

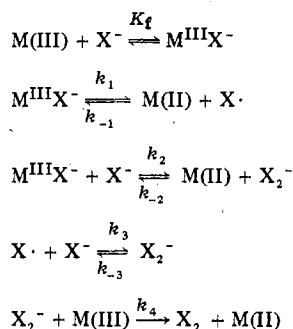
Contribution from the Inorganic Chemistry Department, H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark, and the Chemical Institute AD, Royal Danish School of Pharmacy, DK-2100 Copenhagen Ø, Denmark

Outer-Sphere Oxidation of Iodide and Thiocyanate by Tris(2,2'-bipyridyl)- and Tris(1,10-phenanthroline)osmium(III) in Aqueous Solutions

GWYNETH NORD,*^{1a} BRITTA PEDERSEN,^{1a} and OLE FARVER^{1b}

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The reaction $2M(\text{III}) + 2X^- \rightarrow 2M(\text{II}) + X_2$, where M(III) is one of the title cations and X⁻ is either I⁻ or SCN⁻, occurs through parallel paths. The observed rate expressions are interpreted using a general rate law derived from the reaction sequence



The new values for k_1K_f together with those determined by other workers using Fe(2,2'-bpy)₃³⁺, IrBr₆²⁻, IrCl₆²⁻, NpO₂²⁺, and Mo(CN)₈³⁻ as oxidants extend over a range of 10⁷ and agree with those predicted by the Marcus cross relation when work terms are neglected. A similar correlation of the k_2K_f values is reported and discussed.

Osmium(III) complexes of 2,2'-bipyridyl and of 1,10-phenanthroline² are more robust than the corresponding tris Fe(III) and Ru(III) complexes and, therefore, would be expected to be more suitable for investigating mechanisms of slow electron-transfer reactions. The oxidation of small inorganic ions was of interest to us because it was necessary to invoke the new pathway of nucleophilic attack on the ligand in order to explain activation enthalpies for the oxidation of OH⁻ by these complexes.³

While this work was in progress, an analogous study,⁴ chiefly of Ir(IV) complexes but also including Fe(bpy)₃³⁺ as oxidant, was brought to our notice and a second report of the oxidation rate of SCN⁻ by Fe(phen)₃³⁺ also appeared.⁵ We have been able to correlate our data for Os(III) with those of the above workers and also with the rates of iodide and thiocyanate oxidation by other transition-metal complexes. We show here that in all cases the reactions conform to a general rate law and also that the individual rate constants are those for outer-sphere electron transfer as treated by Marcus.⁶ In many cases the rates of the reverse reactions approach the diffusion-controlled limiting rates.

Experimental Section

The Os(III) complexes were prepared according to the literature methods given in ref 3. Os(bpy)₃³⁺ may be kept without decomposition for long periods (months) in 8 M perchloric acid but it was necessary to prepare new solutions of Os(phen)₃³⁺ for each series of kinetic runs. Analysis and extinction coefficients were in excellent agreement with those given in ref 3.

Potassium iodide and sodium chloride were "AnalaR" BDH chemicals. Sodium thiocyanate was "rein" (Merck) and sodium nitrate "für Analyse" (Riedel de Haën). Water was doubly distilled in an all-quartz apparatus.

Rates of reaction were followed spectrophotometrically either with a Cary 14 recording spectrophotometer or with the stopped-flow apparatus previously described.³

The concentrations of SCN⁻ and I⁻ were always much greater than that of the complex. In most cases the ionic strength (*I*) of the solutions was 1.0 M adjusted with NaCl. Replacing NaCl by NaNO₃ did not alter the rates which were also found to be unaffected by the presence of small concentrations of ClO₄⁻ and of SO₄²⁻. The hydrogen ion

Table I. Oxidation of I⁻ by Os(bpy)₃³⁺ and Os(phen)₃³⁺ ^a

10 ⁵ [Os(bpy) ₃ ³⁺], M		[I ⁻], M	\bar{k} , s ⁻¹	no. of runs
1.5-2.8	0.035 7		24.16 ± 0.25	2
1.5-2.8	0.020		8.14 ± 0.23	3
1.5-2.8	0.010		2.08 ± 0.13	4
1.5-3.6	0.001 428		0.0731 ± 0.0038	2
3.6	0.000 942		0.0447 ± 0.0030	3
2.0	0.000 823		0.0374 ± 0.0007	2 ^c
3.2	0.000 714		0.0312 ± 0.0005	2 ^b
1.7-6.4	0.000 714		0.0348 ± 0.0025	9 ^d
3.5	0.000 714		0.0408 ± 0.0021	2 ^e
1.68-3.16	0.000 704		0.0323 ± 0.0020	3
10 ⁵ × [Os(phen) ₃ ³⁺], M		[I ⁻], M	\bar{k} , s ⁻¹	no. of runs
0.4-0.8	0.020		14.60 ± 0.43	2
0.4-0.8	0.015		8.52 ± 1.25	4
0.4-0.8	0.010		3.90 ± 0.70	11
0.4-0.8	0.005		1.28 ± 0.16	8
0.4-0.8	0.001		0.087 ± 0.002	3
3.0	0.000 67		0.0332 ± 0.0044	2

^a Conditions: 25.0 ± 0.1 °C, *I* = 1.0 M (NaCl), [H⁺] = 0.04-0.05 M, λ 480 nm. ^b λ 405 nm. ^c Extra bipyridyl added, [H⁺] = 0.01 M, [bpy] = 0.9 × 10⁻⁵ M, [bpyH⁺] = 0.64 × 10⁻² M. ^d [H⁺] = 0.04-0.175 M. ^e [H⁺] = 0.457 M.

concentrations were low and rates were constant over the range of acidity used to derive the rate constants (see legends to tables). Parallel kinetic runs in daylight and in the dark showed that the rates followed those of thermal and not of photochemical reactions.

