Electron Transfer. 139. Reductions with Trioxodinitrate, $[N_2O_3]^{2-}$

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Trioxodinitrate ($N_2O_3{}^{2-}$), prepared as its sodium salt (Angeli's salt, $Na_2N_2O_3$) by nitrosation of hydroxylamine using isopropyl nitrate and sodium ethoxide, reacts with a variety of inorganic oxidants. Observed stoichiometries for both le$^-$ and 2e$^-$ reagents at pH values above 4 generally point to conversion mainly to nitrite with both types. Kinetic acidity patterns, pertaining to media where the uninegative ion, $HN_2O_3{}^-$ ($pK_A = 9.3$) predominates, indicate that oxidations by both I_2 and $I_3{}^-$ proceed through the dinegative ion, $N_2O_3{}^{2-}$, but that oxidations by I(V) involve HIO_3 and the monoprotonated reductant. Oxidations with both Cl(I) and I(VII) proceed by multiple paths involving several protonation levels, with the acidity profile for the latter (Figure 1) being unusually complex. It is proposed that oxidations by HOCl proceed by Cl^+ transfer, that iodate and periodate utilize oxygen transfer, and that the le$^-$ oxidants employ a pair of outer-sphere transactions of which the first is rate-determining. The most unusual aspect of each of these transformations appears to be the rapid cleavage of a $N_2O_4{}^{2-}$ intermediate having an N═N double bond. The ease of this splitting is attributed to the marked diminution of bonding action through electron withdrawal by four strongly electronegative oxygen atoms.

Introduction

Although trioxodinitrate was first described as a component of Angeli's salt, $Na_2N_2O_3$, in 1896,[2] it remains the least familiar of the isolable oxynitrogen anions. This, or a related species, has been proposed as an intermediate in the reductions of nitrogen oxides on zeolite catalysts having transition metal centers,[3] as a source of nitroxyl (NOH) through decompositions at low pH,[4] and as a transient in the enzymatic reduction of nitrite to N_2O.[5] Dissociation constants for the parent acid have been documented,[6] the structure of the anion has been shown to feature a N═N double bond,[7] and ligations of Zn(II) and Co(II) species have been reported.[8] Although thermal decompositions of both the anion[9] and the parent acid[10] have been investigated, we find no accounts of the action of trioxodinitrate as a reductant. In the present study, we have examined redox transformations involving both 1e$^-$ and 2e$^-$ oxidants.

Experimental Section

Materials. Sodium chlorate (Baker and Adamson), sodium chlorite (Aldrich), sodium hypochlorite,[11] sodium periodate (Baker and Adamson), sodium iodate (Baker), sodium hexachloroiridate(IV) ($Na_2IrCl_6 \cdot 6H_2O$, Alfa), sodium hexabromoiridate(IV) (Na_2IrBr_6, Alfa), and sodium perchlorate ($NaClO_4 \cdot H_2O$, Aldrich, employed as the supporting electrolyte in kinetics experiments) were used as received. All solutions were prepared from Millipore water which had been boiled for 2 h and then purged with N_2 for 2 h more to remove dissolved O_2.

Table 1. Stoichiometries of the Reactions of Trioxodinitrate ($N_2O_3{}^{2-}$) with Inorganic Oxidants[a]

oxidant (Ox)	λ, nm	$\Delta[Ox]/\Delta[N_2O_3{}^2]$
$IrCl_6{}^{3-}$	489	1.91
$IrBr_6{}^{3-}$	585	1.95
I_2	458	0.99
$I_3{}^-$	365	0.94
$IO_4{}^-$	250	0.94[b]
$IO_3{}^-$	250	0.35
Br_2	392	3.0
OCl^-	250	0.95[c]

[a] Reactions were carried out at 22 °C in acetate buffers, pH 4.7; $\mu = 0.20$ M ($NaClO_4$), unless otherwise indicated (see Experimental Section). [b] Fast reaction preceding the much slower reduction of the $IO_3{}^-$ product. [c] pH = 8.2.

