of positive sodium ions blocks the migration path of Cu(II) into the interphase. The concentration of SHS in these systems is much too small to allow this to be an effective mechanism.

It is of interest to compare the results of Letts and Mackay[14] in the study of the metalation of (TPP)H$_2$ in oil-in-water microemulsions. They obtained a rate of metalation in the presence of sodium dodecyl sulfate (SDS) that is quite similar to ours but were unable to effect any reaction at all in the presence of HPB. They explained their results by invoking a model where virtually all of the copper is bound to the surface of the droplet when SDS is the surfactant but is repelled by coulombic repulsion from the interphase when cationic surfactants are used. This rationale, applied to SDS, is generally consistent with our own observations. It is difficult, however, to explain why the phase-transfer mechanism via formation of copper halide complexes does not seem to be active in their systems, since the effective concentration of bromide in the aqueous phase would appear to be as high as 10^3 greater than that in our experiments.

The effect of addition of the anionic soap, potassium oleate, differs from the results obtained with SHS in that it enhances rather than retards the rate of chemical reaction. As with the cationic surfactants this appears to arise from a phase-transfer mechanism. Reaction of a Cu(II) salt with potassium oleate in aqueous solution produces instantaneous precipitation. The resulting copper oleate complex is totally insoluble in aqueous media but dissolves rapidly when introduced into toluene. As

a consequence, it would appear that the oleate complexes with the copper(II) ion in the water-rich droplet and is then ejected into the oil phase whereupon it reacts with the (TTP)H$_2$.

One further piece of data deserves comment. As is clear from Figure 3, solvent composition affects the metalation rate significantly. Throughout the microemulsion region, up to a mole fraction of 2-propanol slightly in excess of 0.5, the rate of metalation shows only a slight increase with 2-propanol content. Since the increase in 2-propanol content leads to a droplet size decrease and a droplet number increase, the surface area to volume ratio rises. With an increase in the interfacial area and a decrease in volume, the mean free path of migration of copper ions to (TPP)H$_2$ is decreased, enhancing the opportunity of an encounter. Once outside the microemulsion region, above a mole fraction of approximately 0.55, there is a rapid increase in rate with increasing 2-propanol. This implies a breakdown of the interphase leading to a more intimate mixing of the reacting species. This behavior is a dramatic demonstration of the effect of the interfacial barrier on reaction rates.

Registry No. Cu, 7440-50-8; (TPP)H$_2$, 917-23-7; Br$^-$, 24959-67-9; Cl$^-$, 16887-00-6.

Outer-Sphere Oxidation. 2.[1] Pulse-Radiolysis Study of the Rates of Reaction of the $I_2^-\cdot$ and $(SCN)_2^-\cdot$ Radical Anions with the Tris(2,2'-bipyridyl)[2] Complexes of Os(II) and Os(III)

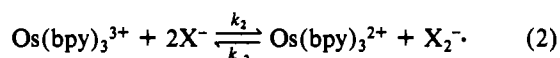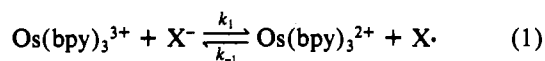GWYNETH NORD,* BRITTA PEDERSEN,[3a] EVA FLORYAN-LØVBORG, and PALLE PAGSBERG[3b]

Received February 20, 1981

The rate constants at 22 °C and an ionic strength of 0.1 M for the following reactions are

$$I_2^-\cdot + Os(bpy)_3^{2+} \underset{(3.33 \pm 0.17) \times 10^4 \, M^{-2} s^{-1}}{\overset{(1.1 \pm 0.3) \times 10^6 \, M^{-1} s^{-1}}{\rightleftharpoons}} 2I^- + Os(bpy)_3^{3+} \qquad I_2^-\cdot + Os(bpy)_3^{3+} \xrightarrow{(1.2 \pm 0.3) \times 10^{10} \, M^{-1} s^{-1}} I_2 + Os(bpy)_3^{2+}$$

$$(SCN)_2^-\cdot + Os(bpy)_3^{2+} \underset{25 \pm 5 \, M^{-2} s^{-1}}{\overset{(2.8 \pm 0.2) \times 10^9 \, M^{-1} s^{-1}}{\rightleftharpoons}} 2SCN^- + Os(bpy)_3^{3+}$$

