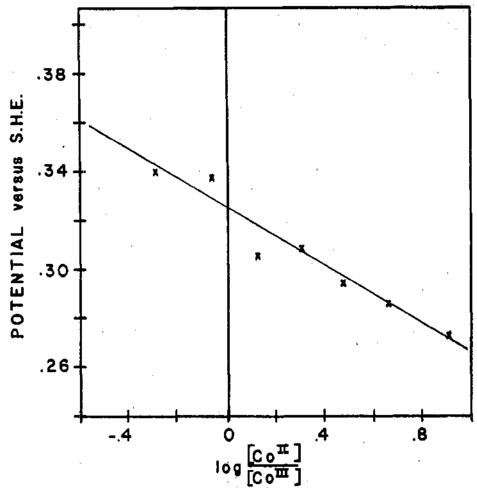

Figure 5. Plot of potential (E) measured at a carbon-rod electrode vs. log ([Co(II)]/[Co(III)]).

our conclusions based on the studies at the mercury electrode.

Before concluding, we should comment about the differences between the potentials determined by Gouzerh and those reported herein. (See the table.) Gouzerh noted that the values he reported were only approximate[3] because of anomalies in the polarograms which may in part be related to the $Co(IDA)_2^-/Hg$ reaction described above. Another consideration is that the polarographic work was carried out at pH 5,[3] and we have found that the $Co(IDA)_2^{2-}$ complex is substantially hydrolyzed at this pH. In fact, an *anodic* shift in the half-wave potential is expected if the reduction product is consumed in a follow-up chemical reaction as discussed previously in connection with the reduction of *trans*-$Co(IDA)_2^-$. Since the above complications have been obviated in our experiments, we suggest that the potentials reported herein are the more reliable.

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Registry No. *trans*-$Co(IDA)_2^-$, 33848-79-2; *trans*-$Co(IDA)_2^{2-}$, 68831-75-4; *cis*-$Co(IDA)_2^{2-}$, 68831-76-5; *cis*-$Co(IDA)_2^-$, 21718-59-2.

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(7) We are indebted to a referee for bringing this point to our attention.
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Catalysis in Substitution on Ruthenium(III) by Iodide

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The kinetics of replacement of water by iodide on *trans*-$[Ru(NH_3)_4(isn)H_2O]^{3+}$ (isn = isonicotinamide) have been studied in 0.1 M acid at 25 °C (reaction 1). In contrast to anation by chloride and bromide, which proceeds with simple first-order dependence on halide, the rate of iodide anation is given by $-d \ln [Ru^{III}H_2O]/dt = k_a[I^-]^{5/2}[I_3^-]^{-1/2} + k_b[I^-]^2$. The first term arises from catalysis of substitution by $[Ru(NH_3)_4(isn)H_2O]^{2+}$ which is maintained at equilibrium with aquoruthenium(III), I^-, and I_3^-. The second term is believed to indicate a presubstitution electron transfer ($I^- \rightarrow Ru(III)$) not involving production of free iodine. The data give a value of $0.20 \pm 0.04\ M^{-1}\ s^{-1}$ for the specific rate of iodide substitution on $[Ru(NH_3)_4(isn)H_2O]^{2+}$. Stopped-flow experiments give the rate of aquation of I^- in $[Ru(NH_3)_4(isn)I]^+$ as $0.91 \pm 0.17\ s^{-1}$. The equilibrium quotient for reaction 1 was determined ($86 \pm 4\ M^{-1}$).

In the course of preparing some Co(III)–Ru(III) complexes with 4,4′-bipyridine bridging the two metal centers, it was observed[1] that SO_4^{2-} on Ru(III) is replaced by I^- at a rate much in excess of that expected for ordinary nucleophilic substitution. It was suspected, and the present work has confirmed this, that the enhanced rate is a special manifestation of the catalysis by Ru(II) of the rate of substitution on Ru(III). Whereas in the cases previously studied[2,3] Ru(II) is produced by an extrinsic process, here we describe a system in which its formation is intrinsic, and this leads to some special kinetic effects. We selected the isonicotinamide complex of Ru(III) for detailed study, and the net change in our system therefore is

$$trans\text{-}[Ru(NH_3)_4(isn)H_2O]^{3+} + I^- = trans\text{-}[Ru(NH_3)_4(isn)I]^{2+} + H_2O \quad (1)$$

