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Reductions by hyponitrite †

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Hyponitrites, salts of the weak acid HO–N=N–OH, hyponitrous acid, react, in aqueous solution (pH 4–8), with an array of inorganic oxidants. With the high potential reagents Br_2 and $[Fe(bipy)_3]^{3+}$ in excess, conversion is mainly to nitrate, whereas with I_2 and $[IrCl_6]^{2-}$, the product is nitrite. Kinetic acidity patterns indicate that nearly all oxidations proceed largely through the conjugate base, $HN_2O_2^-$. With I_2, I_3^-, and Br_2 there is also evidence also for a doubly deprotonated route, possibly involving a halogen–$N_2O_2^{2-}$ complex. The $1e^-$ metal oxidants $[Fe(bipy)_3]^{3+}$ and $[IrCl_6]^{2-}$ probably operate through a series of outer-sphere $1e^-$ steps in which the initial transfer is rate-determining, whereas with I_2 and Br_2, reaction *via* a halogen bridge, resulting in net transfer of X^+ (a $2e^-$ change) is more likely. None of the reaction profiles exhibits irregularities attributable to the intervention of an intermediate formed or destroyed on a time scale commensurate with the initial reaction.

Introduction

Although hyponitrites, salts of the weak acid acid HON=NOH, hyponitrous acid, have been known since 1871,[2,3] interest in this N(I) system has been greatly overshadowed by the vast body of attention bestowed on the higher oxidation states of nitrogen. Acidity constants ($pK_1 = 7.18$; $pK_2 = 11.54$) have been documented,[4] and a *trans*-configuration has been established, both for the dinegative anion,[5] and for the predominant form of the solid parent acid.[5,6]

In principle, a nitrogen(I) transient should be involved in the enzymatic oxidation of ammonia to nitrate (nitrification)[7] and in the biologically significant reductions of nitrite to ammonia[8a] or N_2.[8b] However, attempts to demonstrate the intermediacy of hyponitrous acid or its anion in such biosystems[7,9] have yielded negative or questionable results, suggesting that such species, if they intervene at all, are unusually reactive.

We have extended our interest in the redox chemistry of the lower oxidation states of nitrogen[10] to the hyponitrite system, which, like hydrazine and hydroxylamine, is a powerful but selective reductant. Although detailed investigations into the decomposition of both hyponitrous acid and its salts have been carried out,[11] mechanistic studies of reactions with inorganic oxidants have been more fragmentary. Kinetic studies by Gupta and co-workers[12] embraced a variety of oxidants but generally dealt only with initial reaction rates and utilized quite limited variations in reaction media. The reaction between hyponitrous and nitrous acids (eqn. 1) has been examined at some length,[13]

$$H_2N_2O_2 + HNO_2 \longrightarrow HNO_3 + N_2 + H_2O \qquad (1)$$

and the N_2 formed has been shown[14] to arise from the N(I) acid. Hence this conversion may be considered to be a net reduction, rather than an oxidation, of hyponitrous acid.

Experimental

Materials

Iron(III) perchlorate $[Fe(ClO_4)_3{\cdot}6H_2O]$, sodium *trans*-hyponitrite hydrate ($Na_2N_2O_2{\cdot}xH_2O$), potassium hexachloropalladate(IV) (K_4PdCl_6), tris(2,2′-bipyridine)iron(III) hexafluorophosphate, thallium(III) perchlorate, sodium thiocyanate (NaSCN) (Aldrich products), bromine water (Fisher), sodium hexachloroiridate(IV) ($Na_2IrCl_6{\cdot}6H_2O$), and sodium hexachloroplatinate(IV) (Na_2PtCl_6) (Alfa products) were used as received.

Fresh stock solutions of sodium hyponitrite were prepared daily in aqueous base (1.0 M NaOH) and were standardized spectrophotometrically in 0.1 M NaOH (ε_{248} 6.6×10^3 M^{-1} cm^{-1}).[15] Stock solutions of $[Fe(bipy)_3](PF_6)_3$ were prepared in dry acetonitrile and were filtered to remove insoluble impurities. Stock solutions of Na_2PdCl_6 and Na_2PtCl_6 were prepared in 0.1 M HCl.