Kinetic data were treated graphically except for the SCN⁻ oxidations where the rate law was not simple, and the data were also treated numerically. The computer programs were written in Nu-Algol and the calculations performed using a Univac 1110 computer.

Activation parameters were derived by combining the data used for the tables at 25 °C with those for at least two other temperatures which included 15 or 17 °C and also 33 °C.

The potentials for the metal complex couples in the media also used for the kinetic studies were measured by cyclic voltammetry and/or potentiometric titration, in both methods vs. a saturated calomel electrode at 25 °C.

Table II. Ionic Strength Dependence of the Os(bpy)₃³⁺-I⁻ Reaction Rate^a

10 ⁵ [Os(bpy) ₃ ³⁺], M	[I ⁻], M	[Cl ⁻], M	<i>I</i> , M	<i>k</i> , s ⁻¹	no. of runs
3.2	0.000 709	0.36	0.42	0.0544 ± 0.0010	2 ^b
3.2	0.000 709	0.21	0.27	0.0612 ± 0.0018	2 ^b
3.2	0.000 709	0.14	0.20	0.0661 ± 0.0067	2 ^b
1.6	0.000 399	0.10	0.10	0.0611 ± 0.0037	2
1.6	0.000 299	0.10	0.10	0.0431 ± 0.0008	2
1.6	0.000 199	0.10	0.10	0.0274 ± 0.0009	2

^a [H⁺] = 0.03–0.04 M. ^b [SO₄²⁻] = 0.02 M.

Results and Discussion

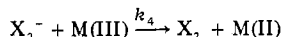
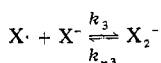
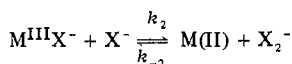
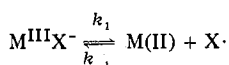
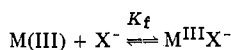
Iodide Oxidations. For both complexes, at all the temperatures studied and in the absence of added product complex, rates were pseudo first order for at least 3 half-lives of the complex. Addition of ligand did not affect the rates. The values for the pseudo-first-order rate constant *k* in s⁻¹ are reported in Tables I and II.

The experimental rate law is

$$-d[M(III)]/dt = k[M(III)] = 2k_1'[I^-][M(III)] + 2k_2'[I^-]^2[M(III)] \quad (1)$$

The rate constants 2*k*₁' and 2*k*₂' and the activation parameters are included in Table V for *I* = 1.0 M. From Table II we find that 2*k*₁' = 122 M⁻¹ s⁻¹ and 2*k*₂' = 7.7 × 10⁴ M⁻² s⁻¹ at *I* = 0.1 M and 25 °C for M(III) = Os(bpy)₃³⁺.

Equation 1 is also that found by Wilmarth et al.⁴ for the oxidation of I⁻ and SCN⁻ by IrBr₆²⁻, IrCl₆²⁻, and Fe(bpy)₃³⁺. It can be derived from the following reaction sequence when X⁻ = I⁻, *k*₁' = *k*₁*K*_f, *k*₂' = *k*₂*K*_f, *k*₋₁[M(II)] ≪ *k*₃[X⁻], *k*₋₃ < *k*₄[M(III)], and *k*₋₂[M(II)] ≪ *k*₄[M(III)]:



The general rate law is as in (2)

$$-d[M(III)]/dt = 2k_4[M(III)]^2[X^-]^2[F] \quad (2)$$

where

$$[F] = \frac{k_3k_1K_f + k_2K_f(k_{-1}[M(II)] + k_3[X^-])}{k_{-1}[M(II)](k_{-3} + k_4[M(III)] + k_{-2}[M(II)]) + k_3[X^-](k_4[M(III)] + k_{-2}[M(II)])}$$

We only consider pseudo-first-order rate constants (excess I⁻) and also do not need to invoke the reverse reaction (*k*₋₄ in the scheme). We have therefore not included, or considered further, the final fast step I₂ + I⁻ ⇌ I₃⁻. The stoichiometry of the SCN⁻ oxidation is discussed in the next section.

According to the preceding scheme the reaction occurs through the parallel paths

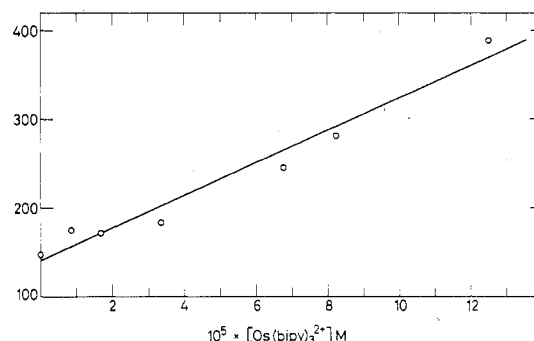


and

**Table III.** The Os(bpy)₃³⁺-I⁻ Reaction with Added Os(bpy)₃²⁺ ([Os(II)]₀)²

10 ⁵ [Os(II)] ₀ , M	<i>k</i> , s ⁻¹	10 ⁵ [Os(II)] ₀ , M	<i>k</i> , s ⁻¹
0	0.007 60	6.76	0.004 88
0.85	0.006 49	8.24	0.004 36
1.67	0.006 63	12.47	0.003 36
3.35	0.006 30		

^a [I⁻] = 2.08 × 10⁻⁴ M, [Os(III)] = 1.5 × 10⁻⁵ M, [H⁺] = 0.031 M, *I* = 1.0 M (NaCl), 25.0 °C.

