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ELECTRON-TRANSFER REACTIONS INVOLVING SIMPLE FREE RADICALS *

WAYNE K. WILMARTH, DAVID M. STANBURY **, JAMES E. BYRD †,
HENRY N. PO ††, AND CHEE-PENG CHUA

Department of Chemistry, University of Southern California, Los Angeles, CA 90007 (U.S.A.)

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A. INTRODUCTION

Despite the various approximations of the model, Marcus' theory and its elaborations have been quite successful in treating the rates of outer-sphere

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* Dedicated to the memory of Wayne Keith Wilmarth.

** To whom correspondence may be addressed at the Department of Chemistry, Rice University, P.O. Box 1892, Houston, TX 77251, U.S.A.

† Present address: Department of Chemistry, California State College, Stanislaus, Turlock, CA 95380, U.S.A.

†† Present address: Department of Chemistry, California State University, Long Beach, CA 90840, U.S.A.

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electron-transfer reactions. The model seems to be most appropriate to reactions between two weakly charged complexes which have substitutionally inert and saturated coordination shells in both oxidation states. The model is quite inappropriate to the oxidation of, for example, iodide by bromine atoms; by analogy with I_2^- and Br_2^- the reaction can be expected to proceed by diffusion-controlled formation of IBr^-, and so the weak overlap approximation is grossly violated. An intermediate class comprises redox reactions between conventional "outer-sphere" redox agents and simple main-group species such as the oxidation of nitrite by hexachloroiridate. Current results, although limited, have shown that in this class Marcus' theory is marginally appropriate.

One major area of research in Professor Wilmarth's laboratories during the 1970s was a broad investigation of the oxidation of simple main-group species by the well-known oxidants $IrCl_6^{2-}$, $IrBr_6^{2-}$ and $Fe(bpy)_3^{3+}$. The majority of these reactions proceed by simple bimolecular kinetics. A few of the reactions also show pathways which are first order in oxidant and second order in reductant; these third-order reactions have already been discussed [1]. The three oxidants were selected in order to provide two similar species and one quite different, differing in charge type, metal center and type of ligand. The two iridium complexes are of interest because although $IrCl_6^{2-}$ is the stronger oxidant, it has a slower self-exchange rate. The main-group species $S_2O_3^{2-}$, I^-, SCN^-, N_3^-, NO_2^-, and SO_3^{2-} also provide a wide variety of properties. The complete set of 18 reactions between these oxidants and reductants is described in this paper. Some additional results are described for the oxidation of CN^-.

B. EXPERIMENTAL

(i) Reagents

K_2IrBr_6 was obtained from A.D. McKay Co., and K_2IrCl_6 and $Na_2IrCl_6 \cdot 6H_2O$ were obtained from Alfa Products. $[Fe(bpy)_3](ClO_4)_2$ was prepared as described by Sutin and Gordon [2]. Other chemicals were of reagent grade and were obtained from Mallinckrodt and J.T. Baker. $NaNO_2$ was recrystallized twice from ethanol solution; NaN_3 and NaCN were recrystallized once from triply distilled water; other reagents were used as supplied. Triply distilled water was used in preparing the solutions. A stock solution of $NaClO_4$ was prepared by neutralizing concentrated $HClO_4$ with Na_2CO_3. The resulting $NaClO_4$ crystals were collected by filtration and were redissolved in water. The CO_2 gas was expelled from the stock solution either by boiling or by deaerating with N_2. The concentration of $NaClO_4$ was determined gravimetrically or by titration of an aliquot which had been passed through an acidic cation exchanger with 0.1N NaOH.

(ii) Analyses

The concentration of $IrCl_6^{2-}$ in solution was determined spectrophotometrically. We have carefully carried out replicate experiments to obtain a value for ε of $3.70 \times 10^3 M^{-1}$ cm^{-1} at 487 nm for $IrCl_6^{2-}$; reported ε values for $IrCl_6^{2-}$ are $3.2 \times 10^3 M^{-1}$ cm^{-1} at 490 nm and $4.06 \times 10^3 M^{-1}$ cm^{-1} at 488 nm. In the stoichiometry studies the Ir(III) product was identified by Cl_2 oxidation and comparison of the resulting spectra with those of authentic $IrCl_6^{2-}$.

(iii) Kinetic measurements

An Aminco-Morrow stopped-flow spectrophotometer was used to follow those reactions with half-lives < 5 s. Other work was performed on Cary 14R and Beckman ACTA VI spectrophotometers. In all cases, the reaction temperature was maintained at 25.0 ± 0.1°C. All of the kinetic runs were performed under pseudo-first-order conditions with a large excess of substrate. Sodium perchlorate and perchloric acid were used to adjust the ionic strength ($\mu = 0.10M$) and the acidity of the solutions. The rate of loss of $IrCl_6^{2-}$ was monitored at 487 nm, and the rate of loss of $IrBr_6^{2-}$ was monitored at 585 nm; in the case of $Fe(bpy)_3^{3+}$, the rate of formation of $Fe(bpy)_3^{2+}$ was monitored at 522 nm. Pseudo-first-order rate constants were obtained from plots of $\log(A - A_\infty)$ vs. time which were linear for at least four half-lives. All the k_{obs} values reported are averages of two to four replicate runs.

Although the aquation rates of the oxidants are all quite slow, fresh solutions were prepared for each run by dissolving the appropriate weight of oxidant in a prethermostated solution. Sulfite and bisulfite solutions were prepared by adding $HClO_4$ to Na_2SO_3 or $Na_2S_2O_5$, and they were then deaerated under N_2 to eliminate the kinetic effects of O_2. Concentrations of HSO_3^- and H^+ in each reaction mixture were calculated from the initial amounts of $HClO_4$ and S(IV) using the values $K_1 = [H^+][HSO_3^-]/[H_2SO_3] = 2.4 \times 10^{-2}M$ and $K_2 = [H^+][SO_3^{2-}]/[HSO_3^-] = 1.2 \times 10^{-7}M$ at 25°C in 0.10M $NaClO_4$ [3].

C. RESULTS

(i) Stoichiometry

The oxidation of $S_2O_3^{2-}$ by $IrCl_6^{2-}$ has been studied by Novoselov and Muzykantova [4]; they found quantitative conversion of $IrCl_6^{2-}$ to $IrCl_6^{3-}$ when excess $S_2O_3^{2-}$ was present. We have measured the consumption of

$IrCl_6^{2-}$ when $IrCl_6^{2-}$ was in excess; the consumption ratio $\Delta[IrCl_6^{2-}]/[S_2O_3^{2-}]_0$ was found to be dependent on the initial concentration ratio $[IrCl_6^{2-}]_0/[S_2O_3^{2-}]_0$, but there was no dependence on $[O_2]$. At neutral pH the concentration ranges of $[IrCl_6^{2-}]_0 = 0.0213\text{–}3.75 \times 10^{-5}$M and $[S_2O_3^{2-}]_0 = 0.0483\text{–}5.0 \times 10^{-4}$M were used to obtain initial concentration ratios ranging from 5 to 220. The consumption ratio increased rapidly from 3.5 to 5 as the initial concentration ratio changed from 5 to 20, and then it slowly increased to 6.75 as the initial concentration ratio reached 220. These results are shown in Fig. 1, and they imply that there is more than one reaction path for the consumption of the primary free radical. The sulfur-containing products were not identified. Extrapolation of the trends in Fig. 1 suggests limiting consumption ratios of 1 and 8. These correspond to the following stoichiometries:

$$2IrCl_6^{2-} + 2S_2O_3^{2-} \rightarrow 2IrCl_6^{3-} + S_4O_6^{2-} \tag{1}$$

and

$$8IrCl_6^{2-} + S_2O_3^{2-} + 5H_2O \rightarrow 8IrCl_6^{3-} + 2SO_4^{2-} + 10H^+ \tag{2}$$

An intermediate stoichiometry of 6 : 1 is also feasible. This is the dithionate formation:

$$6IrCl_6^{2-} + S_2O_3^{2-} + 3H_2O \rightarrow 6IrCl_6^{3-} + S_2O_6^{2-} + 6H^+ \tag{3}$$

The reaction conditions under which the kinetic studies were conducted were always with a 10–200-fold excess of $S_2O_3^{2-}$, and so the limiting stoichiometry of 1 : 1 should apply.