Stoichiometric studies

Stoichiometries of the oxidation of hyponitrite were generally determined with the oxidant in excess. The decrease in absorbance at λ_{max} of the oxidant, after addition of a measured deficiency of hyponitrite and standing for 2–10 min, was used to estimate the loss of oxidant. These changes were compared with those seen when excess hyponitrite was added. Reasonable values could not be obtained for the oxidation by I_3^- because of the competing reaction of the product, HNO_2, with I^- in the supporting medium, nor for oxidation by $[PdCl_6]^{2-}$ because of the attendant decomposition of the oxidant to Cl_2. In the latter case, however, the product was identified as $[PdCl_4]^{2-}$ by its spectrum. Results for other systems are summarized in Table 1.

Kinetic experiments

Reactions, under argon, were generally examined at or near λ_{max} of the oxidant, using either a Shimadzu-1601 instrument or a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Temperatures were kept at 24.0 ± 0.5 °C throughout the entire series of experiments. Ionic strength was regulated by addition of ($NaClO_4$ + $HClO_4$) or (HCl + NaCl). Low pH values (0–2) were maintained with added $HClO_4$ or HCl, and higher pH's by phosphate, acetate or chloroacetate buffers. Solutions of hyponitrite, especially those held at pH 6–8, were used as quickly as possible after preparation to minimize decomposition of this reagent in solution. Reactions were run under pseudo-first order conditions with

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† Electron Transfer, part 142. For part 141, see ref. 1.

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Table 1 Stoichiometry of oxidations of hyponitrite[a]

Oxidant (Ox)	pH	μ/M	λ/nm	$\Delta[\mathrm{Ox}]/\Delta[\mathrm{H_2N_2O_2}]$
I_2	4.0	0.20	456	1.85
Br_2	0.7	0.20	395	3.8[b]
$[IrCl_6]^{2-}$	7.0	0.20	489	3.8
$[Fe(bipy)_3]^{3+}$	6.0	1.0	525	7.4

[a] For reaction conditions, see Experimental section. [b] Value with Br_2 in excess. With hyponitrite in excess, the ratio $[HNO_2]_{formed}/[Br_2]_{consumed}$ was 1.2 ± 0.1.

hyponitrite in greater than tenfold excess. Rate constants were obtained from the resulting profiles by nonlinear least squares fittings to the relationship describing first order decay. All reactions for which reproducible data could be obtained were first order both in hyponitrite and oxidant. Although many of the rates were strongly acid dependent, none of the reactions examined in buffered systems exhibited general acid or general base catalysis. In a few instances reactions were run without protection by argon; results were not significantly affected.

A number of oxidizing species reacted inconveniently slowly, or not at all, with hyponitrite under the conditions examined. Among these were $[Fe(CN)_6]^{3-}$, $[Co(NH_3)_5Br]^{2+}$, $[Fe(NCS)]^{2+}$, Fe(III)$_{aq}$ (pH 0.2), the Ni(IV) complex of 2,6-diacetylpyridine dioxime,[16] the Ag(III) complex of ethylenebis(biguanide),[17] and hydrogen peroxide (both in the presence and the absence of CH_3ReO_3).[18] In contrast, the reaction with $Tl(ClO_4)_3$ (pH 2.8–4.7) was too rapid to follow, even using stopped-flow methods under second order conditions.

Results and discussion

Stoichiometric results summarized in Table 1 indicate that under the conditions chosen, hyponitrous acid is oxidized principally to HNO_2 by I_2 ($E°$ 0.54 V) and $[IrCl_6]^{2-}$ (0.87 V),[19] even when these reagents are employed in excess (eqns. 2 and 3),

$$H_2N_2O_2 + 2\,I_2 + 2\,H_2O \longrightarrow 2\,HNO_2 + 4\,I^- + 4\,H^+ \quad (2)$$

$$H_2N_2O_2 + 4\,[IrCl_6]^{2-} + 2\,H_2O \longrightarrow 2\,HNO_2 + 4\,[IrCl_6]^{3-} + 4\,H^+ \quad (3)$$