**Figure 1.** Test of eq 6: Os(bpy)₃³⁺ + I⁻ with added Os(bpy)₃²⁺. *I* = 1.0 M; 25.0 °C.

For the first-order path alone eq 1 and 2 reduce to equation 5 if the assumptions *k*₋₃ < *k*₄[M(III)] and *k*₋₂[M(II)] < *k* - 2*k*₂'[I⁻]² = 2*k*₃*k*₁'[I⁻]²/(*k*₋₁[M(II)] + *k*₃[I⁻])

(5) *k*₄[M(III)] are retained. As *k*₃ is 8 × 10⁹ M⁻¹ s⁻¹^{7a} and the maximum (diffusion-controlled) value for *k*₋₁ cannot be expected to be much greater than this, we added Os(II) to the reaction mixture at low [I⁻] and low [Os(III)] as a competitor with I⁻ for the radical I[•]. This work was carried out for the bpy system and is recorded in Table III for [I⁻] = 2.08 × 10⁻⁴ M. Pseudo-first-order plots were linear only for about the first half-life with respect to Os(III) and the *k* values given in the table are calculated from the initial slopes of these plots.⁸ Correction for the second-order term (*k*₂') varied from 11 to 24% (see Table V). Equation 5 can be re-formed as eq 6 where

$$1/k_{\text{cor}} = (k_{-1}/2k_1'k_3[I^-]^2)[Os(II)]_0 + 1/2k_1'[I^-] \quad (6)$$

*k*_{cor} is the initial rate constant for the first-order path alone and [Os(II)]₀ is the concentration of Os(II) added to the reaction mixtures. In accordance with this we find a plot of 1/*k*_{cor} vs. [Os(II)]₀ to be linear (Figure 1) although with a rather large scatter. The least-squares intercept is 140 which would correspond to 2*k*₁' = 34 M⁻¹ s⁻¹ (cf. Table V, 2*k*₁' = 33 ± 9 M⁻¹ s⁻¹) and the slope is 1.84 × 10⁶ s M⁻¹. From this and *k*₃ we find *k*₋₁/*k*₁' = 1.29 × 10⁹ so that *k*₋₁ is 2.2 × 10¹⁰ M⁻¹ s⁻¹. The same treatment applied to measurements with [I⁻] = 7.04 × 10⁻⁴ M and [Os(II)]₀ = 4.3 × 10⁻⁵ M to 16.0 × 10⁻⁵ M gave values of *k*₋₁ from 3 × 10¹⁰ M⁻¹ s⁻¹ to 5 × 10¹⁰ M⁻¹ s⁻¹. Within the experimental error the rates were first order throughout but the correction for the *k*₂' term was large (29–53%). We have, therefore, chosen the value of *k*₋₁ from Figure 1 when later in this paper we estimate the standard potential of the I[•]-I⁻ couple.

Thiocyanate Oxidations. For both complexes rates were slower for SCN⁻ than for I⁻. The rate law (7) was derived

$$\begin{aligned} \frac{-d[M(\text{III})]}{dt} &= \frac{[M(\text{III})]^2[\text{SCN}^-]}{[M(\text{III})] + [M(\text{II})]} \left[2k_2'[\text{SCN}^-] + C \right] \\ &= \frac{[M(\text{III})][\text{SCN}^-]}{1 + R[M(\text{II})]/[M(\text{III})]} \left[2k_2'[\text{SCN}^-] \right] + \\ &\quad \frac{[M(\text{III})][\text{SCN}^-]}{1 + R[M(\text{II})]/[M(\text{III})]} C \end{aligned} \quad (7)$$

from the data for the first 80% of the reaction. This would accord with the general rate law (eq 2) where $k_2/k_4 = R = 1$ and where $C = 2k_1'$. The assumption made above that $k_{-1}[M(\text{II})] \ll k_3[X^-]$ is required to still hold. Numerical integrations of (7) showed that the small increase in rate during

Table IV. Oxidation of SCN⁻ by Os(bpy)₃³⁺ and Os(phen)₃³⁺^a

10 ⁵ [Os(bpy) ₃ ³⁺], M	[SCN ⁻], M	k _{obsd} , M ⁻¹ s ⁻¹	kA/[SCN ⁻] ^{2, b} , M ⁻² s ⁻¹
3.66	0.1225	3850	9.38
2.25	0.1225	7070	10.61
4.58	0.1222	3580	10.95
2.46	0.1222	6620	10.89
4.46	0.0668	1068 ± 33	10.67
3.08	0.0668	1759 ± 68	12.14
6.79	0.0622	572	10.03
2.12	0.0622	1826	10.00
2.08	0.0622	2142	11.51
0.76	0.0622	4749	9.34
3.75 ^c	0.0611	992	9.96
2.49 ^d	0.0611	1620 ± 80	10.80
1.18 ^c	0.0611	3576	11.31
4.70	0.0605	773 ± 59	9.93
0.89 ^e	0.0601	4022 ± 78	9.92
4.66	0.0465	456	9.85
4.66	0.0425	372	9.60
4.58	0.0314	198	9.20
4.15 ^f	0.0308	222 ± 3	9.71
4.22 ^g	0.0308	272 ± 5	12.10
4.87	0.0232	96.7	8.75
4.79	0.00852	16.6	10.97
4.69	0.00448	6.40	14.96
2.30	0.00448	12.55	14.38
4.20	0.00388	6.43 ± 0.53	17.93

