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Reaction between Trioxodinitrate and the Pentacyanonitrosylferrate(II) Anion (Nitroprusside)

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Trioxodinitrate ($^-ON^1{=}N^2O_2^-$) and the pentacyanonitrosylferrate(II) anion $[Fe(CN)_5(NO)]^{2-}$ (nitroprusside) react in the pH range 5–11 in the following stages: (1) "immediate" production of free NO_2^- and a complex corresponding to $[Fe(CN)_5(NO^+{-}NO^-)]^{3-}$ by attack at the N═N bond; (2) conversion of the complex, with release of NO, to a 410-nm intermediate identified as $[Fe^{II}(CN)_5(NO)]^{3-}$; (3) slower decomposition of the intermediate, principally to $[Fe(CN)_5(H_2O)]^{3-}$, with continuing release of N_2O. Tracer studies show that the product NO forms primarily but not entirely from the NO^+ group. The N_2O that forms during the second and third stages derives from a combination of NO^- from the N-1 position of $N_2O_3^{2-}$ and NO^+ nitrogen from nitroprusside. Secondary pathways are postulated to account for the appearance of $^{44}(N_2O)$, $^{45}(N_2O)$, and $^{46}(N_2O)$ in reactions with $N_2O_3^{2-}$ containing ^{15}N in the N-1 position. Minor quantities of N_2 product contain no N-1 nitrogen and most likely result from nitroprusside self-decomposition. Rapid nitrosative cleavage of the N═N bond in trioxodinitrate upon interaction with the Fe—NO^+ group, analogous to the known HNO_2 catalysis of $H_2N_2O_3$ decomposition to form NO, also occurs in the reaction between $[Ru(NH_3)_5(NO)]^{3+}$ and $N_2O_3^{2-}$. While both cases involve intermediates containing coordinated nitric oxide, nitrosation by the Fe(II) complex yields free NO_2^- and bound NO^-, whereas the Ru(II) complex yields reduced NO^- (as free NO) and bound NO_2^-. Also, while coordinated NO in the Fe(II) intermediate derives from the NO^- side of $N_2O_3^{2-}$, that in the Ru(II) case comes from the original coordinated NO^+ group.

We have recently reported that the reaction between trioxodinitrate and the nitrosylpentaammineruthenium(II) cation[2] takes place over the pH range 6–14, with a maximum rate at about pH 10. The gas product NO appears in a rapid initial phase of the reaction, its nitrogen atom deriving predominantly from the N-1 position of trioxodinitrate ($^-ON^1{=}N^2O_2^-$), and N_2O is produced by a subsequent, slower reaction of the resulting ruthenium complex. The nitrogen of N_2O also derives in part from the N-1 position but includes contributions from the NO^+ group of the ruthenium complex and the N-2 atom of trioxodinitrate. We now report on the reaction of trioxodinitrate with the pentacyanonitrosylferrate(II) anion (nitroprusside), in further extension of our inquiry into the nature of trioxodinitrate nitrosation by coordinated NO^+ under relatively high pH conditions.

The nitroprusside anion is present as an equilibrium mixture of nitrosyl and nitro forms at high pH,[3] with $K = 1.5 \times 10^6$ M^{-2} at 25 °C. The fraction present in the nitrosyl form is effectively unity at pH values up to 10 but falls to 0.4 at pH 11 and 0.01 at pH 12. Both nitrosyl and nitro forms have an absorption maximum at 398 nm, with molar absorption coefficients of 19 and 832 M^{-1} cm^{-1}, respectively. In alkaline solutions, aquation of the nitro ligand takes place.[3]

The nitroprusside anion is well-known to react with a number of bases, reaction often proceeding via intermediate species in which the bases are bound to the nitrogen atom of the nitrosyl group. Examples of such reactions are those involving azide, hydroxylamine,[4] amines,[5-7] amino acids,[8] and sulfur compounds such as thiols[9] and sulfite.[10]

Experimental Section

Sodium trioxodinitrate was prepared from propyl nitrate and hydroxylamine.[11] The extinction coefficient of the product in 0.1 M alkali was 8300 M^{-1} cm^{-1} at 248 nm, identical with the literature value.[11] All other reagents were the best grade available. Nitroprusside solutions were stored in the dark and freshly prepared every few days. Buffers were made up to literature specifications.[12] Nitrite was measured by a colorimetric method involving the diazotization of sulfanilic acid and coupling with β-naphthol.[13] The azo dye has a maximum absorption at 480 nm with a molar absorption coefficient of 23 500 M^{-1} cm^{-1}.