Experimental Section

Ruthenium Complexes. The species *trans*-$[Ru(NH_3)_4(isn)H_2O]^{3+}$ was produced in situ as follows: Recrystallized *trans*-$[Ru(NH_3)_4(isn)SO_4]Cl$ was prepared by the method of Isied and Taube.[4] About 80 mg of this complex was dissolved in 1 mL of 0.1 N trifluoromethanesulfonic acid, CF_3SO_3H (obtained neat from 3M Chemical Division and vacuum distilled), and then reduced over zinc amalgam with argon bubbling for 20 min. Coordinated sulfate is rapidly aquated from the inner coordination sphere of Ru(II) ($t_{1/2} < 1$ s).[4] The solution was rapidly filtered and the complex was precipitated as deep red crystals of $[Ru(NH_3)_4(isn)H_2O](PF_6)_2$ by saturating with ammonium hexafluorophosphate and then cooling.[5] Microanalysis calculated for the composition above: C, 12.02; H, 3.36; N, 14.02. Found: C, 12.07; H, 3.35; N, 14.02. About 3 mg of $[Ru(NH_3)_4(isn)H_2O](PF_6)_2$ was dissolved in 5 mL of 0.1 N CF_3SO_3H and then oxidized by adding excess manganese dioxide. The deep red color of the solution quickly faded as Ru(II) changed to Ru(III). The remaining manganese dioxide was filtered off, and the filtrate was stored in a freezer until use.

trans-$[Ru(NH_3)_4(isn)I]I_2$ was prepared by dissolving 40 mg of $[Ru(NH_3)_4(isn)SO_4]Cl$ and 0.5 g of sodium iodide in 3 mL of water. The solution was refrigerated overnight. Deep blue crystals containing the iodo complex formed. They were filtered off and washed with acetone and ether and then dried in a vacuum desiccator (yield 65%). Anal. Calcd: C, 10.72; H, 2.70; N, 12.51; I, 56.7. Found: C, 10.85; H, 2.76; N, 12.48; I, 55.4. If the solution is allowed to stand for more than 24 h, a second product is formed, assumed to be the diiodotetraammine complex.

Solutions of $[Ru(NH_3)_4(isn)Br]^{2+}$ were prepared by adding a catalytic amount of $[Ru(NH_3)_4(isn)H_2O](PF_6)_2$ to a solution 1 M in sodium bromide and about 10^{-3} M in $[Ru(NH_3)_4(isn)H_2O]^{3+}$.

All solutions were made from doubly distilled water and all chemicals were reagent grade.

Kinetic Studies. It was observed early in the work that I_2 had to be present if reproducible rate data were to be obtained. Kinetics were done under pseudo-first-order conditions with $[Ru(NH_3)_4(isn)H_2O]^{3+}$ at about 1×10^{-4} M, iodide and triiodide being in large excess. Solutions were prepared from sodium iodide, iodine, sodium *p*-toluenesulfonate (to adjust ionic strength), and CF_3SO_3H to give the desired iodide and triiodide concentrations in 0.1 N CF_3SO_3H at $\mu = 0.7$ M. The solutions were stored under argon to exclude oxygen.

For each run, 2.5 mL of the reaction solution containing all reagents except Ru(III) was brought to 25.0 °C (± 0.1 °C), the solution temperature being monitored by a thermistor probe placed directly into the solution. To initiate reaction, 0.5 mL of temperature-equilibrated $[Ru(NH_3)_4(isn)H_2O]^{3+}$ solution was added and mixed using an all-glass syringe fitted with a platinum needle. The reaction was followed for at least 8 half-lives by the increase in absorbance at 604 nm. A plot of ln $(A_\infty - A_t)$ vs. time gave a straight line with a slope which is defined as $-k_{obsd}$. In general, rate constants were reproducible to within ±4%.

