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Electron Transfer. 61. Reactions of the Nitrosodisulfonate Anion Radical with Inorganic Reductants[1]

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The nitrosodisulfonate anion radical $\cdot ON(SO_3)_2^{2-}$ smoothly oxidizes $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ and H_2O_2 to O_2; in both reactions, the reduction product is $HON(SO_3)_2^{2-}$. The oxidation of $Fe(CN)_6^{4-}$ appears to proceed by parallel outer-sphere paths, one involving the anion radical and the other its conjugate acid. The specific rate for the first of these, in conjunction with earlier potentiometric data, allows us to estimate the self-exchange specific rate in the system $\cdot ON(SO_3)_2^{2-}$–$ON(SO_3)_2^{3-}$ as 9×10^{-6} M^{-1} s^{-1} at 25 °C, i.e., 11–14 powers of 10 below exchange rates in systems featuring aromatic radicals. The reaction with H_2O_2 also follows two routes. The first is peroxide dependent and involves HO_2^-; for this, the suggested rate-determining step is the formation of a N–OOH intermediate with displacement of sulfite. The second path is peroxide independent and may be initiated by heterolysis of the anion radical with loss of sulfite. The nitrosodisulfonate anion radical thus displays significant versatility in exploiting possible reaction paths of several types.

For several years we have been interested in electron-transfer reactions involving radicals and radical ions in aqueous media.[2] One of the simplest and most stable of such odd-electron species is the nitrosodisulfonate radical anion $\cdot ON(SO_3)_2^{2-}$, which is formed by virtually complete homolysis of its dimer, Fremy's salt, when the latter is dissolved in polar solvents (eq 1).[3] This radical anion has been used as an oxidant for a wide

$$\underset{\text{"Fremy's salt"}}{(K^+)_4[(O_3S)_2NO{-}ON(SO_3)_2]^{4-}} \rightarrow 2[\cdot ON(SO_3)_2]^{2-} + 4K^+ \tag{1}$$

variety of organic[4] and inorganic[5] compounds, but mechanistic studies have been reported only for its reactions with sulfite[6] and nitrous acid[7] and for its decomposition in aqueous solution.[3b,8]

The work described in this paper deals with the reductions of nitrosodisulfonate with hexacyanoferrate(II)[9] and with hydrogen peroxide. We here present evidence that these reductants operate, as might be anticipated, through markedly different mechanisms.

Experimental Section

Materials. Inorganic reagents (Fisher Certified or Baker Analyzed Grade) were used as received. Hydrogen peroxide solutions were prepared by dilution of the Fisher 30% solution and were standardized by titration with permanganate.[10] Fremy's salt was prepared by the procedure of Yamada,[11] was stored in a closed container at −15 °C, and was dissolved in buffered aqueous solution to yield the potassium salt of the nitrosodisulfonate radical anion just prior to kinetic runs or stoichiometric experiments.

Table I. Stoichiometries of the Reactions of $\cdot NO(SO_3)_2^{2-}$ (NDS·) with $Fe(CN)_6^{4-}$ and with H_2O_2[a]

A. $Fe(CN)_6^{4-}$ Reaction

[NDS·], M	$[Fe(CN)_6^{4-}]$, M	Δ[NDS·], M	$\Delta[Fe(CN)_6^{3-}]$,[c] M	Δ[NDS·]/ $\Delta[Fe(CN)_6^{4-}]$
0.00055	0.0043		0.000 58	0.94
0.00046	0.0043		0.000 50	0.91
0.0260	0.0134	0.0122		0.89
0.0209	0.0134	0.0119		0.89

B. H_2O_2 Reaction

[NDS·], M	$[H_2O_2]$, M	Δ[NDS·],[b] M	Δ[NDS·]/ $\Delta[H_2O_2]$
0.002 20	0.000 43	0.000 87	2.01
0.002 69	0.000 43	0.000 80	1.87
0.001 89	0.000 43	0.000 76	1.76

C. Evolution of O_2

amt, mmol			
NDS·	H_2O_2	O_2	NDS·/O_2
0.76	8.0	0.34	2.22
0.80	8.0	0.41	1.94
0.87	10.0	0.38	2.28

[a] Nitrosodisulfonate was added as its dimeric potassium salt (Fremy's salt); $Fe(CN)_6^{4-}$ was added as its potassium salt. Reactions with hexacyanoferrate(II) were carried out in a solution 0.10 M in Na_2HPO_4 and 0.20 M in NaH_2PO_4. Reactions with H_2O_2 were carried out in a solution 0.01 M each in Na_2HPO_4 and Na_3PO_4 (see Experimental Section). [b] Determined spectrophotometrically at 540 nm; path length 10.0 cm. [c] Determined spectrophotometrically at 420 nm; path length 1.00 cm.