That the oxidation of I^- by $IrCl_6^{2-}$ quantitatively yields $IrCl_6^{3-}$ has been

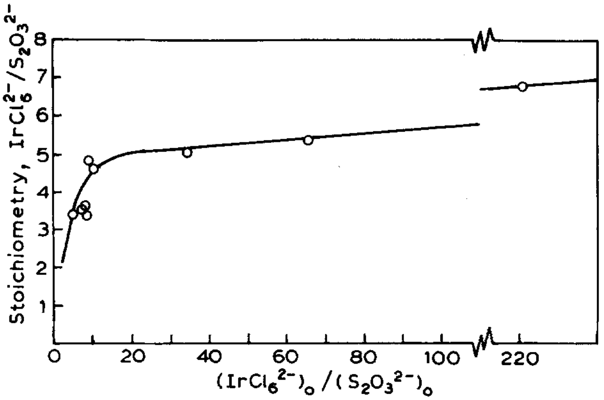

Fig. 1. Stoichiometry variation for the oxidation of $S_2O_3^{2-}$ by $IrCl_6^{2-}$ as a function of initial reactant's concentration ratio.

confirmed by Novoselov and Muzykantova [4] and by ourselves. The yield of I_3^- was determined with a large excess of I^- over $IrCl_6^{2-}$. Under the conditions $[I^-]_0 = 0.01M$, $[H^+] = 1 \times 10^{-3}M$, $[IrCl_6^{2-}]_0 = 1.75 \times 10^{-4}M$, the final spectrum of the solution showed a maximum at 352 nm, corresponding to the expected I_3^- spectrum [5]. The absorbance at that wavelength, after correction for $IrCl_6^{3-}$, was 1.830, and this corresponds to a yield of $7.0 \times 10^{-5}M$ I_3^-. A theoretical yield of $7.6 \times 10^{-5}M$ I_3^- was calculated using the reported [5] equilibrium constant of $1.4 \times 10^{-3}M$ for the reaction $I_3^- \rightleftharpoons I_2 + I^-$. This error of 8.6% is well within expected experimental error, and so the stoichiometry is written as:

$$2IrCl_6^{2-} + 3I^- \rightarrow 2IrCl_6^{3-} + I_3^- \qquad (4)$$

$(SCN)_2$ is presumed to be an intermediate in the oxidation of SCN^- by $IrBr_6^{2-}$, but because of its rapid hydrolysis the ultimate products are SO_4^{2-} and CN^-. Cyanide was determined [6] by distilling HCN from the products arising from mixing 1.92×10^{-5} moles of $IrBr_6^{2-}$ with 8.4×10^{-4} moles of NaSCN in 10 ml of H_2O. The distilled HCN was trapped in ammoniacal Ni(II), and the UV absorbance of $Ni(CN)_4^{2-}$ indicated, by comparison with a calibration curve, a yield of CN^- of $(3 \pm 0.5) \times 10^{-6}$ moles of CN^-. This method was somewhat inaccurate due to turbidity of the Ni(II) solutions, so a titration method was used for the corresponding reaction of $IrCl_6^{2-}$ [1]. A qualitative test for SO_4^{2-} using $Ba(NO_3)_2$ was positive. $IrBr_6^{3-}$ was identified as the iridium-containing product by mixing $2.3 \times 10^{-4}M$ $IrBr_6^{2-}$ and $5.4 \times 10^{-2}M$ SCN^- in a 10-cm cuvette. Comparison with reported [7] spectra of $IrBr_6^{3-}$ and $IrBr_5H_2O^{2-}$ indicated that the major product was $IrBr_6^{3-}$. This conclusion was somewhat complicated by the slow subsequent aquation of $IrBr_6^{3-}$. The stoichiometry is thus given as:

$$6IrBr_6^{2-} + SCN^- + 4H_2O \rightarrow 6IrBr_6^{3-} + SO_4^{2-} + CN^- + 8H^+ \qquad (5)$$

The oxidation of N_3^- by $IrCl_6^{2-}$ was investigated under a variety of conditions. A mixture of 0.1M NaN_3 and $2 \times 10^{-4}M$ $IrCl_6^{2-}$ was allowed to react; it was then acidified with 1.0M $HClO_4$ and oxidized by Cl_2. The excess Cl_2 was eliminated with argon and the visible spectrum was recorded. The peak positions and intensities corresponded with those expected for complete recovery of $IrCl_6^{2-}$. Bubbles were observed to form on the cell walls during the initial reaction. A consumption ratio of 1.02 for $\Delta N_3^-/\Delta IrCl_6^{2-}$ was obtained from a mixture of $1.52 \times 10^{-2}M$ $IrCl_6^{2-}$ and $5.64 \times 10^{-3}M$ NaN_3 after 3 h. Attempts to determine NO_3^- by the chromotropic acid method [8] failed, presumably because of oxidation of $IrCl_6^{3-}$ in concentrated H_2SO_4. A qualitative test for NH_3 formation by the indophenol method [9] was negative.

Although nitrogen oxides are sometimes a product of N_3^- oxidations, the

1/1 consumption ratio argues against this possibility. The results are consistent with:

$$\mathrm{IrCl_6^{2-} + N_3^- \rightarrow IrCl_6^{3-} + \tfrac{3}{2}N_2} \qquad (6)$$

Spectral titrations of solutions containing 0.0107 g K_2IrCl_6 in 100 ml of solution ($\mu = 0.10M$) at 490 and 435 nm with $3.0 \times 10^{-2}M$ NaCN solution were carried out. Both of these experiments yielded a consumption ratio of 1.0, implying the stoichiometry:

$$\mathrm{IrCl_6^{2-} + CN^- \rightarrow IrCl_6^{3-} + \tfrac{1}{2}(CN)_2} \qquad (7)$$

We have confirmed Novoselov and Muzykantova's report [4] that $IrCl_6^{3-}$ is the product of the oxidation of nitrite by $IrCl_6^{2-}$. The consumption ratio was determined by allowing a solution containing $6.98 \times 10^{-5}M$ $NaNO_2$ and $2.41 \times 10^{-4}M$ K_2IrCl_6 to react to completion. This yielded a ratio for $\Delta IrCl_6^{2-}/\Delta NO_2^-$ of 2.08. No attempt was made to isolate the expected NO_3^- ion produced in the reaction. The stoichiometry is concluded to be:

$$\mathrm{H_2O + 2IrCl_6^{2-} + NO_2^- \rightarrow 2IrCl_6^{3-} + NO_3^- + 2H^+} \qquad (8)$$

Sulfite is oxidized by $IrCl_6^{2-}$ with variable stoichiometry. This has been investigated several times [4,10,11], and we have confirmed that $IrCl_6^{3-}$ is the only iridium-containing product of the reaction. As in the previous investigations we have not tried to analyse the sulfur-containing products, but we have measured consumption ratios. When HSO_3^- was added to a solution containing at least a 2-fold excess of K_2IrCl_6 in 0.01M sodium acetate, only 0.6 moles of $IrCl_6^{2-}$ were consumed per mole of S(IV). When the reactions were performed under a N_2 atmosphere with the exclusion of O_2, more consistent results were obtained. Seven measurements were made under the following conditions: $[S(IV)] = (6.86\text{–}7.10) \times 10^{-5}M$; $[K_2IrCl_6] = (1.51\text{–}1.91) \times 10^{-4}M$; and $[NaOAc] = 0.010M$ and in N_2 atmosphere. The average consumption ratio was 2.04 ± 0.08 moles of $IrCl_6^{2-}$ per mole of S(IV). Thus, in the absence of oxygen:

$$\mathrm{2OH^- + 2IrCl_6^{2-} + SO_3^{2-} \rightarrow 2IrCl_6^{3-} + SO_4^{2-} + H_2O} \qquad (9)$$

In the presence of oxygen $IrCl_6^{2-}$ initiates (and terminates) a chain reaction between O_2 and SO_3^{2-}, thus accounting for the low consumption of $IrCl_6^{2-}$. Previous workers [10,11] have found a consumption ratio of < 2 in the absence of O_2 and have attributed this to dimerization of the SO_3^- radical. Our higher ratio seems to be a result of the higher pH in our studies.

(ii) Kinetics

The pseudo-first-order oxidations of thiosulfate by $Fe(bpy)_3^{3+}$, $IrBr_6^{2-}$, and $IrCl_6^{2-}$ were performed in unbuffered solutions at pH ~ 6 and are listed in Table 1. In the case of $Fe(bpy)_3^{3+}$ the reaction was so fast that the dependence on $[S_2O_3^{2-}]$ was not checked at 25°. However, at 10°C the $[S_2O_3^{2-}]$ dependence was determined, and the rate law

$$\frac{+\mathrm{d}\left[\mathrm{Fe(bpy)}_3^{2+}\right]}{\mathrm{d}t} = 2k'\left[\mathrm{Fe(bpy)}_3^{3+}\right]\left[\mathrm{S_2O_3^{2-}}\right] \tag{10}$$

was found to be adequate. This gave a value of k' at 10°C of $(3.06 \pm 0.08) \times 10^4$ $M^{-1}s^{-1}$. At 25°C triplicate runs were performed at $[S_2O_3^{2-}] = 2.00 \times 10^{-4}M$ and a value of k' of $(9.5 \pm 0.8) \times 10^4$ $M^{-1}s^{-1}$ was calculated assuming rate law 10.