The stopped-flow experiments were done with an Aminco-Morow/Beckman DU instrument.[6] The rate constant for the aquation of iodide from $[Ru(NH_3)_4(isn)I]^+$ was measured by mixing a solution of $[Ru(NH_3)_4(isn)I]^{2+}$ with a 500% excess of $[Ru(NH_3)_6]^{2+}$, known to be a rapid and unspecific reducing agent.[19] Solute concentrations were adjusted to give a mixed solution at pH 1 and $\mu = 0.7$ M. The loss of iodide from the inner coordination sphere of $[Ru(NH_3)_4(isn)I]^+$ can be followed by the increase in absorbance at 475 nm (production of aquo complex). Oscilloscope traces of photomultiplier tube voltage vs. time were converted into ln absorbance vs. time data,[6] and k_{obsd} was calculated by the method of least squares.

Electrochemistry. The standard reduction potentials of the $[Ru(NH_3)_4(isn)H_2O]^{3+/2+}$ and $[Ru(NH_3)_4(isn)I]^{2+/+}$ couples were determined by cyclic voltammetry with a PAR Model 173/175 potentiostat/programmer. Current vs. potential traces were recorded on either a Houston Instruments 2000 X-Y recorder or a Tektronix storage oscilloscope. The electrochemical cell was a conventional three-electrode type with an aqueous saturated calomel electrode (SCE) as reference, platinum wire as auxiliary, and carbon paste (or glassy carbon) as the indicator electrode. The reference cell was connected to the sample solution through a fritted glass bridge. The concentration of the electroactive species was $\sim 10^{-3}$ M in a supporting electrolyte of 0.1 M sodium *p*-toluenesulfonate/0.1 M *p*-toluenesulfonic acid. Values for $E_{1/2}$ were taken as the average of anodic and cathodic peak potentials and were converted to NHE scale by adding 0.242 V to the $E_{1/2}$ value vs. SCE.

Equilibrium Quotient Determinations. To measure the equilibrium quotient for reaction 1, an argon-saturated solution 0.020 M in sodium iodide, 0.58 M in sodium *p*-toluenesulfonate, 0.1 M in CF_3SO_3H, and about 1×10^{-4} M in $[Ru(NH_3)_4(isn)I]I_2$ was prepared and transferred to a 10-cm cell. The spectrum from 800 to 350 nm was recorded. A small amount (resultant concentration less than 5×10^{-5} M) of $[Ru(NH_3)_4(isn)H_2O](PF_6)_2$ was then added to act as catalyst. Care was taken to exclude air because the Ru(II) complex is slowly oxidized by oxygen in acidic solution. The visible spectrum was scanned every 10 min until no change was observed (1–2 h). The ratio of $[Ru(NH_3)_4(isn)I]^{2+}$:$[Ru(NH_3)_4(isn)H_2O]^{3+}$ is fixed by the readings of absorbance at 604 nm where only the iodo complex absorbs significantly.

Table I. Results of Spectrophotometric Measurements

species	λ_{max},[a] nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}
trans-$[Ru(NH_3)_4(isn)H_2O]^{2+}$	478	11.7
	256	4.8
	215 sh	
trans-$[Ru(NH_3)_4(isn)H_2O]^{3+}$ [b]	375 sh	
	262	7.2
trans-$[Ru(NH_3)_4(isn)I]^{2+}$ [c]	604	2.6
	335 sh	
	270 sh	
	225	52.0
trans-$[Ru(NH_3)_4(isn)Br]^{2+}$	428	
	335 sh	
	265	
I_3^-	350	26.4
	287	40.0

[a] Except for I_3^-, the values for which are taken from ref 8, all measurements were made in 0.10 M CF_3SO_3H; the temperature was 25 °C. [b] Produced from $[Ru(NH_3)_4(isn)H_2O]^{2+}$ by oxidizing with $S_2O_8^{2-}$. [c] Iodide salt used.

In most cases, the absorbance of the $[Ru(NH_3)_4(isn)H_2O]^{2+}$ added as catalyst at 604 nm was negligible, but, when necessary, a correction for its contribution was made. The correction was never more than 5% of the observed absorbance at 604 nm.