Table I. Dependence of Maximum Absorbance at 410 nm on pH and Trioxodinitrate Concentration[a]

$[N_2O_3^{2-}]_0/M$	pH	A_{410}[b]	$[N_2O_3^{2-}]_0/M$	pH	A_{410}[b]
0.010	5.8	0.492	0.010	8.8	0.150
0.010	6.4	0.471	0.0050	7.1	0.199
0.010	6.8	0.361	0.010	7.1	0.316
0.010	7.1	0.316	0.020	7.1	0.408
0.010	7.5	0.232			

[a] Conditions: $[Fe(CN)_5NO^{2-}]_0 = 0.010$ M; $t = 25.0$ °C. [b] $A_{max} - A_0$. In most cases, reported values are the mean of several determinations.

UV–visible spectroscopy was carried out utilizing Perkin-Elmer Lambda 3 and Pye Unicam 6-550 instruments. Kinetic runs were initiated by the addition of measured amounts of solid trioxodinitrate to thermostated solutions containing all other components and followed directly in 1-cm quartz cells either at fixed wavelength (410 nm) or by scanning at appropriate time intervals. Sodium chloride was used to control ionic strength. Gas mixtures were analyzed with a vacuum line-interfaced GC system using CF_4 as internal reference to determine molar quantities[14] and mechanical vibration of the reaction vessel in time-dependence studies.[15] Trioxodinitrate containing 99% nitrogen-15 at the N-1 position was employed in tracer experiments, and mass spectrometry was carried out on an AEI MS-30 instrument (Stony Brook Mass Spectrometry Facility).

Results

The reaction has been studied over the pH range 5–11, mainly in the concentration range 10^{-3}–10^{-2} M. Evolution of gas products begins immediately upon initiation of the reaction, accompanied by the formation and subsequent slower decay of a yellow color in solution. This intermediate species has intense absorptions in the UV–visible region, exhibiting maxima at 350 and 410 nm. At pH 7 and 25 °C, the intermediate was formed to the maximum extent after about 20-min reaction time, and its decay took place

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Table II. Distribution of Gas Products[a]

pH	mole ratio[b]	% N_2O	% NO	% N_2
4.7	2.58	48.3	50.6	1.1
4.7	0.82	58.5	40.3	1.3
4.7	0.35	64.0	33.8	2.2
7.1	3.00	76.3	22.6	1.1
7.1	1.10	83.3	15.4	1.3
7.1	0.30	89.1	7.8	3.2
9.7	3.00	76.3	18.5	5.2
9.7	1.25	72.8	23.2	4.1
9.7	0.97	68.2	28.4	3.5
9.7	0.47	78.4	20.2	1.5
10.9	3.10	32.3	63.6	4.1
10.9	0.85	31.5	62.6	5.6
10.9	0.39	68.0	27.2	4.8

[a] Conditions: $n_0(Na_2N_2O_3) = 2.05 \times 10^{-5}$ mol; reaction time ~20 h; reaction volume = 10.0 mL; t = 25.0 °C. [b] $[Fe(CN)_5NO^{2-}]_0:[N_2O_3^{2-}]_0$.

Table III. Time Dependence of Gas Product Formation[a]

(a) Mole Ratio = 3.00:1[b]

t/min	10	20	30	50	70	100	130
$10^5n(N_2O)$	0.74	1.51	2.34	3.15	3.25	4.18	4.35
$10^5n(NO)$	1.00	1.51	2.00	2.38	2.52	2.91	2.80
$10^5n(N_2)$	0.08	0.07	0.06	0.08	0.05	0.08	0.18

(b) Mole Ratio = 0.82:1

t/min	5	10	20	30	60	90	120	600
$10^5n(N_2O)$		1.60	2.21	3.45	3.45	3.87	3.76	3.90
$10^5n(NO)$	0.39	0.68	1.01	1.23	1.68	1.78	1.69	1.78
$10^5n(N_2)$	0.15	0.12	0.12	0.2	0.22	0.16	0.15	0.35

(c) Mole Ratio = 1:3.0

t/min	10	20	30	50	70	110	140	450
$10^5n(N_2O)$		1.05	1.53	2.24	2.67	3.17	3.33	3.36
$10^5n(NO)$	0.61	0.83	0.98	1.22	1.33	1.45	1.47	1.52
$10^5n(N_2)$	0.24	0.20	0.18	0.23	0.19	0.29	0.28	0.34

[a] Conditions: $n_0(N_2O_3^{2-}) = 8.20 \times 10^{-5}$ mol; reaction volume = 10.0 mL; pH = 7.1; t = 25.0 °C. [b] $n_0(Fe(CN)_5NO^{2-}):n_0(N_2O_3^{2-})$.