Stoichiometric Studies. The stoichiometry of the reaction between $\cdot ON(SO_3)_2^{2-}$ and $Fe(CN)_6^{4-}$ in HPO_4^{2-}–$H_2PO_4^-$ buffer, with the radical anion in excess, was determined by adding a measured deficiency of the reductant to the radical solution, waiting 30 min for completion of the reaction, and then measuring the decrease in absorbance at 540 nm ($\epsilon_{radical} = 20.8$ M^{-1} cm^{-1}).[8a] With the reductant in excess, the increase in absorbance at 420 nm, the maximum for $Fe(CN)_6^{3-}$ ($\epsilon = 1017$ M^{-1} cm^{-1})[9] was measured.

For the $\cdot NO(SO_3)_2^{2-}$–H_2O_2 reaction, a deficiency of H_2O_2 was added to the radical anion, and after a 3-h waiting period, the decrease in radical absorbance at 540 nm was measured. Stoichiometric results obtained in this manner were confirmed by spectrophotometric titration in which a solution of the radical anion was added slowly to a known quantity of peroxide until the radical color persisted. Oxygen released

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(1) Support of this work by the National Science Foundation (Grant 8022881) is gratefully acknowledged.

(2) See, for example: (a) Chang, C.-R.; Paton, S. J.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1979**, *18*, 1294. (b) Singh, A. N.; Gelerinter, E.; Gould, E. S. *Ibid.* **1982**, *21*, 1232.

(3) (a) Asmussen, R. W. *Z. Anorg. Allg. Chem.* **1933**, *212*, 317. (b) Wilson, B. J.; Hayes, J. M.; Durbin, J. A. *Inorg. Chem.* **1976**, *15*, 1703.

(4) Zimmer, H.; Lankin, D. C.; Horgan, S. W. *Chem. Rev.* **1971**, *71*, 229. Although this extended review deals principally with the reactions of nitrosodisulfonate with organic substrates, it also summarizes physicochemical studies of this anion radical and includes detailed directions for its preparation.

(5) See, for example: (a) Gehlen, H.; Elchlepp, E.; Armak, J. *Z. Anorg. Allg. Chem.* **1953**, *274*, 293. (b) Gehlen, H.; Dase, G. *Ibid.* **1954**, *275*, 327. (c) Cispito, M.; Raspi, G. *Anal. Chim. Acta* **1975**, *74*, 452.

(6) Li, J. C. M.; Ritter, D. M. *J. Am. Chem. Soc.* **1953**, *75*, 5831.

(7) Li, J. C. M.; Ritter, D. M. *J. Am. Chem. Soc.* **1953**, *75*, 5823.

(8) (a) Murib, J. H.; Ritter, D. M. *J. Am. Chem. Soc.* **1952**, *74*, 3394. (b) Wilson, B. J.; Ritter, D. M. *Inorg. Chem.* **1963**, *2*, 974. (c) Wilson, B. J.; Fillmore, D. L. *Ibid.* **1977**, *16*, 1404.

(9) An earlier kinetic study of the reaction of $\cdot ON(SO_3)_2^{2-}$ with $Fe(CN)_6^{4-}$ at 17 °C in 0.01 M KOH (Holba, V.; Volarova, O. *Collect. Czech. Chem. Commun.* **1975**, *40*, 355) determined the order in each reactant and examined the effect of nonparticipating electrolytes. It did not, however, establish a kinetic acidity pattern.

(10) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. "Quantitative Chemical Analysis", 4th ed.; Macmillan: New York, 1969; p 834.