Results

Electrochemistry. The values of $E_{1/2}$ vs. NHE for the couples $[Ru(NH_3)_4(isn)H_2O]^{3+/2+}$, $[Ru(NH_3)_4(isn)I]^{2+/+}$, and $[Ru(NH_3)_4(isn)Br]^{2+/+}$ in 0.10 M sodium *p*-toluenesulfonate/0.10 M *p*-toluenesulfonic acid at 25 °C were measured as 0.427, 0.291, and 0.290 V, respectively (the latter were determined at scan rates high enough so that the results are not biased significantly by aquation of $[Ru(NH_3)_4(isn)X]^+$ ($X^- = I^-, Br^-$)). For $[Ru(NH_3)_5isn]^{3+/2+}$ a value of 0.375 V has been reported.[7]

Spectrophotometry. The absorption characteristics of the complexes we have studied are summarized in Table I. As expected, the properties of the strong band for $[Ru(NH_3)_4(isn)H_2O]^{2+}$ in the visible (λ_{max} 478 nm, ϵ 11.7×10^3 M^{-1} cm^{-1}) agree with those of the corresponding pentaammine complex (λ_{max} 478 nm, ϵ 11.9×10^3 M^{-1} cm^{-1}).[9]

The strong bands for $[Ru(NH_3)_4(isn)I]^{2+}$ and $[Ru(NH_3)_4(isn)Br]^{2+}$ (604 and 428 nm, respectively) can be assigned to halide-to-metal charge transfer. The bands are at lower energies, by 1770 and 1970 cm^{-1}, respectively, than those of the halopentaammine complexes.[10] These shifts are ascribable to the effect of the π-acid ligand in raising the oxidation potential of the Ru(III) center. The increase in oxidation potential as measured electrochemically is ca. 0.32 V, while the observed shifts, when the mean of the two recorded is taken, correspond to 0.23 V. Exact agreement between the spectrophotometric values, which involve final states not necessarily at equilibrium, and the equilibrium values is not expected.

Equilibrium Quotient K_1 for Reaction 1. Three determinations with initial concentrations of $[Ru(NH_3)_4(isn)I]^{2+}$ as 3.47×10^{-5}, 3.58×10^{-5}, and 4.56×10^{-5} M gave values for K_1 of 84.5, 87.7, and 85.1 M^{-1}, respectively. The mean is 85.8 ± 4.3 M^{-1} with error given for a 95% confidence interval.

Rate of Aquation of $[Ru(NH_3)_4(isn)I]^+$. The stock solution used for the stopped-flow experiment was 1×10^{-4} M in $[Ru(NH_3)_4(isn)I]^{2+}$. The separate reducing solution contained $[Ru(NH_3)_6]^{2+}$ at 6×10^{-4} M. The reaction is first order in the iodo complex. Three determinations made at 25 °C gave values of 0.97, 0.92, and 0.85 s^{-1} for the specific rate; the mean is 0.91 ± 0.17 s^{-1}. Cyclic voltammetry, by the method of

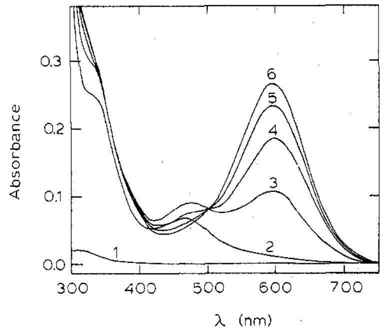

Figure 1. Spectrophotometric traces for reaction of [Ru(NH$_3$)$_4$(isn)H$_2$O] (at 1 × 10^{-4} M) and iodide (at 0.1 M) at 25 °C. Initial trace 1 is a solution of sodium iodide in deaerated 0.1 M trifluoromethanesulfonic acid. Trace 2 is recorded immediately after addition of the ruthenium complex. Subsequent traces 3–6 are recorded at 5-min intervals.