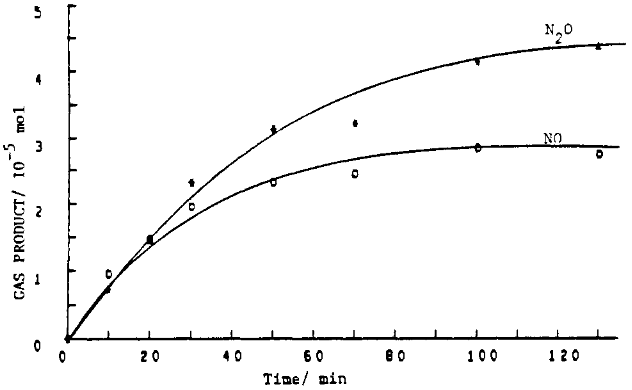


Figure 1. Time course of product gas evolution at pH 7.2 and 25.0 °C, with $[Fe(CN)_5NO^{2-}]_0:[N_2O_3^{2-}]_0 = 3.0:1$.

Table IV. Isotopic Composition of N_2O and NO Products of the Nitroprusside Reaction with Trioxodinitrate Containing 99% ^{15}N in the N-1 Position[a]

mole ratio[b]	3.01	3.01	1.00	0.334
N_2O, *m/e* 46	0.0214	0.0205	0.0500	0.151
N_2O, *m/e* 45	0.196	0.172	0.229	0.239
N_2O, *m/e* 44	0.283	0.308	0.222	0.111
N_2O, *m/e* 31	0.130	0.136	0.167	0.248
N_2O, *m/e* 30	0.370	0.365	0.333	0.252
% ^{15}N, N_2O (44–46)	23.9	21.3	32.9	54.1
% ^{15}N, N_2O (30–31)	26.0	27.1	33.4	49.6
% ^{15}N, NO (30–31)	6.3	8.6	23.2	40.9

[a] Conditions: $n_0(N_2O_3^{2-}) = 1.64 \times 10^{-5}$ mol; reaction volume = 10.0 mL; pH = 7.1; t = 25.0 °C. [b] $n_0(Fe(CN)_5NO^{2-}):n_0(N_2O_3^{2-})$.

over a period of a few hours. At pH 9, the comparable times are about 4 h and several days. The extent of formation of the intermediate decreases with increasing pH (Table I). Attempts to isolate the intermediate did not succeed.

Gas Products. These were found to be N_2O and NO, with a small amount of N_2. Table II shows results obtained over the pH range 4.7–10.9 and at three stoichiometric reactant ratios. It may be seen that in the presence of excess nitroprusside the products N_2O and NO are produced in nearly equimolar amounts at the lowest pH (4.7), that N_2O dominates in >3:1 ratio in the middle pH range (7.1–9.7), and that NO becomes predominant at the highest pH (10.9). Excess trioxodinitrate results in increased production of N_2O, because of self-decomposition. Results closely similar to those shown were obtained after 3 h under all conditions except at pH 10.9, where a major increase in the proportion of NO was observed between 3 and 20 h with trioxodinitrate in excess.

The results of experiments on the time course of gas evolution are shown in Table III and for the case of 3:1 excess nitroprusside in Figure 1. It is seen that release of NO occurs largely in the time period associated with formation of the 410-nm intermediate. Production of N_2O also occurs during this phase of the reaction but continues during the period of decay of the intermediate.

The "infinite time" results of Table III have been used to calculate nitrogen mass balances. Assuming that $[Fe(CN)_5(NO)]^{2-}$ and $N_2O_3^{2-}$ react in 1:1 ratio yielding 1 mol of free nitrite in solution per unit of reaction (vide infra), that all trioxodinitrate either reacts with nitroprusside or is destroyed by its normal self-decomposition reaction, and that all nitroprusside in excess of trioxodinitrate remains unreacted, mass balances of 89.0, 79.7, and 89.5% are obtained for cases a, b, and c, respectively.

