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Kinetics and Mechanism of the One-Electron Reduction of Iodine by $[Ru^{II}(NH_3)_5isn]^{2+}$ in Aqueous Solution

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Iodine oxidizes $[Ru^{II}(NH_3)_5isn]^{2+}$ in mildly acidic ($HClO_4$) aqueous solution at 25 °C according to the reaction $I_2 + 2[Ru^{II}(NH_3)_5isn]^{2+} \rightarrow 2I^- + 2[Ru^{III}(NH_3)_5isn]^{3+}$. The rate law is $-d[Ru(II)]/dt = \{2k_1[I_2] + 2k_2[I_3^-]\}[Ru(II)]$ with $k_1 = 4.3 \times 10^3$ M^{-1} s^{-1} and $k_2 = 80$ M^{-1} s^{-1} at $\mu = 0.10$ M ($NaClO_4$). An outer-sphere electron-transfer mechanism is proposed for both terms of the rate law, with the k_1 term corresponding to the formation of I_2^- and k_2 corresponding to the formation of I_2^- plus I^-. Subsequent reduction of I_2^- by Ru(II) to form I^- is expected to be fast. A value of 2.7 for $\log(k_{22})$ (the I_2/I_2^- self-exchange rate constant) is derived from the Marcus cross relationship.

Introduction

Outer-sphere electron-transfer reactions have been investigated for a number of main-group molecules, and there are indications that the Marcus model is of general applicability in rationalizing the reaction rates.[1] For diatomic molecules, estimates of the self-exchange rate constants have been made for the O_2/O_2^-, NO^+/NO, I_2/I_2^-, Br_2/Br_2^-, and Cl_2/Cl_2^- systems. Of these, only the O_2/O_2^- system has received extensive scrutiny. In the case of the NO^+/NO system, only one reaction has been found that appears to fall in the outer-sphere class.[2] There are scattered reports for the halogen systems, but serious reservations relate to the derived self-exchange rate constants.[1] According to theory, the internal reorganization energy is minimal for the I_2/I_2^- couple (94 kJ mol^{-1}), substantial for the Br_2/Br_2^- couple (154 kJ mol^{-1}), and quite large for the Cl_2/Cl_2^- couple (305 kJ mol^{-1}).[1] One anticipates a wide range of self-exchange rate constants on the basis of these reorganization energies, but that expectation is not fulfilled by the published estimates. As a result, we have initiated a program of study of halogen chemistry. Our first effort focused on the Cl_2/Cl_2^- couple, the results of which serve to indicate the degree of complexity that can arise.[3] In the present report, we discuss reactions pertaining to the I_2/I_2^- couple, which is much less challenging to study.

The first estimate of the I_2/I_2^- self-exchange rate constant (8.5×10^4 M^{-1} s^{-1}) was published in 1974 by Woodruff and Margerum.[4] This result was obtained by applying the Marcus theory to a series of reactions of I_2 with transition-metal complexes. As noted by McDowell et al., the reactions used for this estimate are believed to be inner sphere, which undermines the credibility of the derived self-exchange rate constant.[5] One might hope to derive a self-exchange rate constant from the reaction of I_2^- with $[Os(bpy)_3]^{3+}$, but this reaction is diffusion controlled.[6] The reaction of I_2 with $[Co(sep)]^{2+}$ is clearly outer sphere and is not limited by diffusion control;[7] Woodruff and Margerum's estimate of k_{11} was found to give a satisfactory fit for this reaction. Despite this apparent success, there are reasons to be skeptical of it. One is that the value of $E°$ used for the I_2/I_2^- couple was 0.11 V, while more recent estimates place it at 0.21 V.[8] Nord derived a value of 46 M^{-1} s^{-1} for k_{11} from the same reaction using a value of 0.172 V for $E°(I_2/I_2^-)$.[9] Another difficulty is that work terms were omitted in the Marcus calculations for both estimates. Moreover, the experiments were performed in chloride-containing media; the possibility that the rates were influenced by the reaction of I_2Cl^- was not investigated.

In the present paper, we report on the reaction of I_2 with $[Ru(NH_3)_5isn]^{2+}$ in acidic perchlorate media. This reaction most likely has an outer-sphere electron-transfer mechanism, does not have the possibility of reaction through I_2Cl^-, expands the roster of reactions to be analyzed, and affords an opportunity to apply the Marcus theory with the revised I_2/I_2^- potential plus work terms.

Experimental Section

Reagents and Solutions. Distilled deionized water was obtained by passage of deionized water through a Barnstead pretreatment cartridge and subsequent distillation in a Barnstead Fi-stream all-glass still. A 1 M $HClO_4$ solution was prepared by diluting 70% $HClO_4$ (Baker Analyzed reagent) and was standardized with Trizma base. $NaClO_4$ was recrystallized from hot water. Stock solutions of $NaClO_4$ were standardized by passing an aliquot through a column of Dowex 50W-X8 H^+ and titrating the effluent with Trizma base. Sodium chloride (Fisher, Certified) was used as supplied.

NaI (Certified) was recrystallized from acetone and dried for several days in a vacuum desiccator.[10] Solutions of NaI were standardized by

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titration with $AgNO_3$, using Eosin as indicator.[11] Reagent grade crystalline I_2 was purified by reduced-pressure sublimation. Saturated solutions of I_2 were prepared by mixing pulverized I_2 in hot water, allowing the solution to cool in the dark overnight, and then removing excess I_2 by filtration. The concentration of I_2 was determined by spectrophotometry at 460 nm; this analysis used a value of 750 M^{-1} cm^{-1} for the molar absorptivity of I_2.[12] I_2/I^- solutions were prepared by dissolving I_2 in hot NaI solutions, allowing the solution to cool in the dark overnight, and removing any insoluble impurities by filtration. The concentrations of $[I_2]_{tot}$ and $[I^-]_{tot}$ were obtained from the absorbance at 428 and 440 nm.[12]

The compound $[Ru(NH_3)_5isn](ClO_4)_2$ (isn = isonicotinamide) was prepared by a modification of Gaunder's method, as described by Stanbury et al.[13] To prevent autoxidation,[13] Ru(II) solutions were prepared by adding solid $[Ru(NH_3)_5isn](ClO_4)_2$ to a bubbling flask containing water that had been previously degassed with argon. $[Ru(NH_3)_5isn](TFMS)_3$ ($TFMS = CF_3SO_3^-$) was prepared from $[Ru(NH_3)_5Cl]Cl_2$ as described previously.[13]

Methods. UV−vis spectra were recorded on Hewlett-Packard 8452A and 8453 diode array spectrophotometers with quartz cells of 1.00 cm path length. The spectrophotometers were equipped with thermostated water baths to maintain the temperature at 25.0 ± 0.1 °C.