Copper catalysis was significant in the $IrBr_6^{2-}$ reaction, yielding the rate law:

$$\frac{-\mathrm{d}\left[\mathrm{IrBr_6^{2-}}\right]}{\mathrm{d}t} = \left(k_0 + 2k'[\mathrm{S_2O_3^{2-}}] + k_{\mathrm{Cu}}[\mathrm{Cu^{2+}}]\right)\left[\mathrm{IrBr_6^{2-}}\right] \tag{11}$$

The rate constants were found to be $k_0 = 0.07$ s^{-1}, $k' = 17.5$ $M^{-1}s^{-1}$ and $k_{Cu} = 4.3 \times 10^5$ $M^{-1}s^{-1}$. The physical significance of the k_0 term is unclear, but its magnitude seems to be too large to have arisen from Cu^{2+} impurities in the reagents.

For the $IrCl_6^{2-}$ reaction, Cu^{2+} catalysis was not observed and simple bimolecular kinetics as in eqn. 10 were found. A least-squares fit of the data gave an average deviation of < 5%, a maximum deviation of 14.8%, and a value for k' of $(1.74 \pm 0.01) \times 10^2$ $M^{-1}s^{-1}$.

The oxidation of iodide by $IrBr_6^{2-}$ has been published [1]. Bimolecular oxidation by $IrCl_6^{2-}$ and $Fe(bpy)_3^{3+}$ has also been published recently, but the results obtained were 0.5M H_2SO_4 [12]. Our results in 0.1M $NaClO_4$ are listed in Table 1. The $Fe(bpy)_3^{3+}$ reaction was studied with $[I^-]$ at seven concentrations between 1.5×10^{-4} and $3.0 \times 10^{-4}M$. Because the reaction was so rapid only a restricted range of concentrations were used. A fit of the data to rate law 10 gave a value for k' of 9.5×10^4 $M^{-1}s^{-1}$. The $IrCl_6^{2-}$ reaction was also investigated with respect to various interferences; no significant effect was observed for addition of 0.01M H^+, $10^{-5}M$ Cu^{2+}, 0.046M Br^-, or 0.046M SCN^-. There was a 10% increase in rate at $10^{-3}M$ OH^-, but this may be attributed to the direct reduction of $IrCl_6^{2-}$ by OH^- [13]. A least-squares fit of the data at natural pH to rate law 10 gave an average deviation of 4.4% and a maximum deviation of 8.1%, with a value for k of $(4.09 \pm 0.05) \times 10^2$ $M^{-1}s^{-1}$.

Oxidations of SCN^- by $IrCl_6^{2-}$ and $IrBr_6^{2-}$ have already been reported [1]. The oxidation by $Fe(bpy)_3^{3+}$ was studied at natural pH with $[SCN^-]$ varied from 1.5×10^{-4} to $2.0 \times 10^{-2}M$. The results were consistent with the rate law:

TABLE 1

Pseudo-first-order rate constants [a]

[Substrate] (M)	k_{obs} (s^{-1})	[Substrate] (M)	k_{obs} (s^{-1})
$Fe(bpy)_3^{3+} + S_2O_3^{2-}$ [b]		$IrCl_6^{2-} + N_3^-$ [h]	
2.00×10^{-4} [c]	11.8	1.0×10^{-2}	1.45×10^{-3}
3.00×10^{-4} [c]	18.9	2.0×10^{-2}	2.61×10^{-3}
4.00×10^{-4} [c]	26.3	3.0×10^{-2}	3.75×10^{-3}
5.00×10^{-4} [c]	29.1	4.0×10^{-2}	5.50×10^{-3}
2.00×10^{-4}	35.6	5.0×10^{-2}	7.00×10^{-3}
2.00×10^{-4}	41.0	6.0×10^{-2}	7.88×10^{-3}
2.00×10^{-4}	36.9	$IrCl_6^{2-} + NO_2^-$ [d]	
$IrCl_6^{2-} + S_2O_3^{2-}$ [d]		1.00×10^{-3}	1.82×10^{-2}
1.0×10^{-3}	0.385	2.00×10^{-3}	4.08×10^{-2}
2.02×10^{-3}	0.787	4.00×10^{-3}	7.85×10^{-2}
4.00×10^{-3}	1.37	1.00×10^{-2}	1.94×10^{-1}
5.00×10^{-3}	1.73	2.00×10^{-2}	3.92×10^{-1}
1.00×10^{-2}	3.34	$IrBr_6^{2-} + NO_2^-$ [h]	
1.00×10^{-2} [e]	3.30	5.0×10^{-3}	2.36×10^{-1}
1.00×10^{-2}	3.41	1.0×10^{-2}	5.95×10^{-1}
2.00×10^{-2}	7.06	2.0×10^{-2}	1.08
$IrCl_6^{2-} + I^-$ [d]		3.0×10^{-2}	1.67
1.0×10^{-3}	0.77	4.0×10^{-2}	2.55
2.0×10^{-3}	1.61	5.0×10^{-2}	3.18
4.0×10^{-3}	3.15		
1.0×10^{-2}	8.03		
2.0×10^{-2}	15.2		
4.0×10^{-2}	33.2		
5.0×10^{-2}	40.8		
2.0×10^{-3} [f]	1.67		
2.0×10^{-3} [g]	1.87		

[a] $\mu = 0.10M$ ($NaClO_4$); 25.0°C; average of triplicate runs. [b] $[Oxidant]_0 = 3.0 \times 10^{-5}M$. [c] 10°C. [d] $[Oxidant]_0 = 1 \times 10^{-4}M$. [e] N_2 saturated. [f] 0.01M H^+. [g] 0.001M OH^-. [h] $[Oxidant]_0 = 4.0 \times 10^{-5}M$. [i] acetate buffer at 0.01M. [j] $\mu = 0.15M$. [k] $\mu = 1.0M$.

$$\frac{+d\left[Fe(bpy)_3^{2+}\right]}{dt} = \left(2k'[SCN^-] + 2k''[SCN^-]^2\right)\left[Fe(bpy)_3^{3+}\right] \tag{12}$$

with $k' = 5.5\ M^{-1}s^{-1}$ and $k'' = 7.5 \times 10^3\ M^{-2}s^{-1}$.

Rather complex kinetic behavior was observed for the oxidation of azide. The reaction of $IrCl_6^{2-}$ with a large excess of NaN_3 showed non-first-order kinetics. Semilog plots curved in a way indicative of a second-order component or product inhibition. This curvature was minimized by working at low concentrations of $IrCl_6^{2-}$, but it was never entirely eliminated. Table 1 lists

[S(IV)] (M)	pH	k_{obs} (s^{-1})	[S(IV)] (M)	[H^+] (M)	k_{obs} (s^{-1})
$IrCl_6^{2-} + SO_3^{2-}$ [d,e,i]			$IrBr_6^{2-} + SO_3^{2-}$ [e,h,i]		
2.38×10^{-3}	5.734	14.10	2.00×10^{-3}	1.09×10^{-4}	1.07
2.38×10^{-3}	5.368	7.08	2.00×10^{-3}	9.85×10^{-5}	2.44
2.38×10^{-3}	5.216	4.03	2.00×10^{-3}	3.45×10^{-5}	4.61
2.38×10^{-3}	5.094	3.71	2.00×10^{-3}	1.27×10^{-5}	14.0
2.38×10^{-3}	4.941	2.54	2.00×10^{-3}	6.47×10^{-6}	23.3
2.38×10^{-3}	4.750	1.32	$Fe(bpy)_3^{3+} + SO_3^{2-}$ [b,e]		
2.38×10^{-3}	4.684	1.20	2.00×10^{-3}	2.40×10^{-2}	1.98
4.76×10^{-3}	5.281	9.40	4.00×10^{-3}	2.30×10^{-2}	4.50
4.76×10^{-3}	5.108	5.50	6.00×10^{-3}	2.21×10^{-2}	6.92
4.76×10^{-3}	5.043	4.78	8.00×10^{-3}	2.14×10^{-2}	10.4
4.76×10^{-3}	4.846	3.46	1.00×10^{-2}	2.04×10^{-2}	14.2
4.76×10^{-3}	4.745	2.53	4.00×10^{-3}	4.73×10^{-2}	1.34
9.52×10^{-3}	5.553	35.4	8.00×10^{-3}	4.48×10^{-2}	3.34
9.52×10^{-3}	5.032	11.2	1.60×10^{-2}	4.00×10^{-2}	8.77
9.52×10^{-3}	4.622	5.05	2.00×10^{-2}	3.78×10^{-2}	12.5
1.90×10^{-2}	4.976	24.8	1.00×10^{-2} [j]	9.25×10^{-2}	1.32
1.90×10^{-2}	4.601	8.90	1.50×10^{-2} [j]	8.85×10^{-2}	1.91
1.90×10^{-2}	4.458	7.22	2.00×10^{-2} [j]	8.50×10^{-2}	2.94
1.90×10^{-2}	4.262	4.30	2.50×10^{-2} [j]	8.15×10^{-2}	3.95
1.90×10^{-2}	4.004	2.36	2.50×10^{-2} [k]	8.35×10^{-2}	0.75
			7.50×10^{-2} [k]	5.72×10^{-2}	3.88
			1.00×10^{-1} [k]	4.75×10^{-2}	6.94

first-order rate constants taken from the initial quasi-linear portions of the reaction. These results give an excellent first-order dependence on [N_3^-], leading to a second-order rate constant of $1.34 \times 10^{-1}\ M^{-1}s^{-1}$.