10 ⁵ [Os(phen) ₃ ³⁺], M	[SCN ⁻], M	k _{obsd} , M ⁻¹ s ⁻¹	kA/[SCN ⁻] ^{2, b} , M ⁻² s ⁻¹
2.29	0.0602	6688 ± 452	42.26
2.95	0.0402	3244	59.20
2.3 ± 0.1	0.0372	3399 ± 3	56.45
2.17	0.0279	2352 ± 55	65.59
2.30	0.0201	1573 ± 95	89.55
2.2 ± 0.1	0.0100	777 ± 139	171.0
2.12	0.00929	718 ± 70	176.5
2.4 ± 0.1	0.00502	335	318.7
2.4	0.00104	63 ± 4	1398

^aI = 1 M (NaCl), T = 25.0 ± 0.2 °C, [H⁺] = 1.4 × 10³ [Os(III)].
^bA = [Os(II)] + [Os(III)]. ^c[H⁺] = 0.01 M. ^d[H⁺] = 0.02–0.04 M. ^eI = 1 M (NaNO₃). ^f[H⁺] = 0.058 M. ^g[H⁺] = 0.677 M.

Table V. Activation Parameters and Rate Constants for Os(III)-X⁻ Reactions in 1.0 M NaCl

reactants	2k ₁ '(25 °C), M ⁻¹ s ⁻¹	2k ₂ '(25 °C), M ⁻² s ⁻¹	ΔH ₁ [‡] , kcal mol ⁻¹	ΔS ₁ [‡] , cal K ⁻¹ mol ⁻¹	ΔH ₂ [‡] , kcal mol ⁻¹	ΔS ₂ [‡] , cal K ⁻¹ mol ⁻¹
Os(phen) ₃ ³⁺ + I ⁻	52 ± 12	3.43 × 10 ⁴ ± 0.12 × 10 ⁴	13.7 ± 0.9	-4.0 ± 3.0	7.5 ± 0.2	-13.0 ± 0.7
Os(bpy) ₃ ³⁺ + I ⁻	33 ± 9	1.83 × 10 ⁴ ± 0.05 × 10 ⁴	17.4 ± 2.1	-7.4 ± 7.0	9.1 ± 0.3	-10 ± 1
Os(phen) ₃ ³⁺ + SCN ⁻	<1.4	21.6 ± 5				
Os(bpy) ₃ ³⁺ + SCN ⁻	<0.024	9.8 ± 0.2			10.5 ± 0.5	-18.0 ± 1.7

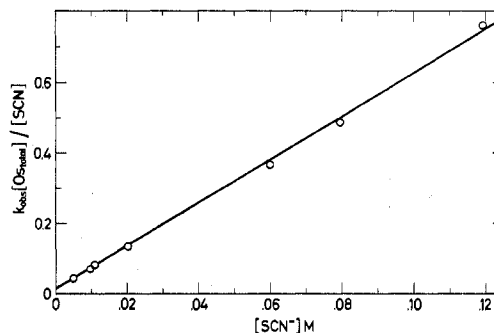


Figure 2. SCN⁻ dependence of the rate constant for oxidation by Os(bpy)₃³⁺. [Os(bpy)₃³⁺] = 2.92 × 10⁻⁵ to 5.06 × 10⁻⁵ M; I = 1.0 M; 17.2 ± 0.1 °C.

the last 10–20% of the reaction could not be accounted for using a constant value of R throughout because this increase is not a function of the ratio $[M(\text{II})]/[M(\text{III})]$. It may possibly reflect reduction of $M(\text{III})$ by intermediates formed during the hydrolysis of $(\text{SCN})_2$ (see below).

Solvent oxidation³ during the time of reaction was negligible in the absence of SCN⁻ (or I⁻). For both reductants the absorption spectra of the product solutions (UV to IR) were those calculated for complete conversion to Os(bpy)₃²⁺ and Os(phen)₃²⁺. No change in absorption occurred after periods of several days. In contrast to this the red color of the less robust Fe(bpy)₃²⁺ produced by the reaction of Fe(bpy)₃³⁺ with SCN⁻ slowly disappears.⁹

The value of $2k_2'$ given in Table V is calculated from the data in Table IV. The activation parameters were derived from analogous data at four other temperatures.

The parameter C was very small for the Os(bpy)₃³⁺-SCN⁻ system and varied from 0.017 M⁻¹ s⁻¹ at 17.2 °C (see Figure 1) to 0.03 M⁻¹ s⁻¹ at 33.0 °C. For Os(phen)₃³⁺ not only was C much larger (see last column of Table IV) but we also found that the second-order path was scarcely detectable at 33 °C and that at this temperature the kinetic data were poorly reproducible.

Our interpretation of the reaction which is second order in SCN⁻ is that this occurs according to eq 4. This is consistent with the following facts.