Table IV gives details of the gas products obtained by using trioxodinitrate ^{15}N-labeled at position N-1. The separated N_2O fraction exhibited product of mass numbers 44, 45, and 46; the relative abundance of fragments at masses 31 and 30 show that the $^{45}(N_2O)$ consists of the isotopomers $^{14}N^{15}NO$ and $^{15}N^{14}NO$ in approximately equal proportions. The doubly labeled species $^{46}(N_2O)$ must be produced by dimerization of NO^- released by trioxodinitrate self-decomposition, consistent with the observation that its abundance was only a few percent in experiments carried out with excess nitroprusside but increased with increasing trioxodinitrate concentration. The species $^{45}(N_2O)$ is a major product and must be formed by combination of nitrogen from the nitroprusside nitrosyl group and the N-1 atom of trioxodinitrate. Its abundance increases with trioxodinitrate concentration, consistent with the expected increase in $^{15}NO^-$ production from self-decomposition. The species $^{44}N_2O$ is produced by dimerization of an NO^- species derived from the NO^+ group, and although it is the major product under excess nitroprusside reaction conditions, its importance declines as increased trioxodinitrate concentration results in increased $^{15}NO^-$ production.

At initial concentration ratio $[Fe(CN)_5NO^{2-}]_0:[N_2O_3^{2-}]_0 = 3:1$, the NO product is derived largely but not entirely from the nitroprusside NO^+ group, but as trioxodinitrate is increased, it forms to an increasing extent from the N-1 atom of trioxodinitrate. The minor quantity of dinitrogen gas product was found to contain essentially natural-abundance nitrogen and is probably derived entirely from nitroprusside self-decomposition.

The isotopic data suggest that the nitrosyl group of nitroprusside is reduced to NO and NO^-, as represented in eq 1–5, in which the ^{14}NO product (eq 1) is not necessarily taken to be an intermediate in the formation of $^{14}NO^-$.

$$Fe^{14}NO^+ \rightarrow Fe^{14}NO \rightarrow Fe^{14}NO^- \tag{1a}$$

$$Fe^{14}NO \rightarrow {}^{14}NO;\ Fe^{14}NO^- \rightarrow {}^{14}NO^- \tag{1b}$$

$$HO^{15}NNO_2^- \rightleftarrows H^{15}NO + NO_2^- \tag{2}$$

$$^{14}NO^- + {}^{14}NO^- \xrightarrow{H^+} {}^{44}N_2O + OH^- \tag{3}$$

$$^{14}NO^- + {}^{15}NO^- \xrightarrow{H^+} {}^{45}N_2O + OH^- \tag{4}$$

$$^{15}NO^- + {}^{15}NO^- \xrightarrow{H^+} {}^{46}N_2O + OH^- \tag{5}$$

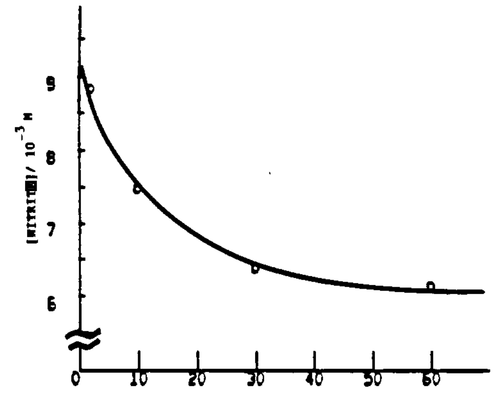


Figure 2. *Apparent* [nitrite] vs time, as determined by the azo-dye method, with $[N_2O_3^{2-}]_0 = 5 \times 10^{-3}$ M, in excess $[Fe(CN)_5NO]^{2-}$.

Analysis for Nitrite by UV and Colorimetric Methods. Analysis of the final reaction solution at several pH values by the colorimetric method shows that nitrate is formed from trioxodinitrate on a 1:1 basis (eq 6). Measured values of the ratio $\Delta[NO_2^-]$:

$$[Fe(CN)_5(NO)]^{2-} + HN_2O_3^- \rightarrow NO_2^- + \text{products} \quad (6)$$

$\Delta[N_2O_3^{2-}]$ lie between 1.10 and 1.20 over the pH range 6–8; the additional 10–20% can be ascribed to NO_2^- production due to trioxodinitrate self-decomposition.