$$(SCN)_2^-\cdot + Os(bpy)_3^{3+} \xrightarrow{(1.0 \pm 0.1) \times 10^{10} \, M^{-1} s^{-1}} (SCN)_2 + Os(bpy)_3^{2+}$$
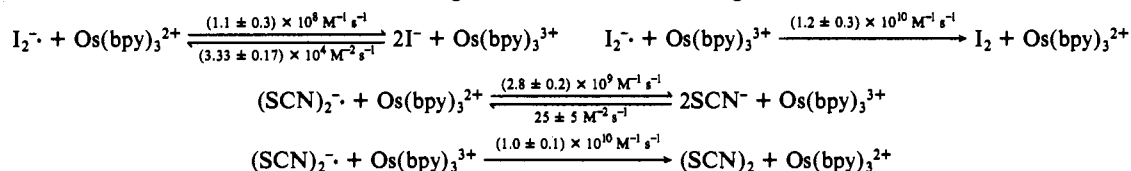
No adduct intermediates were detected. Formal reduction potentials for the following couples under the above conditions are as follows: Os(bpy)$_3^{3+}$–Os(bpy)$_3^{2+}$, 0.857 ± 0.004 V; I$_2^-\cdot$–I$^-$, 1.063 ● 0.011 V; I$_2^-\cdot$–I$_2$, 0.172 ± 0.011 V; (SCN)$_2^-\cdot$–SCN$^-$, 1.331 ± 0.008 V.

It has long been known that the oxidation of I$^-$ and SCN$^-$ by metal complexes such as Os(bpy)$_3^{3+}$, which are one-electron oxidizing agents, occurs through the following parallel paths where X$^-$ is I$^-$ or SCN$^-$:

$$Os(bpy)_3^{3+} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Os(bpy)_3^{2+} + X\cdot \qquad (1)$$

$$Os(bpy)_3^{3+} + 2X^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Os(bpy)_3^{2+} + X_2^-\cdot \qquad (2)$$

The radical products are connected through the equilibrium

$$X\cdot + X^- \rightleftharpoons X_2^-\cdot$$
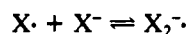
and X$_2^-\cdot$ is oxidized further according to eq 3.

$$X_2^-\cdot + Os(bpy)_3^{3+} \xrightarrow{k_3} X_2 + Os(bpy)_3^{2+} \qquad (3)$$
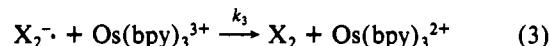
We have earlier found[1] that k_2 obeys a Marcus-type correlation for a series of complexes including Os(bpy)$_3^{3+}$, and in an attempt to gain more insight into the detailed mechanism of this third-order path we have now measured the reverse rate constant (k_{-2}) in solutions of X$_2^-\cdot$ produced by pulse radiolysis. According to (2) and (3), Os(bpy)$_3^{3+}$ and Os(bpy)$_3^{2+}$ compete for X$_2^-\cdot$, and in accordance with this we have been able to calculate both k_{-2} and k_3.

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(1) Part 1: G. Nord, B. Pedersen, and O. Farver, *Inorg. Chem.*, **17**, 2233 (1978).
(2) 2,2'-Bipyridyl is referred to as bpy.
(3) (a) H. C. Ørsted Institute. (b) Risø National Laboratory.

* To whom correspondence should be addressed at H. C. Ørsted Institute.

