Electron Transfer. 132. Oxidations with Peroxynitrite[1]

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Peroxynitrite ($O=N-O-O^-$) is formed by the reaction, at -2 °C, of nitrous acid and hydrogen peroxide, followed by rapid quenching with excess cold base. Unlike its conjugate acid (peroxynitrous acid, $pK_a = 6.5$), which decomposes quickly, the anion can be preserved for several weeks at high pH at -18 °C. Solutions of $ONOO^-$ rapidly oxidize solutions of H_3AsO_3, antimony(III) tartrate, and HSO_3^- (at pH 5−13) and Sn(II) (at pH 10−13) in reactions exhibiting 1:1 stoichiometry. Oxidation of hypophosphite is much slower and that of phosphite is nondetectable. Kinetic acidity patterns for oxidations of As(III), Sb(III), and S(IV) are each in accord with reactions proceeding via three paths featuring different levels of protonation. For H_3AsO_3 and antimony(III) tartrate, reaction involving the monodeprotonated reductant (e.g., $H_2AsO_3^-$) and ONOOH (OxH$^+$ + Red) predominates whereas, for HSO_3^-, reaction is most rapid when both redox partners are protonated (OxH$^+$ + RedH$^+$). All transformations in this study are taken to be oxo-transfer reactions proceeding through O-bridged precursor complexes. The observed reactivity series, $Sn^{II} > Sb^{III} > As^{III} > S^{IV} >> P^I > P^{III}$, is not directly related to the formal potentials of these reducing centers but appears largely to reflect the relative accessibilities of the electron-rich sites of the reductants, with the substitution-inert anions $H_2PO_2^-$ and HPO_3^{2-} being particularly unreactive. The unexpectedly high rates associated with the protonated form of S(IV) may be attributed to the decrease in coordination number of sulfur and the attendant improved availability of the reducing site as the HSO_3^- anion is converted, via protonation, to SO_2, which is recognized to be the preponderant S(IV) species in acidic aqueous solutions.

Recent years have seen a marked intensification of interest, among workers dealing with biosystems, in two quite different odd-electron diatomic species—nitric oxide (NO) and the superoxide anion (O_2^-), The first of these is thought to play a role in such physiological processes as neurotransmission, smooth muscle relaxation, lysis of tumor cells, long-term recall, immune regulation, and male sexual function.[2] Superoxide is an initial product in biological energy transfer reactions involving O_2, specifically the respiration of aerobic organisms.[3]

Despite their ubiquitous participation in bioprocesses, both superoxide and NO are toxic if allowed to accumulate.[4] Superoxide is customarily lost by disproportionation into H_2O_2 and O_2, a conversion strikingly catalyzed by a group of bimetalloproteins (superoxide dismutases).[5] When present, NO offers a second route for superoxide destruction, for the two odd-electron species react at a rate near the diffusion-controlled limit:

$$NO + O_2^- \rightarrow [ONOO]^- \qquad k = 6 \times 10^9 \ M^{-1} \ s^{-1}$$
$$(25 \ °C)^6 \quad (1)$$
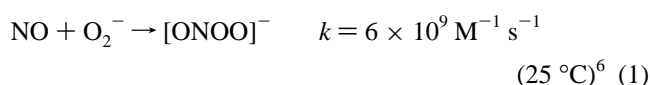
The product, peroxynitrite (or peroxonitrite), is the anion of the unstable weak acid peroxynitrous acid ($pK_a = 6.5$)[7] and can be preserved for several weeks in strongly basic media at -18 °C.[8a]

Raman spectra of the anion, as well as *ab initio* quantum mechanical calculations, point to a predominant *cis* structure.[8b]

Peroxynitrite, which has been found to be cytotoxic,[9] should be formed in instances where superoxide and NO are being generated at the same time. Its production in biosystems has been confirmed,[10] and it has been proposed as an oxidant in reactions associated with vascular injuries[11] and as an agent in development of atherosclerotic lesions.[12]

Although peroxynitrite was virtually unknown to a large fraction of practicing inorganic chemists until the beginning of this decade, a scattering of studies pertaining to this anion and its conjugate acid were carried out before 1975[13] and a detailed review appeared in 1994.[14]

A variety of activation paths are conceivable for reactions of the peroxynitrous acid/peroxynitrite couple, each with precedents in related systems. The acid may undergo heterolysis at the N−O bond (reaction 2), forming the nitrosonium cation, an effective nitrosating agent. Alternatively, the O−O bond may be broken heterolytically (reaction 3) to yield OH$^+$, a strongly

