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Contribution from the Departments of Chemistry, University of Southern California, Los Angeles, California 90005,
California State University, Long Beach, California 90840, and California State College, Stanislaus, Turlock, California 95380

Oxidation of Thiocyanate and Iodide by Iridium(IV)

DAVID M. STANBURY,* WAYNE K. WILMARTH,† SHADA KHALAF, HENRY N. PO, and JAMES E. BYRD

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The outer-sphere electron-transfer reactions between SCN^- and $IrCl_6^{2-}$ and between I^- and $IrBr_6^{2-}$ have the rate law $-d[Ir(IV)]/dt = (k'[X^-] + k''[X^-]^2)[Ir(IV)]$, where X^- is SCN^- or I^-. At $\mu = 0.10$ M ($NaClO_4$), 25.0 °C, pH 2, $k' = 9.1 \times 10^{-3}\ M^{-1}\ s^{-1}$, $k'' = 9.3 \times 10^{-1}\ M^{-2}\ s^{-1}$, $\Delta H_1^{\ddagger} = 15.2$ kcal/mol, $\Delta S_1^{\ddagger} = -16.5$ eu, $\Delta H_2^{\ddagger} = 8.74$ kcal/mol, and $\Delta S_2^{\ddagger} = -29.5$ eu for the SCN^- reaction, and at natural pH $k' = 57.1\ M^{-1}\ s^{-1}$, $k'' = 8.50 \times 10^3\ M^{-2}\ s^{-1}$, $\Delta H_1^{\ddagger} = 7.9$ kcal/mol, $\Delta S_1^{\ddagger} = -24.0$ eu, $\Delta H_2^{\ddagger} = 4.22$ kcal/mol, and $\Delta S_2^{\ddagger} = -26.4$ eu for the I^- reaction. There are no complications due to medium effects, although the SCN^- reaction develops complexities above pH 4.7. One-electron oxidation potentials for I^- and SCN^- are obtained, and a LFER is demonstrated for the k' paths.

Introduction

Redox reactions which involve different changes in oxidation state for the reaction partners are called noncomplementary. They are often mechanistically complex, and so their systematization is still in its infancy. In this paper we report results for some relatively simple noncomplementary reactions and achieve a degree of success in their systematization.

The reactions considered here all have one-electron outer-sphere oxidants as one of the reactants, while the partners are simple main-group substrates. Pelizzetti, Mentasti, and coworkers have been prolific in their similar studies of the oxidation of ascorbic acid, quinols, and the like, and they have found that Marcus theory generally correlates their results.[1] Of more direct relevance, Ng and Henry have found a rough Marcus-type correlation for the overall third-order oxidations of SCN^- by a series of Ferriin derivatives.[2] Finally, analogous studies by Nord and co-workers have recently appeared for which both overall second- and third-order oxidations of SCN^- and I^- have been correlated with Marcus theory.[3]

In this paper we investigate the following aqueous reactions:

$$4H_2O + 6IrCl_6^{2-} + SCN^- \rightarrow 6IrCl_6^{3-} + SO_4^{2-} + CN^- + 8H^+ \quad (1)$$

$$2IrBr_6^{2-} + 2I^- \rightarrow 2IrBr_6^{3-} + I_2 \quad (2)$$

These two reactions proceed by parallel paths first and second order in substrate, and hence they provide entry to two important mechanisms. We find that Marcus theory does not provide the most simple and direct analysis of the paths first order in substrate. The observation of paths second order in substrate is shown to be intimately related to the energetics of formation of $X_2^-\cdot$ from X^- and $X\cdot$.[4]

Experimental Section

Materials. K_2IrBr_6 (A. D. McKay) was used as supplied. $Na_2IrCl_6\cdot 6H_2O$ (Alfa) was recrystallized by Poulsen and Garner's method.[5] Na_3IrCl_6 and Na_3IrBr_6 were recrystallized from concentrated HCl and HBr, respectively, by the addition of 1-propanol after reduction with $NaNO_2$. NaI and NaSCN were recrystallized from acetone/water and dried for several days in a vacuum desiccator. $NaClO_4$, used to maintain ionic strength, was prepared by Na_2CO_3 neutralization of $HClO_4$ and then twice recrystallized; $LiClO_4$ was similarly prepared. Reverse osmosis purified and distilled water was used in all manipulations. Solutions of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ were individually prepared for each run to avoid complications due to hydrolysis. Solutions of NaI were prepared under N_2 and were foil wrapped to avoid autoxidation.

Kinetic Procedures. The oxidation of I^- was observed on an Aminco-Morrow stopped-flow apparatus, and the SCN^- oxidation was observed on a Cary 14 conventional spectrometer. For the stopped-flow work both solutions were thermostated to ±0.1 °C. The absorbance changes were kept to less than 0.3 so that the oscilloscope traces could be approximated as absorbance changes. The conventional kinetics were initiated by injecting aliquots of $IrCl_6^{2-}$ into 1-cm cells containing the substrate solutions thermostated to ±0.05 °C. The kinetics were monitored at 585 nm for $IrBr_6^{2-}$ and at 487 nm for $IrCl_6^{2-}$; these wavelengths are reactant absorbance maxima where the absorbance of products is negligible. Pseudo-first-order rate constants were determined from plots of log $(A_t - A_\infty)$ vs. time. These log plots were linear for at least 3 half-lives, except at the highest temperatures where hydrolysis of $IrBr_6^{2-}$ was fast enough to produce deviations during the third half-life. The activation parameters and rate constants were determined by using the Los Alamos nonlinear least-squares computer program with the temperatures, substrate concentrations, and first-order k_{obsd} values as input variables.

SCN^- Complications. Although the reaction of SCN^- with $IrCl_6^{2-}$ was well-behaved at pH 4.7 or less, complications developed at pH 6.7 which became severe in alkaline media. When buffered at pH 6.7 or greater, solutions saturated in O_2 showed less than first-order kinetics and general acceleration. With increasing pH the rate increased and became cleanly $^1/_2$ order with respect to $IrCl_6^{2-}$. At pH 10 (carbonate buffer), the [SCN^-] dependence of O_2 saturated solutions roughly followed the rate law of eq 3, although the O_2 and

$$-d[Ir(IV)]/dt = (k^0 + k^*[SCN^-]^2)[Ir(IV)]^{1/2}$$
$$k^0 = 4 \times 10^{-5}\ M^{1/2}\ s^{-1} \qquad k^* = 2.8 \times 10^{-1}\ M^{-3/2}\ s^{-1} \quad (3)$$

pH dependences are not included. The rates were somewhat irreproducible. Cl_2 oxidation of the acidified products showed $IrCl_6^{3-}$ as the product. When the reactions were performed in solutions degassed with N_2, the pH effect was much less dramatic; up to pH 10 the reactions were first order for at least 2 half-lives, and the rates increased by only a factor of 3 at pH 10, relative to the rates at pH 2. The key observations seem to be the O_2 dependence, the half-order kinetics, and the irreproducibility; these suggest a chain mechanism involving the reduction of O_2. However, a rough determination of the SCN^- consumption at pH 10 showed that the consumption ratio $\Delta[SCN^-]/\Delta[Ir(IV)]$ was less than 0.3, so there was no strong induction of SCN^- oxidation.

More straightforward kinetics were observed at and below pH 4.7. At pH 4.7 (phthalate buffer) and [SCN^-] = 0.05 M no O_2 effect was discernible. At pH 2, natural [O_2] and [SCN^-] = 0.05 M the same rate was observed as at pH 4.7, and at [SCN^-] = 0.01 M no O_2 effect was seen. We concluded that at pH 2 the complications at higher pH were absent and so the remaining kinetics were performed at pH 2 and natural [O_2].

Results

Stoichiometry. The stoichiometry for the reaction of $IrCl_6^{2-}$ with SCN^- was determined with excess SCN^- in neutral media. One of the products, CN^-, was determined at the initial concentrations of 1.43×10^{-2} M $IrCl_6^{2-}$ and (2, 4, and 6) $\times 10^{-2}$ M SCN^-. CN^- was titrated with Ni^{2+} by Huditz and

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*To whom correspondence should be addressed at the Department of Chemistry, Rice University, Houston, TX 77001.