(11) Yamada, S.; Tsuchida, R. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 721.

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when a known quantity of the radical was treated with a 10-fold excess of H_2O_2 was measured by carrying out the reaction in a gas buret. Results are summarized in Table I.

The reduction product in both systems was identified as hydroxylaminedisulfonate, $HON(SO_3)_2^{2-}$, by treating spent reaction solutions with PbO_2, whereupon the nitrosodisulfonate spectrum was regenerated.

Rate Measurements. Rates were estimated from measurements of changes in absorbance with the use of a Cary 14 recording spectrophotometer. For the $Fe(CN)_6^{4-}$ reaction, runs with excess reductant were followed at 540 nm, whereas runs with excess radical anion were monitored by measuring the formation of $Fe(CN)_6^{3-}$ at 420 nm. All runs with H_2O_2 were followed at 540 nm. Ionic strengths were regulated with use of $NaNO_3$,[12] whereas pH values were maintained by adding measured quantities of NaH_2PO_4, Na_2HPO_4, and NaOH. Rates were not significantly affected by addition of any of the phosphate anions provided that $[H^+]$ was kept constant by maintaining the proper ratio of buffer components. Rates were not altered by addition of the sodium salt of EDTA, indicating that catalysis by trace metal ions in solution was not occurring. In addition, reactions were unaffected by atmospheric oxygen. The $Fe(CN)_6^{4-}$ reaction was first order in each reactant, but kinetic runs were generally carried out under pseudo-first-order conditions with one reagent in at least 10-fold excess over the other. The H_2O_2 reaction, when carried out with peroxide in large excess, yielded logarithmic decay curves; slopes of absorbance–time plots carried out with $\cdot ON(SO_3)_2^{2-}$ in excess, although not constant, decreased less markedly during a given run than corresponded to pseudo-first-order behavior. At the concentration levels used in the kinetic measurements no complications resulting from the evolution of oxygen bubbles were encountered. Data were taken for at least 4 half-lives, and an "infinity reading" was taken after 7 half-lives. Rate constants from successive half-life values in a pseudo-first-order run agreed to within 5%, and average values did not differ significantly from those obtained from slopes of logarithmic plots of absorbance differences against reaction times. Specific rates from replicate runs checked to better than 8%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

The nitrosodisulfonate radical anion did not react with *tert*-butyl hydroperoxide, $Ru(CN)_6^{4-}$, or $Fe(o\text{-phen})_3^{2+}$ under our conditions. In contrast, the reaction with $Co(CN)_5^{3-}$ was too rapid to follow by using ordinary mixing techniques; with both reagents at concentrations of 4×10^{-4} M, reaction was more than 95% complete within 5 s, corresponding to a bimolecular rate constant $>10^4$ M^{-1} s^{-1} (25 °C, 0.1 M NaCN).

Results and Discussion

Our stoichiometric studies (Table I) indicate that the nitrosodisulfonate radical anion, as expected, reacts quite cleanly with $Fe(CN)_6^{4-}$ in a 1:1 ratio (eq 2) and with hydrogen peroxide in a 2:1 ratio (eq 3).

$$\cdot ON(SO_3)_2^{2-} + Fe(CN)_6^{4-} + H^+ \rightarrow HON(SO_3)_2^{2-} + Fe(CN)_6^{3-} \quad (2)$$

$$2\cdot ON(SO_3)_2^{2-} + H_2O_2 \rightarrow O_2 + 2HON(SO_3)_2^{2-} \quad (3)$$

Demonstration that the reduction product is hydroxylaminedisulfonate, $HON(SO_3)_2^{2-}$, confirms this straightforward picture.

Representative kinetic data for the hexacyanoferrate(II) reaction appear in Table II. The reaction is first order in both oxidant and reductant and is seen to be accelerated by increasing acidity. A plot of k_{obsd} vs. $[H^+]$ within the range examined is linear and conforms to the relationship

$$\text{rate} = [\text{NDS}\cdot][\text{Fe}^{II}](k_0 + k_1[H^+]) \quad (4)$$

($k_0 = 0.67$ M^{-1} s^{-1}; $k_1 = 1.56 \times 10^7$ M^{-1} s^{-1}; 25 °C; NDS· = nitrosodisulfonate radical anion).