Performing the reaction under an atmosphere of argon or in the presence of 5×10^{-6}M Cu^{2+} and Fe^{3+} had no effect. However, excess $IrCl_6^{3-}$ had a strong effect; when $Na_3IrCl_6 \cdot 2H_2O$ was added to give the conditions $[IrCl_6^{2-}]_0 = 2.4 \times 10^{-5}$M, $[IrCl_6^{3-}] = 6.1 \times 10^{-4}$M and $[N_3^-] = 9.96 \times 10^{-2}$M the reaction gave a Guggenheim plot linear for three half-lives, with $k_{obs} = 1.64 \times 10^{-3}s^{-1}$. This suggested the rate law:

$$\frac{-\mathrm{d}[\mathrm{IrCl}_6^{2-}]}{\mathrm{d}t}=\frac{k'[\mathrm{IrCl}_6^{2-}][\mathrm{N}_3^-]}{(1+k[\mathrm{IrCl}_6^{3-}])} \tag{13}$$

Using a non-linear least-squares computer program, the integrated form of this rate law was used to fit the time-dependent data obtained at low initial concentrations of $IrCl_6^{3-}$. For these fits runs were used with $[N_3^-]$ ranging from 0.01 to 0.1M and $[IrCl_6^{2-}]_0$ ranging from 2×10^{-4} to 4×10^{-5}M. This fit yielded $k' = (1.06 \pm 0.02) \times 10^{-1}\ M^{-1}s^{-1}$ and $k = (1.31 \pm 0.27) \times 10^3\ M^{-1}$. There were, however, systematic deviations near the ends of the reactions.

A brief investigation of the reaction of $IrBr_6^{2-}$ with N_3^- showed roughly bimolecular kinetics with a rate constant of $6.1 \times 10^{-2}\ M^{-1}s^{-1}$.

The reaction of N_3^- with $Fe(bpy)_3^{3+}$, like that with $IrCl_6^{2-}$, showed strong inhibition by $Fe(bpy)_3^{2+}$. Accordingly, all subsequent experiments were run with added $Fe(bpy)_3^{2+}$ in effectively constant excess. When $[Fe(bpy)_3^{2+}]$ was 1.3×10^{-4}M, and $[N_3^-]$ was varied from 1×10^{-3} to 5×10^{-2}M, the individual runs showed good pseudo-first-order kinetics. A good fit to the data was obtained for:

$$k_{\mathrm{obs}} = k'[\mathrm{N}_3^-] + k_2[\mathrm{N}_3^-]^2 \tag{14}$$

with $k' = 10.8\ M^{-1}s^{-1}$ and $k_2 = 1.75 \times 10^3\ M^{-2}s^{-1}$.

In a second series of experiments at constant $[N_3^-]$ the concentration of $Fe(bpy)_3^{2+}$ was varied from 1×10^{-4} to 6×10^{-4}M. Two such series were run, one at 1×10^{-3}M and one at 2.5×10^{-3}M $[N_3^-]$. Under these conditions the k' path dominates but the k_2 path makes significant contribution at low $[Fe(bpy)_3^{2+}]$. The inhibition by $Fe(bpy)_3^{2+}$ saturates at high $[Fe(bpy)_3^{2+}]$ consistent with the rate law:

$$k_{\mathrm{obs}} = k'[\mathrm{N}_3^-] + \frac{k_2'[\mathrm{N}_3^-]^2}{[\mathrm{Fe(bpy)}_3^{2+}]} \tag{15}$$

with $k' = 10.8\ M^{-1}s^{-1}$ and $k_2' = 0.228\ M^{-1}s^{-1}$. However, insufficient data were obtained to perform a rigorous test of this rate law.

Our study of halide and pseudohalide oxidation concludes with the oxidation of CN^- by $IrCl_6^{2-}$. The kinetics were studied at $[IrCl_6^{2-}] = 1.0 \times 10^{-4}$M, $[CN^-] = 1.00 \times 10^{-3}$ to 2.0×10^{-2}M and pH ~ 10.3. The pH was simply dictated by the basicity of NaCN. Pseudo-first-order kinetics were obtained, but the rates were independent of $[CN^-]$ and were fairly irreproducible. The reaction proved to be highly sensitive to added copper sulfate. A linear dependence on $[Cu^{2+}]$ was found over the concentration range of $(5-10) \times 10^{-4}$M. The rate law is therefore:

$$\frac{-\mathrm{d}[\mathrm{IrCl}_6^{2-}]}{\mathrm{d}t} = k[\mathrm{IrCl}_6^{2-}][\mathrm{Cu}^{2+}][\mathrm{CN}^-]^0 \tag{16}$$

with $k = (2.77 \pm 0.12) \times 10^6\ M^{-1}s^{-1}$. No rate effect was found with $1.0 \times 10^{-5}M\ Ag^+$ or $1.0 \times 10^{-5}M\ Fe(CN)_6^{3-}$ added in the absence of added Cu^{2+}.

Nitrite was found to be oxidized by $IrCl_6^{2-}$ with quite simple kinetics. When the reaction was studied with excess $NaNO_2$ pseudo-first-order kinetics were observed, as shown in Table 1. The linear dependence of k_{obs} on $[NO_2^-]$ indicates a simple second-order rate law as in eqn. 10 with $2k' = (1.96 \pm 0.02) \times 10^1\ M^{-1}s^{-1}$; the average deviation was 3.5% and the maximum deviation was 7% over the 20-fold range in concentrations.

Similar results, also shown in Table 1, were obtained for oxidation of NO_2^- by $IrBr_6^{2-}$. These led to a value for $2k'$ of $56.0 \pm 2.7\ M^{-1}s^{-1}$.

Oxidation of NO_2^- by $Fe(bpy)_3^{3+}$ was studied with the acidity varied from 4.3×10^{-3} to $5.6 \times 10^{-2}M$ while the concentration of nitrite was varied from 5×10^{-4} to $4 \times 10^{-3}M$. Under these conditions N(III) is largely protonated but decomposition of HNO_2 is not a problem. The pseudo-first-order rate constants were adequately described by the rate law:

$$k_{obs} = \frac{2k[HNO_2]}{[H^+]} \qquad (17)$$

with $2k = 71\ s^{-1}$.

Oxidation of sulfite by $IrCl_6^{2-}$ has been investigated previously at an ionic strength of 0.2M maintained with NaCl [11]. Our results were obtained at an ionic strength of 0.1M maintained with $NaClO_4$. The kinetics were run under nitrogen and the pH was maintained with 0.01M acetate buffer. With excess S(IV) the pseudo-first-order rate constants listed in Table 1 were obtained as a function of pH and [S(IV)]. A good fit was obtained for the rate law:

$$\frac{-d\ln[IrCl_6^{2-}]}{dt} = 2k'[SO_3^{2-}] \qquad (18)$$

with $2k' = (1.11 \pm 0.02) \times 10^5\ M^{-1}s^{-1}$ and an average deviation of 11.2%. The rates were found to be independent of buffer concentration but they did decrease slightly in the presence of O_2.

The reaction of $IrBr_6^{2-}$ with SO_3^{2-} was studied under conditions similar to the oxidation by $IrCl_6^{2-}$. However, the total concentration of S(IV) was not varied. Rate law 18 was assumed, and a value for $2k'$ of $(6.36 \pm 0.73) \times 10^5\ M^{-1}s^{-1}$ was obtained from the values of k_{obs} in Table 1.