UV spectrophotometry was used to monitor nitrite directly during the course of the reaction, with the initial objective of determining whether its formation occurs during the periods of formation and/or decay of the 410-nm intermediate. Because of the intense nitroprusside band at 204 nm, the UV spectra of reaction samples did not directly reveal an absorption maximum due to nitrite at 215 nm ($\epsilon = 5600$ M^{-1} cm^{-1}), but a comparison of the ratio of absorbances at 204 and 215 nm in fully reacted solutions with the value for nitroprusside alone confirmed that nitrite had been produced in 1:1 ratio. The accuracy of the method was checked for several standard solutions containing nitroprusside and nitrite in varying proportions. The time dependence of nitrite production was then studied by this method at pH 6.5, 7.0, 7.5, and 8.0. In all cases, it was found to be complete before withdrawal of the first sample (<4 min). Nitrite formation from the nitroprusside–trioxodinitrate reaction therefore occurs entirely in a rapid, early stage of the reaction that is not directly tied either to gas production or to growth and decay of the 410-nm intermediate.

The production of nitrite was also followed during the course of reaction by using the sulfanilic acid–β-naphthol colorimetric method. Individually, neither trioxodinitrate nor nitroprusside gives a positive response to this test. As shown in Figure 2, however, the azo dye formed in samples taken immediately after reaction initiation corresponded to a nitrite content twice the initial molar concentration of $N_2O_3^{2-}$, i.e. to an *apparent* nitrite concentration twice the expected final value. In subsequent samples the apparent nitrite concentration fell and leveled off at the stoichiometric value 1:1, within the time period corresponding to formation of the 410-nm intermediate. Thus, the colorimetric method analyzes both for free nitrite, as detected directly by UV spectroscopy, and for a second nitrosating group that decays during formation of the yellow intermediate. We identify this as the nitroprusside NO^+ group, with its reactivity enhanced in the product formed by interaction with the residual NO^- fragment of trioxodinitrate (eq 7 and 8). The measured rate constants for loss of the additional nitrosating group and for formation of the 410-nm intermediate are similar (1.4×10^{-3} and 1.7×10^{-3} s^{-1}, respectively, at pH 7.1 and 35.0 °C).

$$[Fe(CN)_5(NO)]^{2-} + N_2O_3^{2-} \rightarrow NO_2^- + [Fe(CN)_5(NO^+\text{–}NO^-)]^{3-} \quad (7)$$

$$[Fe(CN)_5(NO^+\text{–}NO^-)]^{3-} \rightarrow \text{410-nm species} + \text{gas products} \quad (8)$$

Table V. Rate Constants for Formation of the 410-nm Intermediate[a]

pH	$[N_2O_3^{2-}]$/M	10^3k_1/s^{-1}	pH	$[N_2O_3^{2-}]$/M	10^3k_1/s^{-1}
5.8	0.010	2.06	7.1	0.0050	2.74
6.0	0.010	2.18	7.1	0.010	2.70
6.8	0.010	2.01	7.1	0.020	2.84
7.5	0.010	2.30			

[a] Conditions: $I = 0.20$ M; $t = 25.0$ °C; $[Fe(CN)_5NO^{2-}]_0 = 0.0010$ M.

Stoichiometry of the 410-nm Intermediate. The extent of formation of the 410-nm intermediate increases with stoichiometric trioxodinitrate excess (Table I). Values of A_{410} at pH 7.1 were determined for a number of solutions in which the total molarity was constant (0.010 M) but relative reactant concentrations were varied, with allowance for contribution to the absorbance from excess nitroprusside in appropriate cases. The maximum value of A_{410} was found at 1:1 ratio of the reactants, showing that the intermediate is formed from 1 mol of each.