Cyclic voltammograms were recorded at room temperature on a BAS-100 electrochemical analyzer, using a glassy carbon working electrode, Ag/AgCl (satd KCl) reference electrode, and a Pt wire auxiliary electrode. Potentials are expressed relative to NHE by adding 0.199 V to the measured potential.[14]

The kinetics studies were performed on a Hi-Tech Scientific model SF-51 stopped-flow apparatus equipped with an SU-40 spectrophotometer and a C-400 circulating water bath that maintained the temperature of the cell compartment at 25.0 ± 0.1 °C. An OLIS 4300 S system was used for data acquisition and analysis. Reactions were monitored at 480 nm, and the rate constants were obtained by fitting the data with OLIS-supplied first-order functions. A nonlinear-least-squares computer program was used to fit the overall rate law to the values of k_{obs}.[15]

An OLIS RSM-1000 rapid-scan UV−vis/USA stopped-flow instrument was used to examine the reaction spectra. This experiment was run at room temperature, the other conditions being $[Ru(II)]_0 = 53$ μM, $[I_2]_0 = 0.47$ mM, $[H^+] = 0.01$ M, and $\mu = 0.1$ M ($NaClO_4$).

Results

Preliminary examination of the solution-phase reaction of excess I_2 with $[Ru^{II}(NH_3)_5isn]^{2+}$ showed that it proceeds homogeneously with rapid consumption of the Ru(II).

Product Analysis. The ruthenium-containing products of the reaction of $[Ru^{II}(NH_3)_5isn]^{2+}$ with I_2 were determined by UV−vis spectrophotometry, cyclic voltammetry (CV), and Osteryoung square-wave voltammetry (OSWV). One set of experiments was performed with no iodide initially in the solution, the other conditions being $[I_2]_0 = 0.5$ mM, $[Ru(II)]_0 = 0.05$ mM, $[HClO_4] = 0.01$ mM, and $[NaCl] = 0.1$ M. After reaction, excess I_2 was removed by extraction with CCl_4. The UV−vis spectrum of the aqueous phase showed a peak at 276 nm, identical in shape with that for an authentic sample of $[Ru^{III}(NH_3)_5isn]^{3+}$. A 97% yield of Ru(III) was calculated by comparing the absorbance at 276 nm with that of pure Ru(III).

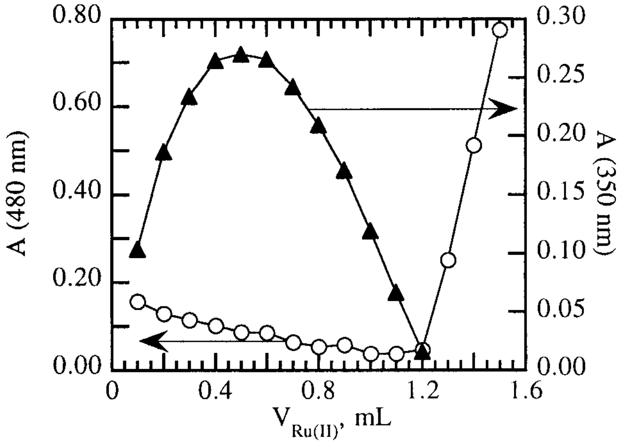

Figure 1. Spectrophotometric titration of I_2 with Ru(II). Absorbance on the left-hand ordinate at 480 nm (circles) is shown as a function of the volume of Ru(II) solution added. Formation and consumption of I_3^- are shown by the corrected absorbance on the right-hand ordinate (triangles) at 350 nm. $[H^+] = 0.01$ M, $[I_2]_0 = 0.25$ mM, $n_0(I_2) = 6.3 \times 10^{-4}$ mmol, [Ru(II) stock] = 1.02 mM, and initial volume of I_2 solution = 2.5 mL.

The CV of the product solution (subjected to the same extraction procedure) showed a reversible wave with $E_f = 375$ mV vs NHE and $\Delta E_{p/p} = 71$ mV, while OSWV yielded an $E_p = 371$ mV. These results may be compared with those for authentic $[Ru^{III}(NH_3)_5isn]^{3+}$ (E_f(CV) = 376 mV vs NHE, $\Delta E_{p/p}$(CV) = 69 mV, and E_p(OSWV) = 375 mV), which confirms the product identification. The difference between $E_f = 375$ mV and the literature value (387 mV)[13] may be due to difference in background electrolyte (NaCl vs HCl). Further confirmation was obtained by adding $Na_2S_2O_3$ to the product solution, which reduced the Ru(III) back to Ru(II); spectrophotometric analysis of this last solution indicated a $[Ru(NH_3)_5isn]^{2+}$ recovery of 100 ± 10%.

Similar analysis under conditions of high I^- concentrations could not be performed because iodide interferes with the extraction of I_2. Thus, the excess I^- was removed by passing the product solution through an anion-exchange column in the chloride form (Dowex 50W-X8). This treatment also removed the excess I_2, making the CCl_4 extraction step unnecessary. The reaction was carried out with $[I_2]_0 = 1.0$ mM, $[I^-]_0 = 90$ mM, $[HClO_4] = 0.01$ M, and $[Ru(II)]_0 = 0.05$ mM. After the ion-exchange treatment, the eluate was concentrated by rotary evaporation and the Ru(III) was reduced back to Ru(II) with $Na_2S_2O_3$. UV−vis spectral analysis of this solution indicated a 66% recovery of the initial Ru(II). The low yield of Ru(II) is attributed to loss of Ru(III) during the ion-exchange and rotary evaporation process.