but is converted predominantly to NO_3^- by the more powerful oxidants, Br_2 (1.06 V) and $[Fe(bipy)_3]^{3+}$ (1.11 V)[20] (eqn. 4 and 5). However, under our kinetic conditions (reductant in excess),

$$H_2N_2O_2 + 4\,Br_2 + 4\,H_2O \longrightarrow 2\,NO_3^- + 8\,Br^- + 10\,H^+ \quad (4)$$

$$H_2N_2O_2 + 8\,[Fe(bipy)_3]^{3+} + 4\,H_2O \longrightarrow 2\,NO_3^- + 8\,[Fe(bipy)_3]^{2+} + 10\,H^+ \quad (5)$$

oxidation by Br_2 yields mainly HNO_2. Tripositive nitrogen doubtless intervenes in the $H_2N_2O_2$–$[Fe(bipy)_3]^{3+}$ reactions, but the oxidation of HNO_2 by this high potential chelate proceeds 40–60 times as rapidly as that of $H_2N_2O_2$ and hence is kinetically silent. None of the reaction profiles in the present study exhibits irregularities attributable to formation or destruction of a transient on a time scale comparable to that of the principal reaction.

Table 2 Kinetic data for the oxidation of hyponitrous acid with iodine and with triiodide[a]

A $H_2N_2O_2 + I_2$		B $H_2N_2O_2 + I_3^-$ [b]	
pH	$k/M^{-1}\,s^{-1}$ [c]	pH	$k/M^{-1}\,s^{-1}$ [c]
3.68	11 (15)	4.00	1.0 (0.81)
3.80	21 (24)	4.50	5.5 (4.5)
3.88	43 (32)	4.65	6.6 (8.1)
3.91	50 (36)	5.05	33 (42)
4.14	99 (87)	5.35	1.2×10^2 (1.5×10^2)
4.29	1.8×10^2 (1.6×10^2)	5.40	1.6×10^2 (1.9×10^2)
4.40	2.5×10^2 (2.5×10^2)	5.48	2.3×10^2 (2.7×10^2)
4.50	3.8×10^2 (3.9×10^2)	5.66	5.5×10^2 (6.0×10^2)
5.08	4.5×10^3 (5.0×10^3)	6.25	8.0×10^3 (7.9×10^3)
5.20	8.8×10^3 (8.7) $\times 10^3$)	6.60	3.4×10^4 (3.4×10^4)
5.22	1.00×10^4 (0.95×10^4)	6.90	1.1×10^5 (1.1×10^5)
5.69	7.3×10^4 (7.9×10^4)		

[a] Reactions were run at 24.5 ± 0.5 °C; μ = 0.20 M ($NaClO_4$). Solutions were buffered using HOAc/OAc$^-$ or $H_2PO_4^-/HPO_4^{2-}$ (0.05 M). [b] $[I^-]_{added}$ = 0.05 M. [c] Parenthetical values were calculated using eqn. 6 and parameters listed in Table 3.

Oxidations by halogen species

Kinetic data for oxidations by I_2 and by I_3^- are assembled in Table 2. Reactions are accelerated by increases in pH, and the trends in rate are decidedly sharper than that characterizing a simple inverse-[H$^+$] relationship. Both oxidations conform to a binomial expression, eqn. 6, where K_1, the first acidity constant

$$k = \frac{a[H^+] + bK_1}{[H^+](K_1 + [H^+])} \quad (6)$$

of the reductant, is taken as 7×10^{-8} M.[4] Refinement of data in terms of eqn. 6 yields the parameters listed in Table 3. Eqn. 6 implies a reaction proceeding through two acidity levels, formed by loss of successive protons from the principal reductant species, which itself is negligibly reactive. The relevant rate law (eqn. 7) in which the rate constants k_{HA} and k_A refer to the

$$k = \frac{1}{[H^+] + K_1}\left[K_1 k_{HA} + \frac{k_A K_1 K_2}{[H^+]}\right] \quad (7)$$

contributing hyponitrite anions, is algebraically equivalent to eqn. 6.