†Professor Wayne K. Wilmarth passed away June 1980.

(1) (a) E. Pelizzetti, E. Mentasti, and E. Pramauro, *Inorg. Chem.*, **17**, 1181 (1978); (b) E. Pelizzetti and E. Mentasti, *Z. Phys. Chem.* (*Frankfurt am Main*), **105**, 21 (1977).

(2) F. T. T. Ng and P. M. Henry, *Can. J. Chem.*, **53**, 3319 (1975).

(3) G. Nord, B. Pedersen, and O. Farver, *Inorg. Chem.*, **17**, 2233 (1978).

(4) Abbreviations: X^- = halide or pseudohalide, Ir(IV) = $IrCl_6^{2-}$ or $IrBr_6^{2-}$.

(5) I. A. Poulsen and C. S. Garner, *J. Am. Chem. Soc.*, **84**, 2032 (1962).

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Table I. Kinetic Results for the Oxidation of SCN^- by $IrCl_6^{2-}$ [a]

[NaSCN], M	10^4k_{obsd}, s^{-1} 25 °C	[NaSCN], M	10^4k_{obsd}, s^{-1} 25 °C
0.00558	0.811	0.0446	21.6
0.01116	2.12	0.0893	85.6
0.0223	6.86		

	10^4k_{obsd}, s^{-1}			
[NaSCN], M	10.0 °C	18.0 °C	32.0 °C	40.0 °C
0.00563	0.291	0.492	1.49	2.96
0.0113	0.817	1.45	3.92	6.82
0.0225	2.41	4.28	10.6	17.4
0.0450	9.17	14.9	35.3	54.7
0.0900	31.5	59.2	125.0	185.6

[a] μ = 0.100 M ($NaClO_4$), pH 2 ($HClO_4$), $[IrCl_6^{2-}]_0 = 2.5 \times 10^{-4}$ M.

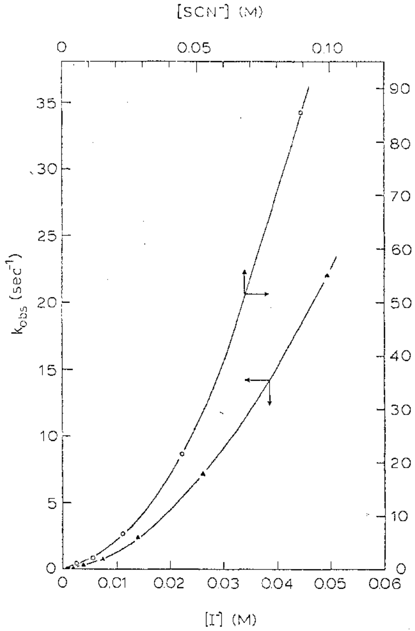

Figure 1. k_{obsd} vs. $[X^-]$ (25.0 °C, μ = 0.1 M): ○ = SCN^-; △ = I^-.

Table II. Kinetic Results for $IrBr_6^{2-}$ Oxidation of I^-

	k_{obsd},[a] s^{-1}			
[NaI], M	16.7 °C	24.1 °C	30.8 °C	35.9 °C
2.0×10^{-3}	0.0996	0.136	0.187	0.215
3.8×10^{-3}	0.244	0.324	0.446	0.526
7.2×10^{-3}	0.613	0.795	1.16	1.33
1.37×10^{-2}	1.81	2.33	2.98	3.22
2.61×10^{-2}	5.47	7.03	8.85	10.0
4.95×10^{-2}	18.4	22.0	28.2	31.4

[NaI], M	medium	temp, °C	k_{obsd}, s^{-1}
3.8×10^{-3}	0.10 M $NaClO_4$, natural pH	25.0	0.0757
3.8×10^{-3}	pH 3	25.0	0.380
3.8×10^{-3}	pH 2	25.0	0.375
2.61×10^{-2}	natural pH	25.0	7.65
2.61×10^{-2}	pH 3	25.0	8.54
2.61×10^{-2}	pH 2	25.0	8.40
2.0×10^{-3}	0.015 M $NaClO_4$	24.4	0.0757
4.0×10^{-3}		24.5	0.180
7.5×10^{-3}		24.9	0.443
12.0×10^{-3}		24.9	0.904
2.0×10^{-3}	0.040 M $NaClO_4$	24.5	0.104
4.0×10^{-3}		24.7	0.243
7.5×10^{-3}		24.9	0.624
12.0×10^{-3}		24.9	1.33
2.0×10^{-3}	0.070 M $NaClO_4$	24.5	0.126
4.0×10^{-3}		24.8	0.315
7.5×10^{-3}		24.9	0.729
12.0×10^{-3}		25.0	1.65
2.0×10^{-3}	0.10 M $LiClO_4$	25.1	0.141
4.0×10^{-3}		25.1	0.352
7.5×10^{-3}		25.1	0.907
12.0×10^{-3}		25.1	2.01
7.0×10^{-3}	5×10^{-3} M H_2SO_4[b]	25.4	1.17[c]
7.0×10^{-3}	5×10^{-3} M H_2SO_4[b]	25.4	0.971

[a] Ionic strength = 0.10 M ($NaClO_4$) unless otherwise specified. $[IrBr_6^{2-}]_0 = 8.0 \times 10^{-5}$ M. [b] μ = 0.10 M ($NaClO_4$). [c] Contains added $IrBr_6^{3-}$ at 5.6×10^{-4} M.

Flaschka's method,[6] and the ratios $\Delta[Ir(IV)]/\Delta[CN^-]$ = 6.61, 6.70, and 6.59, respectively, were obtained. The theoretical ratio of 6 corresponds to a 9% error which can be attributed to HCN volatilization. SO_4^{2-}, another product, was determined qualitatively under conditions similar to those above with $Ba(NO_3)_2$. An attempted quantitative determination of SO_4^{2-} using barium chloranilate[7] gave results consistently too high, presumably due to coprecipitation. $IrCl_6^{3-}$ was identified as the metallic product by reoxidizing with Cl_2 to recover 98.4% of the starting $IrCl_6^{2-}$.[5] The overall stoichiometry can be described by eq 1.

The iodide oxidation stoichiometry was determined with excess iodide in 0.1 M $HClO_4$, monitoring the absorbance at 353 nm where I_3^- and $IrBr_6^{3-}$ are the major chromophores. Initial $[IrBr_6^{2-}]$ was determined by measuring the absorbance of the dilute $IrBr_6^{2-}$ solution at 585 nm and using ϵ_{585} = 3870. The $[IrBr_6^{2-}]_0/[I^-]_0$ ratio was varied from 3.42×10^{-2} to 1.8×10^{-3} with $[I^-]_0$ = (2, 10, and 40) $\times 10^{-3}$ M. By use of Awtrey and Connick's data for ϵ_{I_2}, $\epsilon_{I_3^-}$, and K_{eq} for $I_2 + I^- \rightleftarrows I_3^-$, a consumption ratio $\Delta[I^-]/\Delta[IrBr_6^{2-}] = 0.96 \pm 0.02$ was obtained.[9] $IrBr_6^{3-}$ was identified as a reaction product by Cl_2 oxidation, but a quantitative estimate of percent recovery was impossible due to the large and variable absorbance of I_2. Formation of $IrBr_6^{3-}$ from $I^- + IrBr_6^{2-}$ is in accord with Novoselov and Muzykantova's report.[10] The stoichiometry can be described by eq 2.

$IrCl_6^{2-}$ + SCN^- Kinetics. The oxidation of SCN^- by $IrCl_6^{2-}$ was observed with a large excess of SCN^- by monitoring the loss of $IrCl_6^{2-}$. A preliminary study showed that the kinetics conformed to eq 4. Later, a rather complex pH and O_2 effect

$$-d[Ir(IV)]/dt = (k'[X^-] + k''[X^-]^2)[Ir(IV)] \qquad (4)$$

was discovered which yielded tractable results only below pH 4.7 (see Experimental Section). In solutions more acidic than pH 4.7 there was no O_2 or pH dependence.