$Fe(bpy)_3^{3+}$ was found to be oxidized very rapidly by S(IV) and so strongly acidic conditions were used. It was necessary to account for the formation of "H_2SO_3" in calculating $[SO_3^{2-}]$. A good fit of the data in Table 1 to rate law 18 was obtained with $2k' = 4.1 \times 10^8\ M^{-1}s^{-1}$; additional experiments to test the dependence on ionic strength gave $2k' = 3.76 \times 10^8\ M^{-1}s^{-1}$ at $\mu = 0.15M$, and $2k' = 1.51 \times 10^7\ M^{-1}s^{-1}$ at $\mu = 1.0M$. These high ionic strength results were calculated using $K_1 = 1.27 \times 10^{-2}M$ and $K_2 = 4.57 \times 10^{-7}M$ at $\mu = 1.0M$, and $K_1 = 2.57 \times 10^{-2}M$ and $K_2 = 1.41 \times 10^{-7}M$ at $\mu = 0.15M$ [3].

D. DISCUSSION

The primary objective of this study was to obtain data on a series of reactions involving oxidation of simple inorganic substrates by substitution-inert coordination complexes. The three oxidants selected, $IrCl_6^{2-}$, $IrBr_6^{2-}$, and $Fe(bpy)_3^{3+}$ are well suited to this purpose. They are substitution-inert, moderately strong oxidants (0.892, 0.843 and 1.06 V, respectively), and they have strong visible absorption bands to facilitate observation. The inorganic substrates selected, $S_2O_3^{2-}$, I^-, SCN^-, N_3^-, CN^-, NO_2^-, and SO_3^{2-} are all well characterized, stable in solution, and amenable to oxidation. To a large extent simple stoichiometries and kinetics have been obtained. Derived values of k', the intrinsic bimolecular rate constant, are collected in Table 2. Table 3 presents reduction potentials for the important free radicals.

(i) $S_2O_3^{2-}$

Under conditions pertinent to the kinetic studies, $IrCl_6^{2-}$ oxidized $S_2O_3^{2-}$ to $S_4O_6^{2-}$ while retaining its coordination sphere intact. In this sense, then, the reaction could be called outer sphere. Outer-sphere oxidation was also found for $IrBr_6^{2-}$, and we assume the reaction with $Fe(bpy)_3^{3+}$ is similar.

A mechanism consistent with the kinetics and stoichiometry is

$$\mathrm{Ox} + S_2O_3^{2-} \rightleftharpoons \mathrm{Red} + S_2O_3^{-} \qquad k_1, k_{-1} \tag{19}$$

$$S_2O_3^{2-} + S_2O_3^{-} \rightleftharpoons S_4O_6^{3-} \qquad K_{\mathrm{rad}} \tag{20}$$

$$\mathrm{Ox} + S_4O_6^{3-} \rightarrow \mathrm{Red} + S_4O_6^{2-} \qquad k_2 \tag{21}$$

The rate law derived from this mechanism, applying the steady-state approximation to $S_2O_3^-$ and $S_4O_6^{3-}$, is:

$$\frac{-\mathrm{d}[\mathrm{Ox}]}{\mathrm{d}t} = \frac{2k_1k_2K_{\mathrm{rad}}[\mathrm{Ox}]^2[S_2O_3^{2-}]^2}{k_{-1}[\mathrm{Red}] + K_{\mathrm{rad}}k_2[S_2O_3^{2-}][\mathrm{Ox}]} \tag{22}$$

TABLE 2

Second-order rate constants

Substrate	Oxidant, k' (M^{-1} s^{-1})		
	$IrCl_6^{2-}$	$IrBr_6^{2-}$	$Fe(bpy)_3^{3+}$
$S_2O_3^{2-}$	$(1.74 \pm 0.01) \times 10^2$	17.5	$(9.5 \pm 0.8) \times 10^4$
I^-	$(4.09 \pm 0.05) \times 10^2$	28	9.5×10^4
SCN^-	$(4.55 \pm 0.31) \times 10^{-3}$	—	5.5
N_3^-	$(1.06 \pm 0.02) \times 10^{-1}$	6.1×10^{-2}	10.8
NO_2^-	9.8 ± 0.1	28.0 ± 1.4	3.3×10^4
SO_3^{2-}	$(5.6 \pm 0.1) \times 10^4$	$(3.18 \pm 0.37) \times 10^5$	2.1×10^8

TABLE 3

Free radical reduction potentials

Radical	E^0 (V)	Ref.
$S_2O_3^-$	1.35	this work
I	1.33	1
SCN	1.66	1
N_3	1.37 ± 0.22	this work
CN	2.8	37
NO_2	1.03 ± 0.04	this work
SO_3^-	< 0.89	50

Under the conditions that $k_{-1}[\text{Red}] \ll K_{\text{rad}} k_2[S_2O_3^{2-}][\text{Ox}]$ the rate law simplifies to:

$$\frac{-\text{d}[\text{Ox}]}{\text{d}t} = 2k_1[\text{Ox}][S_2O_3^{2-}] \tag{23}$$

An estimate of the redox potential for the $S_2O_3^{2-}/S_2O_3^-$ couple can be made using pulse-radiolysis data on the $SCN^-/S_2O_3^{2-}$ system [14]. By summing the published equilibria

$$SCNS_2O_3^{2-} \rightleftharpoons SCN^- + S_2O_3^- \qquad K_A \tag{24}$$

$$SCN + S_2O_3^{2-} \rightleftharpoons SCNS_2O_3^{2-} \qquad K_B \tag{25}$$

$$SCN + S_2O_3^{2-} \rightleftharpoons SCN^- + S_2O_3^- \qquad K_A K_B \tag{26}$$

the relative stabilities of SCN and $S_2O_3^-$ may be obtained as $K_A K_B = 2.68 \times 10^4$. Combining this equilibrium constant with our prior E^0 value for the SCN^-/SCN couple [1] gives an E^0 value of 1.35 V for the $S_2O_3^{2-}/S_2O_3^-$ couple.

Equilibrium constants can be calculated for the first electron-transfer step using this value of E^0 and the reduction potentials for the oxidants. Combining these equilibria with the k_1 values leads to k_{-1} by the principle of microscopic reversibility. The values so obtained are 9.6×10^9, 6.5×10^9, and 7.6×10^9 $M^{-1}s^{-1}$ for $IrCl_6^{2-}$, $IrBr_6^{2-}$ and $Fe(bpy)_3^{3+}$, respectively. These rate constants are reasonable for diffusion-controlled reactions.

An essential component of the proposed mechanism is the step in which the "radical dimer" is formed. The formation constant, K_{rad}, was found to be in excess of 10^6 M^{-1}, and the rate constant for forming the dimer was measured at 8×10^8 $M^{-1}s^{-1}$ [15].

With these numbers in hand it can be shown that the inequality required for the derived rate law to reduce to the observed rate law will be satisfied for values of k_2 in excess of 10^2 $M^{-1}s^{-1}$. It is rather difficult to estimate a value for k_2; this step is, of course, thermodynamically favorable, and so the rate constant may well be as fast as 10^7 $M^{-1}s^{-1}$, easily satisfying the inequality. The function of the radical dimer equilibrium then is to draw off the products from the reaction so as to eliminate the effects of reversibility in the rate-limiting step.

There have been a number of other studies of the oxidation of $S_2O_3^{2-}$; for example, by $Au(NH_3)_4^{3+}$ [16], $Fe(CN)_6^{3-}$ [17], $Mo(CN)_8^{3-}$ [18] and OsO_4 [19], but none are of the outer-sphere mechanism having simple bimolecular kinetics. Thus, our data are unique in yielding bimolecular rate constants for a non-bonded electron-transfer process leading to the $S_2O_3^-$ radical.

(ii) I^- and SCN^-

The oxidation of I^- and SCN^- by various oxidants has been discussed in detail previously [1]. However, since then an important study on the oxidation of I^- by a series of Cu(III) peptides has been published [20]. Their conclusions differ significantly from ours.

Briefly, our oxidations of I^- and SCN^- may be accommodated by a mechanism analogous to that proposed above for oxidations of $S_2O_3^{2-}$. In the case of SCN^-, however, an additional fast step must be included to allow $(SCN)_2$ to hydrolyze to CN^-, SO_4^{2-} and SCN^-. We found a linear free-energy relationship (LFER) relating the rates and equilibria for oxidation of I^- by a series of outer-sphere oxidants. The unit slope and small scatter in the LFER were taken to indicate that k_{-1} for the whole series of reactions was diffusion controlled. This led to an estimate of 1.33 V for E^0 for the I^-/I couple. Additional terms were seen in the rate law which were second order in $[I^-]$ and first order in [oxidant]. These were interpreted as involving electron transfer and simultaneous bond formation to make I_2^-. The reverse reactions for these terms were found to be activation controlled, and Marcus theory was found to rationalize the rates.