Kinetics of Formation of the Intermediate. The reaction was followed directly in the thermostated cell compartment of the spectrophotometer by monitoring at 410 nm, with trioxodinitrate typically in 10-fold excess. When the pH was around 6 or when trioxodinitrate was present in only 5-fold excess, there appeared to be an induction period, which was absent at pH 7 or under 10-fold-excess conditions. Since the kinetics as measured pertain to a stage of reaction subsequent to the initial, rapid nitrite-producing step, the time lag indicates that the nitrite-producing stage may be relatively slow under certain conditions. Plots of log ($A_{max} - A_t$) against time, where A_{max} and A_t are maximum values and values at time t of the absorbance at 410 nm, are excellent straight lines, showing the reaction to be first order in the Fe(II) complex formed in the primary reaction. As shown in Table V, the rate constants appear to be essentially independent of trioxodinitriate concentration and independent of pH in the range 5.8–7.1. (As reported in the Experimental Section however, the reaction is substantially slower at pH 9.) Absence of an $[HN_2O_3^-]$ dependence for k_1 suggests a rate-determining rearrangement of an iron complex that has been rapidly and completely formed from the original reactants, as postulated.

Discussion

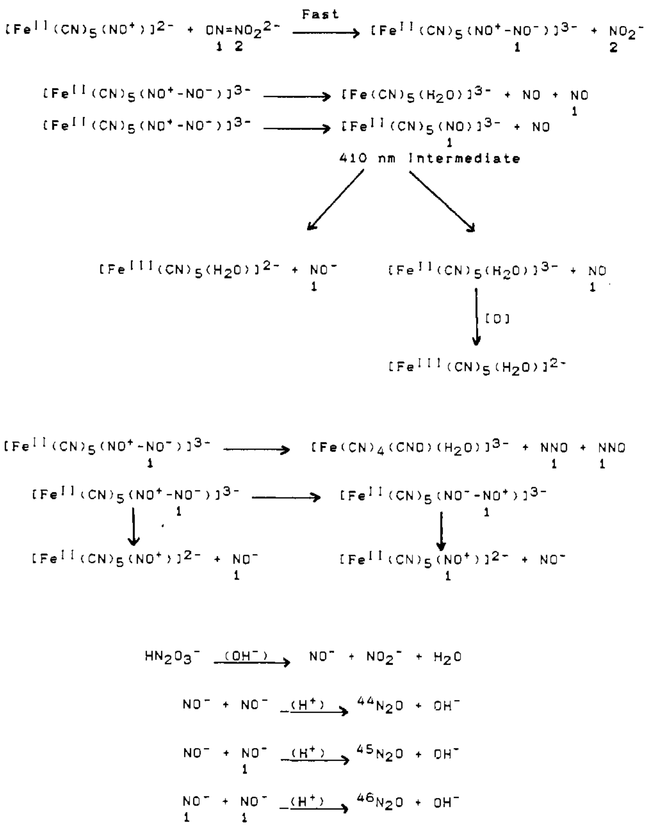
It is clear that the nitroprusside and trioxodinitrate anions react rapidly at 25 °C to give nitrite as one product. The reaction probably involves an attack of the nitroprusside NO^+ group on the N-1 nitrogen atom of trioxodinitrate, with consequent rapid cleavage of the N=N link and formation of free nitrite and a pentacyanoiron(II) complex that contains both the original NO^+ group and the NO^- fragment of trioxodinitrate. In accordance with the known mode of adduct formation in reactions of nitroprusside with a variety of bases in which interaction between NO^+ and the base occurs, this Fe(II) complex probably contains a group with a N–N bond. However, since the Fe(II) complex containing this "N_2O_2" ligand is able to react with sulfanilic acid in the analytical diazotization reaction, it must still be capable of acting as a source of NO^+. Parallels for this behavior are found in recent studies in the nitrosation of secondary amines by nitroprusside, in which a rate law with a square term in amine is found.[5-7] In these cases the adduct $[Fe^{II}\text{–}(NO^+)\text{–amine}]$ is reactive toward a second amine molecule.