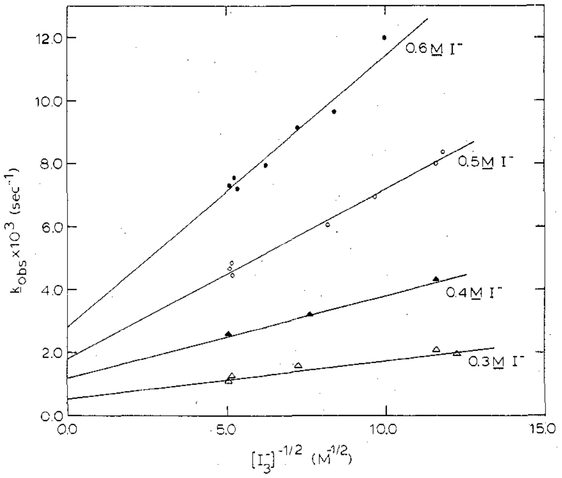

Figure 2. Plot of k_{obsd} vs. $[I_3^-]^{-1/2}$ for reaction 1 at constant iodide concentrations. The values for k_a (=slope/(1.42 × 10^{-2})) and intercepts for calculated lines are, respectively, (●) 3.15 × 10^{-3} M^{-2} s^{-1}, 2.77 × 10^{-3} s^{-1}; (○) 3.07 × 10^{-3} M^{-2} s^{-1}, 1.81 × 10^{-3} s^{-1}; (▲) 2.61 × 10^{-3} M^{-2} s^{-1}, 1.20 × 10^{-3} s^{-1}; (△) 2.50 × 10^{-3} M^{-2} s^{-1}, 5.14 × 10^{-4} s^{-1}.

Nicholson and Shain,[11] set a lower limit of 0.5 s^{-1} on the specific rate for aquation.

Kinetics of Reaction 1. Among the halides Cl$^-$, Br$^-$, and I$^-$, facile substitution into [Ru(NH$_3$)$_4$(isn)H$_2$O]$^{3+}$ is limited to the last; furthermore, the reaction of Ru(NH$_3$)$_5$H$_2$O^{3+} with I$^-$ takes place as a normal substitution.[12] These observations, and the fact that to gain control over the reaction it is necessary to add I$_3^-$ in a known amount, suggest catalysis of substitution in Ru(III) by Ru(II). This assessment is borne out by spectrophotometric observations (cf. Figure 1) on mixtures made up from [Ru(NH$_3$)$_4$(isn)H$_2$O]$^{3+}$ and I$^-$. Referring to this figure we can see that immediately after the Ru(III) aquo ion is added to the solution containing iodide ion absorption appears at 350 and 478 nm, wavelengths characteristic of I$_3^-$[8] and [Ru(NH$_3$)$_4$(isn)H$_2$O]$^{2+}$, respectively (the former as a shoulder on the strong $\pi^* \leftarrow \pi$ band of the ligand). Soon after, a band begins to develop at about 600 nm showing the growth of the product [Ru(NH$_3$)$_4$(isn)I]$^{2+}$. The isosbestic point relating [Ru(NH$_3$)$_4$(isn)H$_2$O]$^{2+}$ and [Ru(NH$_3$)$_4$(isn)I]$^{2+}$ arises, because, when [Ru(NH$_3$)$_4$(isn)H$_2$O]$^{3+}$ is converted to [Ru(NH$_3$)$_4$(isn)I]$^{2+}$, the equilibrium concentration of Ru(II) decreases (the iodoruthenium(III) complex is a weaker oxidizing agent than the aquoruthenium(III) complex) and as a result the following net change involving the catalyst occurs as substitution progresses:

$$2[Ru(NH_3)_4(isn)H_2O]^{2+} + I_3^- = 2[Ru(NH_3)(isn)I]^{2+} + I^-$$

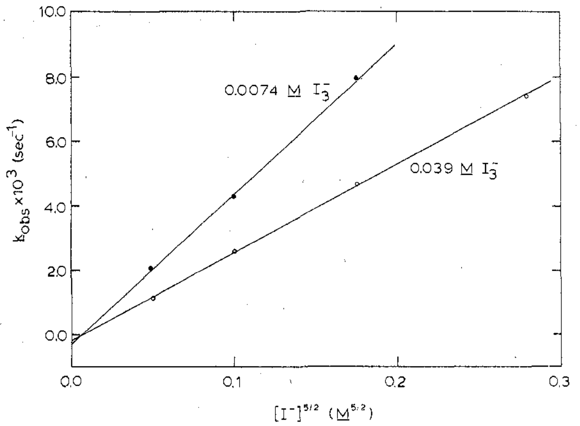

Figure 3. Plot of k_{obsd} vs. $[I^-]^{5/2}$ at constant triiodide concentrations. According to the rate law (eq 2), the slope of these lines is given by $k_a[I_3^-]^{-1/2} + k_b[I^-]^{-1/2}$; therefore perfectly straight lines are not expected. The slopes of the calculated lines shown have no direct relationships to k_a and k_b due to the $[I^-]^{-1/2}$ dependence of the second term. However, the apparent linearity of the points does indicate that the rate law is obeyed, since deviations from linearity will be most pronounced near the origin.