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(1) Sponsorship of this work by the National Science Foundation (Grant 9414113) is gratefully acknowledged.
(2) Review: Stamler, J. S.; Singel, D. J.; Loscalzo, *Science* **1992,** *258,* 1898.
(3) See, for example: (a) Fridovich, I. *Adv. Inorg. Biochem.* **1979,** *67,* 1. (b) Fee, J. A.; Valentine, J. S. In *Superoxide and Superoxide Dismutase*, Michelson, A. M., McCord, J. M., Fridovich, I., Eds.; Academic Press: New York, 1979; p 19.
(4) Radi, R.; Cosgrove, T. P.; Beckman, J. S.; Freeman, B. A. *Biochem. J.* **1993,** *290,* 51.
(5) See, for example: Valentine, J. S.; de Freitas, D. M. *J. Chem. Educ.* **1985,** *62,* 990.
(6) Huie, R. E.; Padmaja, S. *Free Radical Res. Commun.* **1993,** *10,* 221.
(7) Logager, T.; Sehested, K. *J. Phys. Chem.* **1993,** *97,* 6664.
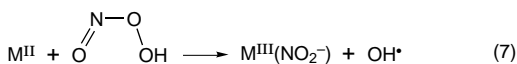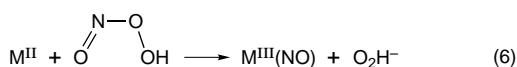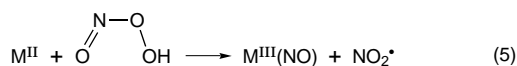
(8) (a) Beckman, J. S.; Chen, J.; Ischiropoulos, H.; Crow, J. P. *Methods Enzymol.* **1994,** *233,* 229. (b) Tsai, J.-H. M.; Harrison, J. G.; Martin, J. C.; Hamilton, T. P.; van der Woerd, M.; Jablonsky, M. J.; Beckman, J. S. *J. Am. Chem. Soc.* **1994,** *116,* 4115.
(9) Zhu, L.; Gunn, C.; Beckman, J. S. *Arch. Biochem. Biophys.* **1992,** *298,* 452.
(10) Ischiropoulos, H.; Zhu, L.; Beckman, J. S. *Arch. Biochem. Biophys.* **1992,** *298,* 446.
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(14) Edwards, J. O.; Plumb, R. C. *Prog. Inorg. Chem.* **1994,** *41,* 599. This review emphasizes the photochemistry of peroxynitrite and its transformations with inorganic coreagents.

$$\text{O=N(O)OH} + H^+ \longrightarrow [NO]^+ + H_2O_2 \qquad (2)$$
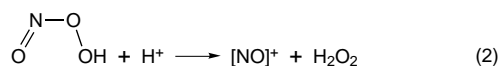
hydroxylating species, but homolysis (reaction 4), which would produce the unusually reactive hydroxyl radical, has been shown to be thermodynamically nonfeasible.[15]

$$\text{O=N(O)OH} + H^+ \longrightarrow HNO_2 + [OH]^+ \qquad (3)$$

$$\text{O=N(O)OH} \not\longrightarrow NO_2 + OH^\bullet \qquad (4)$$
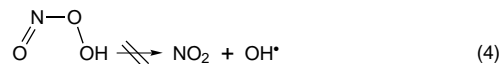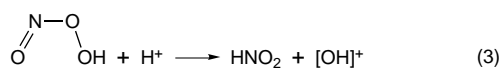
Additional modes are possible in the presence of transition metal ions. Reactions 5−7 entail oxidative changes at the metal

$$M^{II} + \text{O=N(O)OH} \longrightarrow M^{III}(NO) + NO_2^\bullet \qquad (5)$$

$$M^{II} + \text{O=N(O)OH} \longrightarrow M^{III}(NO) + O_2H^- \qquad (6)$$

$$M^{II} + \text{O=N(O)OH} \longrightarrow M^{III}(NO_2^-) + OH^\bullet \qquad (7)$$

center analogous to the familiar Fenton-type activation of peroxo compounds.[16] Each requires a metal featuring at least two accessible oxidation states differing by a single unit.

In still other instances, a metal center can activate the transfer of an electrophilic fragment to a reductant (designated R:) via preliminary coordination, but without a change in oxidation state (eqs 8 and 9), a route which is characteristic of oxyphilic d^0 centers such as Ti(IV) and Mo(VI).[17]

$$\text{O=N(O)O}-M + R: \longrightarrow R:O + M(O-N=O^-) \qquad (8)$$

$$\text{O=N(O)O}-M + R: \xrightarrow{H^+} R:N=O + M(OOH^-) \qquad (9)$$
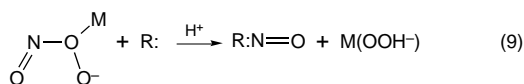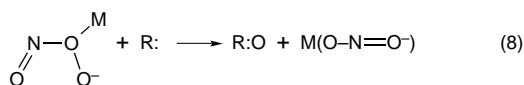
Reflecting the quickening of activity in this area, a flurry of investigations dealing with reactions of peroxynitrite has been reported. Among the inorganic coreagents have been NH₂-OH,[13a] Fe(CN)₆⁴⁻,[18] Ni^II(cyclam),[18] iodide,[13b] and cyanide.[13a] Organic substrates include thiols,[19] thioethers,[20] phenols,[11] 1,2-glycols,[21] and amino acids.[22]