Stoichiometry. The stoichiometry of the reaction between Ru(II) and I_2 was determined in a spectrophotometric titration by adding small aliquots of Ru(II) to a cuvette containing a sample of I_2 solution in 0.01 M $HClO_4$. The cuvette was equipped with a stopcock to prevent loss of I_2 vapor. The solution of Ru(II) was bubbled with argon to prevent autoxidation and was injected through the stopcock and into the cuvette by a syringe equipped with a Pt needle.

Figure 1 shows a plot of the absorbance at 350 nm (corrected as described below) and at 480 nm as a function of the volume of Ru(II) solution added. The data at 480 nm correspond to the Ru(II) spectral absorbance peak. The figure shows an initial weak absorbance at 480 nm due to the I_2 that drops during the titration. At the end point, there is an abrupt change in slope,

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with the absorbance rising as the excess Ru(II) concentration increases. The end point corresponds to a consumption ratio of 1.96 for $n_{Ru(II)}/n_{I_2}$, where n represents the number of moles of reactant. This consumption ratio, combined with the evidence for quantitative conversion of Ru(II) to Ru(III) as described above, supports description of the reaction by eq 1.

$$2[Ru^{II}(NH_3)_5isn]^{2+} + I_2 \rightarrow 2[Ru^{III}(NH_3)_5isn]^{3+} + 2I^- \quad (1)$$

Further support for eq 1 is obtained from the yield of I_3^-, which forms first by the combination of I_2 with I^- produced in the reaction and then decays as the I_2 is consumed. This was determined in the above experiment from the absorbance at 350 nm. It is well-known that I^- reacts rapidly and reversibly with I_2 as in eq 2.[12] Thus reaction 2 must be included in a complete

$$I_2 + I^- \rightleftharpoons I_3^- \qquad K_{eq} = 720\ M^{-1} \quad (2)$$

description of the reaction of I_2 with Ru(II). Unequivocal evidence for this complication is evident from Figure 1, which shows a plot of the corrected absorbance at 350 nm in the above titration. The correction removes the absorbance contribution from Ru(III) as it accumulates during the titration and is calculated as in eq 3, with $\epsilon_{Ru(III)} = 497\ M^{-1}\ cm^{-1}$. The

$$A_{350,corr} = A_{350} - \epsilon_{Ru(III)}[Ru(III)] \quad (3)$$

absorbance at 350 nm due to I_2 can be neglected ($\epsilon = 27\ M^{-1}\ cm^{-1}$), as can be the absorbance of I^-. On the other hand, the absorbance due to I_3^- is significant ($\epsilon = 27\,000\ M^{-1}\ cm^{-1}$).[12] Thus, Figure 1 shows an initial rise due to the formation of I_3^- as I^- is produced by the reduction of I_2. This is followed by a fall in absorbance due to the loss of I_3^- as the I_2 is consumed, the end point corresponding exactly to that found for Ru(II) at 480 nm. The maximum absorbance (0.27), occurring at the half-equivalence point, is in agreement with the value predicted from the stoichiometry of eq 1, the equilibrium constant for eq 2, and the absorptivity of I_3^-.

Kinetics. Qualitative features of the kinetics of the reaction of I_2 with Ru(II) were examined by use of rapid-scan stopped-flow spectrophotometry with a 10-fold excess of I_2 over Ru(II) in mildly acidic media. This experiment revealed that the reaction proceeds in a single phase, characterized by a loss of absorbance due to Ru(II) at 473 nm, a gain due to Ru(III) at 337 nm, and a well-preserved isosbestic point at 397 nm. The initial spectral peak is blue-shifted by 7 nm relative to that of pure Ru(II) because of the background absorption of I_2; the initial spectrum was accurately simulated by summing the individual spectra of the component I_2 and Ru(II) solutions.

Preliminary experiments showed that the kinetics were highly sensitive to the iodine and iodide concentrations, as is to be expected from the rapid and reversible reaction of these two species to form I_3^- as in eq 2. Consequently, all data are reported in terms of $[I_2]_{tot}$ and $[I^-]_{tot}$, defined by eqs 4 and 5.

$$[I_2]_{tot} = [I_2] + [I_3^-] \quad (4)$$

$$[I^-]_{tot} = [I^-] + [I_3^-] \quad (5)$$

In general, the kinetics were studied in acidic solution ($[HClO_4] = 0.010$ M), with $\mu = 0.10$ M ($NaClO_4$) at 25.0 °C. All the reactions were studied with $[I_2]_{tot} \gg [Ru(II)]_0$ by monitoring the loss of Ru(II) at 480 nm, which is the spectral absorbance peak of Ru(II), on a stopped-flow spectrophotometer. Under these conditions, the kinetic traces displayed pseudo-first-order kinetics, with the rate constants, k_{obs}, being defined by the equation

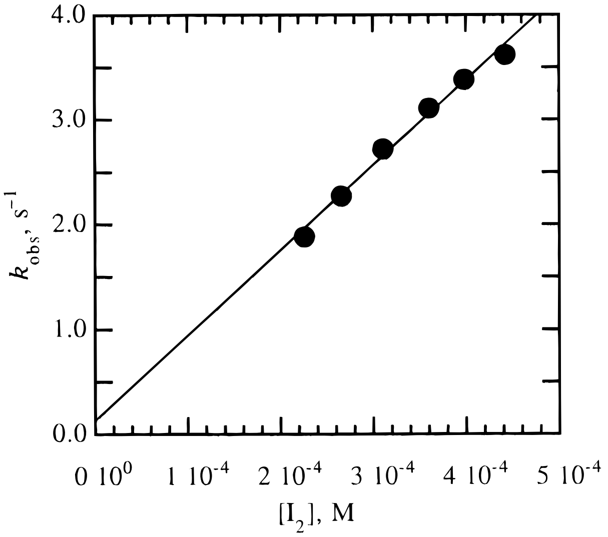

Figure 2. Kinetics of the reaction of Ru(II) with I_2 in the absence of I^-: plot of k_{obs} as a function of $[I_2]$, the slope of which is $8.1 \times 10^3\ M^{-1}\ s^{-1}$. $[HClO_4] = 0.010$ M, $\mu = 0.10$ M, $[Ru(II)]_0 = 5.0 \times 10^{-5}$ M, and 25.0 °C. The values of k_{obs} are given in the Supporting Information (Table S-1).