Under these conditions good first-order plots are obtained; values of k_{obsd} as defined in eq 5 are listed in Table I. A

$$-d[Ir(IV)]/dt = k_{obsd}[Ir(IV)] \qquad (5)$$

complex dependence on $[SCN^-]$ is demonstrated by the nonlinearity of the k_{obsd} vs. SCN^- plot shown in Figure 1. Plots of $k_{obsd}/[SCN^-]$ vs. $[SCN^-]$ were linear over the 16-fold variation in $[SCN^-]$ and had a significant intercept giving a rate law of the form of eq 4. Activation parameters as defined by the Eyring equation were obtained from the temperature dependence and are listed in Table III. Rate constants at 25.0 °C are $k' = (9.09 \pm 0.62) \times 10^{-3}$ M^{-1} s^{-1} and $k'' = (9.32 \pm 0.35) \times 10^{-1}$ M^{-2} s^{-1}.

Iodide Kinetics. The oxidation of I^- by $IrBr_6^{2-}$ was observed with a large excess of I^- by monitoring the loss of $IrBr_6^{2-}$. Rates are listed in Table II. As in the SCN^- reaction, a plot of k_{obsd} vs. I^-, Figure 1, indicates a complex rate law. Plots of $k_{obsd}/[I^-]$ vs. $[I^-]$ were linear over the 20-fold variation in $[I^-]$ indicating a rate law of the form of eq 4. Activation

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(7) R. J. Bertolacini and J. E. Barney, II, *Anal. Chem.*, **29**, 281 (1959).
(8) W. S. Melvin and A. Haim, *Inorg. Chem.*, **16**, 2016 (1977).
(9) A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842 (1951).
(10) R. I. Novoselov and Z. A. Muzykantova, *Russ. J. Inorg. Chem.*, **15**, 1606 (1970).

Table III. Activation Parameters

reaction path	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
k' (SCN^-)	15.22 ± 0.06	−16.5 ± 2.0
k'' (SCN^-)	8.74 ± 0.03	−29.5 ± 1.2
k' (I^-)	7.90 ± 0.55	−24.0 ± 1.9
k'' (I^-)	4.22 ± 0.42	−26.4 ± 1.4

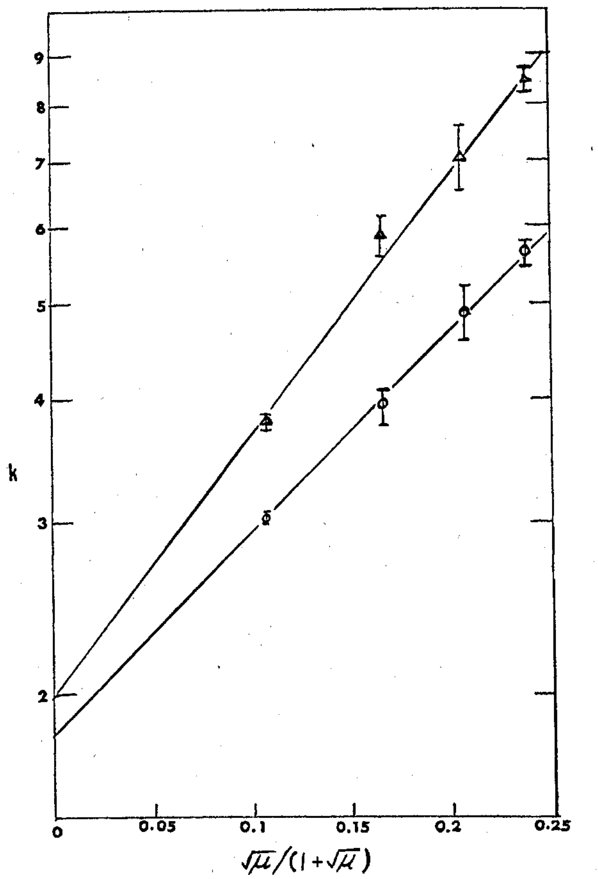

Figure 2. Ionic strength dependence of k' and k'' for the reaction of $IrBr_6^{2-}$ + I^- (25.0 °C, $NaClO_4$): ○ = $10^{-1}k_1$, M^{-1} s^{-1}; ▲ = $10^{-3}k_2$, M^{-2} s^{-1}.

parameters obtained from the temperature dependence are listed in Table III. Interpolated rate constants at 25.0 °C are $k' = 57.1$ M^{-1} s^{-1} and $k'' = 8.50 \times 10^3$ M^{-2} s^{-1}.

Medium effects also listed in Table II were investigated by varying the ionic strength, by substituting Li^+ for Na^+, and by adjusting the pH with $HClO_4$. Plots of log (k' and k'') vs. $\sqrt{\mu}/(1 + \sqrt{\mu})$ are linear as shown in Figure 2. The graph yields slopes of 2.11 for k' and 2.56 for k'' and intercepts $k_0' = 17.8$ M^{-1} s^{-1} and $k_0'' = 1.98 \times 10^3$ M^{-2} s^{-1}. Substituting Li^+ for Na^+ gives $k_{Li}' = 50.7 \pm 1.3$ M^{-1} s^{-1} and $k_{Li}'' = (9.55 \pm 2.6) \times 10^3$ M^{-2} s^{-1}. The small pH effect is probably not important. Overall, the medium effects do not indicate any need to modify eq 3.

The effect of added $IrBr_6^{3-}$ was also investigated. Initial studies were frustrated by the difficulty of isolating pure $Na_3IrBr_6{\cdot}2H_2O$. Subsequently it was found that reaction with $IrBr_6^{3-}$ generated in situ by SO_3^{2-} reduction showed good first-order kinetics. Comparison with the rate (Table II) in an analogous medium made up with H_2SO_4 but no $IrBr_6^{3-}$ showed a small rate enhancement in the presence of $IrBr_6^{3-}$; this was attributed to simple activity effects.

Discussion

Medium Effects. Mechanistic interpretation of the observed rate law hinges on the significance of the k'' term. Such terms may represent either distinct mechanistic paths or strong specific medium effects.[11] Specific anion effects are expressed by eq 6, which for small β is indistinguishable from eq 4.[12]

$$k = k_0[X^-] \exp(\beta[X^-]) \qquad (6)$$

Values of β less than 0.1 are common, although values as high as 4.5 have been considered acceptable.[13] A computer fit of our data to eq 6 gave $\beta = 15.3 \pm 1.6$ and 37.9 ± 4.8 for the SCN^- and I^- reactions, respectively. The deviations of k_{calcd} from k_{obsd} were systematic and much larger than for the fits to eq 3. It can be concluded that eq 6 is not correct and that the two-term rate law represents distinct mechanistic paths.

The other studies of medium effects are in accord with the observed rate law. Specifically, the ionic strength dependence of the k' path is nicely in accord with that expected for the Guggenheim equation; the k'' path has a weaker dependence on ionic strength than expected, but it is difficult to find comparable reactions in the literature. The specific cation effect (Li^+ for Na^+) is almost identical with those reported for the $S_2O_3^{2-}$ + $BrCH_2COO^-$ and I^- + $Mo(CN)_8^{3-}$ reactions.[11] In conclusion, the observed rate law is mechanistically significant.