This study deals with the reactions of peroxynitrite with a series of oxo-substituted anions of main group elements. Since each of these coreagents is generally taken to be a 2-unit reductant, paths featuring straightforward transfer of oxygen

Table 1. Stoichometries of the Reactions of Peroxynitrite (ONOO⁻) with Inorganic Reductants[a]

reductant (Red)	[ONOO⁻], mM	[Red], mM	μ, M	Δ[ONOO⁻], mM	Δ[Red]/ Δ[ONCO⁻]
As(III)	0.45	0.10	0.2	0.11	0.91
	0.45	0.20		0.21	0.95
	0.45	0.33		0.35	0.94
Sb(III)[b]	0.42	0.10	0.6 (NaClO₄)	0.11	0.91
	0.42	0.20		0.23	0.87
	0.42	0.30		0.34	0.88
Sn(II)	0.60	0.15	1.0 (NaCl)	0.13	1.15
	0.60	0.30		0.28	1.07
	0.60	0.45		0.42	1.07

[a] Reactions at 25 °C in 0.20 M NaOH; waiting period 2−5 min. [b] Added as potassium antimony(III) tartrate.

atoms might be anticipated. However, we have encountered some unexpected kinetic acidity patterns.

Experimental Section

Materials. All solutions were prepared with deionized water which had been treated by a Millipore-Q purification system. Sodium hypophosphite, sodium tartrate, antimony potassium *d*-tartrate, and the buffer components ACES (2-(2-acetamido)amino)ethanesulfonic acid), TAPS (3-[tris(hydroxymethyl)methylamino]-1-propanesulfonic acid), and CAPS (3-(cyclohexylamino)propanesulfonic acid) (all Aldrich products) were used as received, as were tin(II) chloride, sodium sulfite (MCB), and arsenic(III) oxide (Fisher).

Peroxynitrite solutions were prepared using slight modifications of literature methods.[15,18,23] Aliquots of 1.2 M H₂O₂ (in 1.0 M HClO₄) and 1.0 M NaNO₂ (in water) (10 cm³ each) were cooled to −2 °C and then quickly mixed. The reaction was immediately quenched by addition of 5 cm³ of cold 7.0 M NaOH. Unreacted H₂O₂ was removed by treatment with excess MnO₂, and the preparation was filtered. The filtrate was then chilled further until 30−40% had solidified, and the liquid phase was decanted. The iced phase, which contained the major portion of the contaminating salts, NaNO₂ and NaNO₃,[24] was discarded, and the yellow supernatant solution, which held the major portion of the peroxynitrite formed (0.2−0.3 M) was kept at −18 °C. Solutions were used for redox experiments no more than 14 days after their preparation. Stock solutions were standardized spectrophotometrically each day ($\epsilon_{302} = 1670$ M⁻¹ cm⁻¹).[6,18]

Stock solutions of As(III) were prepared by dissolving As₂O₃ in hot 0.010 M NaOH and then neutralizing with dilute HClO₄. Tin(II) solutions were prepared by dissolving SnCl₂ in air-free 0.2 M HCl which was also 1.0 M in NaCl. The latter solutions were kept under N₂ and standardized daily iodometrically.[25]

Stoichiometric Studies. Stoichiometries of the peroxynitrite reactions, each with this oxidant in excess, were determined in 0.2 M NaOH by adding deficient quantities of the reductant to a known concentration of the peroxynitrite, waiting 2−5 min, and then measuring the decrease in absorbance at 302 nm. These changes were compared to those occurring when peroxynitrite was treated with excess reductant. Results with As(III), Sb(III), and Sn(II) are summarized in Table 1. The stoichiometry of the slower reactions with hypophosphite and sulfite could not be determined in this manner since self-decomposition of the oxidant in the medium which was taken proceeded at a rate comparable to that of the redox reaction of interest.

Kinetic Studies. Rates were evaluated from measurements of absorbance decreases at 300 nm using a Beckman Model 5260 recording spectrophotometer or a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Temperatures were kept at 25.0 ± 0.5 °C. For reductions by As(III), Sb(III), and sulfite, ionic strength was maintained by addition of NaClO₄, whereas NaCl was

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(17) See, for example: Su, C.-C.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1973**, *12*, 337.
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(22) Ischiropoulos, H.; Zhu, L.; Chen, M.; Tsai, M.; Martin, J. C.; Smith, C. D.; Beckman, J. B. *Arch. Biochem. Biophys.* **1992**, *298*, 431.