$$-d[Ru(II)]/dt = k_{obs}[Ru(II)] \quad (6)$$

Overall, the pseudo-first-order rate constants obey the two-term rate law

$$k_{obs} = 2k_1[I_2] + 2k_2[I_3^-] \quad (7)$$

Simple demonstration of this rate law is a nontrivial task because of the following general equations:

$$[I_2] = \{-(K_{eq}[I^-]_{tot} + 1 - K_{eq}[I_2]_{tot}) + [(1 + K_{eq}[I^-]_{tot} - K_{eq}[I_2]_{tot})^2 + 4K_{eq}[I_2]_{tot}]^{1/2}\}/2K_{eq} \quad (8)$$

$$[I_3^-] = \frac{K_{eq}[I_2][I^-]_{tot}}{1 + K_{eq}[I_2]} \quad (9)$$

Useful approximations can be made under certain limiting conditions. The simplest case is where $[I^-]_{tot} = 0$, such that $[I_2] \sim [I_2]_{tot}$ and $[I_3^-] \sim 0$. A series of experiments of this type was performed as shown in Figure 2, which is a graph of k_{obs} as a function of $[I_2]$. The graph indicates an excellent first-order dependence on $[I_2]$ and has a slope ($2k_1$) of $8.1 \times 10^3\ M^{-1}\ s^{-1}$.

The dependence of k_{obs} on $[I^-]$ is more complex, but it simplifies when the iodide concentration is high enough that most of the I_2 is converted to I_3^-. This occurs when $[I^-]_{tot} \gg [I_2]_{tot}$ and $[I^-]_{tot} \gg 1/K_{eq}$, such that $[I_2]_{tot} \sim [I_3^-]$ and $[I_2] \sim [I_2]_{tot}/(K_{eq}[I^-]_{tot})$. With these approximations eqs 7−9 lead to an inverse dependence on $[I^-]_{tot}$ as given in eq 10. Values of

$$k_{obs} = 2\left(\frac{k_1}{K_{eq}[I^-]_{tot}} + k_2\right)[I_2]_{tot} \quad (10)$$

k_{obs} obtained under these conditions are shown in Figure 3 as a linear plot of k_{obs} vs $1/[I^-]_{tot}$ with slope $= 9.72 \times 10^{-3}\ M\ s^{-1}$ and intercept $= 0.199\ s^{-1}$. When these results are interpreted

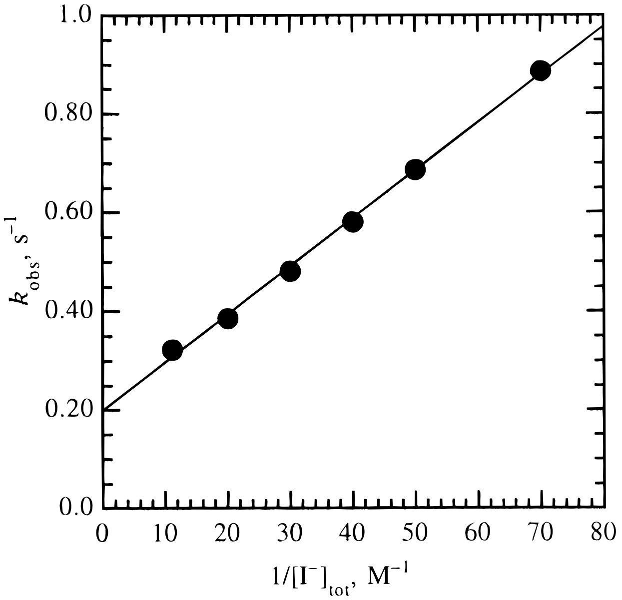

Figure 3. Dependence of the pseudo-first-order rate constant (k_{obs}) on $1/[I^-]_{tot}$ at high $[I^-]_{tot}$. The slope of the line is 9.72×10^{-3} M s^{-1}, and the intercept is 0.199 s^{-1}. $[I_2]_{tot} = 1.0 \times 10^{-3}$ M, $[Ru(II)]_0 = 5.0 \times 10^{-5}$ M, $[H^+] = 0.010$ M, $\mu = 0.10$ M, and 25.0 °C. The values of k_{obs} are given in the Supporting Information as Table S-2.

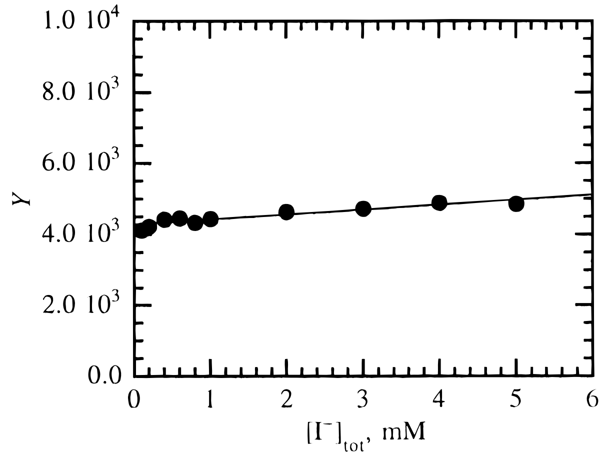

Figure 4. Kinetics at low $[I_2]_{tot}$ and low $[I^-]_{tot}$. $Y = k_{obs}(K_{eq}[I^-]_{tot} + 1)/(2[I_2]_{tot})$; see eq 11. The graph yields an intercept of 4.28×10^3 M^{-1} s^{-1} for k_1 and an ill-defined slope of 1.4×10^5 M^{-2} s^{-1} for k_2K_{eq}. $[I_2]_{tot} = 5 \times 10^{-5}$ M, $[Ru(II)]_0 = 1.0 \times 10^{-5}$ M, $[H^+] = 0.010$ M, 25.0 °C, and $\mu = 0.10$ M. The values of k_{obs} are given in the Supporting Information as Table S-3.