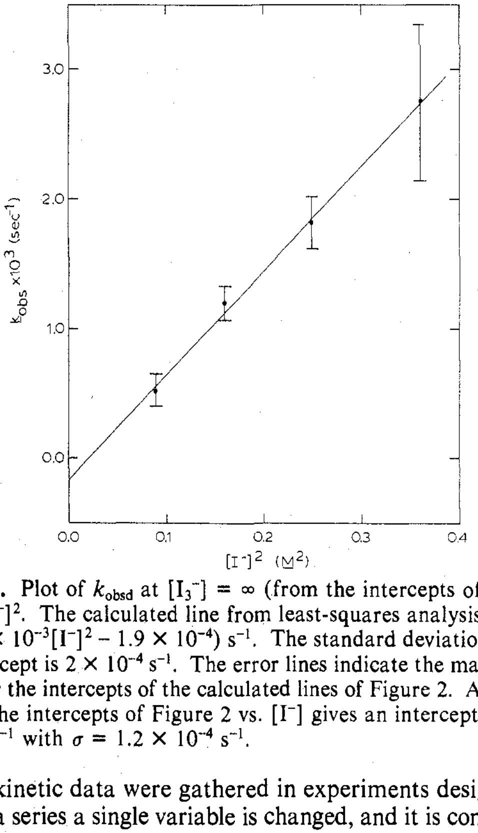

Figure 4. Plot of k_{obsd} at $[I_3^-] = \infty$ (from the intercepts of Figure 2) vs. $[I^-]^2$. The calculated line from least-squares analysis is k_{obsd} = (8.2 × 10^{-3}[I$^-$]^2 – 1.9 × 10^{-4}) s^{-1}. The standard deviation (σ) of the intercept is 2 × 10^{-4} s^{-1}. The error lines indicate the magnitude of 2σ for the intercepts of the calculated lines of Figure 2. A similar plot of the intercepts of Figure 2 vs. [I$^-$] gives an intercept at –1.5 × 10^{-3} s^{-1} with σ = 1.2 × 10^{-4} s^{-1}.

The kinetic data were gathered in experiments designed so that in a series a single variable is changed, and it is convenient to present them in graphical form. Each experiment was done under pseudo-first-order conditions with [Ru(NH$_3$)$_4$(isn)H$_2$O]$^{3+}$ as the limiting agent, and in each experiment a value of k_{obsd}, defined as

$$-d[Ru^{III}H_2O]/dt = k_{obsd}[Ru^{III}H_2O]$$

was determined.

In Figure 2, k_{obsd} is shown as a function of $1/[I_3^-]^{1/2}$, and in Figure 3, some of the same data are used to construct series at constant [I$_3^-$] but with [I$^-$] as the variable. The plots show that an important term in the rate law has the form $k_a[Ru^{III}H_2O][I^-]^{5/2}/[I_3^-]^{1/2}$. From the slopes of the lines in Figure 2, k_a is evaluated as (2.83 ± 0.52) × 10^{-3} M^{-2} s^{-1}. But the data of Figure 2 show clearly that a second term contributes. Of the various simple alternatives for the second term, we find the one represented in the complete rate law (2) best fits the data. According to this rate law, the intercepts on

$$k_{\text{obsd}} = k_{\text{a}} \frac{[\text{Ru}^{\text{III}}\text{H}_2\text{O}][\text{I}^-]^{5/2}}{[\text{I}_3^-]^{1/2}} + k_{\text{b}}[\text{I}^-]^2 \qquad (2)$$

the ordinate in Figure 2 should vary directly with $[\text{I}^-]^2$. Unfortunately, the region of high $[\text{I}_3^-]$ was not accessible owing to precipitation of ruthenium salts above $[\text{I}_3^-] = 4 \times 10^{-2}$ M, so that a long extrapolation was necessary. However, as shown in Figure 4, the intercepts from Figure 2 do seem to vary with $[\text{I}^-]^2$ and the constant k_{b} as determined from the plot in Figure 4 is $(8.2 \pm 2.4) \times 10^{-3}$ M^{-2} s^{-1}. For reasons which are obscure, the data at the highest concentrations of I^-, 0.60 M, were less reproducible than those under other conditions; hence the wide error limits for the data point representing the high $[\text{I}^-]$ experiments.