Proposed Stoichiometric Mechanism. A general mechanistic scheme consistent with the observed stoichiometry and kinetics is shown in eq 7–11. When the steady-state approximation

$$\mathrm{Ir(IV)} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ir(III)} + X\cdot \qquad (7)$$

$$\mathrm{Ir(IV)} + 2X^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Ir(III)} + X_2^-\cdot \qquad (8)$$

$$\mathrm{Ir(IV)} + X_2^-\cdot \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Ir(III)} + X_2 \qquad (9)$$

$$X\cdot + X^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} X_2^-\cdot \qquad (10)$$

$$4H_2O + 3(SCN)_2 \xrightarrow{k_5} 5SCN^- + HCN + SO_4^{2-} + 7H^+ \qquad (11)$$

is applied to this mechanism, assuming k_5 is rapid and neglecting k_{-3}, rate law 12 obtains. With the assumptions

$$-d[\mathrm{Ir(IV)}]/dt = [2k_3[\mathrm{Ir(IV)}]^2[X^-]^2(k_4k_1 + k_2k_4[X^-] + k_2k_{-1}[\mathrm{Ir(III)}])]/[k_{-1}k_{-4}[\mathrm{Ir(III)}] + (k_4[X^-] + k_{-1}[\mathrm{Ir(III)}])(k_{-2}[\mathrm{Ir(III)}] + k_3[\mathrm{Ir(IV)}])] \qquad (12)$$

$k_{-2}[\mathrm{Ir(III)}] << k_3[\mathrm{Ir(IV)}]$, $k_{-1}[\mathrm{Ir(III)}] << k_4[X^-]$, and $k_{-1}k_{-4}[\mathrm{Ir(III)}] << k_4k_3[X^-][\mathrm{Ir(IV)}]$, eq 12 reduces to the observed rate law, where $k' = 2k_1$ and $k'' = 2k_2$. These approximations are justifiable assuming that k_{-1} and k_4 are diffusion controlled (ca. 10^{10} M^{-1} s^{-1}), that k_3 is close to diffusion controlled, and that k_{-2} is somewhat less than diffusion controlled, as discussed below. k_4 and k_{-4} have been measured;[14] the associated free radicals, despite their strong absorptivity, are precluded from direct observation because of their low steady-state concentrations.[15]

While $(SCN)_2$ is implicated as a reaction intermediate, the various studies of its hydrolysis indicate that it hydrolyzes

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(11) A. D. Pethybridge and J. E. Prue, *Prog. Inorg. Chem.*, **17**, 327 (1972).

(12) T. W. Newton, "The Kinetics of the Oxidation-Reduction Reactions of Uranium, Neptunium, Plutonium and Americium in Aqueous Solutions", TID-26506, U.S. Energy Research and Development Administration, Springfield, Va., 1975, p 11.

(13) J. Cooper, W. D. Reents, Jr., M. Woods, R. Sjoblom, and J. C. Sullivan, *Inorg. Chem.*, **16**, 1030 (1977).

(14) J. H. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, **64**, 2389 (1968).

(15) A mechanism in which I· dimerizes can be ruled out because I· will much more quickly form $I_2^-\cdot$ in the presence of 0.01 M I^-. Disproportionation of $I_2^-\cdot$ can also be ruled out; the steady-state concentration of $I_2^-\cdot$ in eq 7–11 is so low (~10^{-8} M) that the second-order disproportionation should not compete with the pseudo-first-order reaction with Ir(IV).

rapidly to give the observed final products. The actual rate law and mechanism of $(SCN)_2$ hydrolysis are controversial.[16] The problem is complicated by the necessarily large number of unknown intermediates. There is a possibility that $(SCN)_2$ and some of its hydrolysis products react with Ir(IV), giving the same stoichiometry.

If this occurs, then the factor of 2 in the derived rate law could be increased to a maximum of 6. Evidence is presented below, however, which militates against this possibility.

From the proposed mechanism one may well wonder why the reactions do show first-order kinetics. Competition between paths k_{-1}, k_{-2}, and k_3 might be expected to yield an Ir(III) dependence. Calculation of the values of k_{-1} and k_{-2} by microscopic reversibility using the reduction potentials discussed below shows that k_{-1} is about 2 orders of magnitude greater than k_{-2}. One estimates that k_3 is very fast due to its large favorable free energy and the high reactivity of X_2^-.[17] The excess substrate scavenges the X· to form X_2^- before it can react via the k_{-1} path, and then the X_2^- reacts via the more rapid k_3 path; thus there is no strong Ir(III) dependence. It is evident though, that at very high [Ir(III)] the reverse paths should become significant. This effect was investigated for the reaction of $IrCl_6^{2-}$ with I^-. $IrCl_6^{2-}$ was chosen because no complications were expected from k_2 and k_{-2}, the k_2 term being absent in the observed rate law.[18] Indeed, significant inhibition was observed at $[IrCl_6^{3-}] = 1 \times 10^{-2}$ M, and so rate law 12 seems reasonable.

Intimate Mechanism. To establish the observed rates at a predictive level demands attention to the intimate mechanism. Important questions are the extent to which k_{-1} and k_{-2} are diffusion controlled. Scheme I details the two steps. Applying the steady-state approximation to the several ion pairs allows identification in eq 13 and 14 of k_1 and k_2 in eq 7 and 8 as functions of a prior rapid ion-pair formation, intra-ion-pair electron transfer, and product separation. These elementary processes should be amenable to theoretical analysis.

Scheme I

$$Ox + X^- \rightleftharpoons Ox,X^- \quad K_{1ip}$$

$$Ox,X^- \rightleftharpoons Red,X\cdot \quad k_{1et}, k_{-1et}$$

$$Red,X\cdot \rightleftharpoons Red + X\cdot \quad k_{1d}, k_{-1d}$$

$$Ox,X^- + X^- \rightleftharpoons Ox,2X^- \quad K_{2ip}$$

$$Ox,2X^- \rightleftharpoons Red,X_2^-\cdot \quad k_{2et}, k_{-2et}$$

$$Red,X_2^-\cdot \rightleftharpoons Red + X_2^-\cdot \quad k_{2d}, k_{-2d}$$

$$k_1 = K_{1ip}k_{1et}k_{1d}/(k_{-1et} + k_{1d}) \tag{13}$$

$$k_2 = K_{1ip}K_{2ip}k_{2et}k_{2d}/(k_{-2et} + k_{2d}) \tag{14}$$

We first consider the k_1 path. Depending on the relative values of k_{-1et} and k_{1d}, there are two limiting forms:

$$k_1 = K_{1ip}k_{1et}k_{1d}/k_{-1et} = K_{1eq}k_{-1d} \tag{15}$$

$$k_1 = K_{1ip}k_{1et} \tag{16}$$

K_{1eq} is the equilibrium constant for reaction 7. It is not a priori obvious which form should dominate, since both k_{-1et} and k_{1d} are expected to be very fast. The problem is conveniently addressed with a linear free energy relationship (LFER).

LFER for the k_1 Paths. The existence in the literature of several outer-sphere oxidations of I^- having bimolecular rate laws allows exploration of a LFER. This is best shown as a plot of log (k_1) as a function of log (K_{1eq}), where k_1 and K_{1eq} refer to reaction 17. Thus k_1 is $k'/2$ as in eq 4, and K_{1eq} is

$$I^- + Ox \rightleftharpoons I\cdot + Red \tag{17}$$

simply defined by the formal $E°$ of I· and of the various oxidants. An experimental $E°$ of I· is not available, but an estimate of +1.42 V has been made by using the known $\Delta G°_f$ for I^-(aq) and I·(g) and an estimated $\Delta G°_{hyd}$ of I·.[19] As a test of this value, k_{-1} was calculated for $IrCl_6^{2-}$,[18] $IrBr_6^{2-}$, $Fe(bpy)_3^{3+}$,[20] and $Mo(CN)_8^{3-}$[21] by using the relationships $23.06\Delta E° = -RT \ln (K_{eq})$ and $k_1/k_{-1} = K_{1eq}$. The obtained k_{-1} are (3.39, 1.08, 1.22, and 3.06) $\times 10^{11}$ M^{-1} s^{-1}, respectively. A reasonable upper limit to k_{-1} is only 1.2×10^{10} M^{-1} s^{-1}; this upper limit is supported by the Smoluchowski equation (7×10^9 M^{-1} s^{-1} for reactants of equal radii),[22] by the measured rates of OH· reactions (1.2×10^{10} M^{-1} s^{-1} for the reaction with I^- and 1.02×10^{10} M^{-1} s^{-1} for the reaction with $Os(CN)_6^{4-}$),[23] and by the measured rate of reaction of I· with I^- (1.3×10^{10} M^{-1} s^{-1}).[24] The excessive calculated values for k_{-1} imply that the $E°$ for I· is in error. A value of +1.33 V gives k_{-1} values close to 1.2×10^{10} M^{-1} s^{-1}, and it is therefore used in the construction of the LFER.

