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Reactions of the nitrosodisulfonate anion radical with s^2 reducing centers †

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The nitrosodisulfonate anion radical, $^\bullet NO(SO_3)_2^{2-}$, a single electron oxidant, reacts rapidly with the $2e^-$ metal-based reductants, Sn(II) and Ge(II) ($k = 10^4$–10^5 M^{-1} s^{-1}), less rapidly with sulfite ($k = 0.24$ M^{-1} s^{-1}) and very slowly (10^{-3}–10^{-2} M^{-1} s^{-1}) with the nonmetal-based donors, $H_2AsO_3^-$, Sb^{III}(tartrate), hyponitrite, and hypophosphite. Reductions yield the product $HON(SO_3)_2^{2-}$. Kinetic profiles exhibit no irregularities attributable to generation or loss of a transient on a time scale comparable to the principal conversion, indicating that rates are determined by the original $1e^-$ transfer and that the "follow-up" step is rapid. Reductions by sulfite (pH 4.2–8.6) are retarded by partial conversion to HSO_3^-, whereas those by Sn(II) and Ge(II) (in 0.1–1.0 M H^+) are accelerated by H^+. Rates for Sn(II) are markedly enhanced by chloride, suggesting stabilization of intervening chloro-ligated Sn(III).

Introduction

In line with our extended interest in electron-transfer reactions involving radicals and radical ions in aqueous media,[2] we have been particularly drawn to the nitrosodisulfonate radical anion, $[^\bullet NO(SO_3)_2]^{2-}$, one of the simplest and most stable of such odd electron species. This is formed by the nearly complete homolysis of its dimer, Fremy's salt, when the latter is dissolved in polar solvents [eqn. (1)][3] and has been used as an oxidant for a wide variety of organic[4] and inorganic[5] compounds. Mechanistic studies have been reported for its reactions with nitrous acid,[6] sulfite,[7] and $Mn(acac)_2$,[8] and for its decomposition in aqueous solution.[9]

$$\underset{\text{“Fremy's salt”}}{(K^+)_2[(O_3S)_2NO\text{-}ON(SO_3)_2]^{4-}} \rightarrow 2[^\bullet ON(SO_3)_2]^{2-} + 4K^+ \quad (1)$$

Little attention has thus far been directed to the interaction of this radical with reductants which are characteristically considered to undergo two-electron transactions. The present study deals mainly with such "non-complementary" redox systems. The recently described preparation of aqueous solutions of Ge(II)[10] allows us to include a less usual oxidation state. The ease with which these reductants react with this odd-electron oxidant may be taken to reflect their capacity to donate electrons in separate steps. We observe differences in such versatility, calling to mind those perceived in earlier experiments involving Cr(VI),[11] but the present contrasts are more marked.

Experimental

Materials

Solutions were prepared from Millipore water which had been boiled for two hours and then sparged with pure argon for two hours more to remove O_2. Sodium sulfite, tin(II) chloride, germanium dioxide, sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), sodium hyponitrite ($Na_2N_2O_2 \cdot xH_2O$)], iron(II) ammonium sulfate, potassium antimonyl tartrate hydrate [$K(SbO)C_4H_4O_6 \cdot xH_2O$], and the buffer components ACES (2-(2-acetamido)-aminoethanesulfonic acid) and TAPS {3-[tris(hydroxymethyl)-methylamino]-1-propanesulfonic acid} (all Aldrich products) were used as received.

Potassium nitrosodisulfonate dimer (Fremy's salt) was prepared as orange microcrystals as described by Yamada[4,12] and kept at −18 °C. Concentrations of the anion radical in solution were determined spectrophotometrically (ε_{540} = 20.8 M^{-1} cm^{-1}).[13]

Tin(II) solutions were prepared by dissolving $SnCl_2$ in deareated aqueous HCl–NaCl and centrifuged before kinetic experiments. They were analyzed spectrophotometrically at 353 nm by reaction with I_3^-.[14] Germanium(II) solutions in HCl were prepared and analyzed as described by Babich *et al.*[10]

Stoichiometric studies

Stoichiometries of the reduction of nitrosodisulfonate were examined at 540 nm. Measured deficient quantities of each reductant were added to a known excess of the oxidant. Decreases of absorbance were compared to those resulting from addition of excess reductant. This procedure was not applicable to the very slow reactions of hyponitrite, hypophosphite, As(III), and Sb(III); in these cases, decomposition of nitrosodisulfonate competed with the redox reactions of interest. Results are summarized in Table 1.