Sodium trioxydinitrate was prepared from hydroxylammonium chloride by using slight modifications of the methods of Brauer[12] and Hunt,[9] but substituting isopropyl nitrate (Aldrich) for ethyl nitrate as the nitrosating agent. This salt was recrystallized three times from 20/1 methanol−water and kept in a closed container at −18 °C; $\epsilon_{250}^{\max} = 8.2 \times 10^3\ M^{-1}\ cm^{-1}$ in 0.1 M NaOH (lit.,[9] 8.15×10^3). Material subjected to fewer recrystallizations exhibited erratic kinetic behavior in subsequent experiments.

Stoichiometric Studies. Stoichiometries of the redox conversions were most often determined, with trioxydinitrate in excess, by adding a measured deficiency of the oxidant, waiting 30 min for completion of the reaction, and then measuring the decrease in absorbance at 250 nm. These changes were then compared to those observed when trioxydinitrate was treated with excess oxidant. When the oxidant was strongly colored (e.g., $IrBr_6{}^{2-}$, $I_3{}^-$), the procedure was reversed. Results are summarized in Table 1.

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[2] (a) Angeli, A. *Gazz. Chim. Ital.* **1896**, *26*, 18. (b) The anion has been designated also as oxyhyponitrite, hyponitrate, and trioxodinitrate(II).

[3] Valyon, J.; Hall, W. K. *J. Catal.* **1993**, *143*, 520.

[4] (a) Hendrickson, D. N.; Jolly, W. L. *Inorg. Chem.* **1969**, *8*, 693. (b) Bazylinski, D. A.; Hollecher, T. C. *Inorg. Chem.* **1985**, *24*, 4285.

[5] (a) Hulse, C. L.; Averill, B. A.; Tiedje, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 2322. (b) For an opposing view, see: Goretski, J.; Hollecher, T. C. *J. Biol. Chem.* **1990**, *265*, 889.

[6] Sturrock, P. E.; Ray, J. D.; McDowell, J.; Hunt, H. R., Jr. *Inorg. Chem.* **1963**, *2*, 649.

[7] Hope, H.; Sequeira, M. R. *Inorg. Chem.* **1973**, *12*, 286.

[8] Chuy, C.; Falvello, L. R.; Libby, E.; Santa-Maria, J. C.; Tomas, M. *Inorg. Chem.* **1997**, *36*, 2004.

[9] Bonner, F. T.; Ravid, B. *Inorg. Chem.* **1975**, *14*, 558.

[10] Hunt, H. R.; Cox, J. R., Jr.; Ray, J. D. *Inorg. Chem.* **1962**, *1*, 938.

[11] The NaClO solution, analyzed by using a reported procedure (Furman, N. H. *Standard Methods of Chemical Analysis*, 6th ed.; Van Nostrand: Princeton, NJ, 1963; Vol. 1, part A, pp 264, 341) was found to be 1.2 M.

[12] Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press: New York, 1963; p 517.

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Kinetic Studies. Rates were evaluated from measurements of absorbance changes using a Shimadzu 1601 recording spectrophotometer or a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Most usually, decreases at 250 nm due to loss of trioxodinitrate were followed, but in some cases, the change in a colored coreagent was monitored. Temperatures were kept at 22.0 ± 0.5 °C. Ionic strength was maintained at 0.20 M by addition of $NaClO_4$. Acidities were regulated by measured quantities of buffering acids and NaOH. For kinetic runs, solutions of the oxidant and the buffering acid were added to solutions of $N_2O_3^{2-}$ in base, thus minimizing the loss of the reductant by acid-catalyzed self-decomposition[9] prior to mixing; pH values of the redox mixtures were checked at the conclusion of each reaction. Except as noted below, conversions were first order each in trioxodinitrate and oxidant but were customarily run under pseudo-first-order conditions with one reagent in greater than 10-fold excess. Rate constants were obtained by nonlinear least-squares fitting to the relationship describing exponential decay. Values from replicate runs generally agreed to better than 6%. Rates measured under anaerobic conditions did not differ systematically from those determined in contact with air.