Table I. Molar Extinction Coefficients (ϵ, M^{-1} cm^{-1})

λ, nm	312	475	630
$\epsilon_{SCN_2^-}$	2.3×10^2	7.6×10^3	4.4×10^2
$\epsilon(SCN)_2$	$\sim 4 \times 10^2$	negligible	negligible

λ, nm	380	400	630
$\epsilon_{I_2^-}$	1.60×10^4	1.14×10^4	$(1.5 \pm 0.2) \times 10^3$
$\epsilon_{I_3^-}{}^a$	1.5×10^4 ^{b}	5.8×10^3	1.1×10

^{a} At 0.1 M I$^-$ all I$_2$ is effectively converted to I$_3^-$.[10] ^{b} From ref 10.
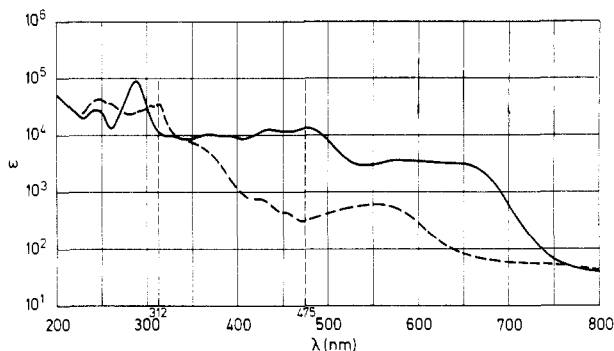
Figure 1. Absorption spectra of Os(bpy)$_3^{2+}$ (—) and of Os(bpy)$_3^{3+}$ (---).

The contribution of (1) is negligible because of the high concentrations of X$^-$ used in the present work. The complete reaction scheme includes (2), (3), and (4) together with the

$$2X_2^- \cdot \xrightarrow{k_4} X_2 + 2X^- \qquad (4)$$
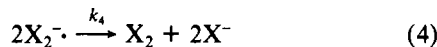
preliminary reactions which are complete within 2 μs[4-6] and which describe the effectively complete conversion of ·OH radicals to X$_2^-$·.

Experimental Section

All materials were of analytical reagent purity and were used without further treatment. Os(bpy)$_3$(ClO$_4$)$_2$ was prepared according to the literature methods given in ref 1. All solutions for pulse radiolysis were prepared with triply distilled water and deaerated with N$_2$O. N$_2$O, He, and Ar were of reagent grade and used without purification.

The pH was adjusted with solutions of HClO$_4$ or NaOH.

The rates of the slow reactions were followed as in ref 1. The spectra of Os(bpy)$_3^{2+}$ after irradiation was checked with a Cary-14 spectrophotometer, and no change at any pH could be seen.
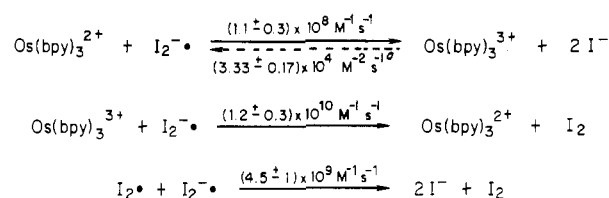
All measurements were made at 22 ± 1 °C.

The pulse-radiolysis experiments were carried out with 1.0-μs, 10-MeV, 1100-mA pulses from a HRC Lineac. The cell, optical arrangement, and analyzing light were as described in ref 7. The data were collected and processed with a digital storage oscilloscope, Explorer 3, Nicolet series 2090. Some of the experiments were duplicated with a Field Emission Corp. Febetron 705 B, which provides single-electron pulses of 30 ns and an energy of 2 MeV and a 3000-mA beam. The irradiation technique, cell, light source, and analyzing monochromator were as in ref 8 and 9.

The irradiation dose varied from 1 to 10 krd, being typically 1 krd. The absolute dose was determined by a 10^{-3} M K$_4$Fe(CN)$_6$, N$_2$O-saturated dosimeter using $G_{e_{aq}^-} + G_{OH} = 5.8$.