according to eq 10 with the literature value of 720 M^{-1} for K_{eq}, they yield $k_1 = 3.5 \times 10^3$ M^{-1} s^{-1} and $k_2 = 99.8$ M^{-1} s^{-1}.[12]

At small $[I^-]_{tot}$ most of the I_2 is not converted to I_3^-, and hence eq 10 is not appropriate. Simplifications can be obtained when $[I_2]_{tot} \ll 1/K_{eq}$, such that $[I_2] \sim [I_2]_{tot}/(1 + K_{eq}[I^-]_{tot})$ and $[I_3^-] \sim K_{eq}[I^-]_{tot}[I_2]_{tot}/(1 + K_{eq}[I^-]_{tot})$. These approximations lead to eq 11. Data obtained under these conditions are shown

$$\frac{k_{obs}(K_{eq}[I^-]_{tot} + 1)}{2[I_2]_{tot}} = k_1 + k_2K_{eq}[I^-]_{tot} \qquad (11)$$

in Figure 4 as a plot of the left-hand side of eq 11 vs $[I^-]_{tot}$, the literature value of 720 M^{-1} for K_{eq} being used.[12] The graph demonstrates an excellent fit to eq 11 and yields $k_1 = 4.3 \times 10^3$ M^{-1} s^{-1}. The value of k_2 has a large uncertainty because the slope is not well defined by these data.

A comprehensive fit to all the kinetic data with eq 7 and with $[I_2]$ and $[I_3^-]$ defined as in eqs 8 and 9 was achieved by use of a nonlinear-least-squares computer program. Attempts to fit the data with k_1, k_2, and K_{eq} as adjustable parameters failed to converge. On the other hand, convergence was obtained with k_1 and k_2 as adjustable parameters and the value of K_{eq} held fixed. When a series of fits was performed while systematically varying the value of K_{eq}, the lowest variance was obtained for $K_{eq} = 718$ M^{-1}. The close agreement between this value of K_{eq} and that given in the literature supports the inferred rate law. When the data were fit with the literature value of 720 M^{-1} for K_{eq},[12] the following results were obtained: $k_1 = (4.28 \pm 0.05) \times 10^3$ M^{-1} s^{-1}, $k_2 = 80 \pm 5$ M^{-1} s^{-1}. In summary, the overall rate law has the form

$$-d[Ru(II)]/dt = 2(k_1[I_2] + k_2[I_3^-])[Ru(II)] \qquad (12)$$

A number of control experiments were also performed. Thus, reaction between Ru(II) and I_2 at pH 1 and 3 showed no significant pH dependence when studied with a 10-fold excess of I_2. Likewise, for a series of experiments with 0.01 M H^+, $[I^-]_{tot} = 4.0$ mM, and $[I_2]_{tot} = 0.5$ mM, variation in $[Ru(II)]_0$ over the range from 10 to 80 μM led to no significant effect on the kinetics. As a test for possible metal ion catalysis, addition of 1 mM $Na_2C_2O_4$ had no effect under conditions of $[I_2]_{tot} = 1.0$ mM, $[I^-]_{tot} = 3.2$ mM, 0.10 M H^+, and 0.10 mM Ru(II). A test for the effect of O_2 was performed comparing the kinetics under two reaction conditions. First, both the Ru(II) and I_2/I^- solutions were purged with argon prior to the kinetics run; then the I_2/I^- solution was briefly sparged with air prior to the next kinetics run. This procedure was followed in order to minimize the effects of the inevitable loss of I_2 during sparging. Essentially identical rate constants were obtained for the two runs, showing that O_2 has no significant effect. The effect of Ru(III) was studied under conditions of $[Ru(II)]_0 = 54$ μM, $[I_2]_{tot} = 0.50$ mM, $[I^-]_{tot} = 2.4$ mM, and $[HClO_4] = 0.10$ M. Without Ru(III), the value of k_{obs} was 0.96 s^{-1}, and it was virtually unchanged at 0.97 s^{-1} with the addition of 0.5 mM Ru(III). Thus, Ru(III) has no influence on the reaction.

Discussion

Proposed Mechanism. A mechanism consistent with the rate law and stoichiometry is given by eqs 13–15, where steps 13 and 14 are rate-determining.

$$Ru(II) + I_2 \rightleftharpoons Ru(III) + I_2^- \qquad k_1, k_{-1}, K_1 \qquad (13)$$

$$Ru(II) + I_3^- \rightleftharpoons Ru(III) + I_2^- + I^- \qquad k_2, k_{-2}, K_2 \qquad (14)$$

$$Ru(II) + I_2^- \rightarrow Ru(III) + 2I^- \qquad k_3 \qquad (15)$$

The steady-state approximation for $[I_2^-]$ leads to

$$[I_2^-]_{ss} = \frac{(k_1[I_2] + k_2[I_3^-])[Ru(II)]}{k_{-1}[Ru(III)] + k_{-2}[Ru(III)][I^-] + k_3[Ru(II)]} \qquad (16)$$

and the overall rate law

$$-\frac{d[Ru(II)]}{dt} = \frac{2(k_1[I_2] + k_2[I_3^-])k_3[Ru(II)]^2}{k_{-1}[Ru(III)] + k_{-2}[Ru(III)][I^-] + k_3[Ru(II)]} \qquad (17)$$