Rate measurements of the very slow oxidations of trioxodinitrate by H_2O_2, BrO_3^-, and ClO_3^- (each at pH 4−5) could not be carried out due to the competing self-decomposition of the reductant in this medium. At the other extreme, oxidations by Br_2 were so rapid that only a lower rate limit (10^6 M^{-1} s^{-1} at pH 4) and no rate law could be obtained. Reactions with hypochlorite and chlorite gave irreproducible autocatalytic curves in acetate buffers, and the reactions were strongly catalyzed by added chloride. These complications were minimized for hypochlorite (but not for chlorite) by working in borate buffers. Oxidations by $IrCl_6^{2-}$ and $IrBr_6^{2-}$ exhibited second-order rate constants that were very nearly $[H^+]$ independent in the region pH 3−4, but rates appeared to increase at greater pH values while becoming more poorly reproducible. Moreover, the apparent kinetic acidity profiles were not consistent with the reported[6] pK_a values of $H_2N_2O_3$. Oxidations with $Fe(CN)_6^{3-}$ yielded mixed order decay curves which could not be interpreted in their entirety, but comparisons of initial rates indicated that this reaction was first order in both redox partners with a rate constant near 4 M^{-1} s^{-1} (22 °C, pH 4.7, $\mu = 0.20$ M).

Results and Discussion

The reported dissociation constants for the parent trioxo acid ($pK_1 = 2.51$; pK_2 9.70)[6] indicate that the uninegative ion $HN_2O_3^-$ is the principal dinitrogen species in the acetate buffers used in most of the experiments considered. Each trioxodinitrate is seen (Table 1) generally to consume very nearly two units of single-electron reagents (e.g., eq 1) but one unit of 2e⁻ oxidants

$$HN_2O_3^- + 2IrCl_6^{2-} + H_2O + 3\,OAc^- \rightarrow 2IrCl_6^{3-} + 2NO_2^- + 3HOAc \quad (1)$$

$$HN_2O_3^- + HOCl + 2HPO_4^{2-} \rightarrow Cl^- + 2NO_2^- + 2H_2PO_4^- \quad (2)$$

(e.g., HOCl in eq 2). The implication here is that nitrite is the predominant oxidation product with both types.

The approach to 1:3 stoichiometry for oxidation by iodate is consistent with net conversion to iodide (eq 3), whereas the 3:1 ratio observed with excess Br_2 points to further oxidation of NO_2^- to NO_3^- (eq 4).

$$IO_3^- + 3HN_2O_3^- + 3\,OAc^- \rightarrow I^- + 6NO_2^- + 3HOAc \quad (3)$$

$$3Br_2 + HN_2O_3^- + 3H_2O + 7\,OAc^- \rightarrow 6Br^- + 2NO_3^- + 7HOAc \quad (4)$$

Since the reaction of IO_4^- is very much more rapid than that of IO_3^- under similar conditions, the two processes are kinetically separable.

Table 2. Kinetic Data for the Reaction of Trioxodinitrate ($N_2O_3^{2-}$) with I_2 and OCl^- [a]

I_2 reactions		OCl^- reactions	
pH	$10^{-3}k$, M^{-1} s^{-1} [b]	pH	k, M^{-1} s^{-1} [b]
5.95	27 (29)	13.0	0.112 (0.119)
5.72	17.4 (18.4)	12.70	0.200 (0.160)
5.36	7.4 (7.4)	12.19	0.25 (0.32)
5.29	6.1 (6.4)	12.00	0.60 (0.44)
4.98	3.1 (3.1)	11.70	0.81 (0.80)
4.95	3.2 (2.9)	10.10	25 (26)
4.60	1.01 (1.30)	9.64	66 (65)
4.39	0.71 (0.79)	9.12	161 (162)
4.15	0.28 (0.35)	8.96	2.3×10^2 (2.1×10^2)
3.86	0.24 (0.23)	8.57	5.0×10^2 (5.0×10^2)
3.70	0.163 (0.160)	8.15	7.9×10^2 (8.0×10^2)

[a] Reactions were carried out at 22 °C; $\mu = 0.20$ M ($NaClO_4$). Reactions with I_2 were followed at 460 nm; those with OCl^- were followed at 250 nm. [b] Second-order rate constants; parenthetical values were calculated by using the relationships and parameters in Table 3.