The reaction rates were followed spectrophotometrically over a series of wavelengths including 312, 475, and 630 nm for the thiocyanate system corresponding to a minimum, a maximum, and negligible
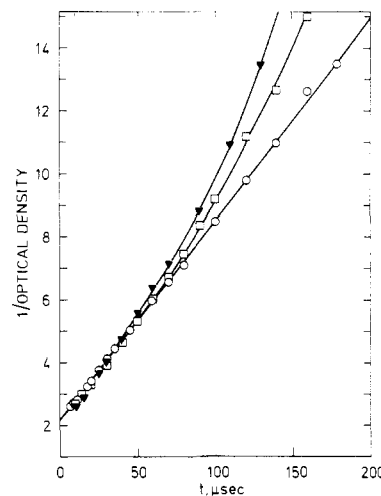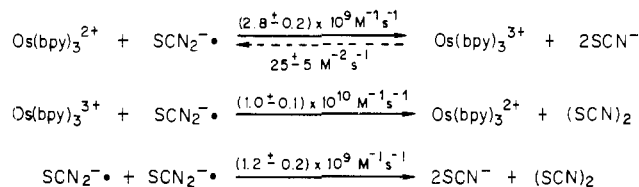
(4) J. H. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, **64**, 2389 (1968).
(5) D. Behar, P. L. T. Bevan, and G. Scholes, *J. Phys. Chem.*, **76**, 1537 (1972).
(6) Hch. Büchler and R. E. Bühler, *Chem. Phys.*, **16**, 9 (1976).
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(10) A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842 (1951).

Scheme I

^{a} From ref 1.

Scheme II

Figure 2. pH dependence of the disproportionation rate of (SCN)$_2^-$· ([SCN$^-$] = 0.10 M; dose = 1.9 ± 0.1 krd): O, pH 3; □, pH 7; ▼, pH 11.

absorption by SCN$_2^-$· (see Table I). The iodide system included measurements at 380 and 630 nm. The first wavelength corresponds to a maximum of absorption by I$_2^-$· (see Table I). It was necessary to use the latter wavelength with the higher concentrations of the Os(II) complex, $>2 \times 10^{-5}$ M, because of the high ϵ value of this species (see Figure 1).

All operations were made in an Ar or He atmosphere. The pulse to pulse dose variation for single pulses repeated at 10-min intervals was less than ±5%.

The concentrations of X$^-$ were always much greater than the concentration of the complex which varied between 10^{-5} M to 10 $\times$ 10^{-5} M. The concentration of X$^-$ was always great enough for OH· to be effectively all converted to I$_2^-$· or SCN$_2^-$· within less than 2 μs. The multistep processes producing I$_2^-$· and SCN$_2^-$· during this 2 μs are well documented.[4-6]

Rates were measured with and without added Os(bpy)$_3^{2+}$, and in the mixed solutions the starting concentration ratio [Os(bpy)$_3^{2+}$]:[X$_2^-$·] varied from 1.5 to 12.0.

With use of the complete reaction sequence given in Schemes I and II together with the starting concentrations of all reactants, the individual rate constants were determined by iteration using the computer simulation program described in ref 9 and 11.

The potentials for the metal complex couples in the media also used for the kinetic studies were measured as in ref 1.

Results

Microsecond Time Scale Kinetic Data. $2I_2^- \cdot \rightarrow I_2 + 2I^-$. In the absence of metal complex, the decay of I$_2^-$· was strictly

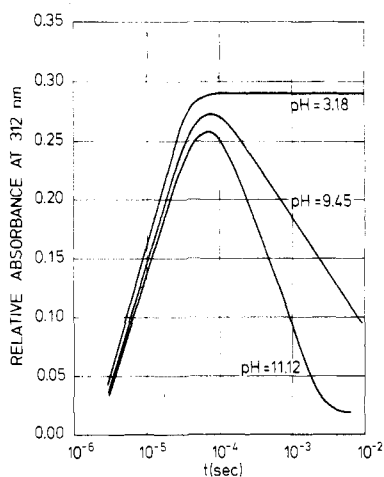(11) O. Lang Rasmussen, Risø Report No. 395 Risø National Laboratory, Roskilde, Denmark, 1979.

Figure 3. Illustration of the lack of complexity of $(SCN)_2^{-\cdot}$ reactions in sufficiently acid solutions (10^{-5} M Os(bpy)$_3$(ClO$_4$)$_2$ in 0.10 M NaSCN, N$_2$O saturated; dose = 1.04 ± 0.07 krd).
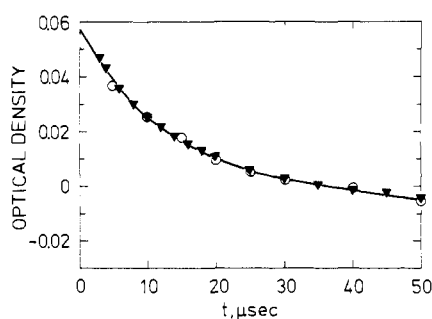

Figure 4. Simulated (▲) and experimental (○) decay rate of optical density (λ = 630 nm). The initial concentrations are [I$^-$] = 0.10 M, [Os(bpy)$_3^{2+}$] = 1.0 × 10^{-4} M, and [H$^+$] = 0.0010 M. Dose = 1.3 krd.

second-order throughout. The rate constant (see Scheme I) was that previously reported by other workers.[6] Changing the pH of the solution did not affect the rate of this reaction.