Table II. Kinetic Data for the Reaction of $\cdot ON(SO_3)_2^{2-}$ (NDS·) with $Fe(CN)_6^{4-}$ [a]

10^3[NDS·], M	$10^3[Fe(CN)_6^{4-}]$, M	pH	k_{obsd},[b] M^{-1} s^{-1}
4.03	53.2	11.81	0.64
4.03	24.4	11.81	0.67
30.0	2.7	11.81	0.69
4.00	24.4	10.70	0.63
4.00	24.4	7.90	0.89
4.00	24.4	7.50	1.33
4.00	24.4	7.09	2.2
4.00	24.4	6.90	2.7
4.00	24.4	6.74	3.5
4.00	24.4	6.60	4.5

[a] Reactions were carried out at 25.0 °C; $\mu = 0.5$ M ($NaNO_3$); pH values were maintained with measured quantities of NaH_2PO_4, Na_2HPO_4, and NaOH. [b] $k_{obsd} = (-d[\text{NDS}\cdot]/dt)[\text{NDS}\cdot]^{-1}\cdot[Fe(CN)_6^{4-}]^{-1}$.

Rate law 4 implies that the observed reaction proceeds by a combination of two paths, one involving the oxidant in its protonated form and the second involving the oxidant in a nonprotonated form. Since there is no indication of kinetic saturation at pH values as low as 6.6, the latter species can constitute only a minor fraction of the total added radical at and above this pH; i.e., pK_A of the anion radical must fall below 5.6. The bimolecular specific rate for reduction of the protonated radical, $H\dot{O}N(SO_3)_2^-$, obtained by multiplying k_1 in (4) by K_A, then exceeds 40 M^{-1} s^{-1}. Protonation, as expected, greatly facilitates electron transfer to the radical oxidant.

The substitution-inert character of $Fe(CN)_6^{4-}$ precludes any mechanism for this oxidation involving prior dissociation of cyanide. Alternatively, one cannot assemble a transition state in which a cyano group links the reductant and oxidant without subjecting the latter to an obvious violation of the octet rule. It is thus reasonable to consider the $\cdot ON(SO_3)_2^{2-}$–$Fe(CN)_6^{4-}$ reaction simply as a pair of outer-sphere processes at different protonation levels.

We may use the value of k_0, the specific rate for the nonprotonated path, to estimate the rate constant for self-exchange in the system $\cdot ON(SO_3)_2^{2-}$–$ON(SO_3)_2^{3-}$ ($NDS^{2-/3-}$). For this path, which features a difference in half-cell potentials of only about −0.010 V,[13-15] Marcus's treatment[16] yields the approximate relationship

$$k_{NDS,Fe} = (k^{ex}_{NDS}k_{Fe(2,3)}K_{NDS,Fe})^{1/2} \quad (5)$$

where $k_{NDS,Fe}$ is the specific rate for the redox reaction at hand at a very high pH (k_0 in eq 4), k^{ex}_{NDS} is the self-exchange rate in the nitrosodisulfonate system, $k_{Fe(2,3)}$ is that in the $Fe(CN)_6^{4-/3-}$ system (taken to be 7×10^4 M^{-1} s^{-1} at 25 °C),[17,18] and $K_{NDS,Fe}$ is the equilibrium constant for the reaction (here estimated as 0.7). The calculated nitrosodisulfonate self-exchange rate constant is 9×10^{-6} M^{-1} s^{-1} at 25 °C. Note that

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(12) Attempts to prepare crystalline samples of the Na^+ analogue of Fremy's salt, which would presumably allow experiments with less strongly complexing ClO_4^- as the counterion of the supporting electrolyte, were unsuccessful. This salt does not appear to have been reported.

(13) E_0 for the $Fe(CN)_6^{3-/4-}$ half-reaction in the basic medium employed has been estimated as −0.36 V (Kolthoff, I. M.; Tomsicek, W. J. *J. Phys. Chem.* **1935**, *39*, 945).