The resulting bimolecular rate constant, k_{HA}, pertaining to uninegative hyponitrite, is 2.3×10^4 $M^{-1}\,s^{-1}$ for reduction of I_2 and 7.2×10^2 $M^{-1}\,s^{-1}$ for I_3^-. As expected, the more electrophilic uncharged X_2 molecule is the more reactive.

Extension of this reasoning to the inverse-[H$^+$] term in eqn. 7 to calculate rates for dinegative hyponitrite requires division by K_1K_2 and leads to k_A values of 1.3×10^{10} $M^{-1}\,s^{-1}$ for I_3^- and 2×10^{12} $M^{-1}\,s^{-1}$ for I_2, both of these exceeding the diffusion controlled limit[21] for bimolecular reactions in water. We therefore conclude, with some hesitancy (for the data are suggestive rather than compelling) that this kinetic contribution stems instead either from deprotonation of a different species (possibly a halogen–$HN_2O_2^-$ precursor) or from intervention of a reactive halogen–OH^- adduct.

Rates for the much more rapid oxidation by Br_2 could be measured only at higher acidities (0.005–0.20 M H$^+$). The three-term rate law, eqn. 8 in Table 4, tells us that an additional path ($k = 9 \times 10^3$ $M^{-1}\,s^{-1}$) involving the parent acid, $H_2N_2O_2$, has become operative. Moreover, the calculated kinetic contribution for $HN_2O_2^-$ (1×10^6 $M^{-1}\,s^{-1}$) is over 40 times that for the corresponding component for I_2. Here again, refinement indicates a doubly deprotonated route, the nature of which is subject to the same questions as those for oxidations by I_2 and I_3^-.

Reactions with metal-center oxidants

Data for oxidations by $[Fe(bipy)_3]^{3+}$ and $[IrCl_6]^{2-}$ appear in Table 5. The simpler rate expressions (Table 4, eqns. 9 and 10) correspond to partition of the reductant into parent acid and monoanion, and with the Fe(III) chelate, only the latter

Table 3 Kinetic parameters for oxidation of hyponitrous acid[a]

Oxidant	μ/M	Parameters[b]
I_2	0.20	$K_1 = 7 \times 10^{-8}$ M;[c] $k_{HA} = (2.3 \pm 0.1) \times 10^4$ M^{-1} s^{-1}; $b = (3.39 \pm 0.03) \times 10^{-7}$ s^{-1}
I_3^-	0.20	$k_{HA} = (7.2 \pm 0.5) \times 10^2$ M^{-1} s^{-1}; $b = (2.60 \pm 0.03) \times 10^{-9}$ s^{-1}
Br_2	0.20	$k_{H_2A} = (9.0 \pm 0.3) \times 10^3$ M^{-1} s^{-1}; $k_{HA} = (1.03 \pm 0.02) \times 10^6$ M^{-1} s^{-1}; $b = (7.2 \pm 0.4)$ M s^{-1}
$[Fe(bipy)_3]^{3+}$	1.0	$k_{HA} = (4.0 \pm 0.1) \times 10^4$ M^{-1} s^{-1}
$[IrCl_6]^{2-}$	0.50	$k_{H_2A} = 0.83 \pm 0.02$ M^{-1} s^{-1}; $k_{HA} = 413 \pm 3$ M^{-1} s^{-1}
$[PtCl_6]^{2-}$	0.50	$k_{HA} = 33 \pm 3$ M^{-1} s^{-1}
$[PdCl_6]^{2-}$	1.0	$k_1 = 8 \times 10^4$ M^{-1} s^{-1}; $k_2 = 4 \times 10^3$ M^{-2} s^{-1}

[a] Reactions were run at 24.5 ± 0.5 °C; μ was generally regulated using $NaClO_4/HClO_4$. [b] Parameters are those in the rate laws listed in Table 4. [c] K_1, the first acidity constant for hyponitrous acid, is taken as 7.0×10^{-8} M throughout (ref. 8).