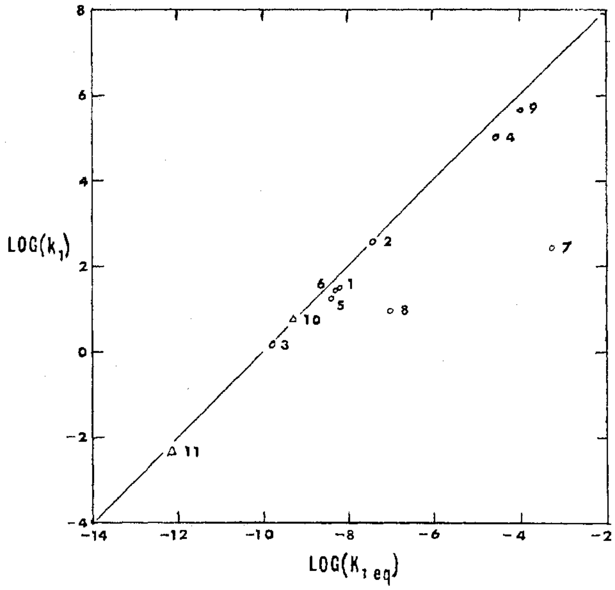

Figure 3. LFER for oxidations of I^- and SCN^-. Points are numbered as in Table IV: no. 9, $Fe(o\text{-phen})_3^{3+} + I^-$, log $k_1 = 5.51$,[36] $E° = 1.096$ V;[35] no. 10, $Fe(bpy)_3^{3+} + SCN^-$, log $k_1 = 0.74$;[20] no. 11, $IrCl_6^{2-} + SCN^-$. Δ = SCN^- reactions; O = I^- reactions.

The LFER is plotted in Figure 3. The solid line has been drawn with a slope of 1 and an intercept of log (k_1) = 10. To the left of that line is a forbidden region wherein k_{-1} exceeds the diffusion-controlled limit. With the exception of the points for Pu(VI) and Np(VI) the *LFER is obeyed within the probable error in $E°$ for the oxidants* for 6 orders of magnitude. The remarkable correlation exists despite large variations in ligand type, charge type, and metal center. The insensitivity of the rates to the nature of the oxidant, aside from its $E°$, suggests that eq 15 rather than eq 16 is the dominant expression of the intimate mechanism; that is, the rate-limiting

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Table IV. Marcus Calculations for the k_1 Paths with I^- [a]

no.	oxidant	k_1, $M^{-1}\ s^{-1}$	$E°$, V	k_{22}, $M^{-1}\ s^{-1}$	$k_{11,calcd}$, $M^{-1}\ s^{-1}$	k_{22}/K_{eq}, $M^{-1}\ s^{-1}$
1	$IrBr_6^{2-}$	28	0.843[g]	2×10^8 [l]	5.16×10^4	3.40×10^{15}
2	$IrCl_6^{2-}$	409[b]	0.892[h]	2×10^5 [m]	1.39×10^9	5.14×10^{12}
3	$Mo(CN)_8^{3-}$	1.5[c]	0.75[i]	3×10^4 [n]	1.93×10^8	1.94×10^{14}
4	$Fe(bpy)_3^{3-}$	1×10^5 [d]	1.06[j]	5×10^8 [o]	4.44×10^6	1.82×10^{15}
5	$Os(bpy)_3^{3-}$	16.5[e]	0.8437[e]	1.8×10^8 [e]	2.33×10^4	3.94×10^{16}
6	$Os(o\text{-phen})_3^{3+}$	26.0[e]	0.840[e]	3.1×10^8 [e]	3.43×10^4	5.26×10^{16}
7	NpO_2^{2+}	263[f]	1.1378[k]	105[f]	1.89×10^6	1.91×10^5
8	PuO_2^{2+}	8.49[f]	0.9164[k]	105[f]	7.02×10^7	1.05×10^9

[a] $E°(I\cdot(aq)) = 1.33$ V. [b] Reference 18. [c] Reference 21. [d] Reference 20. [e] Reference 3. [f] Reference 13. k_{22} for PuO_2^{2+} is assumed to be the same as for NpO_2^{2+}. [g] Obtained from $E°$ for $IrCl_6^{2-}$ and k_{eq} for $IrCl_6^{2-} + IrBr_6^{3-} \rightleftharpoons IrCl_6^{3-} + IrBr_6^{2-}$.[30] [h] Reference 31. [i] Reference 32. [j] Reference 33. [k] Reference 12. [l] Calculated by using eq 23, the rate and equilibrium constant of electron transfer between $IrCl_6^{2-} + IrBr_6^{3-}$ and k_{22} for $IrCl_6^{2-/3-}$.[30] [m] Reference 30. [n] Reference 34. [o] Reference 35.

step is not electron transfer but diffusion apart of the products.[57]

In photochemical studies of quenching by electron transfer the rates frequently approach the diffusion-controlled limit. Since these rates are measured directly, an estimate of the diffusion-limited rate often allows separation of the activation-controlled rate. In a recent paper by Sutin et al. a similar analysis was performed on ground-state electron transfer between $Ru(n\text{-}n)^{3+}$ and Cu(I) formed in a quenching process.[38] An analogous separation of the effects of activation and diffusion control cannot accurately be made in our system because to do so would require a very good value of $E°$ during the manipulations of microscopic reversibility. Nevertheless, the lack of scatter in the LFER implies that diffusion control is dominant. Aside from systems such as those mentioned above there seems to be little recognition of the dominant role which k_d, diffusion apart of the products, can play in defining the kinetics of simple inorganic reactions.

The adjustment of $E°$ for I· to +1.33 V was made because of the constraint that k_{-1} could not exceed the diffusion-controlled limit; the subsequent understanding that k_{-1} is actually at the diffusion-controlled limit allows us to fix $E°$ at $+1.33 \pm 0.03$ V. Margerum's estimate of $E°$ at +1.42 V was based on presumably very good thermochemical data and the reasonable assumption that $\Delta G°_{hyd}$ of I· was the same as of Xe.[19] The error in his estimate implies that I· is solvated by 2.1 kcal/mol more than Xe. This may occur through a bonding interaction with water similar to that of I· with I^-.

The only reactions having reliable values of k_1 for the oxidation of SCN^- are those of $IrCl_6^{2-}$ and $Fe(bpy)_3^{3+}$.[20,41] With only these two points an analysis similar to the above for I^- is not meaningful. However, it is possible to estimate $E°$ for SCN· by using the data of Schoneshofer et al.[25] They measured the following two equilibria, from which we obtain K_{eq} for eq 20. Combination of this K_{eq} with our $E°$ for I· gives $E° = +1.66$ V for SCN·.

$$ISCN^{-}\cdot \rightleftharpoons I^- + SCN\cdot \tag{18}$$

$$I\cdot + SCN^- \rightleftharpoons ISCN^{-}\cdot \tag{19}$$

$$I\cdot + SCN^- \rightleftharpoons I^- + SCN\cdot \tag{20}$$

With this $E°$ for SCN·, the $IrCl_6^{2-}$ and $Fe(bpy)_3^{3+}$ data have been included in Figure 3. The excellent coincidence of these two points with the line for the I^- points provides support for both the above $E°$ for SCN· and the use of $k_1 = k'/2$ rather than $k_1 = k'/6$. It is concluded that k_{-1} for the SCN^- reactions as well as for the I^- reactions is simply at the diffusion-controlled limit.

A useful outcome of this work is a reasonable estimate of $\Delta H°_f$ of SCN· in the gas phase; direct gas-phase measurements of this value have been quite variable.[26] Estimating $\bar{S}°_{SCN\cdot(g)} = \bar{S}°_{COS(g)} = 56.7$ eu (corrected for spin)[27] and estimating $\Delta H°_{hyd,SCN\cdot} = \Delta H°_{hyd,SO_2}$,[27] in combination with our $E°$ for SCN· yields $\Delta H°_f = 66.4$ kcal/mol for SCN· in the gas phase. This estimate is probably good to within 3 kcal/mol.