(14) Aoyagui, S.; Kato, F. (*J. Electroanal. Chem. Interfacial. Electrochem.* **1972**, *38*, 243) record a formal potential of −0.122 V for $NDS^{2-/3-}$ in strongly basic media, but the primary data of these authors (their Figure 2) indicate that this value must be adjusted to −0.350 V in line with their use of a saturated KCl–calomel reference electrode.

(15) Despite the small difference in potentials, reactions carried out under the conditions of our kinetic runs resulted in greater than 95% conversions at our highest pHs. At lower pH values, NDS· becomes more strongly oxidizing,[14] and conversions approach 100%.

(16) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(17) Shporer, M.; Ron, G.; Loewenstein, A.; Navon, G. *Inorg. Chem.* **1965**, *4*, 361. The value of $k_{Fe(2,3)}$ here utilized has been estimated from the specific rate at 32 °C and the activation energy reported by these authors, both applicable to systems in which the two cyano complexes are 0.25 M. This reaction has been shown to be exceedingly sensitive to variations in medium.[18]

(18) See, for example: Campion, R. J.; Deck, C. F.; King, P., Jr.; Wahl, A. C. *Inorg. Chem.* **1967**, *6*, 672.

Table III. Kinetic Data for the Reaction of $\cdot ON(SO_3)_2{}^{2-}$ (NDS·) with H_2O_2[a]

$10^3[H_2O_2]$, M	$10^{12}[H^+]$, M	μ	$10^3 k_{obsd}$,[b] s^{-1}
1.03	2.92	0.50	2.1
1.40	2.92		2.6
2.14	2.92		3.4
2.82	2.92		4.5
5.80	2.92		6.8
11.6	2.92		12.6
29.1	2.92		26
5.75	17.0	0.50	2.6
5.75	10.8		3.3
5.75	7.6		4.8
5.75	4.5		6.3
5.75	1.90		8.4
5.75	0.20		21
5.75	0.10		19.9
5.75	0.050		21
29.9	17.0	0.70	10.3
29.9	11.3		13.9
29.9	8.1		19.2
29.9	4.5		26
29.9	2.92		35

[a] Reactions were carried out at 25.0 °C; the supporting electrolyte was $NaNO_3$. pH values were maintained with measured quantities of Na_2HPO_4 and NaOH. $[NDS\cdot]_0 = 4.4 \times 10^{-4}$ M throughout. [b] $k_{obsd} = (-d[NDS\cdot]/dt)[NDS\cdot]^{-1}$.

this value falls far below the rates (10^6–10^9 M^{-1} s^{-1}) reported for a host of aromatic radicals.[19] The magnitude of the gap reminds us that, just as with metal-center reactions, alterations in molecular geometry resulting from electron transfer (which tend to retard) are most serious when the migrating electron cannot be delocalized over a conjugated system.

Kinetic data for the reaction with hydrogen peroxide are assembled in Table III. This reaction is first order in the radical anion. At the highest concentrations of peroxide used, rates are nearly proportional to $[H_2O_2]$, but at lower concentrations of the latter, the dependence is less steep. The transformation is accelerated by the increase in pH, but rates are seen to approach a limiting value near pH 13. There is, in addition, a positive kinetic salt effect.

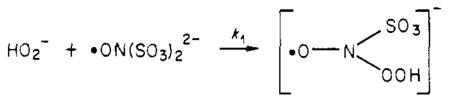
Data from measurements made at $\mu = 0.50$ are in accord with rate law 6, with kinetic parameters (25 °C) $k_1 = 2.8$ M^{-1}

$$\text{rate} = \frac{k_1[NDS\cdot][H_2O_2]}{\dfrac{[H^+]}{K_A} + 1} + k_0[NDS\cdot] \qquad (6)$$

s^{-1}, $k_0 = 8.6 \times 10^{-4}$ s^{-1}, and $K_A = 2.1 \times 10^{-12}$ M. Although the k_0 term does not include $[H_2O_2]$, it does not pertain to loss of the anion radical by disproportionation or by reaction with base, for these side reactions are neglibibly slow under our conditions. The binomial form of (6) is consistent with the generation of kinetic curves having nonintegral order in reactions where the peroxide is in deficiency. The value of K_A corresponds to the acidity constant recorded for H_2O_2 ($pK_A = 11.65$ at 25 °C).[20]