It should be noted that eq 2 calls for curvature in the plot of Figure 3 as $[\text{I}^-]^{5/2}$ becomes small, but the data shown stop short of the concentration region in which the plot would become sensitive to the existence of two terms of slightly differing order in $[\text{I}^-]$.

The possibility that the k_{b} term is spurious and that it is an artifact of the reaction not proceeding to completion have been considered (note that K_1 is 86 ± 4 M^{-1}). The simplest form for a path which is the reverse of the k_{a} term is $k_{-\text{a}} \cdot [\text{I}^-]^{3/2}[\text{Ru}^{\text{III}}]/[\text{I}_3^-]^{1/2}$ and the coefficient multiplying $([\text{Ru}^{\text{III}}\text{H}_2\text{O}]_t - [\text{Ru}^{\text{III}}\text{H}_2\text{O}]_\infty)$ in the rate law for approach to equilibrium will then be $k_{\text{a}}[\text{I}^-]^{5/2}/[\text{I}_3^-]^{1/2} + k_{-\text{a}}[\text{I}^-]^{3/2}/[\text{I}_3^-]^{1/2}$. The important point is that since reaction 1 does not involve I_3^- as a reactant or product, the reverse reaction must show the same dependence on $[\text{I}_3^-]$ that the forward reaction does, and thus the nonzero intercepts shown in Figure 2 cannot arise from the reverse reaction. Any effect that the k_{-a} term has will bias the plots in Figure 3, but not until $[\text{I}^-]$ is low. It should be noted that in most of the experiments, at equilibrium, more than 95% of the $\text{Ru}^{\text{III}}\text{H}_2\text{O}$ is converted to the iodo complex.

Discussion

The k_{a} term of the rate law is accounted for by the mechanism

$$2\text{Ru}^{\text{III}}\text{H}_2\text{O} + 3\text{I}^- = 2\text{Ru}^{\text{II}}\text{H}_2\text{O} + \text{I}_3^- \qquad K_3 \qquad (3)$$

$$\text{Ru}^{\text{II}}\text{H}_2\text{O} + \text{I}^- \rightarrow \text{Ru}^{\text{II}}\text{I} + \text{H}_2\text{O} \qquad k_4 \qquad (4)$$

$$2\text{Ru}^{\text{II}}\text{I} + \text{I}_3^- = 2\text{Ru}^{\text{III}}\text{I} + 3\text{I}^- \qquad K_5 \qquad (5)$$

With reaction 3 maintained as an equilibrium and reaction 5 as rapid compared to 4, k_{a} becomes $K_3^{1/2}k_4$. The value of K_3 can be calculated ($K_3 = 2.0 \times 10^{-4}$) from the electrochemical data and the value of $E°$ for the I_3^-/I^- couple[13] and thus k_4 is fixed by the value of k_{a} which was measured ($k_{\text{a}} = (2.83 \pm 0.52) \times 10^{-3}$ M^{-2} s^{-1}). The rate constant k_4 so determined is 0.20 ± 0.04 M^{-1} s^{-1}. This value seems reasonable when compared to other data. The specific rate for substitution into *trans*-$[\text{Ru(NH}_3)_4(\text{isn})\text{H}_2\text{O}]^{2+}$ by the neutral ligand isonicotinamide is observed[14] to be 5×10^{-3} M^{-1} s^{-1}; the negatively charged ligand I^- is expected to react more rapidly than isonicotinamide.