(23) Halfpenny, E.; Robinson, P. L. *J. Chem. Soc. A* **1952**, 928.
(24) Both nitrite and nitrate were shown to be without significant effect on the stoichiometry and kinetics of the oxidations examined here when these anions were present at concentrations comparable to, or less than, that of peroxynitrite.
(25) Swift, E. H. *A System of Chemical Analysis*; Prentice-Hall: Englewood Cliffs, NJ, 1938; p 277.

used for reactions of Sn(II). Reductions by Sn(II) were carried out anaerobically, but those by As(III), Sb(III), sulfite, and hypophosphite were not significantly affected by exposure to air under our conditions. Acidities were regulated by measured quantities of the buffering acids and NaOH. For reductions with As(III), kinetic runs using the "biological buffers" ACES, TAPS, and CAPS were more successful than those using phosphate and carbonate systems. For reductions with antimony(III) tartrate, on the other hand, individual buffer-related kinetic effects were observed with the biological buffers, but such complications were minimal with phosphate and borate buffers provided excess tartrate (0.15 M) was present. For kinetic runs, solutions of the reductant and buffering acid were added to peroxynitrite in base, thus minimizing loss of the oxidant by self-decomposition[15,18] prior to mixing; pH values of the redox mixtures were checked after completion of the reactions. Conversions were first-order each in peroxynitrite and reductant but were generally carried out under pseudo-first-order conditions with the reductant in greater than 10-fold excess. Rate constants were obtained by nonlinear least-squares fitting to the relationship describing first-order decay. Values calculated from replicate runs agreed to better than 5%.

Precise measurements of the rate of the very slow reduction of peroxynitrite by hypophosphite ($H_2PO_2^-$) were seriously complicated by the self-decomposition of the oxidant. Even with [$H_2PO_2^-$] as great as 0.5 M, the loss of oxidant via decomposition constituted 30−40% of the total loss observed, at both high and low pH. Although attempts were made to correct for this component, rate constants for reduction by $H_2PO_2^-$ (0.12 M^{-1} s^{-1} at pH 8.8; 0.016 M^{-1} s^{-1} at pH 9.8; 0.004 M^{-1} s^{-1} at pH 10.4), which were estimated from initial rates, must be considered approximate. This reaction was not perceptibly catalyzed by the metal salts $NaReO_4$, $(NH_4)MoO_4$, Na_3VO_4, and $Cu(NO_3)_2$ (each added at the 10^{-4} M level). Moreover, reaction of peroxynitrite with phosphite (HPO_3^{2-}) was found to be immeasurably slow.

Results and Discussion

Each mole of peroxynitrite is seen (Table 1) to consume very nearly 1 mol of As(III), Sb(III), and Sn(II). Since each of these reductants is a 2e reagent, conversions are predominantly to nitrite in each case:

$$As(III)/Sb(III) \xrightarrow{ONOO^-} As(V)/Sb(V) + NO_2^- \quad (10)$$

$$Sn(II) \xrightarrow{ONOO^-} Sn(IV) + NO_2^- \quad (11)$$
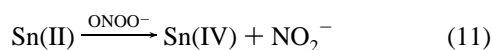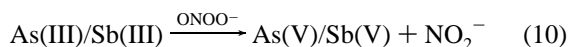
An analogous conclusion may be drawn for the (slow) reductions by hypophosphite and sulfite, for which stoichiometric data could not be obtained. The slight positive departures observed for Sn(II) may be reasonably attributed to consumption of this reductant by adventitious traces of O_2.

Rate data pertaining to the reactions of peroxynitrite with these reductants appear in Tables 2−4. The kinetic acidity pattern for As(III) (Table 2) exhibits a maximum near pH 7.7, with rate constants diminishing to low (but measurable) values at greater and lesser acidities. The bell-shaped curve reflecting this [H^+] dependence (Figure 1A) implies reaction components proceeding through three transition states, each featuring the two redox partners, but at different protonation levels, with the middle level much more reactive than the most basic and the most acidic. If the most rapid route is assigned to the combination ($H_2AsO_3^- + ONOOH$),[26] the rate may be expressed as eq 12, where K_a^O and K_a^R are the acidity constants for peroxynitrous acid and As(OH)$_3$, with k_1, k_2, and k_3 denoting rate constants for the three contributing paths: k_1 for ($ONO_2^- + H_2AsO_3^-$), k_2 for ($ONO_2H + H_2AsO_3^-$), and k_3 for (ONO_2H

(26) This route necessarily includes a contribution from the combination ($ONO_2^- + H_3AsO_3$). Since, however, redox reactions are generally favored by protonation of the oxidant and deprotonation of the reductant (rather than the reverse), the alternate combination may be assumed to predominate greatly.