For the Cu(III) peptide oxidations of I^- a number of different conclusions were obtained, although the same rate law was found. For the paths first order in $[I^-]$ an LFER was obtained with a slope of 0.56 instead of 1.0. Applying the principle of microscopic reversibility a value for E^0 of 1.2 V was obtained instead of 1.33 V. The paths second order in $[I^-]$ gave an LFER of 0.95 instead of the value of 0.5 predicted from Marcus' theory.

We believe that the bulk of the results on the Cu(III) peptide/I^- system can be accommodated by our mechanism and interpretation. The LFER of slope 0.95 for the second-order paths does not come as a surprise; we agree with Raycheba and Margerum that the reaction may involve substitution at the axial position. Using our E^0 value of 1.04 V instead of their value of 0.9

V for the $I_2^-/2I^-$ couple we calculate a reverse rate constant of 1×10^7 $M^{-1}s^{-1}$. This is consistent with an inner-sphere mechanism because substitution rates for axial water on the Cu(II) complexes are expected to be about 3×10^8 $M^{-1}s^{-1}$ [20b]. Furthermore, an inner-sphere mechanism is expected because an estimate of the outer-sphere rate constant using Marcus' theory is somewhat slower than observed. At this point we are not prepared to rationalize the slopes of LFERs obtained for inner-sphere reactions.

Turning to the paths first order in $[I^-]$ we note that their estimate of E^0 for the I^-/I couple depends on an estimate of 3×10^9 $M^{-1}s^{-1}$ as the diffusion-controlled limit. This estimate was obtained from the Smoluchowski equation and from measurements of the rates of electron transfer between two coordination complexes [21]. A value of 1.2×10^{10} $M^{-1}s^{-1}$ is more appropriate to reactions between coordination complexes and I·. This higher estimate is supported by direct measurement of the reaction of I· with I^- ($k = 1.3 \times 10^{10}$ $M^{-1}s^{-1}$) [22], and by measurements of reactions of OH· ($k = 1.2 \times 10^{10}$ $M^{-1}s^{-1}$ with I^-, $k = 1.02 \times 10^{10}$ with $Os(CN)_6^{4-}$, $k = 1.25 \times 10^{10}$ $M^{-1}s^{-1}$ with $Fe(CN)_6^{4-}$) [23]. This difference accounts for only part of the difference between our E^0 estimates.

The LFER for the Cu(III) paths first order in $[I^-]$ was defined by four points, with the point for $Cu^{III}(H_{-2}Aib_3)$ deviating strongly. An LFER can be constructed with the same data by including $Cu^{III}(H_{-2}Aib_3)$ and treating $Cu^{III}(H_{-3}G_4)^-$ and $Cu^{III}(H_{-3}G_4a)$ as outliers instead; this yields a slope of unity. The deviation for $Cu^{III}(H_{-3}G_4a)$ may be due to medium effects; the k_{obs} values show systematic deviations from the rate law, so when data at $[I^-] < 0.13M$ are considered, the second-order rate constant drops by a factor of almost 5. This correction is sufficient to bring the point onto the new LFER. Since $Cu^{III}(H_{-3}G_4)^-$ was the only anionic oxidant in the series, a correction of E^0 for ionic strength effects would shift the point in the appropriate direction. However, a correction by as much as 0.01 V leaves the point still a factor of 7 too fast. The kinetics for the $Cu^{III}(H_{-3}G_4)^-$ reaction with I^- had a fairly complex pH dependence, but data were obtained at only three different acidities. It is conceivable that the complete rate law was not in hand. Neglecting this outlier leads to an LFER with a slope of unity; calculating the reverse rate constants using a value of E^0 of 1.33 V for the I^-/I couple leads to a value of $\sim 3 \times 10^9$ $M^{-1}s^{-1}$; correcting for the effects of ionic strength may well result in rate constants closer to the diffusion-controlled limit.

It should be noted that even by Raycheba and Margerum's estimate, the reverse rate constants for the paths first order in $[I^-]$ exceed the substitution rate on Cu(II), and thus support an outer-sphere mechanism.

A recent investigation of the oxidation of I^- by Ni^{III}cyclam was discussed in terms of an outer-sphere mechanism [24]. Unfortunately, the reduction potential was measured in coordinating sulfate medium [25], and so it is difficult to discuss this work in the present context. In another recent study [26], I^- was oxidized by $Ni^{III}(H_{-2}Aib_3)$. The rate law for this reaction was found to be quite complex, having no terms analogous to those under consideration here.

With regard to the oxidation of SCN^-, the reactions with a series of Ni^{III}macrocycles have recently been studied [27]. The reactions were found to be second order in $[Ni^{III}]$ and so here too there is no simple comparison with the reactions we have studied.

(iii) N_3^-

It is rather difficult to interpret our results for the oxidation of N_3^- because no fully satisfactory rate law was obtained. Nevertheless, certain features of the data merit discussion. Of particular note is the strong inhibition of the kinetics by the reduced metal complex. This was observed in the reactions with $IrCl_6^{2-}$ and $Fe(bpy)_3^{3+}$, and we can assume that it could be observed in the reaction with $IrBr_6^{2-}$ also. This behavior stands in contrast with oxidations of the other pseudohalides and halides. Attempts to observe the radical dimer N_6^- using pulse radiolysis met with no success [28]. Presumably the formation constant is fairly small. If azide was oxidized in the first step by a simple bimolecular pathway as seen for $S_2O_3^{2-}$, there would be no rapid subsequent scavenging of N_3 by N_3^-, and so the reverse reaction could become significant. A probable fate of the azide radical is fragmentation to N_2 plus N. The fragmentation process, although spin-forbidden, is close to thermoneutral [29].

$$IrCl_6^{2-} + N_3^- \rightleftharpoons IrCl_6^{3-} + N_3 \qquad k_1, k_{-1} \tag{27}$$

$$N_3 \rightarrow N_2 + N\cdot \qquad k_2 \tag{28}$$

$$2N\cdot \rightarrow N_2 \qquad \text{fast} \tag{29}$$

This mechanism leads to the rate law

$$\frac{-d[IrCl_6^{2-}]}{dt} = \frac{k_1[IrCl_6^{2-}][N_3^-]}{1 + \frac{k_{-1}}{k_2}[IrCl_6^{3-}]} \tag{30}$$

when the steady-state approximation is applied to $[N_3]$.

This rate law was roughly observed, and the deviations after long time periods could have been due to reactions of N · other than dimerization. If it is assumed that k_{-1} is diffusion controlled, as found for the other pseudohalides, then $k_2 = 8 \times 10^6\ s^{-1}$. This is not an unreasonable rate for such a symmetry-forbidden process [30].

For this mechanism the steady-state concentration of N_3 is given by:

$$[N_3]_{ss} = \frac{k_1[N_3^-][IrCl_6^{2-}]}{k_2 + k_{-1}[IrCl_6^{3-}]} \qquad (31)$$

This leads to a value for $[N_3]_{ss}$ under our conditions of $\sim 10^{-14}$M, and so a pathway involving dimerization of the radical to form "N_6" is highly unlikely.

Presumably the same mechanism applies to the reactions with $IrBr_6^{2-}$ and $Fe(bpy)_3^{3+}$. In the case of $IrBr_6^{2-}$ the concentration of $IrBr_6^{2-}$ must have been small enough that product inhibition was not a problem. In the case of $Fe(bpy)_3^{3+}$ the presence of a second term, second order in $[N_3^-]$, is not in doubt; the exact nature of the inhibition by $Fe(bpy)_3^{2+}$ is less certain. In view of the apparent instability of N_3 it is difficult to propose a mechanism for the second term which involves this species. We are currently at a loss to explain this term.

An estimate of E^0 for the N_3^-/N_3 couple can be made using a recent determination of ΔH_f for $N_{3(g)}$ [31]. ΔH_f for $N_{3(aq)}$ may then be estimated on the assumption that the hydration enthalpy of N_3 is similar to that of N_2O (-5.1 kcal) [32], ClO_2 (-6.7 kcal) [32], or CO_2 (-4.9 kcal) [33]. $\bar{S}_0$ for $N_{3(aq)}$ was assumed to be the same as $\bar{S}_0$ for $CO_{2(aq)}$ plus a correction of Rln2 for spin [33]. Combining these estimates with conventional thermochemical data for $H_{2(g)}$, $H^+_{(aq)}$, and $N^-_{3(aq)}$ results in an E^0 value of 1.37 ± 0.22 V for the N_3^-/N_3 couple. With the assumption that k_{-1} is 1.2×10^{10} $M^{-1}s^{-1}$, k_1 for the $IrCl_6^{2-}$ reaction gives a value of 1.54 V for the N_3^-/N_3 couple. This is within the thermochemical estimate range. Similar estimates using data for the $IrBr_6^{2-}$ and $Fe(bpy)_3^{3+}$ yield values of 1.52 and 1.59 V, respectively.