The experimental evidence is that Ru(III) has no effect on the

Table 1. Marcus Calculations for Reactions of Metal Complexes with I_2

reactants	r,[a] Å	E_f,[f] V	$\Delta G°_{12}$,[j] kJ mol^{-1}	k_{11}, M^{-1} s^{-1}	$k_{12,cal}$,[m] M^{-1} s^{-1}	$k_{12,exp}$, M^{-1} s^{-1}	k_{-12},[o] M^{-1} s^{-1}
$[Ru(NH_3)_5isn]^{2+} + I_2$	4.0[b]	0.387[g]	17.1	1.1×10^5 [k]	4.3×10^3	4.3×10^3 [n]	4.3×10^6
$[Co(sep)]^{2+} + I_2$	4.1[b]	−0.30[h]	−49.2	5.1[h]	4.7×10^6	5.9×10^4 [h]	1.4×10^{-4}
$V^{2+}(aq) + I_2$	3.3[d]	−0.26[c]	−45.4	1.0×10^{-2} [l]	5.5×10^3	7.5×10^3 [l]	8.3×10^{-5}
$Fe^{2+}(aq) + I_2$	3.3[d]	0.74[c]	51.1	3.7[l]	3.3×10^{-3}	5.0×10^{-3} [l]	4.6×10^6
$[Co(EDTA)]^{2-} + I_2$	4.6[b]	0.37[c]	15.5	4.0×10^{-7} [l]	6.4×10^{-4}	5.2×10^{-4} [l]	2.7×10^{-1}
$[Fe(EDTA)]^{2-} + I_2$	4.6[b]	0.12[c]	−8.7	3.0×10^4 [l]	2.7×10^4	1.6×10^6 [l]	4.8×10^4
$[Fe(CN)_6]^{4-} + I_2$	4.1[c]	0.42[c]	20.3	1.9×10^4 [c]	4.4×10^2	1.4×10^3 [q]	5.0×10^6
$[Os(bpy)_3]^{3+} + I_2^-$ [p]	6.8[e]	0.857[i]	−62.4	8.0×10^9 [i]	9.1×10^{10}	1.2×10^{10} [i]	3.2×10^{-1}

[a] Mean radius of the metal complex. For the I_2/I_2^- couple a radius of 2.4 Å was used, which was calculated as $^1/_2(d_1d_2d_3)^{1/3}$,[30] from the structural parameters of crystalline I_2.[20,21] [b] Estimated from CPK models. [c] Reference 31. [d] Calculated from crystal structural data[32,33] and from covalent and van der Waals radii, as given in ref 34. [e] Reference 35. [f] E_f for the complex couples vs NHE. [g] Reference 13. [h] Reference 7. [i] Reference 6. [j] $\Delta G°_{12}$ was calculated from $E_{f,M}$ and $E_{f,I_2/I_2^-}$ which equals 0.21 V. [k] Reference 36. [l] Reference 4 and references therein. [m] $k_{12,cal}$ was calculated from k_{22} for the I_2/I_2^- couple = 486 M^{-1} s^{-1} by using the Marcus cross equation. [n] This work. [o] $k_{-12} = k_{12,exp}/K$; K was calculated from $\Delta G°_{12}$. [p] This reaction is the reverse of the reaction of $[Os(bpy)_3]^{2+} + I_2$.[6] [q] Reference 37.

kinetics, which implies that the first two terms in the denominator of eq 17 can be neglected. With this approximation, eq 17 simplifies to the observed rate law, eq 12.

Justification for the neglect of the two Ru(III) terms in eq 17 can also be made by considering the probable magnitudes of the rate constants involved. The standard reduction potentials for the I_2/I_2^- and Ru(III)/Ru(II) couples have been reported as 0.21 and 0.387 V.[8,13] These potentials lead to a value of 1.0×10^{-3} for K_1, from which a value of 4×10^6 M^{-1} s^{-1} for k_{-1} can be calculated from the experimental value of k_1 and the principle of detailed balancing. Use of the literature value[12] of 720 M^{-1} for K_{eq} then leads to a value of 1.4×10^{-6} for K_2, from which a value of 6×10^7 M^{-2} s^{-1} is calculated for k_{-2}. An estimate of 2.3×10^9 M^{-1} s^{-1} for k_3 can be made on the assumption that it is the same as the rate constant for the corresponding reaction of I_2^- with $[Ru(NH_3)_5py]^{2+}$.[16] With these estimates in hand, it can be shown that the two Ru(III) terms in eq 16 can be safely neglected for the first 4 half-lives in all our experiments.

All three steps in the mechanism proposed above are considered to be outer-sphere electron-transfer processes. This assignment is based on the facts that both Ru(II) and Ru(III) are substitution inert and that the overall reaction products indicate that the coordination sphere at ruthenium is conserved. Parenthetically, note that an inner-sphere mechanism with formation of a $Ru^{III}-I$ product may be anticipated when $[Ru(NH_3)_4(isn)H_2O]^{2+}$ is present in solution.[17] The first step, outer-sphere reduction of I_2 to I_2^-, has been observed in several other reactions and is discussed in detail below. The second step, outer-sphere reduction of I_3^-, entails cleavage of a bond in I_3^- and has been observed previously in the reaction of I_3^- with $[Co^{II}(sep)]^{2+}$ (sep = sepulchrate);[7] this bond cleavage could occur after the electron-transfer event or be concerted with it. The third step, outer-sphere reductive cleavage of I_2^-, is a well-known process, which quite likely has electron transfer concerted with bond cleavage.[9,18]

Alternative Mechanisms. In the proposed mechanism, I_2^- is a reactive intermediate that is consumed by reaction with Ru(II). A conceivable alternative decay path is its well-established self-reaction as given in eq 18. The question of whether it could

$$I_2^- + I_2^- \rightarrow I_3^- + I^- \qquad k_4 = 4 \times 10^9\ \mathrm{M^{-1}\ s^{-1}} \qquad (18)^{19}$$

be competitive with the reaction of I_2^- with Ru(II) can be assessed by calculating the steady-state concentration of $[I_2^-]$ as in eq 16. Under the conditions of all the experiments in Figures 3 and 4, the calculated value of $[I_2^-]_{ss}$ never significantly exceeds 10^{-11} M. This low steady-state concentration ensures that the second-order decomposition of I_2^- can be ignored safely.