Kinetic experiments

Reactions, under argon, were generally examined at or near 540 nm, using either a Shimadzu-1601 instrument or a Durum-Gibson stopped flow spectrophotometer interfaced with an OLIS computer system. Temperatures were kept at 22.0 ± 0.5 °C. For reductions by Ge(II) and Sn(II), ionic strength was regulated by addition of HCl/NaCl/$NaNO_3$. Reactions by Sn(II), Ge(II) and Fe(II) were too rapid for pseudo-first order measurements, even with stop flow, but rates could be estimated under second-order conditions.[13] The slower reductions by sulfite, hypophosphite, As(III), antimony(III) tartrate, and hyponitrite were examined with the reductant in greater than tenfold excess, and rate constants were evaluated by nonlinear least-squares fittings to the relationship describing exponential decay. All reactions were first-order in the two redox partners. Of the slower reductants, only sulfite exhibited significant kinetic acidity dependence within the range examined.

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Table 1 Stoichiometries of reductions of ${}^{\bullet}\mathrm{ON(SO_3)_2}^{2-}$ (${}^{\bullet}$NDS)[a]

Reductant (Red)	[Red]/mM	[${}^{\bullet}$NDS]/mM	Δ[${}^{\bullet}$NDS][b]/mM	Δ[${}^{\bullet}$NDS]/Δ[Red]
$\mathrm{SO_3}^{2-}$ [c]	1.99	35.9	3.82	1.92
	3.95	31.9	7.70	1.95
	7.79	31.9	15.1	1.94
Ge(II)	2.73	23.9	5.34	1.96[d]
	2.66	13.4	5.20	1.95[d]
	3.37	8.29	6.79	2.01[e]
	2.62	7.96	5.15	1.97[e]
Sn(II)	1.92	9.43	3.73	1.94[f]
	1.86	16.7	3.64	1.96[f]
	2.21	5.29	4.30	1.95[g]
	2.78	5.73	5.50	1.96[g]
Fe(II)[h]	4.24	9.86	3.91	0.92
	8.38	9.98	7.72	0.92
	3.83	16.7	3.66	0.95
	4.76	16.7	4.56	0.95

[a] Reactions were carried out at 22.0 ± 0.5 °C. Nitrosodisulfonate (${}^{\bullet}$NDS) was added as its dimeric potassium salt (Fremy's salt). [b] Determined spectrophotometrically at 540 nm (ε = 20.8 $\mathrm{M^{-1}\ cm^{-1}}$), and corrected for self-decomposition of ${}^{\bullet}\mathrm{NO(SO_3)_2}^{2-}$. [c] Reactions in 0.01 M NaOH/ 0.50 M $\mathrm{NaNO_3}$. [d] Reactions in 0.5 M NaOH/0.8 M NaCl. [e] Estimated from kinetic curves in 1.0 M HCl/1.0 M NaCl. [f] Reactions in 0.1 M NaOH/1.0 M NaCl. [g] Estimated from kinetic profiles in 0.2 M HCl/0.8 M NaCl. [h] Reactions in acetate buffer (pH 4.30) containing 20 mM $\mathrm{Na_4EDTA}$; isosbestic point at 464 nm.