$2(SCN)_2^{-\cdot} \rightarrow (SCN)_2 + 2SCN^-$. In the absence of metal complex, the decay of $(SCN)_2^{-\cdot}$ was second order at pH 3, but deviations occurred at higher pH (see Figure 2). According to Henglein et al.,[12] the rate of hydrolysis of $(SCN)_2$ in alkaline solution is comparable to its rate of formation; however, in order to explain the deviations at higher pH in terms of hydrolysis it is necessary for one or more of the intermediates formed during hydrolysis[13] to oxidize $(SCN)_2^{-\cdot}$. This interpretation would also accord with the pH dependence and slow consecutive reduction of Os(bpy)$_3^{3+}$ which we find in alkaline solutions (Figure 3). The disproportionation rate constant for $(SCN)_2^{-\cdot}$ at pH 3 ($2k$ = (2.4 ± 0.2) × 10^9 M^{-1} s^{-1}, see Scheme II) is less than the literature values (4.2 × 10^9 M^{-1} s^{-1}[15] and 5.4 × 10^9 M^{-1} s^{-1}[4]), and we attribute this to the fact that the latter refer to neutral solutions and at least in one case were determined from the half-life of $(SCN)_2^{-\cdot}$ only.

$I_2^{-\cdot}$ + **Os(bpy)$_3^{3+}$ and** $I_2^{-\cdot}$ + **Os(bpy)$_3^{2+}$.** The change in optical density with time together with that calculated with the simulation program is illustrated in Figure 4. The reaction scheme together with the rate constants is given in Scheme
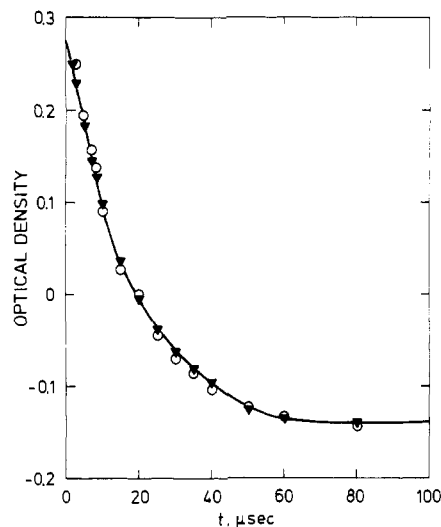

Figure 5. Simulated (▲) and experimental (○) decay rate of optical density (λ = 475 nm). The initial concentrations are [SCN$^-$] = 0.10 M, [Os(bpy)$_3^{2+}$] = 1.0 × 10^{-5} M, and [H$^+$] = 0.001 M. Dose = 1.3 krd.
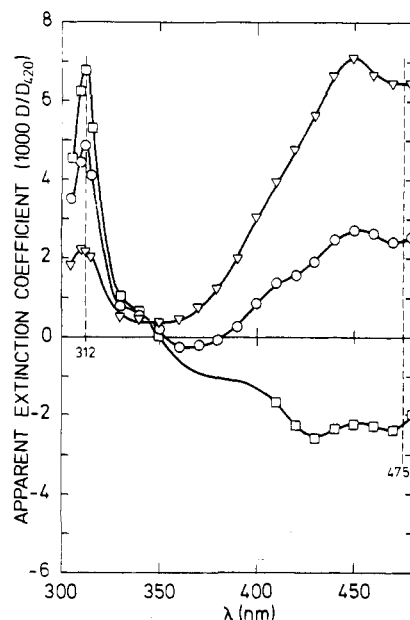

Figure 6. Example of transient spectra used to confirm the absence of an absorbing adduct. The initial concentrations are [SCN$^-$] = 0.10 M and [Os(bpy)$_3^{2+}$] = 1.0 × 10^{-5} M. Dose = 1.89 krd. ▽ = 2.5 μs; ○ = 10 μs; □ = 35 μs.