Table 4 Rate laws for oxidations of hyponitrous acid

Oxidant (Ox)	λ/nm	Rate law[a]	Eqn. no.
I_2	456	Rate = [Ox][Red] $(K_1k_{HA} + b[H^+]^{-1})([H^+] + K_1)^{-1}$	7′[b]
I_3^-	352		7′[b]
Br_2	395	Rate = [Ox][Red] $(k_{H_2A} + K_1k_{HA}[H^+]^{-1} + b[H^+]^{-2})$	8[c]
$[Fe(bipy)_3]^{3+}$	525	Rate = [Ox][Red]$(K_1k_{HA})([H^+] + K_1)^{-1}$	9
$[IrCl_6]^{2-}$	489	Rate = [Ox][Red]$(k_{H_2A}[H^+] + K_1k_{HA})([H^+] + K_1)^{-1}$	10
$[PtCl_6]^{2-}$	270	Rate = [Ox][Red] $K_1k_{HA}[H^+]^{-1}$	11[c]
$[PdCl_6]^{2-}$	340	Rate = [Ox][Red] $(k_1 + k_{Cl}[Cl])$	12[d]

[a] K_1 is the first acidity constant for hyponitrous acid. Parameters k_{H_2A} and k_{HA} refer to kinetic contributions associated with unionized hyponitrous acid and its mononegative anion, $HN_2O_2^-$. [b] Eqn. 7′ is an adaption of eqn. 7 in the text with the kinetically inadmissible $K_1K_2[H^+]^{-1}$ term (see text) replaced by parameter b. [c] Oxidations examined with $[H^+] \gg K_1$. [d] Reaction rate independent of $[H^+]$ in the range 0.1–1.0 M.

Table 5 Kinetic data for oxidation of hyponitrous acid with $[Fe(bipy)_3]^{3+}$ and with $[IrCl_6]^{2-}$[a]

A $H_2N_2O_2 + [Fe(bipy)_3]^{3+}$[b]		B $H_2N_2O_2 + [IrCl_6]^{2-}$[c]	
pH	$10^{-3}k$/M^{-1} s^{-1}[d]	pH	k/M^{-1} s^{-1}
5.02	0.38 (0.38)	4.76	3.4 (4.0)
5.38	0.75 (0.85)	5.07	6.6 (6.0)
5.60	1.36 (1.39)	5.56	13.9 (14.2)
5.90	2.5 (2.7)	5.89	28 (27)
6.08	3.5 (3.9)	6.13	50 (44)
6.30	5.2 (6.1)	6.33	77 (64)
6.56	9.5 (9.9)	6.68	95 (117)
6.62	10.0 (11.0)	7.06	2.0×10^2 (2.0×10^2)
7.20	27 (24)	7.23	2.4×10^2 (2.3×10^2)
7.50	28 (30)		

[a] Reactions were run at 24.5 ± 0.5 °C. Solutions were buffered using $HOAc/OAc^-$ or $H_2PO_4^-/HPO_4^{2-}$ (0.05 M). [b] $\mu = 1.0$ M ($NaClO_4$). At pH values below 5.0, the system was complicated by the reaction of HNO_2 with $[Fe(bipy)_3]^{3+}$. [c] $\mu = 0.50$ M ($NaClO_4$). Rates were not significantly affected by addition of 0.01–0.10 M Cl^-. [d] Parenthetical values were calculated using the rate equations in Table 4 and the parameters in Table 3.

contributes significantly. The substitution-inert Fe(III) complex may be assumed to be an outer-sphere 1e⁻ acceptor, and this is probably the case also for $[IrCl_6]^{2-}$, for the reducing agent is devoid of a positive center that might utilize a chloro bridge. Since there is no evidence for the intervention of a transient which is generated or consumed on a time scale similar to that of the primary conversion, the overall rates may be taken to be determined by the initial act of electron transfer (*e.g.* eqn. 13), with subsequent steps being much more rapid.

$$[Fe(bipy)_3]^{3+} + HN_2O_2^- \longrightarrow [Fe(bipy)_3]^{2+} + HN_2O_2^{\bullet} \qquad (13)$$