Marcus Theory for the k_1 Paths. The reactions in Figure 3 are probably of the outer-sphere type, and so the Marcus theory should be suitable for calculating the rate of electron transfer.[28] In equation 21, the cross relation, k_{11} and k_{22} are

$$\begin{gathered} k_{12} = (k_{11}k_{22}K_{eq}f)^{1/2} \\ \log (f) = (\log^2 (K_{eq}))/(4 \log (k_{11}k_{22}/Z^2)) \end{gathered} \tag{21}$$

the reactant self-exchange rates (eq 22), K_{eq} is the 1 e⁻

$$M_{Ox} + M^*_{Red} \rightarrow M_{Red} + M^*_{Ox} \tag{22}$$

equilibrium constant, and Z is the collision rate ($10^{11}\ M^{-1}\ s^{-1}$). In terms of Scheme I, $k_{12} = K_{IIP}k_{1et}$, i.e., the bimolecular rate of electron transfer.

Two interrelated problems arise here. One problem is the significance and limits which can be placed on k_{11}, the $I\cdot/I^-$ self-exchange rate. The other is that previous workers have met with some success in calculating k_1 using the assumption that $k_1 = k_{12}$,[3] while our work indicates $k_1 = k_{12}k_{1d}/k_{-1et}$.

k_{11} cannot be measured because I· reacts with I^- to form $I_2^{-}\cdot$ at the diffusion-controlled limit.[24] It is possible to estimate k_{11} in cases where k_{12}, k_{22}, and K_{eq} are known, by using eq 23, the quadratic solution to eq 21. The positive root in eq

$$\log (k_{11}) = (b \pm (4 \log (K_{eq}Z/k_{12}) \log (Z/k_{12}))^{1/2})/2 \tag{23}$$

$$b = -\log (k_{22}^2K_{eq}/(Z^2k_{12}^2))$$

23 corresponds to the "inverted region" which is currently of doubtful significance,[29] and so the negative root is used here. In our case, k_{12} is not known, but k_1 provides a lower limit to k_{12} because $k_{1d}/k_{-1et} < 1$; this results in values of k_{11} cal-

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Table V. Reactions Involving $(SCN)_2^-$ (Marcus Calculations)[a]

oxidant	$E°$,[b] V	$k_{2,\text{exptl}}$, $M^{-1}\,s^{-1}$	k_{22},[b] $M^{-1}\,s^{-1}$	$k_{2,\text{calcd}}$, $M^{-1}\,s^{-1}$	k_{-2}, $M^{-1}\,s^{-1}$
$IrBr_6^{2-}$	0.843	1.53[f]	2×10^8	25.9	5.52×10^7
$IrCl_6^{2-}$	0.892	0.466	2×10^5	3.96	2.49×10^6
$Fe(bpy)_3^{3+}$	1.06	7.5×10^3 [g]	5×10^8	8.95×10^3	5.81×10^7
$Fe(4,7\text{-}Me_2phen)_3^{3+}$	0.86[c]	60[h]	5×10^8 [e]	60.5	1.12×10^9
$Fe(5\text{-}Me(phen))_3^{3+}$	1.02[c]	7×10^3 [h]	5×10^8 [e]	3.48×10^3	2.57×10^8
$Fe(o\text{-}phen)_3^{3+}$	1.06[c]	1.4×10^4 [h]	5×10^8 [e]	8.95×10^3	1.09×10^8
$Fe(5\text{-}Cl(phen))_3^{3+}$	1.12[c]	1.87×10^5 [h]	5×10^8 [e]	3.53×10^4	1.40×10^8
$Fe(5\text{-}Br(phen))_3^{3+}$	1.13[c]	1.75×10^5 [h]	5×10^8 [e]	4.40×10^4	8.99×10^7
$Fe(5\text{-}NO_2phen)_3^{3+}$	1.25[c]	5.00×10^5 [h]	5×10^8 [e]	5.57×10^5	2.37×10^6
$Os(bpy)_3^{3+}$	0.837	4.90[i]	1.8×10^8	21.0	2.24×10^8
$Os(o\text{-}phen)_3^{3+}$	0.840	10.8[j]	3.1×10^8	28.8	4.39×10^8
UO_2^{2+}	0.06[d]	2.34×10^{-12} [j]	52[k]	9.61×10^{-12}	1.46×10^9

[a] $k_{11} = 3.02 \times 10^3\ M^{-1}\,s^{-1}$; $E° = -1.29$ V for $(SCN)_2^-$. [b] References as in Table IV. [c] Reference 33. [d] Reference 40. [e] Assumed the same as for $Fe(bpy)_3^{3+}$. [f] Reference 41. [g] Reference 20. [h] Reference 2. [i] Reference 3. [j] Reference 42. [k] Reference 43.

Table VI. Reactions Involving I_2^- (Marcus Calculations[a])

oxidant	$E°$,[b] V	$k_{2,\text{exptl}}$, $M^{-2}\,s^{-1}$	k_{22}, $M^{-1}\,s^{-1}$	k_{-2}, $M^{-1}\,s^{-1}$	$k_{2,\text{calcd}}$, $M^{-2}\,s^{-1}$
$IrBr_6^{2-}$	0.843	4.25×10^3	2×10^8	9.10×10^6	7.69×10^3
V(III)	−0.255[c]	1.82×10^{-14} [e]	1×10^{-2} [j]	1.43×10^8 [h]	5.26×10^{-14}
$Os(o\text{-}phen)_3^{3+}$	0.840	1.72×10^4 [f]	3.1×10^8	4.13×10^7	8.90×10^3
$Os(bpy)_3^{3+}$	0.837	9.15×10^3 [f]	1.8×10^8	2.47×10^7	6.38×10^3
NpO_2^{2+}	1.1378	1.15×10^3 [g]	105	3.03×10^2	6.73×10^2
PuO_2^{2+}	0.9164		105		2.91×10
Fe(III)	0.771[d]	8.0[h]	3.7[k]	2.83×10^5 [h]	2.51×10^{-1}
$Fe(bpy)_3^{3+}$	1.06		5×10^8		1.12×10^6
$Fe(CN)_6^{3-}$	0.34[d]		5×10^3 [l]		2.06×10^{-4}
$Mo(CN)_8^{3-}$	0.75		3×10^4		1.29×10
$W(CN)_8^{3-}$	0.57[f]		4×10^6 [l]		1.65
VO_2^+	1.000[c]	4.7×10^{-1} [i]	5.2×10^{-13}	2.23	1.12×10^{-5}
$IrCl_6^{2-}$	0.892		2×10^5		7.46×10^2

[a] k_{22} for VO_2^+ calculated by using eq 4.15 for the reaction of $VO^+ + Fe(bpy)_3^{3+}$; see J. Birk, *Inorg. Chem.*, 11, 95 (1972); $k_{2,\text{calcd}}$ uses $E° = -1.04$ V for I_2^-, and $k_{11} = 1.15 \times 10^3\ M^{-1}\,s^{-1}$. [b] References as in Table IV. [c] Reference 44. [d] Reference 40. [e] Calculated from K_{-2}. [f] Reference 3. [g] Reference 13. [h] Reference 45. [i] Reference 46. [j] Reference 47. [k] Reference 48. [l] Reference 34.

culated from eq 23 being only lower limits. Table IV lists values of k_{11} calculated in this way; the large calculated variation in k_{11} is expected because it is a lower limit. The analysis thus suggests a highest lower limit of $1.39 \times 10^9\ M^{-1}\,s^{-1}$ for k_{11}. The physical meaning of this number is that the $I^{-/0}$ couple is highly reactive, having almost no intrinsic reactivity barrier.

The second problem is how Nord's application of the Marcus cross relation nevertheless has given a fairly good correlation of the data. In general, one should note that for large free energy changes, the f factor in the cross relation implies a diminished sensitivity of k_{12} to the self-exchange rates and a more linear dependence of k_{12} on K_{eq}. The cross relation also reduces to the observed LFER (when f is neglected) as long as k_{22}/K_{eq} is a constant. Inspection of Table IV shows that this ratio is indeed similar for many of the oxidants which obey the LFER. Of the greatest deviations here, the $IrCl_6^{2-}$ reaction is notable in giving the worst fit with the cross relation. The above considerations show that k_{11} is a relatively free parameter, and so by proper choice of k_{11} the Np(VI) rate can also be correlated because of its slow values for k_{12} and k_{11}. Thus it is possible for the cross relation to "predict" many of the observed data. We stress, however, that, with the exception of the actinide reactions, the data adhere within a factor of 2 in rate to the LFER, and so they imply a tighter mechanistic constraint than activation-controlled electron transfer, namely, separation of the products.