I. The additivity of the absorption of the species Os(bpy)$_3^{3+}$, Os(bpy)$_3^{2+}$, $I_2^{-\cdot}$, and I^{3-} clearly showed that no adduct formation is detectable.

$SCN_2^{-\cdot}$ + **Os(bpy)$_3^{3+}$ and** $(SCN)_2^{-\cdot}$ + **Os(bpy)$_3^{2+}$.** Analogous data to those in Figure 4 are given in Figure 5. The reaction scheme together with the rate constants is given in Scheme II. The contribution of the disproportionation (the last reaction in Scheme II) was less for $(SCN)_2^{-\cdot}$ than for the analogous $I_2^{-\cdot}$ system. The transient absorption and decay in the 300–480-nm range is given in Figure 6 and could, for this system also, be reproduced without extra absorption from an adduct.

For all the above reactions, simulated data were obtained over a range of complex concentration (1.0 × 10^{-5} M–1.0 × 10^{-4} M), dose (0.9–2.2 krd), and excess X$^-$ concentration (0.01–0.1 M),[16] and in all cases the experimental optical

(12) M. Schöneshöfer, G. Beck, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **74**, 1011 (1970).

(13) The complicated series of reactions occurring during the hydrolysis of (SCN)$_2$ has recently been discussed.[12] We have carefully confirmed that there are no contributions due to hydrolysis of (SCN)$_2$ during the reactions in the acid solutions which are the subject of the present paper.[18]

(14) D. M. Stanbury, W. K. Wilmarth, S. Kalaf, H. N. Po, and J. E. Byrd, *Inorg. Chem.*, **19**, 2715 (1980).

(15) R. Wilbrandt, N. H. Jensen, P. Pagsberg, A. H. Sillesen, K. B. Hansen, and R. E. Hester, *Chem. Phys. Lett.*, **60**, 315 (1979).

(16) These values replace those given in a preliminary report for the SCN$^-$ system.[17] There is no large ionic strength effect.

Table II

$$M_{Ox} + 2X^- \underset{k_{-2}}{\overset{k_2'}{\rightleftharpoons}} M_{Red} + X_2^- \cdot \quad \text{(Ionic Strength = 0.1 M)}$$

M_{Ox}	X^-	k_2', M⁻¹ s⁻¹	k_{-2}, M⁻¹ s⁻¹	$E°'_M$, V	$E°'_X$, V	k_{11}, M⁻¹ s⁻¹	k_{22}, M⁻¹ s⁻¹
Os(bpy)₃³⁺	SCN⁻	25	2.8 × 10⁹	0.857	1.331	(4.57 × 10²)	(8 × 10⁹)
Fe(bpy)₃³⁺	SCN⁻	7.5 × 10³ [a,d]	(1.08 × 10⁸)	1.085	1.331	(4.57 × 10²)	(4 × 10⁹)
Os(bpy)₃³⁺	I⁻	3.33 × 10⁴ [b]	1.1 × 10⁸	0.857	1.063	(1.0 × 10³)	(8 × 10⁹)
IrBr₆²⁻	I⁻	4.25 × 10³ [a,c]	(2.2 × 10⁷)	0.843[a]	1.063	(1.0 × 10³)	2 × 10⁸ [a]

[a] From ref 14, 25 °C; this work, 22 °C. The values in parentheses are calculated. [b] $k_1 = 61.71$ M⁻¹ s⁻¹. [c] $k_1 = 28$ M⁻¹ s⁻¹. [d] $k_1 = 5.25$ M⁻¹ s⁻¹.

density vs. time curves could be reproduced within the limits illustrated in Figures 4 and 5.