Table 2. Kinetic Data for Reaction of Peroxynitrite with As(III)[a]

buffer	pH	[HA], mM[b]	[A⁻], mM[b]	$10^{-1}k_{obsd}$[d]
ACES	5.78	50.0	5.0	50 ± 2 (51)
	6.27	60.0	20.0	80 ± 4 (76)
	6.76	50.0	50.0	114 ± 4 (110)
	7.81	5.0	50.0	138 ± 4 (139)
TAPS	7.37	50.0	5.0	128 ± 5 (144)
	7.89	60.0	20.0	145 ± 8 (143)
	8.25	47.0	33.0	147 ± 5 (134)
	8.43	50.0	50.0	134 ± 4 (125)
	8.41	25.0	25.0	128 ± 4 (124)
	8.92	20.0	60.0	104 ± 2 (89)
	9.39	5.0	50.0	52 ± 1 (51)
CAPS	9.36	50.0	5.0	44 ± 1 (50)
	9.88	60.0	20.0	23 ± 1 (21)
	10.37	50.0	50.0	8.0 ± 0.3 (9.1)
	10.41	25.0	25.0	8.5 ± 0.3 (8.9)
	10.85	20.0	60.0	4.9 ± 0.2 (4.8)
	11.38	5.0	50.0	4.1 ± 0.2 (4.2)
none	12.0			2.7 ± 0.1 (2.7)
	13.3			2.3 ± 0.1 (2.6)

[a] Reactions were carried out at 25 °C and monitored at 300 nm; μ = 0.2 M (NaClO$_4$); [As^{III}] = 2.0−12 mM; [peroxynitrite] = 0.10 mM. [b] Buffering acid. [c] Buffering conjugate base. [d] Observed second-order constants, in M^{-1} s^{-1}; parenthetical values were calculated from eq 12, using parameters listed in Table 5.

Table 3. Kinetic Data for Reaction of Peroxynitrite with S(IV)[a]

buffer	pH	k_{obsd}[b]	k_{calcd}[c]
$H_2PO_4^- + HPO_4^{2-}$	5.20	$(2.7 ± 0.1) \times 10^4$	2.8×10^4
	5.80	$(1.84 ± 0.09) \times 10^4$	2.1×10^4
	6.30	$(1.12 ± 0.02) \times 10^4$	1.06×10^4
	6.85	$(3.0 ± 0.01) \times 10^3$	2.7×10^3
	7.10	$(1.27 ± 0.03) \times 10^3$	1.23×10^3
	7.55	272 ± 8	271
TAPS	7.65	159 ± 5	196
	8.40	22 ± 1	22
	9.15	3.2 ± 0.1	3.5
$HPO_4^{2-} + PO_4^{3-}$	10.40	0.25 ± 0.01	0.24
	10.85	0.095 ± 0.003	0.102
	11.50	0.059 ± 0.002	0.064
none	12.30	0.056 ± 0.002	0.051
	13.30	0.051 ± 0.002	0.049

[a] Reactions were carried out at 25 °C and monitored at 300 nm; μ = 1.0 M (NaClO$_4$); [S^{IV}] = 2.0−100 mM (added as Na$_2$SO$_3$); [peroxynitrite] = 0.1−0.5 mM. [b] Observed second-order rate constants in M^{-1} s^{-1}. [c] Second-order rate constants calculated from eq 12, using parameters in Table 5.

$$\text{rate} = [Ox][Red]\frac{k_1 K_a^O K_a^R + k_2 K_a^R[H^+] + k_3[H^+]^2}{(K_a^O + [H^+])(K_a^R + [H^+])} \quad (12)$$

+ H_3AsO_3). Refinement of these data in terms of eq 12 yields $k_1 = 25.7 ± 0.6$, $k_2 = (4.6 ± 0.9) \times 10^5$, and $k_3 = (3.2 ± 0.5) \times 10^2$ M^{-1} s^{-1}, with pK_a^O = 6.6 and pK_a^R = 9.1. The pK_a values are in agreement with those reported for peroxynitrous acid (6.5)[7] and H$_3$AsO$_3$ (9.09).[27] Varying the concentrations of buffer components while keeping their ratio (hence the pH of the medium) constant resulted in no rate changes, thus ruling out significant general- acid or general-base catalysis. Rate constants calculated using eq 12 are compared with observed values at the right of Table 2 and (on a logarithmic scale) in Figure 1.

The acidity pattern governing the reduction by sulfite (Table 3) features a region between pH 6 and 10 in which the variation in rate is somewhat steeper than that corresponding to a first-order [H^+] dependence. If paths involving three degrees of