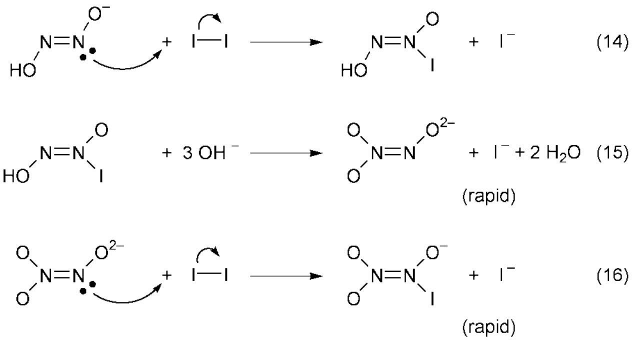
The greater net rate observed for $Fe[(bipy)_3]^{3+}$ may be attributed[22] in part to its more positive potential ($E°_{Fe(III)} = 1.11$ V; $E°_{Ir(IV)} = 0.87$ V),[19,20] in part to its more rapid self-exchange ($10^{8.5}$ *vs.* $10^{5.4}$ M^{-1} s^{-1}),[19] and, to a lesser extent, to partial anion-cation association in the Fe(III) system. The combination of these effects generates[22] a calculated kinetic advantage of 10^4 for $[Fe(bipy)_3]^{3+}$. Agreement with the observed ratio, ($k_{Fe(III)}/k_{Ir(IV)} = 10^{2.0}$, Table 5), although approximate, is comparable to agreements resulting from similar applications of the Marcus model[23] to other redox systems.[24]

A formal potential for the 1e⁻ oxidation of $HN_2O_2^-$ has not yet been reported but probably lies near 0.70 V, slightly below that of $Fe^{II,III}$(aq). This estimate, in conjunction with the "k_{HA}" values in Table 3, leads to calculated self-exchange rates in the range $10^{-4.8 \pm 1.5}$ M^{-1} s^{-1} for $(HN_2O_2)^{-1,0}$.

Rate constants for oxidations by the 2e⁻ reagents $[PtCl_6]^{2-}$ ($E°_{Pt(II,IV)}$ 0.73 V) and $[PdCl_6]^{2-}$ ($E°_{Pd(II,IV)} = 1.47$ V)[25] are seen to be similar to those of single electron oxidants of similar 1e⁻ potential. Outer-sphere 2e⁻ transactions, if they occur at all, should be considerably slower, reflecting a more severe Franck–Condon barrier. For these oxidants, however, reaction through a chloro bridge is reasonable, but a sequence of 1e⁻ transfers (with the initial step rate determining), cannot be excluded. Evidence for an odd-electron Pt(III) transient has been cited for other reactions.[26,27]

Does the oxidation by I_2 involve successive 1e⁻ transactions? We think not. The high rate constant for the principal path, 2×10^4 M^{-1} s^{-1}, considered in conjunction with the weakly oxidizing potential for I_2/I_2^- (0.21 V),[28] points instead to utilization of an iodine bridge (I^+ transfer) (eqn. 14), analogous to that demonstrated[29] for the $HOCl–NO_2^-$ reaction.

Subsequent hydrolysis of the N–I species (eqn. 15) and further attack on the trioxodinitrate intermediate ($N_2O_3^{2-}$) (eqn. 16)



may be taken to be rapid[10c] in relation to the proposed initial step. Analogous halogen-bridged sequences may be assigned to the slower oxidation by I_3^- and, at least in part, to the more rapid reaction of Br_2. As with oxidations of trioxodinitrate (hyponitrate),[10c] cleavage of the N=N double bond to yield the predominant product, nitrous acid, probably reflects the diminution of bonding action by the attached strongly electronegative oxygen atoms.

In summary, hyponitrite, like trioxodinitrate,[10c] exhibits considerable versatility of action in its redox behavior. Reaction sequences may be initiated by transfer of a single electron to an outer-sphere type oxidant when the latter features a sufficiently positive potential. Oxidants having a somewhat lower potential may operate *via* $2e^-$ paths provided that the redox step also entails transfer of a bridging atom to the reductant. With Br_2, both paths may compete.

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