Additional Data. $Os(bpy)_3^{3+} + 2SCN^- \rightarrow Os(bpy)_3^{2+} + (SCN)_2^- \cdot$. We earlier found that at an ionic strength of $\mu = 1.0$ M it was possible to use concentrations of SCN⁻ and H⁺ great enough so that only the k_2' path was experimentally observable ($k_2' = 4.9 \pm 0.2$ M⁻² s⁻¹, 25.0 °C, $\mu = 1.0$, see Table V of ref 1). We have now found that k_2' at 22.0 °C, $\mu = 0.1$, and [H⁺] = 0.5 M[18] is 25 ± 5 M⁻² s⁻¹. The ratio of the ionic strength dependence is within experimental error equal to that for the analogous but faster $Fe(bpy)_3^{3+} + SCN^-$ and $Os(bpy)_3^{3+} + I^-$ systems. In 0.10 M NaCl the formal standard potential $E°'$ (22.0 °C) of the $Os(bpy)_3^{3+}-Os(bpy)_3^{2+}$ couple is found to be 0.857 ± 0.004 V, and $E°'_{Fe(bpy)_3^{3+} - Fe(bpy)_3^{2+}}$ at 22.0 °C is 1.085 ± 0.004 V ($E°'_{IrCl_6^{2-} - IrCl_6^{3-}}$ at 25.0 °C is 0.913 V[1]).

Molar Extinction Coefficients. The absorption spectra of $Os(bpy)_3^{2+}$ and $Os(bpy)_3^{3+}$ are given in Figure 1. The absorption of $(SCN)_2^- \cdot$ and of $I_2^- \cdot$ was obtained by extrapolating to zero time the kinetic plots in the absence of complex. The duration of the pulse was 1 μs, less than 0.5% of the time for completion of the disproportionation reactions. Molar extinction coefficients at the wavelengths used for elucidation of the rate constants are given in Table I. The extinction coefficients for $(SCN)_2^- \cdot$ were obtained from a G value of 5.8 for OH·. The value of $(7.6 \pm 0.3) \times 10^3$ M⁻¹ cm⁻¹ at $\lambda = 475$ nm is in agreement with that found by earlier workers on the system[4,19] as was also the absorption for $I_2^- \cdot$, which has λ max at 380 nm and a maximum extinction coefficient of $(1.6 \pm 0.1) \times 10^4$ M⁻¹ cm⁻¹.[6]

Discussion

The new data enable us first to resolve the ambiguities for the SCN⁻ oxidation in part 1 of this series and secondly to confirm the applicability of the treatment of the intimate mechanism suggested in a recent publication from the school of the late Wayne K. Wilmarth.[14]

The stoichiometry of the SCN⁻ oxidation in the acid media used was earlier assumed[1,14] to be the same as that for the I⁻ oxidation: this is correct. In part 1, however, we also assumed that $k_{-2} = k_3$ for the SCN⁻ system, and this is incorrect. This error means that both the method used for calculating the overall standard potential for the $(SCN)_2-SCN^-$ couple and also the value for this given in part 1 are incorrect.[20]

The formal potentials for the $X_2^- \cdot -X^-$ couples have been calculated with the new rate constants. $E°'_{(SCN)_2^- \cdot -SCN^-}$ is 1.331 ± 0.008 V, in good agreement with the previously estimated values (1.31,[1] 1.29 V[14]). $E°'_{I_2^- \cdot -I^-}$ is 1.063 ± 0.011 V, also in agreement with earlier estimates (1.08,[1] 1.04 V[14]).

There seems little doubt that the marcus relation (eq 5)

$$k_{12} = (k_{11}k_{22}K_{eq}f)^{1/2}$$
$$\log f = (\log^2 K_{eq})/(4 \log (k_{11}k_{22}/Z^2)) \tag{5}$$

could accurately predict the rate of the path which is second order in SCN⁻ or I⁻ for all the oxidants which are listed in ref 1, 14, and 23.

k_{22}, the self-exchange rate constant for $Os(bpy)_3^{3+} + Os(bpy)_3^{2+}$, is not accurately known in either of the chloride solutions so that we can therefore only use our new data to calculate the product $k_{11}k_{22}$, where k_{11} is the self-exchange rate constant for $X_2^- \cdot + 2X^-$. $k_{11}k_{22}$ is 8.0×10^{12} M⁻² s⁻² for I⁻ and 3.6×10^{12} s⁻² for SCN⁻. The absolute values for k_{11} and k_{22} given in Table II are based on k_2, k_{22}, and $E°'_{Ox-Red}$ for the oxidation of I⁻ by $IrBr_6^{2-}$ in 0.1 M NaCl taken from ref 14.