The reactions of Np(VI) and Pu(VI) remain a problem. Their deviations in Figure 3 are sufficient to imply that $k_1 = K_{eq}k_{et} = k_{12}$. However, a value of k_{11} compatible with the cross relation ($1.89 \times 10^6\ M^{-1}\,s^{-1}$) would result in the prediction of much greater scatter in the LFER than observed. The anomalous behavior may be due to the f orbitals (there is increasing suspicion that f-orbital reactants, in general, may not obey the cross relation because of nonadiabaticity).[37]

The k_2 Paths. The k_2 paths for the oxidations of SCN^- and I^- are overall third order, but in the reverse direction they are second order. A systematic treatment of the reactions is therefore more simple when the reverse paths are considered. Values of k_{-2} can be determined if $E°$ for $X_2^-\cdot$ is known. Use of $E°$ values for I· and SCN· and published equilibria for formation of $X_2^-\cdot$ (eq 10)[24,39] yields $E° = +1.29$ and +1.04 V for $(SCN)_2^-\cdot$ and $I_2^-\cdot$ respectively. Tables V and VI list values for k_{-2} so obtained. Inspection reveals that most of the k_{-2} are significantly less than diffusion controlled. This is not

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(41) The reaction of SCN^- with $IrBr_6^{2-}$ was studied with less than satisfactory results. $IrBr_6^{3-}$ was shown to be the major Ir(III) product, and 6 ± 1 mol of CN^- was produced per mole of $IrBr_6^{2-}$; thus the stoichiometry was analogous to the $IrCl_6^{2-}/SCN^-$ reaction. The kinetics showed a stronger O_2/OH^- effect than did the $IrCl_6^{2-}/SCN^-$ reaction; even at pH 1, a weak O_2 effect was observed at low $[SCN^-]$. This O_2 effect was negligible at pH 1 at higher $[SCN^-]$, and so a fairly reliable value of $k'' = 3.0\ M^{-2}\,s^{-1}$ was obtained.

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unexpected in view of the considerable bond lengthening attendant on reduction of $X_2^-\cdot$ to $2X^-$. In terms of Scheme I then, $k_2 = K_{1ip}K_{2ip}k_{2et}$ because $k_{-2et} << k_{2d}$; thus electron transfer is the rate-limiting step in the k_2 paths.

The applicability of Marcus theory to the k_2 paths was suggested by Ng and Henry,[2] and Nord et al. have recently extended the idea.[3] Since the reactions in Tables V and VI are outer sphere and the concepts of Frank–Condon restrictions and reorganizational energies are applicable here, the use of Marcus theory is well motivated. The implicit definition of k_{11}, eq 24, is difficult to appreciate. Since k_{11} is a third-order

$$*X_2^-\cdot + 2X^- \rightarrow X_2^-\cdot + 2{*X^-} \qquad (24)$$

rate constant, there is a mismatch of units in f in the cross relation. Perhaps k_{11} should be understood as the product of the formation constant for I$^-$,I$^-$ and the bimolecular self-exchange of $I_2^-\cdot$ with I$^-$,I$^-$.

There is a good correlation of k_2 calculated from eq 21 using a nonlinear least-squares computer program to optimize k_{11}, as demonstrated in Tables V and VI. In these tables only the first four reactions of I$^-$ were used in the optimization, while all the entries for SCN$^-$ were used. Note that the I$^-$/V(III) and SCN$^-$/U(VI) reactions were actually observed in the reverse direction by flash generation of $X_2^-\cdot$ in the presence of the reduced metal species. The fit of $k_{2,\text{calcd}}$ with $k_{2,\text{obsd}}$ in these tables is generally good within a factor of 5, except for the Ir(IV) reactions with SCN$^-$ which are off by about a factor of 10. Since the reactants and products are all charged species, electrostatic effects should be significant. We have not been able to devise a quantitative scheme to account for such effects because of the high molecularity and asymmetry of the activated complex. Qualitatively the deviations for the Ir(IV)/SCN$^-$ reactions are in the direction expected for their charge type. It may be concluded that eq 21 is empirically useful, even with neglect of the work terms.

Table VI also lists values for $k_{-2,\text{calcd}}$ for several reactions for which the actual mechanism is doubtful or for which k_2 paths were not observed. Some interesting implications arise from these calculations. We found that the estimated k_2 for the $IrCl_6^{2-}$ reaction with I$^-$ was so slow that only the k_1 path would be observable at reasonable concentrations of I$^-$, as found. The estimated k_2 for Np(VI) + I$^-$ compares favorably with an effect attributed to medium effects. The VO_2^+ + I$^-$ k_2 is calculated to be 5 orders of magnitude too slow, thus lending support to the inner-sphere mechanism. The Fe(III) + I$^-$ reaction has been reported as inner sphere in the reverse direction and was suggested by the same authors to be outer sphere in the forward direction; we estimate an outer-sphere rate constant somewhat slower than the measured rates and suggest that the inner-sphere path may be dominant. The reactions of $W(CN)_8^{3-}$ and $Fe(CN)_6^{3-}$ with I$^-$ are first order in "inert" electrolyte; we estimate k_2 to be small enough that it would not have been observable at the ionic strengths used in the experiments. The calculated k_2 for the reactions of $Mo(CN)_8^{3-}$ and $Fe(bpy)_3^{3+}$ with I$^-$ are so small relative to k_1 that a significant contribution by the k_2 path would occur at rates beyond the limits of our instrumentation. The flash photolytic study of $(SCN)_2^-\cdot$ with UO_2^+ is nicely estimated indicating that the authors' tentative assignment of mechanism is correct.

The classification of the k_2 paths as having electron transfer as the rate-limiting step is interesting. In the case of $I_2^-\cdot$, Badger's rule[49] allows an estimate to be made of the bond length by using the Andrews et al. vibrational data of 3.10 Å.[50] The ionic crystal radius of I$^-$ is 2.04 Å,[51] and so there must be a compression of 0.98 Å on oxidation to $I_2^-\cdot$. The Frank–Condon principle implies that a good portion of this compression occurs prior to electron transfer. This extraordinary conclusion suggests a charge-transfer interaction between Ir(IV) and I$^-$.

Activation Enthalpies. With our improved understanding of the intimate mechanism, it is more meaningful to consider the activation enthalpies. In terms of eq 7–11 we can define $\Delta H^\circ_{X_2^-}$ in eq 25; $\Delta H^\circ_{X_2^-}$ thus refers to eq 10. Equation 25

$$\Delta H^\circ_{X_2^-} = \Delta H^\ddagger_2 - \Delta H^\ddagger_{-2} - (\Delta H^\ddagger_1 - \Delta H^\ddagger_{-1}) \qquad (25)$$

can be rewritten as eq 26. $\Delta H^\ddagger_2$ and $\Delta H^\ddagger_1$ have been de-

$$\Delta H^\ddagger_2 - \Delta H^\ddagger_1 = \Delta H^\circ_{X_2^-} + (\Delta H^\ddagger_{-2} - \Delta H^{\ddagger-1}) \qquad (26)$$

termined in this work, and $\Delta H^\circ_{X_2^-}$ has been measured by Baxendale and Bevan using pulse radiolysis.[52] Within the limits of experimental error, $\Delta H^\ddagger_2 - \Delta H^\ddagger_1 = \Delta H^\circ_{X_2^-}$ for both the I$^-$ and SCN$^-$ reactions with Ir(IV). This means that $\Delta H^\ddagger_{-2} - \Delta H^\ddagger_{-1} \sim 0$, which is understandable in view of the intimate mechanism. Both $\Delta H^\ddagger_{-1}$ and $\Delta H^\ddagger_{-2}$ should be small positive numbers, $\Delta H^\ddagger_{-1}$ being simply $\Delta H^\ddagger$ for diffusion and $\Delta H^\ddagger_{-2}$ being $\Delta H^\ddagger$ for a very fast ($\sim 10^7$ M^{-1} s^{-1}) electron-transfer reaction. An alternate expression of these results is that the enthalpy of activation for the k_2 path is stabilized by the enthalpy of formation of the nascent X_2^-.