A further check on the mechanism is made possible by the measurement of the rate of aquation of $[\text{Ru(NH}_3)_4(\text{isn})\text{I}]^+$, governed by the specific rate k_{-4}. The overall equilibrium quotient K_1 for reaction 1 has been measured as 86 ± 4 M^{-1}. The net change represented by eq 1 is given by taking reactions 3, 4, and 5 in the stoichiometric ratios $^1/_2{:}1{:}^1/_2$, and thus $K_1 = K_3^{1/2}K_4K_5^{1/2}$. The quotient K_3 has already been calculated. K_5 is given by the electrochemical data on the $[\text{Ru(NH}_3)_4(\text{isn})\text{I}]^{2+/+}$ couple together with $E°$ for the I_3^-/I^- couple, and K_4 is given by the ratio of k_4/k_{-4} ($=0.22 \pm 0.06$). When these quantities are taken together, K_1 is calculated as 44 M^{-1}. The agreement with the value measured directly is satisfactory considering the error limits on the measurements and the absolute errors attending the calculation of K_3 and K_5 from electrochemical data.

The origin of the k_{b} term in the rate law is much more obscure than that of the k_{a} term. It suggests the interesting possibility of substitution coupled to electron transfer. In an encounter between $[\text{Ru(NH}_3)_4(\text{isn})\text{H}_2\text{O}]^{3+}$ and I^-, substitution on ruthenium would be much facilitated were Ru(III) converted to Ru(II), with, of course, concomitant formation of I. The loss to substitution reactivity of converting I^- to I would amount to only a factor of about 10–100,[20] while the increase in lability of the ruthenium center on being converted to the 2+ state might be as much as a factor of 10^4 or 10^5.[21] The redox path for substitution of course requires the energy barrier for converting $\text{Ru}^{\text{III}}\text{H}_2\text{O} + \text{I}^-$ to $\text{Ru}^{\text{II}}\text{H}_2\text{O} + \text{I}$ to be surmounted, and this can account for the role of the second iodide in the activated complex. The older literature is replete[15–17] with observations bearing on the stabilization of atomic halogen by halide ion, and the conclusions reached on the basis of the earlier kinetic evidence have been borne out and amplified by modern pulse radiation techniques.[18] The major role of the second iodide then is to lower the energy barrier for electron transfer, but it can be construed as contributing also by facilitating the substitution reaction because of the negative charge.

In the absence of a special mechanism such as has been suggested, the reaction of I^- with $\text{Ru}^{\text{III}}\text{H}_2\text{O}$ would be expected to be simply first order in each reagent and governed by a specific rate much like that which we observed for Br^- substituting on $[\text{Ru(NH}_3)_4(\text{isn})\text{H}_2\text{O}]^{3+}$ or as 2×10^{-5} M^{-1} s^{-1}. In 0.10 M iodide, the lowest concentration dealt with in our studies, the k_{b} path is 40 times more rapid than this.

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Registry No. I^-, 20461-54-5; *trans*-$[\text{Ru(NH}_3)_4(\text{isn})\text{H}_2\text{O}]^{3+}$, 63323-64-8; $[\text{Ru(NH}_3)_4(\text{isn})\text{H}_2\text{O}](\text{PF}_6)_2$, 68853-52-1; *trans*-$[\text{Ru(NH}_3)_4(\text{isn})\text{I}]\text{I}_2$, 63251-17-2; *trans*-$[\text{Ru(NH}_3)_4(\text{isn})\text{Br}]^{2+}$, 68833-17-0; Br^-, 24959-67-9; *trans*-$[\text{Ru(NH}_3)_4(\text{isn})\text{I}]^{2+}$, 68833-18-1; *trans*-$[\text{Ru(NH}_3)_4(\text{isn})\text{H}_2\text{O}]^{2+}$, 60208-50-6; $[\text{Ru(NH}_3)_4(\text{isn})\text{I}]^+$, 68853-53-2; I_3^-, 14900-04-0; *trans*-$[\text{Ru(NH}_3)_4(\text{isn})\text{SO}_4]\text{Cl}$, 60209-67-8.

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(21) For example, compare the rates for chloride anation at 25 °C of $[\text{Ru(NH}_3)_5\text{H}_2\text{O}]^{3+}$ (about 2×10^{-5} M^{-1} s^{-1}, estimated from the data of ref 12) and $[\text{Ru(NH}_3)_5\text{H}_2\text{O}]^{2+}$ (7 M^{-1} s^{-1} [20]).