(27) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1976; Vol. 4, p 132.
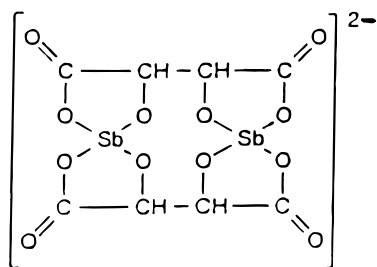
Table 4. Kinetic Data for the Reaction of Peroxynitrite with Sb(III)[a]

buffer	pH	[Sb(III)], mM[b]	$10^{-3}(k)_{obsd}$[c]
$H_2PO_4^- + HPO_4^{2-}$	5.95	1.0	4.0 ± 0.2 (4.2)
	5.95	5.0	4.0 ± 0.2 (4.2)
	6.50	1.0	6.4 ± 0.3 (6.1)
	6.80	1.0	9.7 ± 0.3 (9.4)
	7.49	1.0	20.6 ± 1.0 (18.8)
	7.58	1.0	21.4 ± 1.2 (20.5)
$H_3BO_3 + B(OH)_4^-$	8.00	5.0	24 ± 1 (28)
	8.21	1.0	29 ± 1 (31)
	8.62	1.0	34 ± 1 (34)
	9.08	1.0	34 ± 1 (35)
	9.41	1.0	35 ± 1 (35)
	9.95	1.0	30 ± 1 (33)
$HPO_4^{2-} + PO_4^{3-}$	9.98	1.0	29 ± 1 (33)
	10.98	1.0	18.1 ± 0.4 (18.4)
	11.70	1.0	9.2 ± 0.2 (8.5)
none	12.28	1.0	2.13 ± 0.04 (2.28)
	13.30	5.0	0.85 ± 0.03 (0.77)

[a] Reactions were carried out at 25 °C and were monitored at 300 nm; $\mu = 0.6$ M (NaClO$_4$); [peroxynitrite] = 1.0×10^{-4} M; [tartrate]$_{added}$ = 0.15 M. [b] Added as potassium antimony(III) tartrate. [c] Second order rate constants in M^{-1} s^{-1}; parenthetical values were calculated from eq 12, using parameters in Table 5.

protonation are again assumed, the [H$^+$]^2 term in eq 12 has become relatively more prominent than is the case with As(III) reductions. Treatment of these data, in conjunction with the reported[27] pK_a of HSO$_3^-$ (6.34), leads to the contributing rate constants listed in Table 5. Observed and calculated rates are compared in Figure 1B.

Because of the very low solubility of antimony(III) oxide in water, kinetic studies dealing with Sb(III) over a broad range of acidities require a soluble but slightly dissociated complex of this center. The familiar reagent potassium antimony(III) tartrate, in the crystalline state, has been shown to feature a binuclear tartrato-bridged anion (**I**) in which quadridentate

I

tartrate ligands form four five-membered rings with the two Sb atoms.[28] Kinetic data for the very rapid reduction of peroxynitrite by solutions of this complex are summarized in Table 4. The bell-shaped pH dependency (Figure 1C) resembles that for reductions by As(III) and may likewise be described by eq 12. Kinetic parameters assigned to the three protonation levels in this system have been included in Table 5.

Values of k_{Sb} in HPO$_4^{2-}$-buffered solutions are sensitive also to [tartrate]$_{added}$. Representative data, pertaining to pH 6.8, appear in Table 6. Rate constants are consistent with a preliminary equilibrium of the type (13), applying to exchange

$$Sb(HPO_4) + T^{2-} \overset{Q}{\rightleftharpoons} Sb(T^{2-}) + HPO_4^{2-} \qquad (13)$$
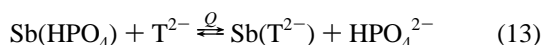
(28) (a) Gress, M. E.; Jacobson. *Inorg. Chim. Acta* **1974**, *8*, 209. (b) For an earlier study of aqueous solutions of this complex, see: Anderegg, G.; Malik, S. *Helv. Chim. Acta* **1970**, *53*, 577.
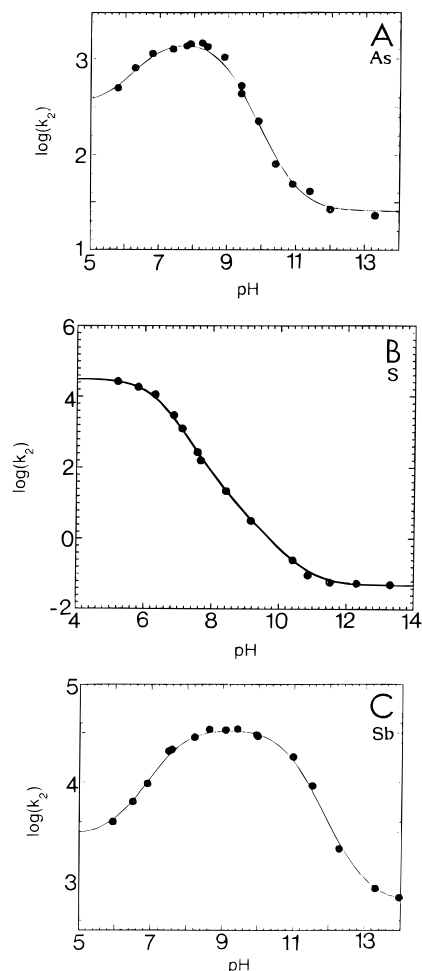
Figure 1. Variation, with pH, of the observed second-order rate constants (plotted as log k_2) for reactions of peroxynitrite (25 °C) with As(III) (A; $\mu = 0.2$ M), S(IV) (B; $\mu = 1.0$ M), and Sb(III) (C; $\mu = 0.6$ M, [tartrate] = 0.15 M). [Red] = 1.0–100 mM; [O=NOO$^-$] = 1.0×10^{-4}; $\lambda = 302$ nm. The supporting electrolyte was NaClO$_4$. The solid circles denote observed values, whereas the solid lines are those calculated using eq 12 and the kinetic parameters listed in Table 5.