The rate constants (k_1 and k_2) for *both* paths are known for $IrBr_6^{2-} + I^-$ and $Os(bpy)_3^{3+} + I^-$ in 0.10 M NaCl (see Table II). The k_1 path has been shown to approximately obey a Marcus correlation[1] and to more accurately follow a LFER.[14] We show below that it is the latter which is applicable.

The LFER for the k_1 path and the Marcus cross correlation for the k_2 path accord with the Wilmarth mechanism[14] if $k_1 = K_{1\,eq} k_{-1\,d}$ and $k_2 = K_{2\,eq} k_{-2\,et}$. The ratio $K_{2\,eq}{:}K_{1\,eq}$ for I⁻ is the ratio of the forward and reverse rate constants of the I· + I⁻ $\rightleftharpoons I_2^- \cdot$ reaction and is 1.3×10^5 M⁻¹.[4] $k_{-1\,d}$ is 2×10^{10} M⁻¹ s⁻¹, which is in excellent agreement with that calculated from k_2 and $K_{2\,eq}$ alone and given in Table II. A similar treatment for the SCN⁻ system, with the rate constants[14] for both paths and with $K_{2\,eq}/K_{1\,eq} = 2.06 \times 10^5$ M⁻¹,[4] gives $k_{-2} = k_2/K_{2\,eq} = 1.0 \times 10^8$ M⁻¹ s⁻¹ and $k_{2\,et} = 2.5 \times 10^{-8}$ M⁻¹ s⁻¹ for Fe(bpy)₃³⁺ and $k_{-2} = k_2/K_{2\,eq} = 2.5 \times 10^7$ M⁻¹ s⁻¹ and $k_{-2\,et} = 1.6 \times 10^7$ M⁻¹ s⁻¹ for $IrCl_6^{2-}$.[24] An analogous calculation for Os(bpy)₃³⁺ and I⁻ gives $k_{-2\,et} = 1.0 \times 10^8$ M⁻¹ s⁻¹, which is the *experimental* value.

Registry No. Os(bpy)₃²⁺, 23648-06-8; Os(bpy)₃³⁺, 30032-51-0; I₂⁻·, 12190-71-5; (SCN)₂⁻·, 34504-17-1.

(17) E. Floryan-Løvborg, P. Pagsberg, G. Nord, and B. Pedersen, "Fast Reactions in Solution, Discussion Group Meeting, Sept 3–5, 1980", The Chemical Society, London, and Max-Planck Gesellschaft, Göttingen, 1980, p 45.

(18) The plateau illustrated at pH 3 in Figure 3 does not extend to the second time range for air-saturated solutions.[14] Decreasing the [H⁺] from ≥0.05 to 0.001 M leads to an increase in the rate of the Os(bpy)₃³⁺ reduction.

(19) R. H. Schuler, L. K. Patterson, and E. Janata, *J. Phys. Chem.*, **84**, 2088 (1980).

(20) $E°'_{I_2 - I^-} = 0.6197$ V[21] so that we find $E°'_{I_2^- \cdot -I^-} = 0.172 \pm 0.001$ V. The generally accepted literature value for $E°_{(SCN)_2-SCN^-}$ (0.77 V[22]) leads to $E°'_{(SCN)_2^- \cdot -(SCN)_2} \simeq E°'_{I_2^- \cdot -I_2}$.

(21) W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, **12**, 962 (1973).

(22) N. Bjerrum and A. Kirschner, *K. Dan. Vidensk. Selsk. Skr., Naturvidensk. Math. Afd.*, [8] 1 (1918).

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

(24) To be consistent with Table II, k_{22} for $IrCl_6^{2-} + IrCl_6^{3-}$ is required to be 10^5 M⁻¹ s⁻¹, not 2×10^5 M⁻¹ s⁻¹ as used in ref 14.