In summary, although the rate laws for the oxidation of azide have not been satisfactorily defined, they are consistent with a mechanism involving reversible formation of the azide radical and subsequent fragmentation of the radical.

Although there have been many studies of the oxidation of azide [34], they have generally been inner-sphere reactions. The one unambiguous exception to this is the recent investigation of the oxidation by $Ni(bpy)_3^{3+}$ [35]. Although the exact reduction potential of $Ni(bpy)_3^{3+}$ is unknown, it is estimated to be 1.71 V [36]. Therefore, the oxidation step to the azide radical is downhill, and, as expected, no inhibition by $Ni(bpy)_3^{2+}$ is observed. Using a value of 3×10^{-5}M for the K_a of HN_3 at $\mu = 2$M, their data in acidic media give a rate constant of 3×10^6 $M^{-1}s^{-1}$ for the reaction of N_3^- with $Ni(bpy)_3^{3+}$. On the basis of the redox potentials we would have predicted a rate somewhat faster, but extrapolation from data at 0.1M to 2M ionic strength for the reduction potential of N_3, and from acetonitrile to water for the reduction potential of $Ni(bpy)_3^{3+}$, clearly introduces severe approximations.

(iv) CN^-

The reduction potential of the cyanogen radical, CN, has been estimated at 2.8 V [37]. The radical has been postulated to be an intermediate in the photolysis of $Mo(CN)_8^{3-}$, but the evidence is not definitive [38]. The difficulty in generating the species is further highlighted by the failure of pulse-radiolytic methods [39]. For this reason the intervention of catalytic paths is to be expected.

Cu(II) has been found to oxidize cyanide to cyanogen and $Cu(CN)_3^{2-}$ on the stopped-flow time scale [40]. The reaction is second order in [Cu(II)] and thereby avoids generating the cyanogen radical. Strong catalysis of the oxidation of CN^- by $Fe(CN)_6^{3-}$ has been observed [41]. Our observation of catalysis by Cu(II) in the oxidation by $IrCl_6^{2-}$ hardly comes as a surprise. A reasonable mechanism is:

$$2Cu(II) + 8CN^- \rightarrow 2Cu(CN)_3^{2-} + (CN)_2 \quad \text{fast} \qquad (32)$$

$$IrCl_6^{2-} + Cu(CN)_3^{2-} \rightarrow IrCl_6^{3-} + Cu(II) \quad k_1 \qquad (33)$$

Thus our measured second-order rate constant is k_1.

(v) NO_2^-

Nitrite was oxidized by $IrCl_6^{2-}$ and $IrBr_6^{2-}$ with simple bimolecular kinetics. The oxidation by $Fe(bpy)_3^{3+}$ was expressed in terms of $[HNO_2]$ and an inverse dependence on $[H^+]$. If it is assumed that NO_2^- is the reactive species, then we can express the rate constant as $2k = 2k'/K_a$ using a value of K_a of 1.1×10^{-3} M^{-1} [42]. This leads to a rate constant of 3.3×10^4 $M^{-1}s^{-1}$ for the reaction of $Fe(bpy)_3^{3+}$ with NO_2^-.

A common mechanism can be proposed for the three reactions:

$$HNO_2 \rightleftharpoons H^+ + NO_2^- \quad K_a \qquad (34)$$

$$NO_2^- + Ox \rightarrow NO_2 + Red \quad k_1 \qquad (35)$$

$$Ox + NO_2 + H_2O \rightarrow Red + NO_3^- + 2H^+ \quad k_2 \text{ fast} \qquad (36)$$

or

$$H_2O + 2NO_2 \rightarrow NO_2^- + NO_3^- + 2H^+ \quad k_3 \text{ fast} \qquad (37)$$

Since k_3 is second order in $[NO_2]$, a fairly high steady-state concentration of NO_2 would develop if k_3 was the dominant pathway for loss of NO_2. N_2O_4 is an intermediate in this disproportionation, and its rate of hydrolysis has been reported to be $\sim 1 \times 10^3$ s^{-1} [43,44]. It is conceivable that N_2O_4 would be oxidized directly by the oxidant; alternately NO_2 may be rapidly oxidized by path k_2.

A good estimate of E^0 for the NO_2^-/NO_2 couple can be made using various well-established thermochemical data for $NO_{2(aq)}^-$ and $NO_{2(g)}$ [33]. The solubility of NO_2 of 1.2×10^{-2}M atm^{-1} estimated by Schwartz and White [45] then leads to a value of E^0 of 1.03 ± 0.04 V. The reverse of k_1 can be calculated using the forward rate constants and the E^0 values, and it is found that at its fastest, for $IrBr_6^{3-}$ it is $\sim 4 \times 10^4$ M^{-1}s^{-1}. This is slow enough that the postulated reactions 36 and 37 could easily scavenge NO_2 and thus prevent significant effects from the reverse of k_1. This explains the simple pseudo-first-order kinetics which were observed.

Oxidations of NO_2^- have recently been reviewed [34]. However, none of the reactions unambiguously involves outer-sphere electron transfer of the type we have been describing. There is a report of the *reduction* of NO_2 by $Fe(CN)_6^{4-}$ [46]; the rate constant was reported as 4.3×10^6 M^{-1}s^{-1}. This reaction, apparently, is the reverse of the reactions described above.

The situation is quite different for oxidations of NO_2^- than for oxidations of $S_2O_3^{2-}$, I^-, SCN^-, N_3^- or CN^- because the NO_2^- reactions are diffusion controlled in neither direction. This raises the possibility of applying Marcus' theory of electron transfer to reactions of NO_2^-. The approach is to use the cross relationship to determine effective self-exchange rates for the NO_2^-/NO_2 couple. Since the oxidants to be compared have a variety of charges it is necessary to correct for work terms. The equation used [47] is

$$k_{11} = \left(\frac{k_{12}}{W_{12}}\right)^2 \frac{1}{k_{22}K_{12}f_{12}}; \qquad W_{12} = \exp\left(\frac{-(w_{12} + w_{21} - w_{11} - w_{22})}{2RT}\right)$$

$$\ln f_{12} = \frac{\left(\ln K_{12} + \frac{w_{12} - w_{21}}{RT}\right)^2}{4\left(\ln \frac{k_{11}k_{22}}{Z^2} + \frac{w_{11} + w_{22}}{RT}\right)}; \qquad w = \frac{4.23 \times 10^{-8} Z_A Z_B}{a\left(1 + 2.38 \times 10^7 a\sqrt{\mu}\right)} \qquad (38)$$

where k_{11} is the self-exchange rate constant for the NO_2^-/NO_2 couple; k_{22} is the self-exchange rate constant for the Ox/Red couple; k_{12} and K_{12} are the rate constant and equilibrium constants, respectively, for the forward reaction; Z is the collision rate constant, taken to be 1×10^{11} M^{-1}s^{-1}; and a is the center-to-center distance between the relevant reactants when touching. Data are given in Table 4. Calculated values of k_{11} range over a factor of 13. This is a reasonable spread for a calculation of this type since errors are magnified by the squared term in eqn. 38. Remarkably, the $Fe(CN)_6^{4-}$ reaction is treated very well by the Marcus cross-relation. The results imply an effective self-exchange rate for the NO_2^-/NO_2 couple of $\sim 1 \times 10^{-2}$ M^{-1}s^{-1}.