Table 5. Kinetic Parameters for Oxidations by Peroxynitrite[a]

$$\text{rate} = [Ox][Red]\frac{k_1 K_a^O K_a^R + k_2 K_a^R[H^+] + k_3[H^+]^2}{(K_a^O + [H^+])(K_a^R + [H^+])}$$

Red	As(III)	Sb(III)[b]	S(IV)
pH range	5.78–13.3	5.95–13.3	5.20–13.3
μ, M	0.2	0.6	1.0
k_1[c]	25.7 ± 0.6	$(6.0 \pm 0.3) \times 10^2$	$(4.9 \pm 0.1) \times 10^{-2}$
k_2[c]	$(4.6 \pm 0.9) \times 10^5$	$(9.5 \pm 0.7) \times 10^7$	$(13.5 \pm 0.7) \times 10^2$
k_3[c]	$(3.2 \pm 0.5) \times 10^2$	$(3.4 \pm 0.2) \times 10^3$	$(3.1 \pm 0.1) \times 10^4$
pK_a^O	6.6	7.1	6.5
pK_a^R	9.1	11.0	6.34[d]
$E°$, V (pH 9.0)[e]	-0.12	> -0.09	-0.55

[a] Reactions were run at 25 °C; supporting electrolyte was NaClO$_4$. Parameters resulted from nonlinear least-squares refinement of data in Tables 2–4 in terms of eq 12. [b] Solutions were prepared from potassium antimony(III) tartrate and were 0.15 M in added tartrate. [c] Rate constants (in M^{-1} s^{-1}) pertain to routes at three protonation levels, with k_1 referring to the least protonated path (see text). [d] Reference 27. [e] Reference 30.

at just one coordination position, with the phosphate-rich and tartrate-rich reductants, Sb(HPO$_4$) and Sb(T^{2-}), then reacting at individual specific rates k_P and k_T. This competition between paths leads to eq 14. Refinement in accordance with (14) leads to $k_P = (3.4 \pm 0.1) \times 10^4$, $k_T = (6.7 \pm 0.9) \times 10^3$ M^{-1} s^{-1},

Table 6. The Peroxynitrite−Sb(III) Redox Reaction: Effect of Added Tartrate[a]

[tartrate]$_{added}$, M[b]	$10^{-3} k_{obsd}$[c]	$10^{-3} k_{calcd}$[c,d]
0.0010[e]	34 ± 2	33
0.010[e]	24.9 ± 1.2	26.3
0.010[f]	24.8 ± 0.6	26.3
0.030[f]	18.8 ± 0.8	19.2
0.050[f]	16.6 ± 0.8	15.9
0.150[f]	10.2 ± 0.5	10.6

[a] Reactions were carried out at 25.0 °C and pH 6.8. $[H_2PO_4^-]$ = $[HPO_4]^{2-}$ = 0.050 M; [peroxynitrite] = 1.0×10^{-4} M; $[Sb^{III}]$ = 1.0×10^{-3} M. [b] Added as sodium tartrate. [c] Rate constants in $M^{-1} s^{-1}$. [d] Values calculated from eq 14 in text, taking k_P as $3.4 \times 10^4 M^{-1} s^{-1}$, k_T = $6.7 \times 10^3 M^{-1} s^{-1}$, and Q = 2.0. [e] μ = 0.2 M (NaClO$_4$). [f] μ = 0.6 M (NaClO$_4$).

$$k_{obsd} = \frac{k_P[HPO_4^{2-}] + k_T Q[T^{2-}]}{[HPO_4^{2-}] + Q[T^{2-}]} \quad (14)$$

and $Q = 2.0 \pm 0.4$. The last value appears to be nearly invariant with ionic strength within the range 0.2−0.6 M.

Reduction by Sn(II) was still more rapid but could be examined only within the pH range 10.15−13.0. Limited data (five acidities) for this reaction are consistent with the rate law (15). At the other extreme, reactions with hypophosphite are

$$\text{rate} = [Ox][Sn^{II}](1.4 \times 10^5 + 9/[OH^-]) \, M^{-1} \, s^{-1}$$
$$(\mu \, 1.0 \, M) \quad (15)$$

so slow that self-decomposition of the oxidant competes seriously with the redox process. Approximate rate constants are 4.2 $M^{-1} s^{-1}$ at pH 6.5 and 0.12 $M^{-1} s^{-1}$ at pH 8.8 (25 °C, μ = 1.0 M).