In the second phase of the reaction, the original nitrosyl NO^+ group (present now in the "N_2O_2" ligand) becomes converted to NO, although the isotopic evidence does indicate that a fraction of the NO is derived from the N-1 trioxodinitrate fragment. The latter pathway could result from decomposition of the (N_2O_2) group to give two molecules of NO, one each derived from the nitrosyl NO^+ and trioxodinitrate NO^- groups (eq 9). However,

$$[Fe(CN)_5(N_2O_2)]^{3-} \rightarrow [Fe(CN)_5(H_2O)]^{3-} + 2NO \quad (9)$$

the predominance of production of NO from the NO^+ group suggests that the second nitrogen fragment tends to remain bound to the iron center to form the 410-nm intermediate. It will be

Scheme I



recalled that the rates of formation of NO and the 410-nm intermediate are similar. This reaction is represented in eq 10, in

$$[Fe(CN)_5(N_2O_2)]^{3-} \rightarrow [Fe(CN)_5NO)]^{3-} + NO \quad (10)$$

which the 410-nm intermediate is taken to be the species $[Fe(CN)_5(NO)]^{3-}$ (vide infra). The existence of parallel reactions (eq 9 and 10) can account for the decreased formation of the 410-nm intermediate observed at the higher pH values.

The intermediate is characterized both by its absorption maximum at 410 nm and its instability in aqueous solution; e.g., at pH 7 it decomposes completely over a period of several hours to yield an almost colorless solution. This species appears to be identical with the known yellow-brown anionic species $[Fe(CN)_5(NO)]^{3-}$, prepared by reduction of nitroprusside[17-19] and usually regarded as a d^6 complex $[Fe^{II}(CN)_5(NO)]^{3-}$, involving coordinated NO behaving as a 2-electron donor.

The final phase of the reaction involves the decay of the 410-nm intermediate. The species $[Fe(CN)_5(NO)]^{3-}$ is known to decompose to the aquopentacyanoferrate(II) species in the absence of O_2 and to the Fe(III) aquo complex in the presence of air.[20] In the present studies the absorption characteristic of $[Fe(CN)_5(H_2O)]^{3-}$ was not found in the spectrum of the final reaction solution, and it appears that the Fe(III) aquo complex may form directly in this reaction setting or that oxidation has occurred during the relatively long time interval preceding final characterization of these solutions (see Scheme I).

The mechanistic postulates advanced above, in general agreement with our reported experimental results, are summarized in Scheme I. The gas analysis data show that NO is produced in the second stage of reaction (during formation of the 410-nm intermediate) while N_2O formation continues through the third stage, so it may be that the 410-nm species decomposes directly to the aquoiron(III) complex and NO^-, which then dimerizes to give N_2O. The discussion presented so far allows only for the production of $^{46}(N_2O)$ in the presence of N-1-labeled trioxodinitrate reactant. This arises from self-decomposition of trioxodinitrate and possibly also from decomposition of the 410-nm intermediate in the manner noted above. The observed formation of $^{44}(N_2O)$ and $^{45}(N_2O)$ requires participation of the nitrosyl (NO^+) nitrogen. The species $[Fe(CN)_5(NO^+{-}NO^-)]^{3-}$ could decompose to give $^{45}(N_2O)$ (containing equal amounts of $O^{15}NN$ and $ON^{15}N$) with concomitant oxidation of one cyanide ligand to cyanate. Alternatively, direct release of NO^- from the bound "N_2O_2" ligand may occur to a limited extent, preceded by an internal exchange process that would account for the appearance of $^{14}NO^-$ in product N_2O. It should be stressed, however, that the identity of the original NO^+ group appears to be conserved to a substantial extent, probably because it is bound to the iron center.

There are striking parallels between the reaction of trioxodinitrate with nitroprusside and that between trioxodinitrate and the $[Ru(NH_3)_5(NO)]^{3+}$ cation.[2] In both cases, nitrosative attack of the NO^+ group on trioxodinitrate brings about rapid cleavage of the N=N bond. In this regard both reactions are consistent with the view that the catalytic cleavage of trioxodinitrate by nitrous acid, which yields two molecules of NO, is initiated by a nitrosation reaction.[16] Furthermore, both reactions appear to involve intermediates containing coordinated NO (rather than NO^+ or NO^-), but in the nitroprusside reaction the NO ligand is derived from the NO^- fragment of trioxodinitrate while in the ruthenium(II) reaction it is formed from the nitrosyl NO^+ group. A further interesting and fundamental difference is that different halves of the trioxodinitrate anion become associated with the metal center in these two cases: reaction with nitroprusside yields free nitrite and bound NO^-, while reaction with the Ru(II) complex yields free NO (from NO^-) and bound nitrite.

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Registry No. $^-ON^1{=}N^2O_2^-$, 15435-67-3; $[Fe(CN)_5(NO)]^{2-}$, 15078-28-1.

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