Another set of pathways for loss of I_2^- arises through its well-known, rapid, and reversible dissociation to form iodide and iodine atoms:

$$I_2^- \rightleftharpoons I + I^- \qquad k_5, k_{-5} \qquad (19)$$

$$Ru(II) + I \rightarrow Ru(III) + I^- \qquad k_6 \qquad (20)$$

$$I + I \rightarrow I_2 \qquad k_7 \qquad (21)$$

Convincing arguments have been made that a value of about 1×10^{10} M^{-1} s^{-1} can be estimated for the oxidation of Ru(II) by iodine atoms, k_6,[9] while a value of 8×10^9 M^{-1} s^{-1} has been measured for iodine atom recombination, k_7.[19] As the steady-state concentration of iodine atoms can never approach that of Ru(II), the second-order recombination of iodine atoms is too slow to compete with their reaction with Ru(II) and hence k_7 can be ignored.

The contribution of reaction of iodine atoms with Ru(II) (eq 20) can be determined by applying the steady-state approximations to $[I_2^-]$ and [I] as they arise in the set of reactions comprising eqs 13−15, 19, and 20. These approximations lead to

$$[I_2^-]_{ss}/[I]_{ss} = (k_{-5}[I^-] + k_6[Ru(II)])/k_5 \qquad (22)$$

Experimental values of 8.8×10^4 M^{-1} s^{-1} and 1.1×10^{10} M^{-1} s^{-1} are available for k_5 and k_{-5}.[19] These data plus the value of k_6 estimated above indicate that the ratio of $[I_2^-]_{ss}/[I]_{ss}$ exceeds 10 for all the experiments with added iodide, while it is about 5 for the experiments without added iodide (data in Figure 2). Thus, the major pathway for loss of I_2^- is through its reaction with Ru(II) in the experiments with added iodide. On the other hand, in reactions with no added iodide, the two loss pathways could have comparable rates. Irrespective of which of these two pathways is dominant, the same overall rate law, eq 12, is obtained.

Details of the I_2 Pathway. With values of k_{11} for Ru(II), E_f for the Ru(III)/Ru(II) couple, and E_f for the I_2/I_2^- couple in hand, it is now possible to calculate the self-exchange rate constant for the I_2/I_2^- redox couple and to conduct an analysis of the rates of reduction of I_2 by using the Marcus theory. The relevant data are presented in Table 1. In this table, $r_{I_2} = 2.4$

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Å, which was evaluated from the structural parameters of crystalline I_2.[20,21] E_f for the I_2/I_2^- couple = 0.21 V.[8] The cross relationship of the Marcus theory is a basis for understanding the data in Table 1. For the present purposes the following equations are used:[22]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{23}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\ln(k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT} \tag{24}$$

$$W_{12} = \exp[(-w_{12} - w_{21} + w_{11} + w_{22})/2RT] \tag{25}$$

$$w_{ij} = 4.23 \times 10^3 Z_i Z_j/(r(1 + 0.328r(\mu)^{1/2}) \tag{26}$$

In these equations, k_{12} represents the rate constant for electron transfer from reductant to I_2, k_{11} is the self-exchange rate constant for the various complex couples, and k_{22} is the self-exchange rate constant for the I_2/I_2^- couple. K_{12} is the equilibrium constant for the various electron-transfer reactions. Z in eq 24 is the collision rate, for which a value of 1×10^{11} M^{-1} s^{-1} has been used. Z_i and Z_j in eq 26 are the ionic charges of the respective species, and R is the gas constant (kcal mol^{-1} K^{-1}). r is the center-to-center distance (Å) when the species are touching.

Our measured value of k_{12} for the I_2/Ru(II) reaction was used in solving the above form of the Marcus cross relationship to obtain a value of 486 M^{-1} s^{-1} for the self-exchange rate constant of the I_2/I_2^- couple. This value for k_{22} was then used in the Marcus cross relationship to calculate values of k_{12} for a series of other reactions, as indicated in Table 1. Good agreement between $k_{12,cal}$ and $k_{12,exp}$ is found for the reactions of I_2 with V^{2+}(aq), Fe^{2+}(aq), $[Co(EDTA)]^{2-}$, and $[Fe(CN)_6]^{4-}$. In the case of the reaction between $[Os(bpy)_3]^{3+}$ and I_2^-, the value of $k_{12,cal}$ is very high, but it gives good agreement with $k_{12,exp}$ after correction for the effects of diffusion control. There is evidence that the reaction of $[Fe(EDTA)]^{2-}$ with I_2 has an inner-sphere mechanism,[4] so the low value of $k_{12,cal}$ in this case is not unexpected. The only reaction in Table 1 that disagrees significantly with expectations is that of $[Co(sep)]^{2+}$; potential explanations for this disagreement are explored below.

Rate constants for the reactions of $[Ru^{II}(NH_3)_5isn]^{2+}$ and $[Co^{II}(sep)]^{2+}$ with the two different oxidants, I_2 and O_2, are now available from the present work and prior studies, as indicated in eqs 27−29.[7,13,23] The values at 25 °C are $k_8 = 5.9 \times 10^4$

$$[Co^{II}(sep)]^{2+} + I_2 \rightarrow [Co^{III}(sep)]^{3+} + I_2^- \qquad k_8 \tag{27}$$

$$[Ru^{II}(NH_3)_5isn]^{2+} + O_2 \rightarrow [Ru^{III}(NH_3)_5isn]^{3+} + O_2^- \qquad k_9 \tag{28}$$

$$[Co^{II}(sep)]^{2+} + O_2 \rightarrow [Co^{III}(sep)]^{3+} + O_2^- \qquad k_{10} \tag{29}$$

M^{-1} s^{-1}, $k_9 = 1.08 \times 10^{-1}$ M^{-1} s^{-1}, and $k_{10} = 43$ M^{-1} s^{-1}. These rate constants allow us to compare the relative reactivity of Ru(II) and Co(II) in their reactions with I_2 and O_2, the pertinent ratios being $k_1/k_8 = 7.3 \times 10^{-2}$ and $k_9/k_{10} = 2.5 \times 10^{-3}$. Simple Marcus theory suggests that these ratios should be similar, although in fact they differ by a factor of 30.