Representative rate data for oxidations by I_2 and ClO^- appear in Table 2. Data for hypochlorite were taken at much greater pH values to avoid catalysis by the product, Cl^-, which is significant in more acidic media.[13] Note that oxidations by ClO^- are accelerated by increases in acidity (doubtless reflecting partial conversion to the more strongly oxidizing species, HOCl), whereas oxidations by iodine are more rapid at higher pH, indicating partition of the reductant between its uninegative and (the more reactive) dinegative anion. Rate laws describing the reactions of the oxidants taken are summarized in Table 3. Also included are kinetic parameters resulting from refinements of observed rates in terms of these expressions. Rate constants calculated from these parameters are compared with observed values in Table 2.

Like oxidations by I_2, reactions of I_3^- are seen to proceed at rates proportional to $1/[H^+]$, indicating that both conversions involve the conjugate base, $N_2O_3^{2-}$, of the principal dintrogen species in acetate buffer. The bimolecular specific rates pertaining to the reactive form, obtained by dividing the tabulated inverse-acid k's by the reported[6] K_2 of the parent acid, 5.4×10^{-10}, are 6.0×10^7 M^{-1} s^{-1} for I_2 and 3.9×10^6 for I_3^-. As expected, attachment of I^- to the iodine molecule makes it a less effective electron acceptor.

Oxidation by IO_3^- is very nearly first order in H^+. The reaction then proceeds through the protonated form of one of the redox species, in this case almost certainly the oxidant. Here, the rate constant referring to HIO_3, obtained by multiplying k_H by the acidity constant for HIO_3 ($pK_A = 0.4$)[14] is 3.6×10^5 M^{-1} s^{-1}, reminding us that the slow conversions observed with this system reflect the very low concentration of the active oxidant rather than its potency. Note that the kinetic profiles give no indication of intermediates formed or destroyed on a time scale comparable to that for the measured disappearance of the reductant. Hence, the initial act in which $N_2O_3^{2-}$ is consumed must be rate-determining. Subsequent participation of the oxidant, although reflected in the overall reaction stoichiometry, is kinetically silent.

The rate law (7) for oxidation by $HOCl/ClO^-$ features a three-term numerator, pertaining to three different protonation levels

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(13) Rate enhancement by Cl^- at high acidity may be reasonably attributed to the formation of chlorine ($HOCl + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O$) which, in analogy to Br_2, would be expected to oxidize $N_2O_3^{2-}$ at a rate constant $>10^6$ M^{-1} s^{-1}.

(14) Naidich, S.; Ricci, J. F. *J. Am. Chem. Soc.* **1939**, *61*, 3268. The value recorded by these authors (0.79, $\mu = 0$) has been adjusted to $\mu = 0.20$ M.

Table 3. Rate Laws and Kinetic Parameters for the Oxidations of Trioxodinitrate ($N_2O_3^{2-}$)[a]

oxidant (Ox)	rate law[b]	eq no.	parameters[c]
I_2	$k'/[H^+]$	5	$k' = (3.25 \pm 0.02) \times 10^{-2}\ s^{-1}$
I_3^- [d]	$k'/[H^+]$	5	$k' = (2.1 \pm 0.2) \times 10^{-3}\ s^{-1}$
IO_3^- [e]	$k_H[H^+]$	6	$k_H = (9.1 \pm 0.2) \times 10^5\ M^{-2}\ s^{-1}$
Br_2	k		$k > 1 \times 10^6\ M^{-1}\ s^{-1}$ (pH 4.7)
HOCl	$(k_0K_{ox}K_{red} + k_1K_{ox}[H^+] + k_2[H^+]^2)/ (K_{ox} + [H^+])(K_{red} + [H^+])$	7	$k_0 = 0.084 \pm 0.016\ M^{-3}\ s^{-1}$ $k_1 = 178 \pm 16\ M^{-3}\ s^{-1}$ $k_2 = (4.0 \pm 0.5) \times 10^3\ M^{-3}\ s^{-1}$ $K_{ox} = 3.2 \times 10^{-8}$; $K_{red} = 5 \times 10^{-10}$ [f]
$IrCl_6^{2-}$			$k = (1.5 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$ [g]
$IrBr_6^{2-}$			$k = (4.6 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$ [g]
$Fe(CN)_6^{3-}$	k		$k = 3.8 \pm 0.4\ M^{-1}\ s^{-1}$ [e,h]

[a] Reactions were carried out at 22 °C; $\mu = 0.20$ M ($NaClO_4$). [b] Rate laws describe $(-d[Red]_T/dt)[Ox]_T^{-1}[Red]_T^{-1}$, where $[Red]_T$ and $[Ox]_T$ designate the total concentrations of dioxotrinitrate and oxidant taken. [c] K_{ox} and K_{red} refer to the acidity quotients of HOCl and $HN_2O_3^-$. [d] Reactions in 0.020 M I^-. [e] Obtained from comparisons of initial rates. [f] Reference 6. [g] pH = 3.7−4.4. [h] pH = 6.6.

