_2 = 0.047 \pm 0.002$ M^{-1} s^{-1} at 25.0 °C. A dinitrosyl Fe(II) species bearing both formal NO^+ and formal NO^- in a cis relation, and in rapid exchange equilibrium, is postulated, and a possible mechanism for the major (second-order) pathway is discussed.

We have reported that the threshold for reduction of NO by Fe(II) to N_2O occurs at about pH 4, that HNO (or NO^-) is the primary product of this process, and that further reduction to N_2 does not occur below ca. pH 8.[2] The apparent inhibition of electron transfer by H^+ in this case is unusual and reflects remarkable stability on the part of the well-known "brown ring" complex, $Fe(H_2O)_5NO^{2+}$. The complexation equilibrium

$$Fe^{2+} + NO \rightleftharpoons Fe(NO)^{2+} \qquad (1)$$

and the redox reaction

$$Fe^{II} + NO + H^+ = Fe^{III} + {}^1/_2N_2O + {}^1/_2H_2O \qquad (2)$$

are closely related and broadly relevant to both inorganic and biochemical processes. Nitrosyliron chemistry is important in providing ESR probes, and in other ways, in the study of hemoglobin, cytochrome *c*, and other heme and nonheme proteins.[3,4] Iron is present at the active sites of both nitrite and nitrate reductases;[5,6] it is probable that nitrosyliron chemistry plays a role in microbial denitrification and possibly in nitrification processes as well. Nitrosyliron compounds have been postulated as intermediates in the transformation of inorganic nitrogen in soils.[7]

There are three principal literature reports concerning equilibrium 1. Manchot and Haunschild[8] measured the equilibrium constant by measurement of initial and final pressures of NO brought in contact with a large volume of solution of ferrous ammonium sulfate and reported values of 4.07, 1.58, and 0.661 atm^{-1}, at 0, 18, and 25 °C, respectively, for

$$K_1 = [FeNO^{2+}]/[Fe^{2+}]P_{NO} \qquad (3)$$

Abel et al.,[9] using a similar method with $FeSO_4$, reported a value of 0.637 atm^{-1} at 25 °C. Kustin, Taub, and Weinstock[10] reported forward and reverse rate constants for eq 1 to be $k_1 = 6.2 \times 10^5$ M^{-1} s^{-1} and $k_{-1} = 1.4 \times 10^3$ s^{-1} (25 °C); in combination with their own value for NO solubility these data yield $K = 0.63$ atm^{-1}.

Griffith, Lewis, and Wilkinson[11] characterized the complex $Fe(H_2O)_5NO^{2+}$ as high spin, with magnetic susceptibility showing three unpaired electrons, and described the bonding as NO^+ coordinated to Fe(I). This description was based in part on observation of an NO stretching frequency of 1765 cm^{-1}, near the upper edge of the region 1600–1750 cm^{-1} that

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