(a) At 25 °C $2k_2'$ for Os(phen)₃³⁺ is about twice that for Os(bpy)₃³⁺ and this is also the ratio not only for the corresponding reaction with I⁻ but also for the self-exchange rates of the two complexes.¹⁰

(b) The rate law found is also that for the Fe(H₂O)₆³⁺ oxidation of both I⁻¹¹ and SCN⁻¹² and also for the Fe(CN)₆³⁻-I⁻ reaction.^{13,14} It is, however, worthy of note that $R \neq 1$ for the Fe(H₂O)₆³⁺ reactions and also that these may occur by both inner- and outer-sphere mechanisms. $R = 1$ for the Fe(CN)₆³⁻-I⁻ reaction but the transition state also contains K⁺.¹⁵ We show later in this paper that the inclusion of such a cation in the transition state of the analogous Mo(CN)₈³⁻-I⁻ reaction probably does not necessitate a drastic change of mechanism. In all of the above cases the overall free-energy change is large and positive and the oxidation rates were interpreted using the mechanism also given here. This was originally postulated for the Fe(CN)₆³⁻-I⁻ reaction long

Table VI. Test of the Marcus Cross Relation for the Reaction $M_{Ox} + X^- \rightarrow M_{Red} + X \cdot$ at 25 °C^a

M_{Ox}	X^-	$\log k_{11}$	$-\log K_{12}$	$\log k_{12}$	
				obsd	calcd
$Os(phen)_3^{3+}$	I^-	8.49 ^b	9.13	1.41 ^c	1.58
$Os(bpy)_3^{3+}$	I^-	8.25 ^b	9.13	1.22 ^c (1.79) ^c	1.52
$Fe(bpy)_3^{3+}$	I^-	7.39 ^b	5.32	4.42 ^d (4.98) ^f	4.07
NpO_2^{2+}	I^-	2.02 ^g	4.06	2.42 ^g	2.32
$Mo(CN)_8^{3-}$	I^-	4.48 ^h	10.20	-0.47 ^j	-0.59
$IrCl_6^{2-}$	I^-	5.36 ⁱ	(7.90)	(2.60) ^f	(1.43)
$IrBr_6^{2-}$	I^-	8.21 ^e	(8.70)	(1.54) ^f	(1.86)
$Fe(bpy)_3^{3+}$	SCN^-	7.39 ^b	9.38	0.93 ^c (0.72) ^f	1.06
$IrCl_6^{2-}$	SCN^-	5.36	(11.95)	(-1.76) ^f	(-1.65)

^a For values in parentheses, $I = 0.1$ M; for others, $I = 1.0$ M. ^b Calculated from ref 10 (see text). ^c This work. $k_{22} = 10^7$ M⁻¹ s⁻¹ (see text); k_{12} and k_{11} are in M⁻¹ s⁻¹. ^d Calculated from the ionic strength dependence of the preceding reaction in the table. ^e Calculated from the rate of the $IrCl_6^{2-} + IrBr_6^{3+}$ reaction given in ref 22 using eq 8. ^f Reference 4. ^g Reference 20. ^h Reference 21. ⁱ Reference 22. ^j $I \rightarrow 0$; reference 23.

before the species X_2^- had been detected.¹⁶

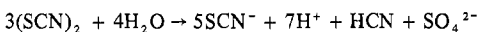
In addition to the above we note that the experimental values of $2k_2'$ agree well with those calculated using a Marcus-type correlation (see Table VII).

We cannot assume that k_{-2} is equal to k_4 because both are diffusion controlled (see discussion below and ref 33). That R for SCN^- is greater than for I^- is, however, explicable in terms of the potentials of the $X_2^- - 2X^-$ couples which are derived later in this paper (see also Table VIII).

We deduce that C does not equal $2k_1'$ but includes contributions from reactions other than the one given in eq 3. This is necessary in order to explain the following: (a) C is very much larger for $Os(phen)_3^{3+}$ than for $Os(bpy)_3^{3+}$.¹⁷ (b) Addition of $Os(II)$ and of ligand at the lowest SCN^- concentrations greatly increased the rates which also were poorly reproducible. Within the experimental error this was consistent with an extra term which was first order in $Os(III)$, $Os(II)$, and SCN^- .

In addition to the above we find that values for $2k_1'$ calculated using the Marcus correlation would be very much less than those found for C (cf. Table VI and also Scheme II).

The stoichiometry of the reaction can be derived to be $6M(III) + SCN^- + 4H_2O \rightarrow 6M(II) + HCN + SO_4^{2-} + 7H^+$ by combining $2M(III) + 2SCN^- \rightarrow 2M(II) + (SCN)_2$ with the hydrolysis of $(SCN)_2$.^{18,19}



This is the stoichiometry which was found in the presence of excess oxidant for the $Fe(phen)_3^{3+} - SCN^-$ reaction⁵ and which was assumed¹² for the $Fe(H_2O)_6^{3+} - SCN^-$ reaction. Both schools of workers who have studied the hydrolysis of thiocyanogen agree that the rapid preequilibrium



is succeeded by a rate-determining reaction of $SCNOH$. At pH ~ 5 this is said to be a slow reaction with solvent;¹⁹ at higher acid concentrations it is attributed to a faster disproportionation. We are unable to use the published data to calculate the rate of hydrolysis in our media. We note, however, that the rates of oxidation of SCN^- by $M(III)$ are acid independent in the restricted range of $[H^+]$ which we use (≤ 0.06 M).