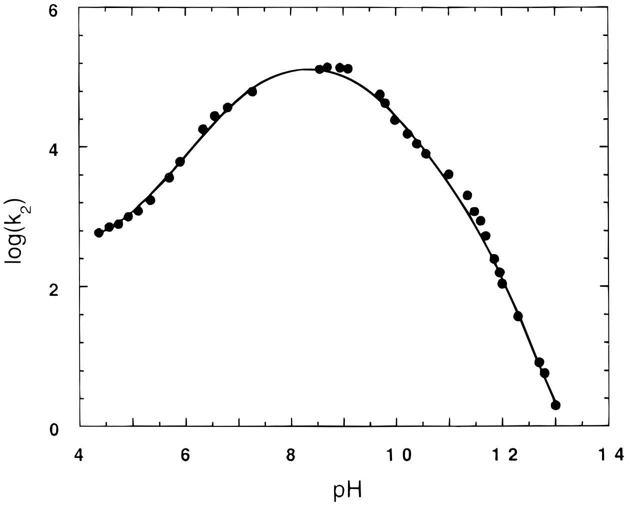

Figure 1. Variation, with pH, of the observed second-order rate constants (plotted as log k_2) for the reaction of trioxodinitrate ($N_2O_3^{2-}$) with I(VII); 22 °C, $\mu = 0.20$ M ($NaClO_4$). Reactions between pH 4.37 and 5.69 were buffered using HOAc/OAc^-, those between 5.90 and 6.60 using $H_2PO_4^-/HPO_4^{2-}$, those between 8.55 and 9.70 by $H_3BO_3/H_2BO_3^-$, and those between 9.80 and 11.35 by "CAPS". The solid circles denote observed values, whereas the solid line is that calculated using eq 8 and the parameters in the text following this equation.

and corresponding to separate bimolecular paths involving the three pairs, ($N_2O_3^{2-} + OCl^-$), ($N_2O_3^{2-}$ + HOCl), and ($HN_2O_3^-$ + HOCl). Refinement of rate data, in conjunction with the known acidity constants for HOCl (3.2×10^{-8}) and $HN_2O_3^-$ (5×10^{-10}),[6] yields a trio of rate constants which increase markedly with protonation. The high value for the monoprotonated component ($k_2 = 178\ M^{-3}\ s^{-1}$) indicates that the major portion of this path is carried by $N_2O_3^{2-}$ + HOCl, rather than by the kinetically equivalent pair, $HN_2O_3^- + OCl^-$, although in terms of concentrations, the latter combination predominates at that level.

The complications associated with the HOCl reactions at low pH values (see Experimental Section) do not extend to oxidations by I(VII). Hence, kinetic acidity data involving periodate embrace an unusually wide range. The resulting profile (pH = 4−13, Figure 1) features a rate maximum near pH 8 and a drop between pH 10 and 13 sharper than that corresponding to an inverse-$[H^+]$ dependence, pointing to two kinetically significant deprotonations in strongly basic media. The distribution between reaction paths is analogous to that for oxidations by HOCl, but two levels of protonation of the oxidant (K_2^{Ox} and K_3^{Ox}) must be considered. (The first deprotonation of HIO_4, pK_1 = 1.6,[15] does not enter the picture in the pH range examined.) In addition, the precipitous rate drop near pH 13 points to reversible conversion, by OH^-, to an inactive form of trioxodinitrate. Since no acidic protons are present on the $N_2O_3^{2-}$ anion, we suspect a relatively loosely bound OH^- adduct (K^{RdOH} ca. 10), possibly involving interaction with the N═N double bond. The four-term rate law, eq 8, describes this distribution of paths