Results

From our stoichiometric studies (Table 1) we see that the nitrosodisulfonate radical anion reacts quite cleanly with sulfite, tin(II), and germanium(II), and also with iron(II) (a one-electron reductant included for comparison). In each case, the observed mole ratio indicates that the reduction product is hydroxylaminedisulfonate, $\mathrm{HON(SO_3)_2}^{2-}$ [eqns. (2) and (3)]:

$$\mathrm{Sn(II)} + 2{}^{\bullet}\mathrm{ON(SO_3)_2}^{2-} + 2\mathrm{H}^+ \longrightarrow \mathrm{Sn(IV)} + 2\mathrm{HON(SO_3)_2}^{2-} \quad (2)$$

$$\mathrm{Fe(II)} + {}^{\bullet}\mathrm{ON(SO_3)_2}^{2-} + \mathrm{H}^+ \longrightarrow \mathrm{Fe(III)} + \mathrm{HON(SO_3)_2}^{2-} \quad (3)$$

Moreover, the close approach to 2 : 1 stoichiometry in the reduction by sulfite rules out significant conversion to dithionate, $\mathrm{S_2O_6}^{2-}$, as has been encountered in several reactions with $1\mathrm{e}^-$oxidants.[16]

Kinetic data for reductions by S(IV) in buffered solutions (pH 4.2–8.6), summarized in Table 2, show the reaction to be accelerated by increases in basicity. Since the oxidant features no acidic center having a pK_A in the range examined, this dependency is attributed to deprotonation of $\mathrm{HSO_3}^-$ [eqn. (4)];

$$\mathrm{HSO_3}^- \rightleftarrows \mathrm{SO_3}^{2-} + \mathrm{H}^+ \quad K_{HA} = 5 \times 10^{-7}\ (\mu = 1.0\ \mathrm{M})^{17} \quad (4)$$

Rates are correlated by eqn. (5)

$$(k)_{\mathrm{obsd}} = \frac{-\mathrm{d}[{}^{\bullet}\mathrm{NDS}]/\mathrm{d}t}{[{}^{\bullet}\mathrm{NDS}][\mathrm{S^{IV}}]} = \frac{k_A K_{HA} + k_{HA}[\mathrm{H}^+]}{K_{HA} + [\mathrm{H}^+]} \quad (5)$$

where k_A and k_{HA} are kinetic contributions from $\mathrm{SO_3}^{2-}$ and $\mathrm{HSO_3}^-$. Refinement of data in terms of (5) yields k_A = (0.236 ± 0.007) $\mathrm{M^{-1}\ s^{-1}}$ and k_{HA} = (0.050 ± 0.003) $\mathrm{M^{-1}\ s^{-1}}$. Calculated and observed rates are compared at the right of Table 2. As expected, conversion of $\mathrm{HSO_3}^-$ to $\mathrm{SO_3}^{2-}$ makes it a more effective donor, but the effect is modest. The value of k_A, representing the limiting rate at high basicities, lies slightly above 0.18 $\mathrm{M^{-1}\ s^{-1}}$ recorded by Li and Ritter[7] for this reaction in 1.0 M NaOH. Note that the earlier study did not include pH variation and was carried out under conditions where hydrolytic degradation competes significantly with the redox transformation.

Table 2 Kinetic data for the reduction of nitrososodisulfonate (${}^{\bullet}$NDS) by sulfite[a]

pH	K^b/$\mathrm{M^{-1}\ s^{-1}}$	pH	k^b/$\mathrm{M^{-1}\ s^{-1}}$
4.20	0.048 (0.051)	6.88	0.22 (0.20)
4.57	0.054 (0.053)	7.05	0.23 (0.21)
4.97	0.057 (0.058)	7.32	0.26 (0.22)
5.42	0.073 (0.071)	7.85	0.19 (0.23)
5.88	0.109 (0.101)	8.05	0.20 (0.23)
6.25	0.161 (0.137)	8.24	0.22(0.23)
6.52	0.169 (0.166)	8.44	0.24 (0.23)
6.69	0.183 (0.182)	8.60	0.23 (0.24)

[a] Reactions were carried out at 22.0 ± 0.5 °C, μ = 1.0 M ($\mathrm{NaNO_3}$); $[\mathrm{S(IV)}]_{\mathrm{total}}$ = 32.0 mM; [NDS${}^{\bullet}$] = 5.00 mM. Solutions were buffered with HOAc/$\mathrm{OAc^-}$, TAPS, or ACES. [b] Parenthetical values were obtained from rate law (5), taking K_{HA} as 5 × 10^{-7}, k_{HA} as 0.050 $\mathrm{M^{-1}\ s^{-1}}$, and k_A as 0.236 $\mathrm{M^{-1}\ s^{-1}}$.