General Discussion

The first step in the reaction scheme is a rapid preequilibrium involving the species formulated as $M^{III}X^-$. The equilibrium constant is required to be less than unity because no deviations from eq 1 and 7 were detectable in the range of $[X^-]$ studied. This species is most simply envisaged as an ion pair so that its free energy of formation includes the electrostatic work terms in the Marcus treatment of outer-

Table VII. Test of the Marcus Cross Relation for the Reaction $M_{Ox} + 2X^- \rightarrow M_{Red} + X_2^-$ at 25 °C

M_{Ox}	X^-	$-\log K_{12}'$	$\log k_{12}'$	
			obsd	calcd
$Os(phen)_3^{3+}$	I^-	4.06	4.23 ^b	3.81
$Os(bpy)_3^{3+}$	I^-	4.06	3.96 ^b (4.59) ^b	3.69
NpO_2^{2+}	I^-	-1.01	3.17 ^c	3.32
$IrBr_6^{2-}$	I^-	(3.62)	(3.64) ^d	3.95
$Fe(bpy)_3^{3+}$	SCN^-	4.14	3.29 ^b (3.86) ^d	3.23
$Fe(phen)_3^{3+}$	SCN^-	4.14	3.44 ^e	3.35
$Os(phen)_3^{3+}$	SCN^-	7.94	1.03 ^b	1.28
$Os(bpy)_3^{3+}$	SCN^-	7.94	0.69 ^b	1.18
$IrCl_6^{2-}$	SCN^-	(6.71)	(-0.49) ^d	0.69

^a For values in parentheses, $I = 0.1$ M; for others, $I = 1.0$ M. $k_{22} = 4 \times 10^3$ M⁻² s⁻¹ (see text). k_{12}' is in M⁻² s⁻¹. k_{11} for $Fe(phen)_3^{3+}$ is 4.3×10^7 M⁻¹ s⁻¹ and is calculated from data in ref 10. E° ($Fe(phen)_3^{3+} - Fe(phen)_3^{2+}$) taken as 1.065 V. ^b This work. ^c Reference 20. ^d Reference 4. ^e Reference 5.

sphere electron-transfer reactions. Tables VI and VII include the results of applying eq 8, which is the simplified Marcus

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad (8)$$

cross relation,⁶ to the reactions studied here and also to the oxidation of I^- and SCN^- by some other complexes. In eq 8 $\log f = (\log K_{12})^2 / 4 \log (k_{11}k_{22}/Z^2)$ and $Z = 10^{11}$ M⁻¹ s⁻¹. We use the usual terminology: k_{11} is the electron exchange rate constant for the metal complex, and K_{12} (Table VI) and K_{12}' (Table VII) are equilibrium constants. K_{12} is k_1'/k_{-1} for reaction 3 and K_{12}' is k_2'/k_{-2} for reaction 4. The data in Table VI are correlated using the average value 10^7 M⁻¹ s⁻¹ for k_{22} which formally would be the electron exchange rate of X^- with $X \cdot$. For Table VII we have used the average value 4×10^3 M⁻² s⁻¹ for k_{22}' , the "electron exchange rate" of $2X^-$ with X_2^- .

The value of k_{11} for $M(III)$ with $M(II)$, where the metal is Fe, Ru, Os, has been measured in acetonitrile together with that for $Fe(phen)_3^{3+}$ with $Fe(phen)_3^{2+}$ in D_2O .¹⁰ We have derived the exchange rate constants given in Table VI by combining the rate constant in D_2O with the ratio of the rate constants for Fe and Os in acetonitrile. It is possible that the true values in the medium we have used (1.0 M Cl^-) are consistently slightly larger than those recorded in the table because the measurements reported in ref 10 were made in more dilute solutions (~ 0.05 M ClO_4^-).

$E^{\circ}(I-I)$ is estimated to be 1.38 V (cf. ref 25) from K_{12}^{-1} for $Os(bpy)_3^{3+} + I^- = 1.3 \times 10^9$ (see above) and $E^{\circ}(Os(bpy)_3^{3+} - Os(bpy)_3^{2+}) = 0.84$ V (see Table VIII). The value determined for k_{-3} in ref 7 is 6.0×10^4 s⁻¹ leading to 1.3×10^5 M⁻¹ for the equilibrium constant of the reaction $I \cdot + I^- \rightleftharpoons I_2^-$ so that $E^{\circ}(I_2-2I^-)$ becomes 1.08 V.²⁷

In order to estimate $E^{\circ}(SCN^- - SCN^-)$ we have assumed that k_{-1} for $SCN^- + Fe(bpy)_3^{2+}$ has the value 2.2×10^{10} M⁻¹

Table VIII. Formal Reduction Potentials at 25 °C

couple	E° , V	method ^a	medium
Os(phen) ₃ ³⁺ -Os(phen) ₃ ²⁺	0.84 ^b	A	0.95 M NaCl + 0.05 M HCl
Os(bpy) ₃ ³⁺ -Os(bpy) ₃	0.835 ^b	A	0.95 M NaCl + 0.05 M HCl
	0.838 ^b	B	0.95 M NaCl + 0.05 M HCl
Fe(bpy) ₃ ³⁺ -Fe(bpy) ₃ ²⁺	1.065 ^b	B	0.95 M NaCl + 0.05 M HCl
NpO ₂ ²⁺ -NpO ₂ ⁺	1.14 ^c		1.0 M HClO ₄
Mo(CN) ₈ ³⁻ -Mo(CN) ₈ ⁴⁻	0.777 ^b	A	0.1 M HCl
	0.75 ^d		I → 0
IrCl ₆ ²⁻ -IrCl ₆ ³⁻	0.964 ^b	B	1.0 M NaCl
	0.913 ^b	B	0.1 M NaCl
IrBr ₆ ²⁻ -IrBr ₆ ³⁻	0.866	from the equilibrium constant for IrCl ₆ ²⁻ + IrBr ₆ ³⁻ ⇌ IrCl ₆ ³⁻ + IrBr ₆ ²⁻ in 0.1 M KNO ₃ and also 0.1 M NaNO ₃ ^e and E° for IrCl ₆ ²⁻ -IrCl ₆ ³⁻ in 0.1 M NaCl	I = 0.10
I-I ⁻	1.38 ^b	see text	I = 1.0 (NaCl + HCl)
I ₂ -2I ⁻	1.08 ^b	see text	I = 1.0 (NaCl + HCl)
SCN ⁻ -SCN ⁻	1.62 ^b	see text	I = 1.0 (NaCl + HCl)
(SCN) ₂ -2SCN ⁻	1.31 ^b	see text	I = 1.0 (NaCl + HCl)