The acidity patterns for reductions by As(III) and tartrate-bound Sb(III) within the same pH range (Table 5) are seen to be similar. The k_2 component (pertaining to interaction of the protonated oxidant and deprotonated reductant) predominates in both, with the ratio k_{Sb}/k_{As} = 10^1–10^2 for each term. Since the structure of crystalline reductant **I** does not feature acidic protons, we suspect that the dinuclear complex is largely dissociated when dissolved, yielding a mononuclear anion having an Sb(III)-bound water which may function as a weakly acidic (pK_a = 11.0) center. Both Anderegg[28b] and Riehlen[29] favor a bicyclic species of type **II**. The straightforward reactant

II
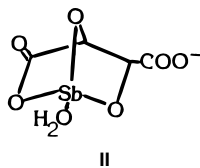
ratios and reproducible kinetic acidity patterns observed for the reactions of peroxynitrite with the 2e reductants As(III), Sb(III), and Sn(II) contrast with the behavior of this oxidant toward the single-electron donors I^-, $Fe(CN)_6^{4-}$, and Ni^{II}(cyclam), which exhibit nonintegral and irregular stoichiometries.[18] Reactions in the present study may be assumed to proceed through O-bridged precursor complexes, for outer-sphere transfers of two oxidation units have not yet been reported.

Correlations of the relative reactivities of the reducing centers considered here are complicated by the plurality of reaction paths available to each. Qualitatively, however, these reductants clearly conform to the series

$$Sn^{II} > Sb^{III} > As^{III} > S^{IV} >> P^I > P^{III}$$
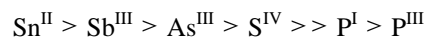
Driving forces for oxo-transfer reactions have been considered by Holm,[30] who has constructed thermodynamic scales of "oxo-transfer half-reactions" analogous the usual potential scale for electron transfers, but these do not yet include Sb(III) and P(I) derivatives and, in any case, do not deal with reaction rates. Moreover, there is no obvious relation between observed reactivities and formal potentials for the two-unit changes, approximate values of which at pH 9.0 (near the center of the pH ranges examined) are included in Table 5.[31]

If the rapid oxidations in this series are taken to proceed via nucleophilic substitution by the reducing center, E:, at the terminal peroxo oxygen of the oxidant (e.g., eq 16), it is
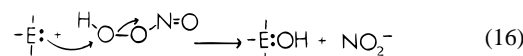
reasonable to attribute the observed trend in reactivities to the relative availability of the electron-rich site of the reductant. This is most accessible when associated with a large center bearing a small positive formal charge but becomes progressively less so as the nucleophilic center becomes smaller (and more highly charged), allowing it to nestle more snugly in the polyhedron of oxy groups comprising its first coordination sphere. A closely analogous trend has been reported for oxidations by bromite (BrO_2^-).[32] As extreme examples, the oxidation of hypophosphite ($H_2PO_2^-$) is found to be unusually slow and that of phosphite (HPO_3^-) undetectable, despite the strongly reducing formal potentials of these anions. The substitution-inert character of the coordinatively saturated P(I) and P(III) centers in these reductants militates against formation of the precursor required for rapid redox.

Perhaps the least expected facet of this study is the relatively high rate associated with the protonated form of the S(IV) reductant (k_3 in Table 5). The prominence of this component probably reflects the decrease in coordination number (and the attendant increase in availability of the nucleophilic site) as the HSO_3^- anion is converted, via protonation, to H_2O and SO_2. The latter (loosely solvated) molecule is recognized to be the preponderant S(IV) species in acidic aqueous solutions.[33,34]

(29) Riehlen, H.; Hezel, E. *Justus Liebigs Ann. Chem.* **1931**, *487*, 213.

(30) (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (b) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571.
(31) Formal potentials pertaining to 2e oxidations at pH 9.0 were estimated from compilations by: (a) Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solutions*; Marcel Dekker: New York, 1985. (b) Latimer, W. M. *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952. Only a lower limit for Sb(III) is tabulated, since ligation by tartrate would be expected to make its potential less negative. Additional estimated values: $H_2PO_2^-$, −1.20 V; HPO_3^{2-}, −0.82 V; Sn^{II} (pH 11), −0.67 V.
(32) Jhanji, A. K.; Gould, E. S. *Int. J. Chem. Kinet.* **1991**, *23*, 229.
(33) See, for example: Kolbe, K. E.; Hellwig, K. C. *Ind. Eng. Chem.* **1955**, *47*, 1116.
(34) With respect to our eq 16, a reviewer asks why we favor transfer of the "terminal" rather the internal oxygen of peroxynitrous acid. Since the transferred oxygen is acting in an electrophilic capacity, its action should be favored by protonation. Moreover, breakage in the manner indicated is consistent with the formation of nitrite.