$$\frac{\text{Rate}}{[\text{Ox}]_T[\text{Red}]_T} = \frac{k_1[H^+]^4 + k_2'[H^+]^3 + k_3'[H^+]^2 + k_4'[H^+]}{([H^+]^2 + K^{Rd}[H^+] + K^{Rd}K_w/K^{RdOH})([H^+]^2 + K_2^{Ox}[H^+] + K_2^{Ox}K_3^{Ox}} \tag{8}$$

where $k_2' = k_2(K_3^{Ox} + K^{Rd})$, $k_3' = k_3K^{Rd}K_3^{Ox}$, and $k_4' = k_4(K^{Rd}K_2^{Ox}K_3^{Ox} + K^{Rd}K_2^{Ox}K_w/K^{RdOH})$. (Here k_1, k_2, k_3, and k_4 are the bimolecular rate constants for paths at four protonation levels and K_w (=10^{-14}) is the autoprotolysis constant for water.)

Refinement of I(VII) data holding K^{Rd} at 4.8×10^{-10},[6] yields $k_1 = (4.1 \pm 0.4) \times 10^2$, $k_2 = (1.7 \pm 0.1) \times 10^5$, $k_3 = (6 \pm 3) \times 10$, and $k_4 = 3.2 \pm 0.6\ M^{-1}\ s^{-1}$. The refined value for K_2^{Ox} (pK = 7.6) is slightly below that of Crouthamel[15] (which pertains to $\mu = 0$). Agreement between our K_3^{Ox} (pK = 12.1) and the earlier pK (11) is not impressive, but both values must be considered highly approximate. Observed specific rates are compared to those calculated from eq 8 (the solid line) in Figure 1.

Oxyhalogen anions and their parent acids are generally, although not invariably,[16] considered to be $2e^-$ oxidants. Since outer-sphere transfers of two oxidation units have not yet been reported, we may infer intervention of bridged intermediates in these cases. Thus, for example, the reaction of $N_2O_3^{2-}$ with $H_4IO_6^-$, to which the predominant k_2 term in (8) pertains, may be taken to be initiated by oxygen transfer (9) to the more nucleophilic of the two nitrogens, yielding the tetraoxo anion, I, which, in analogy to the known[7] structure of its $N_2O_3^{2-}$ precursor, is taken to be a symmetric anion featuring a N═N double bond. Since the observed kinetic patterns give no hint that this intermediate accumulates, we infer that it undergoes rapid symmetric scission (10) to two NO_2- ions, the predominant product

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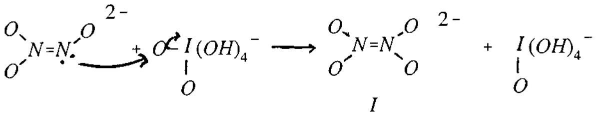
(15) Crouthamel, C. G.; Hayes, A. M.; Martin, D. S. *J. Am. Chem. Soc.* **1951**, *73*, 82. Complications in the I(VII) system due to the rapid equilibrium between the IO_4^- anion and its hydrated form, $H_4IO_6^-$, appear to play no part in the present study. We here cite the "apparent acidity constants" recorded by these workers. These describe equilibria between protonation levels but not between (kinetically indistinguishable) hydration levels.

(16) See, for example: (a) Bakac, A.; Thornton, A. T.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 274. (b) Gordon, G.; Tewari, P. H. *J. Phys. Chem.* **1976**, *70*, 200.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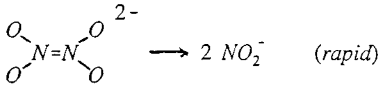
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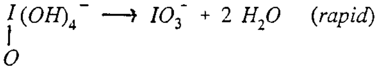
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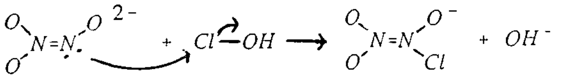
The proposed follow-up step (10) features the rapid fission of an N═N double bond. If correct, it is the most unusual aspect of this transformation, although it has been previously suggested in connection with the $Br_2-NO_2^-$ reaction.[17] The apparent ease of this splitting may be attributed to the marked shrinkage of bonding action through electron withdrawal by all four strongly electronegative oxygen atoms. The process brings to mind the breakage of the N═N bond during the thermal[9] and photolytic[18] decompositions of $N_2O_3^{2-}$ itself and the observed S−S scission[19] in $S_2O_4^{2-}$, although it is obviously more facile.