Kinetic data for the much more rapid reductions by Sn(II) and Ge(II) are summarized in Table 3. These reactions were carried out at higher acidities, and with chloride added, to avoid precipitation of metal hydroxides, which occurs in the pH range used for the S(IV) studies. Reductions by both dipositive centers are accelerated by H^+, but less markedly than corresponds to a direct [H^+]-proportionality, and both are catalyzed by chloride with the kinetic dependence particularly steep for Sn(II).

Dipositive tin undergoes partial anation by Cl^- at several ligation levels;[17]

$$\mathrm{Sn^{II}} + \mathrm{Cl}^- \rightleftarrows \mathrm{SnCl}^+\ (K_1 = 11.2) \quad (6)$$

$$\mathrm{Sn^{II}} + 2\mathrm{Cl}^- \rightleftarrows \mathrm{SnCl_2}\ (K_2 = 32) \quad (7)$$

$$\mathrm{Sn^{II}} + 3\mathrm{Cl}^- \rightleftarrows \mathrm{SnCl_3}^-\ (K_3 = 14) \quad (8)$$

Rates for tin(II) reductions conform to rate law (9),

$$(k)_{\mathrm{obsd}} = \frac{-\mathrm{d}[{}^{\bullet}\mathrm{NDS}]/\mathrm{d}t}{[{}^{\bullet}\mathrm{NDS}][\mathrm{Sn^{II}}]} = \frac{K_3[\mathrm{Cl}^-]^3(k_0 + k_H[\mathrm{H}^+])}{1 + K_1[\mathrm{Cl}^-] + K_2[\mathrm{Cl}^-]^2 + K_3[\mathrm{Cl}^-]^3}$$

Table 3 Kinetic data for reactions of nitrosodisulfonate ($^{\bullet}$NDS) with tin(II) and germanium(II)[a]

Reductant (Red)	[Red]/mM	[$^{\bullet}$NDS]/mM	[H^+]/M	[Cl^-]/M	$10^{-4}\,k^b/M^{-1}\,s^{-1}$
Sn(II)	3.24	6.73	0.10	1.00	0.46 (0.48)
	3.24	6.73	0.30	1.00	0.96 (0.96)
	3.24	6.73	0.40	1.00	1.14 (1.20)
	3.24	6.73	0.50	1.00	1.43 (1.44)
	2.16	4.54	1.00	1.00	2.66 (2.64)
	2.43	5.29	0.20	0.20	0.077 (0.071)
	3.41	7.45	0.20	0.40	0.21 (0.23)
	3.05	6.73	0.20	0.60	0.43 (0.40)
	2.43	5.29	0.20	0.80	0.58 (0.57)
	2.70	6.01	0.20	1.00	0.73 (0.72)
Ge(II)	1.61	7.84	0.30	1.00	3.3 (3.2)
	2.12	7.84	0.40	1.00	3.5 (3.5)
	2.48	7.84	0.50	1.00	3.8 (3.8)
	2.60	5.07	0.80	1.00	4.7 (4.7)
	2.60	5.07	1.00	1.00	5.3 (5.3)
	2.30	6.61	0.50	0.50	4.2 (4.1)
	2.30	8.17	0.50	0.70	3.9 (4.0)
	2.30	7.45	0.50	0.80	4.0 (3.9)
	2.30	6.30	0.50	0.90	3.9 (3.9)
	2.30	7.79	0.50	1.00	3.8 (3.8)

[a] Reactions were carried out at 22.0 ± 0.5 °C, $\mu = 1.0$ M ($HCl/NaCl/NaNO_3$). [b] Second-order rate constants evaluated as described by Espenson.[15] Parenthetical values were calculated from eqns. (9) and (10) and parameters in Table 4.