One possible explanation of these divergent results is that the rate constant for the I_2/Ru(II) reaction is anomalously large (by a factor of 30). This could arise from a specific interaction between I_2 and the aromatic isn ligand, which could lead to either strong electronic coupling between the reactants or an unusually large association constant for the reactants. If such an effect is occurring, it is not detectable in rapid-scan spectra taken immediately after initiating the reaction. This should be considered a negative result, as the spectrum of the I_2/Ru(II) association complex could be formed only weakly and might not be distinct. One reason to reject the idea of an anomalously fast I_2/Ru(II) reaction is that this reaction leads to good agreement for the majority of reactions in Table 1. An alternative explanation for the apparent kinetic advantage of Ru(II) in the I_2 reaction in terms of unaccounted reactivity of I_2Cl^- in the Co(II) reaction is untenable, as correction for this effect would increase the discrepancy in the ratios. Yet another explanation is suggested by the analysis of O_2 reactions performed by Zahir et al.[24] These workers found that the reaction of O_2 with $[Co(sep)]^{2+}$ gives a value of k_{22} for the O_2/O_2^- couple that is about a factor of 10 less than that obtained from the reaction of O_2 with $[Ru(NH_3)_5isn]^{2+}$. Thus, the reaction of O_2 with $[Co(sep)]^{2+}$ is anomalously slow, perhaps because of nonadiabaticity. Likewise, the reaction of $[Co(sep)]^{2+}$ with Fe^{3+}(aq) is significantly slower than predicted by the Marcus theory.[25] This may also be the case in the $I_2/[Co(sep)]^{2+}$ reaction, although to a greater degree than in the $O_2/[Co(sep)]^{2+}$ reaction.

With the Marcus theory it is possible to estimate the internal contribution to ΔG^* for the I_2/I_2^- self-exchange reaction by making the harmonic oscillator approximation and minimizing the energy of the transition state under the constraint that the two reactants have identical geometries. The appropriate equation is

$$\Delta G_i^* = f_1 f_2 (\Delta r)^2/(f_1 + f_2) \tag{30}$$

In this equation, f_1 and f_2 are the force constants for I_2 and I_2^- and Δr is the difference in bond length between the two molecules. This equation was used previously with a value of 0.43 Å for Δr, which was obtained from spectroscopic data for I_2 and from a Badger's rule estimate for I_2^-.[13] After rectification of a math error, a value of 23.5 kJ mol^{-1} was obtained for ΔG_i^*.[1] However, there is now a more accurate value for Δr of 0.56 Å.[26] This revision leads to a significant increase in the calculated value of ΔG_i^*, which is now 38 kJ mol^{-1}. The corresponding value of λ_i, taken as $4\Delta G_i^*$, is 152 kJ mol^{-1}.

A direct comparison can be made with the behavior of the Br_2/Br_2^- couple, for which a value of 154 kJ mol^{-1} was reported for λ_i.[1] As in the case of the I_2/I_2^- system, this result was based on a Badger's rule estimate of 0.52 Å for Δr. The more accurate data now available give a value of 0.57 Å for Δr in the Br_2/Br_2^- system, which is only a modest adjustment.[26] The

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corresponding revised value of λ_i is 180 kJ mol^{-1}. Plotkin and Haim recently derived a value of 150 M^{-1} s^{-1} for the Br_2/Br_2^- self-exchange rate constant.[27] Thus, for both the I_2/I_2^- and Br_2/Br_2^- systems, the values of λ_i are similar and substantial and appear to be reflected in the corresponding values of k_{22}. On the other hand, the O_2/O_2^- system has a smaller value of λ_i and a smaller value of k_{22}; this apparent discrepancy can be resolved if the solvent reorganization energy is larger, as would be expected for the smaller molecular size of O_2.

Details of the I_3^- Pathway. It is fairly common to find rate laws with terms corresponding to direct electron transfer to I_3^-. In the present work, we find that I_3^- is less reactive than I_2 by a factor of 0.019. In the reaction of $[Co(sep)]^{2+}$ the rate constants are more equivalent, with the ratio being 0.66.[7] For V^{2+}(aq), the ratio is 0.13,[28] while it is 0.0040 for $[Fe^{II}(CyDTA)]^{2-}$,[29] 0.0028 for $[Fe^{II}(EDTA)]^{2-}$,[4] 0.060 for $[Co^{II}(EDTA]^{2-}$,[4] and 0.34 for $[Co^{II}(CyDTA)]^{2-}$.[4] As some of these reactions may have inner-sphere mechanisms, such comparisons may not be very meaningful. Nevertheless, it appears to be a general trend that electron transfer is somewhat slower to I_3^- than to I_2. This kinetic disadvantage for I_3^- is not unexpected in view of the associated bond cleavage that must accompany electron transfer.

A similar kinetic disadvantage is often seen for reduction of Br_3^- relative to Br_2.[4] As the formation constant is a factor of 0.015 less favorable for Br_3^- than for I_3^-, detection of Br_3^- pathways can be more difficult. Indeed, reactivity via Br_3^- has not been observed in any reactions of outer-sphere reductants.[27]

Conclusions. $[Ru(NH_3)_5isn]^{2+}$ is oxidized by both I_2 and I_3^- through outer-sphere electron-transfer mechanisms, forming I_2^- as a reactive intermediate. Marcus' theory accounts satisfactorily for the rates via the I_2 pathway, both from the point of view of the cross relationship and from considerations of structural changes and bond force constants.

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Supporting Information Available: Listings of kinetic data (2 pages). Ordering information is given on any current masthead page.

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