The oxidation by hypochlorous acid may, in principle, proceed by oxygen atom transfer, by Cl^+ transfer, or by a combination of the two routes. The demonstrated predominance of chlorine bridging in the $HOCl-NO_2^-$ reaction[20] leads us strongly to favor such a path for $N_2O_3^{2-}$ as well.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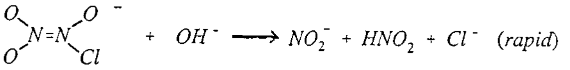
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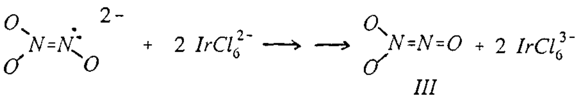
The stoichiometry of the reactions of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ (Table 1) indicates very nearly quantitative conversion to nitrite, as is the case with the oxyhalogen species. The structures of these substitution-inert $1e^-$ oxidants, in conjunction with the high redox rates, rule out a bridged transition state. Instead, these reactions may be assumed to proceed via successive outer-sphere electron transfers to two acceptor Ir(IV) centers, after which the uncharged intermediate, **III**, may undergo hydration, and thence scission in a manner analogous to (10).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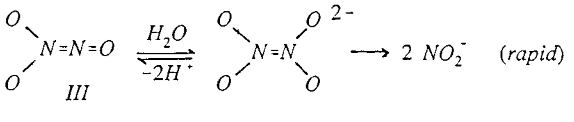
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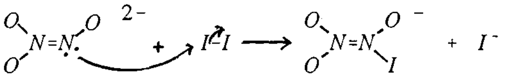
Again, reaction profiles yield no evidence that an intermediate species grows or decays on a time scale comparable to that of the primary reaction, indicating that the second act of electron transfer and the subsequent hydration are both much more rapid than the initial transfer and are therefore kinetically undetectable.

Oxidations by I_2 may conceivably also proceed by successive outer-sphere $1e^-$ transactions. However, the high bimolecular rate constant for the $I_2-N_2O_3^{2-}$ reaction, 6×10^7 M^{-1} s^{-1}, considered along with the weakly oxidizing potential for I_2/I_2^- (0.21 V),[21] points instead to passage through an iodine bridge (I^+ transfer) (16) in analogy with the route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suggested for HOCl.

The rate constant for the initial outer-sphere reduction of $Fe(CN)_6^{3-}$ (4 M^{-1} s^{-1}) allows us to estimate an upper limit for electron self-exchange in the system $N_2O_3^{-/2-}$. Marcus's model[22] leads to the approximate[23] relationship (17)

$$k_{N_2O_3,Fe} = (k^{ex}_{N_2O_3}\, k_{Fe(2.3)} K_{N_2O_3,Fe})^{1/2} \tag{17}$$

where $k_{N_2O_3Fe}$ is the rate constant for this reduction, $k^{ex}_{N_2O_3}$ is the self-exchange rate for $N_2O_3^{-/2-}$, $k_{Fe(2,3)}$ is the self-exchange rate for $Fe(CN)_6^{4-/3-}$ (taken to be $10^{4.8}$ M^{-1} s^{-1} at 25 °C),[24] and $K_{N_2O_3Fe}$ is the equilibrium constant for this reaction. If the latter is assumed to be at least unity, the self-exchange rate for the N_2O_3 anion couple is calculated to lie below $10^{-3.7}$ M^{-1} s^{-1}. This figure, like the self-exchange rate estimated[24] for the system $^{\bullet}ON(SO_3)_2^{2-}/ON(SO_3)_2^{3-}$ and the upper limit proposed[22] for $N_2H_4^+/N_2H_4^0$ (0.3 M^{-1} s^{-1}),[25] serves to remind us that electron self-exchange involving singly bonded molecules and their derived radicals fall well below rates ($10^6 - 10^9$ M^{-1} s^{-1}) reported for aromatics[26] in which the migrating electron can be delocalized over a conjugated system.

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