TABLE 4

Marcus calculations for oxidation of NO_2^-

Oxidant	$2k$ ($M^{-1}s^{-1}$)	E^0 (V)	K_{eq} [b]	k_{-1} ($M^{-1}s^{-1}$)	k_{22} ($M^{-1}s^{-1}$)	r[d] (Å)	w_{12} [e] (kcal)	w_{22} [f] (kcal)	W_{12} [f]	f[f]	k_{22} [f] ($M^{-1}s^{-1}$)
$IrCl_6^{2-}$	19.58	0.892 [a]	5.2×10^{-3}	1.9×10^{3} [c]	2×10^{5} [a]	4.4	0.91	1.73	2.0	0.92	2.5×10^{-2}
$IrBr_6^{2-}$	57	0.843 [a]	7.7×10^{-4}	3.7×10^{4} [c]	2×10^{8} [a]	4.7	0.86	1.62	1.9	0.78	1.9×10^{-3}
$Fe(bpy)_3^{3+}$	6.5×10^{4}	1.06 [a]	36	9.0×10^{3} [c]	5×10^{8} [a]	6.0	−1.01	1.11	6.0	1.0	1.6×10^{-2}
$Fe(CN)_6^{3-}$	2.1×10^{-5} [h]	0.34 [a]	2.4×10^{-12}	4.3×10^{6} [g]	5×10^{3} [a]	4.5	1.34	3.36	5.5	2.4×10^{-2}	1.2×10^{-2}

[a] Ref. 1. [b] Calculated from E^0 in Table 3. [c] Calculated from K_{eq} and k_1. [d] Estimated. [e] w_{21} and w_{11} are zero because NO_2 is uncharged. [f] Calculated from eqn. 38; r for NO_2 estimated as 1.9 Å. [g] Ref. 50. [h] Calculated from K_{eq} and k_{-1}.

(vi) SO_3^{2-}

Sulfite is oxidized to SO_4^{2-}, and the kinetics generally show second-order rate laws. A mechanism consistent with these observations is:

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \qquad K_a \qquad (39)$$

$$Ox + SO_3^{2-} \rightarrow Red + SO_3^- \qquad k_1 \qquad (40)$$

$$Ox + SO_3^- + H_2O \rightarrow Red + SO_4^{2-} + 2H^+ \qquad k_2\text{, fast} \qquad (41)$$

Thus our measured rate constants, k', are equal to k_1. The existence of SO_3^- in aqueous solutions is quite well documented [48]. To our knowledge, there have been no direct investigations of its reactions with outer-sphere redox agents [49]. Recent results from Anast and Margerum [50], however, suggest that the radical can be oxidized to SO_4^{2-} via SO_3 quite rapidly. Anast and Margerum also place an estimate on the upper limit for E^0 for the SO_3^-/SO_3^{2-} couple of 0.89 V. This limit is consistent with the good pseudo-first-order kinetics we observe, which imply that the reverse of k_1 is insignificant.

The enhanced consumption of SO_3^{2-} in the presence of O_2 is accounted for by including chain-propagation steps in the mechanism:

$$SO_3^- + O_2 \rightarrow SO_5^- \qquad (42)$$

$$SO_5^- + SO_3^{2-} \rightarrow SO_4^{2-} + SO_4^- \qquad (43)$$

$$SO_4^- + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^- \qquad (44)$$

This is essentially the mechanism proposed by Hayon et al. [48b].

A direct comparison of our kinetic results with $IrCl_6^{2-}$ may be made with Stapp and Carlyle's investigation [11] of the same reaction, but at 0.2M ionic strength (NaCl). They observe the same rate law, but obtain a rate constant slower by a factor of 5.5. This deviation can be explained by the differing ionic media and differing choices of K_a for HSO_3^-. Another comparison may be made between our study of the oxidation by $Fe(bpy)_3^{3+}$ and Carlyle's study [51] with $Fe(phen)_3^{3+}$ at $\mu = 1.0M$ ($NaClO_4$). There was a term in his rate law analogous to ours, leading to a value for k_1 of 4.6×10^6 $M^{-1}s^{-1}$. Although $Fe(phen)_3^{3+}$ is a somewhat stronger oxidant than $Fe(bpy)_3^{3+}$, the rate is a factor of 45 slower. This must be due in part to the difference in ionic strength.

Reactions between such highly charged species are expected to be sensitive to ionic strength. Indeed, our study of the dependence on ionic strength for the reaction between $Fe(bpy)_3^{3+}$ and SO_3^{2-} shows this strikingly. A set of data at 0.1M ionic strength has been reported for oxidations of SO_3^{2-} by $Ru(bpy)_3^{3+}$, $Os(bpy)_3^{3+}$ and $Ru^*(bpy)_3^{2+}$ [52]. We concur with their interpre-

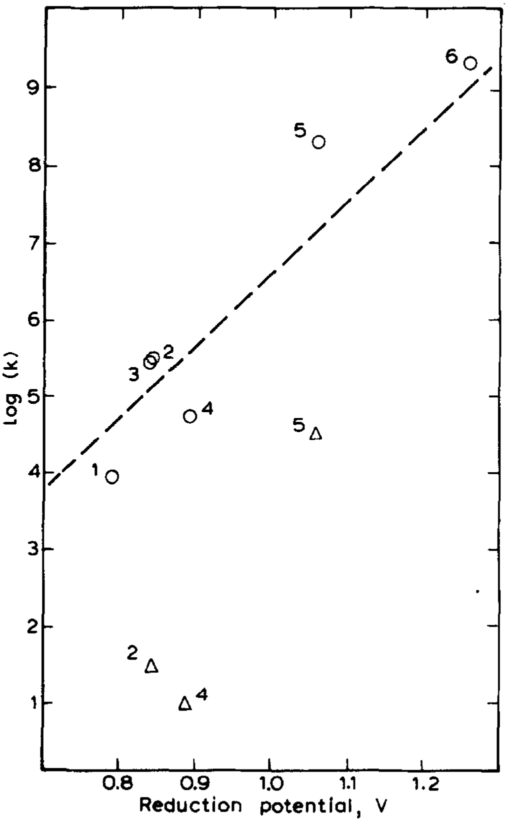

Fig. 2. Log(k) vs. E^0 for the oxidation of SO_3^{2-} (○) and NO_2^- (△) by $Os(bpy)_3^{3+}$ (1); $IrBr_6^{2-}$ (2); $Ru^*(bpy)_3^{2+}$ (3); $IrCl_6^{2-}$ (4); $Fe(bpy)_3^{3+}$ (5); and $Ru(bpy)_3^{3+}$ (6). The line is drawn with slope 0.6.

tation that an LFER is roughly obtained from a plot of log k_1 vs. E^0 as shown in Fig. 2. The results for $IrCl_6^{2-}$ and $IrBr_6^{2-}$ are also roughly compatible with the LFER. The wide scatter in the plot is consistent with the reverse reactions not being diffusion controlled, and the slope of ~ 0.6 is consistent with Marcus' theory of electron transfer. Figure 2 also shows data for oxidations of NO_2^-. Since the reactions of NO_2^- fit Marcus' theory, the similarity of the patterns shown in Fig. 2 for oxidations of SO_3^{2-} and NO_2^- is further support for the validity of Marcus' theory for oxidations of SO_3^{2-}. Further attempts to refine the interpretation require a good value of E^0 for the SO_3^{2-}/SO_3^- couple. Anast and Margerum only provide an estimate of the upper limit [50]. An attempt to estimate E^0 using the electron affinity of SO_3 is frustrated because only a lower limit is known for that quantity [53].

(vii) General considerations

With the exception of CN^-, which was oxidized exclusively by a copper-catalyzed pathway, all the substrates in this study exhibited rate laws for their oxidation from which rate constants could be extracted for simple bimolecular electron transfer. Two distinct types of behavior have been found. (1) Oxidations of $S_2O_3^{2-}$, I^-, SCN^-, and probably N_3^- are limited by the rate of diffusion of the products, i.e., the reduction of the free radicals is diffusion controlled. As a consequence, good LFERs with slope unity are obtained from a plot of log k_1 vs. log K_{eq}. (2) Oxidations of NO_2^- and SO_3^{2-} are activation controlled and have electron transfer as the rate-limiting step, i.e., reduction of the free radicals is not diffusion controlled. Consequently, the reactions can be treated by Marcus' theory, show LFERs with slope ~ 0.5 and with considerable scatter—a result of the sensitivity to the self-exchange rates of the oxidants.

This classification of reactivity is reflected in the electronic structure of the free radicals [54]. The unpaired electron in $S_2O_3^-$, SCN and N_3 resides in a non-bonding molecular orbital and so little change in geometry is expected to occur during oxidation to these species. I, of course, has no bonds and so it is included in this class. For NO_2 and SO_3^- the unpaired electron resides in π^* and σ^* orbitals, respectively. Good structural data are in hand for the NO_2^-/NO_2 couple; the bond angle increases from 115 to 134° and the bond length decreases from 1.24 to 1.19 Å [55]. In the case of SO_3^{2-}/SO_3^- the bond angle changes from 106 [55] to 111° [54] (estimated from ESR data), but the bond lengths in SO_3^- are unknown.

The fact that NO_2^- and SO_3^{2-} must undergo significant structural reorganization for electron transfer to occur explains the significant activation barrier for the process. For I^-, SCN^-, $S_2O_3^{2-}$ and N_3^- the reorganization is limited to the solvent sphere.

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