Table 4 Rate laws and kinetic parameters for reductions of nitrosodisulfonate ($^{\bullet}$NDS)[a]

Red	Medium	Rate law	Eqn. no.	Parameters
SO_3^{-2}	pH 4.2–8.6	$[^{\bullet}NDS][Red]\dfrac{k_A K_{HA} + k_{HA}[H^+]}{K_{HA} + [H^+]}$	(5)	$k_A = 0.236 \pm 0.007\ M^{-1}\,s^{-1}$ $k_{HA} = 0.050 \pm 0.003\ M^{-1}\,s^{-1}$ $K_{HA} = 5 \times 10^{-7}$
Sn^{II}	$[H^+] = 0.1–1.0$ M $[Cl^-] = 0.2–1.0$ M	$\dfrac{[^{\bullet}NDS][Red]K_3[Cl^-]^3(k_0 + k_H[H^+])}{1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3}$	(9)	$K_1 = 11.2$; $K_2 = 32$; $K_3 = 14$ $k_0 = (1.0 \pm 0.3) \times 10^4\ M^{-1}\,s^{-1}$ $k_H = (1.0 \pm 0.2) \times 10^5\ M^{-2}\,s^{-1}$
Ge^{II}	$[H^+] = 0.3–1.0$ M $[Cl^-] = 0.5–1.0$ M	$[^{\bullet}NDS][Red]\dfrac{k_0 + k_H[H^+]}{1 + K_{Cl}[Cl^-]}$	(10)	$k_0 = (2.8 \pm 0.1) \times 10^4\ M^{-1}\,s^{-1}$ $k_H = (3.6 \pm 0.1) \times 10^4\ M^{-2}\,s^{-1}$ $K_{Cl} = 0.20$
Fe^{II}	20 mM EDTA pH 4.5	$k[^{\bullet}NDS][Red]$	(13)	$k = (3.6 \pm 0.1) \times 10^4\ M^{-1}\,s^{-1}$
As^{III}	0.1 M NaOH		(13)	$k = 1.2 \times 10^{-3}\ M^{-1}\,s^{-1}$
Sb^{III}	pH 7,[b] (TAPS)		(13)	$k = 1.3 \times 10^{-2}\ M^{-1}\,s^{-1}$
$N_2O_2^{-2}$	pH 12		(13)	$k = 1.6 \times 10^{-2}\ M^{-1}\,s^{-1}$
$H_2PO_2^-$	pH 3.8–8.5		(13)	$k = 0.010–0.012\ M^{-1}\,s^{-1}$

[a] Reactions at 22.0 ± 0.5 °C, $\mu = 1.0$ M ($HCl/NaCl/NaNO_3/NaOH$). [b] Sb(III) added as tartrate complex.

in which the terms in the denominator describe speciation of the reductant and k_0 and k_H respectively to kinetic contributions by nonprotonated and protonated paths. Refinement of data, (using literature values of K_1 and K_2),[17] yields $k_0 = (1.0 \pm 0.3) \times 10^4\ M^{-1}\,s^{-1}$, $k_H = (1.0 \pm 0.2) \times 10^5\ M^{-2}\,s^{-1}$, and $K_3 = (1.4 \pm 0.4) \times 10$.

Reductions by Ge(II) are much less sensitive to alterations in medium. Rates vary in accord with rate law (10);

$$(k)_{obsd} = \frac{-d[^{\bullet}NDS]/dt}{[^{\bullet}NDS][Ge^{II}]} = \frac{k_0 + k_H[H^+]}{1 + K_{Cl}[Cl^-]} \qquad (10)$$

here k_0 and k_H again pertain respectively to acid-independent and $[H^+]$-proportional kinetic components and the denominator describes the partition of Ge(II). Since the predominant Ge(II) species in this medium is reported to be $GeCl_3^-$,[18] K_{Cl} (earlier estimated as 0.20)[19] may be taken to reflect slight conversion to unreactive $GeCl_4^{2-}$. Refinement yields $k_0 = (2.8 \pm 0.1) \times 10^4$ and $k_H = (3.6 \pm 0.1) \times 10^4\ M^{-2}\,s^{-1}$.

Rate laws and kinetic parameters are summarized in Table 4. Included also, for comparison, are the 1e$^-$ donor, Fe(II), and the very slowly reacting centers, As(III), antimony(III) tartrate, hyponitrite, and hypophosphite.