Expression 6 implies the operation of two reaction paths. The first, which predominates under our conditions, involves the hydroperoxide anion, HO_2^-, in, or prior to, the rate-determining step. In the alternate (minor) path, peroxide appears to intervene subsequent to this step. We suggest sequence (7)–(11) for the peroxide-dependent route. It is proposed that

$$H_2O_2 \underset{}{\overset{K_A}{\rightleftharpoons}} H^+ + HO_2^- \qquad (7)$$



$$HO_2^- + \cdot ON(SO_3)_2{}^{2-} \xrightarrow{k_1} [\cdot O{-}N(SO_3)(OOH)]^- + SO_3{}^{2-} \qquad (8)$$

$$[\cdot O{-}N(SO_3)(OOH)]^- \longrightarrow HO_2\cdot + ONSO_3^- \qquad (9)$$

$$ONSO_3^- \xrightarrow{H^+} HONSO_3 \xrightarrow{SO_3^{2-}} HON(SO_3)_2{}^{2-} \qquad (10)$$

$$HO_2\cdot + \cdot ON(SO_3)_2{}^{2-} \rightarrow O_2 + HON(SO_3)_2{}^{2-} \qquad (11)$$

the rate-determining step in this sequence is (8), the formation of a N–OOH intermediate with displacement of sulfite,[21] and that subsequent steps, the homolysis of this intermediate (9), the reattachment of sulfite (10), and the reaction of $HO_2\cdot$ with a second NDS· (11), are rapid.

We further suspect that the peroxide-independent path is initiated by unimolecular heterolysis of the anion radical (eq 12), followed by rapid hydrogen transfer (eq 13). Subsequent steps correspond to those completing the peroxide-dependent path.

$$\cdot ON(SO_3)_2{}^{2-} \xrightarrow{k_0} \cdot ONSO_3 + SO_3{}^{2-} \qquad (12)$$

$$\cdot ONSO_3 + H_2O_2 \rightarrow HONSO_3 + HO_2\cdot \qquad (13)$$

In sum, our experiments indicate that the nitrosodisulfonate anion radical exhibits a significant degree of versatility in exploiting reaction paths of different types. On examining just two reactions, we have encountered evidence that, given the appropriate coreagents and conditions, this species may react readily: (a) by outer-sphere electron transfer (accelerated by acid); (b) through intervention of a N-bound precursor (accelerated by base); (c) via hydrogen atom transfer to an electron-deficient intermeidate. Additional oxidations by this anion radical are under study.

Registry No. Ferrocyanide, 13408-63-4; hydrogen peroxide, 7722-84-1; nitrosodisulfonate, 15177-44-3.

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(19) See, for example: Hirota, N. In "Radical Ions"; Kaiser, E. T., Kevan, L., Eds.; Interscience: New York, 1968; p 80.

(20) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum: New York, 1976; Vol. 4, p 75.

(21) Identification of the reaction product as $HON(SO_3)_2{}^{2-}$ appears to rule out mechanisms involving displacement of sulfate, for under the mild conditions employed, this poorly nucleophilic species would be expected to remain unchanged.

(22) A reviewer asks why we have rejected, for the reaction between NDS· and $Fe(CN)_6{}^{4-}$, an inner-sphere path passing through the intermediate $[(NC)_5FeCN{-}N(SO_3)O\cdot]^{4-}$, formed presumably by substitution of $SO_3{}^{2-}$ by bound cyanide (which retains an unshared electron pair of nitrogen) on NDS·. We feel that such a route, requiring displacement of a strongly nucleophilic anion by a feebly nucleophilic center, is much less reasonable than the outer-sphere path here proposed. The same reviewer questions our assumption that the H^+-dependent component of this reaction involves protonation of the oxidant, rather than the reductant, $Fe(CN)_6{}^{4-}$. Since the reaction is accelerated at lower pH values (Table II and eq 4), the protonated path is more rapid than the nonprotonated. We point out that protonation of a reductant almost invariably makes it a less effective donor, whereas except in special cases (e.g., reactions involving chelation) protonation of an oxidant makes it a more effective acceptor.