^a A, cyclic voltammetry; B, potentiometric titration. ^b This work. ^c From ref 20. ^d From ref 24. ^e From ref 22.

s⁻¹ which is that found for the Os(bpy)₃²⁺ + I[•] reaction. Since the rate of the forward reaction, Fe(bpy)₃³⁺ + SCN⁻, in our medium is 8.5 ± 2.5 M⁻¹ s⁻¹⁸ and E° (Fe(bpy)₃³⁺-Fe(bpy)₃²⁺) = 1.065 V, we find E° (SCN[•]-SCN⁻) to be 1.62 V. All correlations of rates of SCN⁻ oxidations in both tables depend on this assumption because E° ((SCN)₂-2SCN⁻) is derived from E° (SCN[•]-SCN⁻) using 2.1 × 10⁵⁷ as the equilibrium constant for SCN[•] + SCN⁻ ⇌ (SCN)₂⁻.

Using k_1' from ref 4 corrected for ionic strength gives E° (SCN[•]-SCN⁻) = 1.67 V. Alternatively, if it is assumed that $k_{22} = 4 \times 10^3$ M⁻² s⁻¹ for I₂⁻ + 2I⁻ and also for (SCN)₂⁻ + 2SCN⁻ (cf. Table VII) and the values of k_2' (Table V) for the reaction of Os(bpy)₃³⁺ with 2I⁻ and of Os(bpy)₃³⁺ with 2SCN⁻ are substituted in the Marcus equation (8) together with log K_{12}' for Os(bpy)₃³⁺ + 2I⁻, we find log K_{12}' for Os(bpy)₃³⁺ + 2SCN⁻ to be -9.01. This together with E° (Os(bpy)₃³⁺-Os(bpy)₃²⁺) = 0.837 V, which is the average of the values in Table VIII, gives E° ((SCN)₂-2SCN⁻) = 1.37 V so that E° (SCN[•]-SCN⁻) = 1.68 V. For consistency we have used the value given in Table VIII, 1.62 V, throughout the remainder of this paper but can only state with confidence that from our work E° (SCN[•]-SCN⁻) is found to be in the range 1.62-1.68 V. The dissociation constants for the equilibria ISCN⁻ ⇌ I[•] + SCN[•] and ISCN⁻ ⇌ I[•] + SCN⁻ are reported to be 1.3 × 10⁻⁸ and 4.8 × 10⁻⁴ M, respectively.²⁹ These and E° (I-I) = 1.38 V give E° (SCN[•]-SCN⁻) = 1.65 V.

The observed rate constants in the tables are well reproduced using eq 8. The k_{22} values, however, are best regarded as useful parameters for predicting rates rather than as the true electron exchange rates of X[•] with X⁻ and X₂⁻ with 2X⁻ because they are very sensitive to small changes in the E° values used to derive K_{12} .

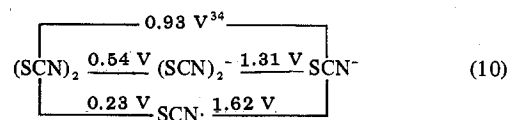
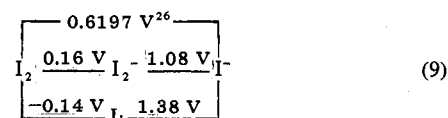
The fact that the rates of the NpO₂²⁺ + I⁻ reactions correlate well with those of the other complexes in Tables VI and VII is of particular interest for the following reasons. First, an inner-sphere mechanism cannot be eliminated; second, it is the only reaction in Table VI for which k_1' may not be almost equally well reproduced as $k_1' = K_{12}k_d$ with $k_d = 2.2 \times 10^{10}$ M⁻¹ s⁻¹. Analogously from Table VII we find that k_2 is much less for NpO₂²⁺ than for the other oxidants. The authors²⁰ of the NpO₂²⁺-I⁻ work have also studied the PuO₂²⁺ + I⁻ reaction.³⁰ From Table III of their paper we find for this that $2k_1' = 16.4$ M⁻¹ s⁻¹ and $2k_2' = 43$ M⁻² s⁻¹. E° (PuO₂²⁺-PuO₂⁺) is 0.9164 V but k_{11} for PuO₂²⁺ + PuO₂⁺ is not known. We calculate this to be 1.04 × 10⁴ M⁻¹ s⁻¹ by using eq 8 with $k_{22} = 10^7$ M⁻¹ s⁻¹ and note that although this is greater than k_{11} for NpO₂²⁺-NpO₂⁺, the ratio of the two rate constants is much less than the value 10⁴ found for k_{11} (Pu-

(III)-Pu(IV)) and k_{11} (Np(III)-Np(IV)) which have also been derived³¹ using the Marcus cross relation.