Discussion

The most notable result of this study is the ease with which the metal center reductants Sn(II) and Ge(II) react with the radical oxidant, in contrast to the sluggish action of the nonmetal-based states, As(III), Sb(III), and P(I). Rates with Sn(II) and Ge(II) (10^3–$10^4\ M^{-1}\,s^{-1}$) fall near the rapid end of the stopped-flow range, whereas the nonmetal rates (10^{-3}–$10^{-2}\ M^{-1}\,s^{-1}$) are so low that measurement is complicated by self-decomposition of the oxidant. The selectivity of $^{\bullet}$NDS toward our donors is thus quite different from that observed for reductions of peroxynitrite at high pH,[20] conversions which are taken to proceed through oxygen atom transfer.

Reactions of each two-electron center requires a pair of transactions involving the radical, but kinetic profiles of these reactions exhibit no irregularities attributable to generation or consumption of an intermediate species on a time scale comparable to the principal transformation. We infer then that the observed rates are determined by the initial transfer and that the "follow-up" step is rapid and therefore kinetically silent; *e.g.*, for Ge^{II}:

$$\mathrm{Ge^{II}} + {}^{\bullet}\mathrm{NO(SO_3)_2}^{2-} \longrightarrow :\mathrm{NO(SO_3)_2}^{3-} + \mathrm{Ge^{III}} \quad (11)$$

$$\mathrm{Ge^{III}} + {}^{\bullet}\mathrm{NO(SO_3)_2}^{2-} \longrightarrow :\mathrm{NO(SO_3)_2}^{3-} + \mathrm{Ge^{IV}} \ \text{(rapid)} \quad (12)$$

Reductions by S(IV) are retarded by increases in acidity, whereas those by Sn(II) and Ge(II) are accelerated. This difference in response mainly reflects pH ranges where the reactions were carried out. At pH 4–9, protonation converts a portion of added sulfite to uninegative HSO_3^-, a less effective reducing species. [H$^+$]-proportional increases with Sn(II) and Ge(II) at pH 0–1 are best attributed to partial protonation of our oxidant, an effect already reported[5b] for the $^{\bullet}$NDS–$Fe(CN)_6^{4-}$ reaction. Since there is no hint of kinetic saturation in the pH range examined, the protonated form can constitute only a minor fraction of the total, and pK_A must fall below -1. The bimolecular specific rate for reduction of the protonated radical by Sn(II) (obtained by multiplying k_H by K_A) then exceeds 10^6 M^{-1} s^{-1}.

The very strong [Cl$^-$]-dependence observed for the Sn(II) reaction [eqn. (9)] points to a transition state with three chloro ligands. A favored path involving $SnCl_3^-$ probably reflects structural resemblance to a Sn(III) intermediate $Sn^{III}Cl_3(H_2O)_3$, a similarity which should lower the Franck–Condon barrier to the initial electron transfer act. Evidence for analogous stabilization of a Sn(III) transient in Co(III)–Sn(II) systems at high [Cl$^-$] has been described by Wetton and Higginson.[21] Why the $^{\bullet}$NDS–Ge(II) reaction is not similarly facilitated at high [Cl$^-$] remains a puzzling point.

For the rapid reductants in this series (SO_3^{-2}, Sn^{II}, and Ge^{II}), electrons to be transferred are nonbonding in character and may be considered to be more accessible than those in the very slowly reacting anion, $H_2PO_2^-$, in which all valence electrons of P(I) are involved in covalent bonding to hydrogen or oxygen.

Reagents $H_2AsO_3^-$, Sb^{III}(tartrate), and hyponitrite are oxidized slowly, despite the presence of nonbonding electrons at the reducing centers. Their sluggishness may be related to their potentials. Recorded 2e$^-$ values (As^{III}, -0.67 V; Sb^{III}, 0.36 V; $HN_2O_2^-$, -0.14 V)[22] lie well below that reported[5c] for 1e$^-$ oxidation of $^{\bullet}$NDS (0.64 V at pH 7), and thus favor reaction. However, past studies of stepwise removal of electrons from 2e$^-$ donors[23] indicate that departure of the first of the two electrons is significantly more difficult than loss of the second: the difference in 1e$^-$ potentials sometimes exceeds 0.5 V. Since the initial transfer act is rate-determining in each case, the low rates observed may be attributed, at least in part, to such gaps.

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