Extensions. The propensity of the substrate to form a radical dimer $X_2^-\cdot$ is obviously an important factor in the reaction mechanism. The greater frequency of k_2 paths for SCN$^-$ than for I$^-$ may in part be ascribed to their relative K_{eq}'s for reaction 10. Schoneshofer has measured similar equilibria for the formation of $ISCN^-\cdot$,[25] $BrSCN^-\cdot$,[53] and $S_2O_3SCN^{2-}\cdot$.[53] This suggested the possibility of overall third-order paths which were first order in two substrates under mixed conditions.

A search for such paths in the I$^-$/SCN$^-$ and SCN$^-$/Br$^-$ reactions with $IrCl_6^{2-}$ and the SCN$^-$/Br$^-$ reaction with $IrBr_6^{2-}$ was unsuccessful. The I$^-$/SCN$^-$ reaction with $IrBr_6^{2-}$ showed a small but significant effect, consistent with a mixed substrate rate constant of 4.4×10^3 M^{-2} s^{-1}. The predominant absence of such paths can be justified noting that the relevant formation constants are about 2 orders of magnitude less than those for the symmetric radical dimers.

Pulse radiolytic studies have also demonstrated quite favorable formation constants for the radical dimers similar to those expected from the outer-sphere oxidations of thiourea and thiomalic acid.[54] With the anticipation of k_2 paths, we tried to oxidize thiourea with $IrCl_6^{2-}$ and thiomalic acid with $IrBr_6^{2-}$. In both cases irreproducible results obtained. This was traced to Cu$^+$ catalysis which gave sixfold rate increases at $[Cu^{2+}] = 5 \times 10^{-6}$ M (pH 6 for thiourea and pH 1 for thiomalic acid). The effects were similar to those reported for $Fe(CN)_6^{3-}$ oxidations of some thiols.[55] The thiourea reaction has been further investigated;[56] the thiomalic acid reaction was not pursued.

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Conclusions. The outer-sphere oxidations of SCN^- and I^- can proceed through paths first order in substrate and second order in substrate and via medium-catalyzed paths. The free energy of the first-order path usually determines its rate, while the second-order path is more often influenced by the self-exchange rates. While we cannot yet predict the rates of the medium-catalyzed paths, it should be noted that they seem to dominate for reactions of weak highly charged oxidizing agents such as $Fe(CN)_6{}^{3-}$ and $W(CN)_8{}^{3-}$.

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Registry No. $IrCl_6{}^{2-}$, 16918-91-5; $IrBr_6{}^{2-}$, 16919-98-5; SCN^-, 302-04-5; I^-, 20461-54-5; $SCN\cdot$, 15941-77-2; $I\cdot$, 14362-44-8; $(SCN)_2{}^-$, 66555-10-0; $I_2{}^-$, 12190-71-5.

Contribution from Istituto di Chimica Analitica ed Elettrochimica,
University of Pisa, 56100 Pisa, Italy

Equilibria and Kinetics of Reduction by Iodide Ion of the Vanadium(V)–Hydrogen Peroxide System

FERNANDO SECCO

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The equilibrium constant (K_1) for the formation of the red vanadium(V)–monoperoxo complex $VO_3{}^+$ from $VO_2{}^+$ and H_2O_2 and the equilibrium constant (K_2) for the formation of the yellow vanadium(V)–diperoxo complex $VO_5{}^-$ from $VO_3{}^+$ and H_2O_2 have been determined by spectrophotometry, their values being $K_1 = (3.7 \pm 0.4) \times 10^4\ M^{-1}$ and $K_2 = 0.6 \pm 0.1$ M at 25 °C and at an ionic strength of 0.3 M ($NaClO_4$). The kinetics of reduction by iodide of acidic mixtures of H_2O_2 and $VO_2{}^+$ have been investigated at the same temperature and ionic strength of the equilibrium measurements. The results agree with the rate law $V/[I^-] = (1.2 \times 10^{-3}/[H^+] + 1.3 \times 10^{-2} + 1.8 \times 10^{-1}[H^+])[VO_3{}^+] + (0.73 + 154[H^+])[VO_5{}^-]$ and are interpreted in terms of nucleophilic attack by iodide ion on differently protonated forms of $VO_3{}^+$ and $VO_5{}^-$ ions.

Introduction

The catalytic effect exerted by transition-metal derivatives on reactions involving hydrogen peroxide as an oxidant and on the decomposition of the hydrogen peroxide itself are well-known and have been extensively investigated.[1] Although the formation of peroxo compounds of transition metals has been envisaged as playing a fundamental role in the above mentioned processes, in most of the investigated systems the metal–peroxo compounds are present only as labile intermediates whose composition is seldom identified with certainty.[2] In their review on the development in redox chemistry of peroxides Jones et al.[3] stressed the importance of two-electron-equivalent processes in a field of chemistry where free-radical interpretations are perhaps superabundant.

The present study of the oxidation of iodide ion by the hydrogen peroxide–vanadium(V) system is an attempt to elucidate the mechanism of action of peroxidic species that are formed in nonnegligible amounts and whose compositions in aqueous solution are quite well established.[4,5]

Experimental Section

Materials. Stock solutions of the reactants were prepared by dissolving chemicals of analytical grade in triply distilled water, which was also used as a reaction medium. Nonstabilized hydrogen peroxide was used, and its content was frequently checked by permanganate titrations. Sodium vanadate was used as a source of vanadium(V); perchloric acid and sodium perchlorate were used to obtain the desired acidity and ionic strength.

Equilibrium Constants. These were measured by spectrophotometry using a Perkin-Elmer E 200 apparatus. The extinction coefficients of the absorbing species were measured at $\lambda = 455$ nm, their values being $\epsilon_{VO_2{}^+} = 3.9$, $\epsilon_{VO_3{}^+} = 278$, and $\epsilon_{VO_5{}^-} = 25\ M^{-1}\ cm^{-1}$. The ionic strength was kept constant at 0.3 M, and the temperature was 25.0 ± 0.1 °C throughout.

Kinetic Runs. Initial rates were measured by titrating with sodium thiosulfate. The iodine developed in the course of the reaction according to the procedure already described.[6,7] Care was taken to exclude the presence of oxygen by flushing the reacting mixture with a stream of purified nitrogen. The temperature and ionic strength were as in the equilibrium experiments. The reaction rates remained unaffected by changing the amount of starch added in order to reveal the developed iodine,[6,7] meaning that radical involvement is absent.

Results

Equilibrium Constants. In solutions more acidic than about 0.01 M, vanadium(V) exists mainly as the oxo cation $VO_2{}^+$ (or $H_4VO_4{}^+$). It forms, with hydrogen peroxide, the red monoperoxo complex $VO_3{}^+$ and the yellow diperoxo complex $VO_5{}^-$ according to the reactions

$$VO_2{}^+ + H_2O_2 \overset{K_1}{\rightleftharpoons} VO_3{}^+ + H_2O \qquad (1)$$

$$VO_3{}^+ + H_2O_2 \overset{K_2}{\rightleftharpoons} VO_5{}^- + 2H^+ \qquad (2)$$

Equilibrium 2 is strongly dependent on $[H^+]$, contrary to equilibrium 1. This allows the equilibrium constants K_1 and K_2 to be determined from independent sets of measurements, by choosing the appropriate ranges of hydrogen ion and hydrogen peroxide concentrations. The two peroxo complexes are known to lose oxygen in acid solution.[8,9] However the process of decomposition is so slow, at the acid and hydrogen peroxide concentrations of this investigation, that it can be safely neglected.

The absorbancies of solutions containing equal concentrations of $NaVO_3$ and H_2O_2 ranging between 5.0 and 20 × 10^{-4}

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