Because of the common rate law for the Fe(CN)₆³⁻ + I⁻ and Os(III) + SCN⁻ systems and also the correlation of the Mo(CN)₈³⁻ + I⁻ rate with the other reactions given in Table VI, it is unlikely that the inclusion of an alkali metal cation in the transition state requires an essentially new mechanism. It has been suggested²³ that differences in coordination number may be mechanistically significant and explain the differences in order of reaction in I⁻, 2 and 1, respectively, found for the Fe(CN)₆³⁻ and Mo(CN)₈³⁻ reactions. We note, however, that the experimental conditions used for the two systems were very different. The Mo(CN)₈³⁻ oxidation was studied only at very low concentrations of I⁻ where the k_1' term may well predominate, while conversely the Fe(CN)₆³⁻ oxidation rates were confined to concentrated I⁻ solutions where the major contribution to the rate would, by analogy with the other systems studied here, be expected to be the second-order k_2' path.

It has been noted by Wilmarth et al.⁴ that for IrBr₆²⁻ + I⁻ and for IrCl₆²⁻ + SCN⁻ the difference in enthalpy of activation between the two reaction paths is within the experimental error equal to ΔH° for the corresponding ion-radical equilibrium X[•] + X⁻ ⇌ X₂⁻. For X⁻ = I⁻, $\Delta H^{\circ} = -5.6$ kcal mol⁻¹ and for X⁻ = SCN⁻, $\Delta H^{\circ} = -6.4$ kcal mol⁻¹.^{7b} From Table V, then, $\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}$ for I⁻ with both Os(phen)₃³⁺ and Os(bpy)₃³⁺ also are within this range. We envisage an oriented ion triplet [M_{ox}X⁻...X⁻] as an intermediate for path 2. The X⁻-X⁻ bond formation in the succeeding precursor complex for electron transfer is required to be essentially that of the X₂⁻ radical.

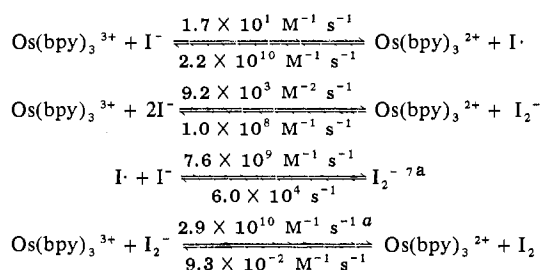
The success of the Marcus cross relation when applied to the oxidation of I⁻ and of SCN⁻ has led us to use this to construct the potential diagrams 9 and 10. We have also used



the Os(bpy)₃³⁺ oxidations of I⁻ and SCN⁻ as examples for calculating the rates of all steps in a mechanism which is simplified in that $k_1K_f = k_1'$ and $k_2K_f = k_2'$. These are given in Scheme I and Scheme II.

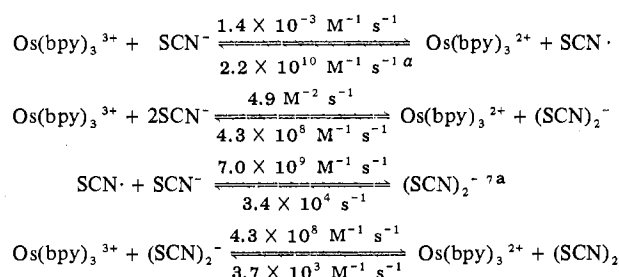
The value of k_4 for the I⁻ system is calculated using the Marcus equation (8) together with the electron exchange rate, k_{22} , of I₂ + I₂⁻ (8.5 × 10⁴ M⁻¹ s⁻¹) taken from ref 32. We note

Scheme I



^a Calculated using the Marcus equation. Other rates were either measured or calculated from the respective equilibrium constants (see text and Table VIII).

Scheme II



^a Assumed. Other rates were either measured or calculated from the respective equilibrium constants (see text and Table VIII).

that from eq 7, k_4 for the SCN^- system is k_{-2} and therefore is k_{12}'/K_{12}' from Table VII. The potential $E^\circ((\text{SCN})_2^-/(\text{SCN})_2^-)$ comes from the equilibrium constant for the $\text{Os}(\text{bpy})_3^{3+} + (\text{SCN})_2^-$ reaction which was calculated by using the Marcus equation and the preceding k_4 values (for I_2^- and $(\text{SCN})_2^-$) and assuming that the electron exchange rates (k_{22}) were the same.³³

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Registry No. $\text{Os}(\text{bpy})_3^{3+}$, 30032-51-0; $\text{Os}(\text{phen})_3^{3+}$, 47837-53-6; $\text{Fe}(\text{bpy})_3^{3+}$, 18661-69-3; NpO_2^{2+} , 18973-22-3; $\text{Mo}(\text{CN})_8^{3-}$, 17845-99-7; IrCl_6^{2-} , 16918-91-5; IrBr_6^{2-} , 16919-98-5; I^- , 20461-54-5; SCN^- , 302-04-5.

References and Notes

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- (33) If k_{-2} and k_4 are both assumed to be $2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, then $E^\circ(\text{SCN}^-/\text{SCN} \cdot)$ can be derived to be 1.71 V. This value together with $E^\circ(\text{Fe}(\text{bpy})_3^{3+}/\text{Fe}(\text{bpy})_3^{2+})$ and k_1' for $\text{Fe}(\text{bpy})_3^{3+} + \text{SCN}^-$ gives the improbably large value of $7 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ for the reverse rate constant k_{-1} .
- (34) This is much larger than that derived in ref 18 ($E^\circ((\text{SCN})_2^-/2\text{SCN}^-) = 0.77 \text{ V}$) using the equilibrium $\text{Au}(\text{SCN})_4^- \rightleftharpoons \text{Au}(\text{SCN})_2^- + (\text{SCN})_2$.