as for sample compounds. These investigations were supported in part by National Research Council of Italy (CNR) and by the U. S. National Science Foundation, through Grants GP 27264 and GP 27984X to the University of Southern California.

Registry No. $Co(PnAO)(N_3)_2$, 41371-80-6; $[Co(PnAO)(H_2O)N_3](ClO_4)$, 53011-16-8; $Co(PnAO)(NO_2)_2$, 41371-79-3; $[Co(PnAO)(H_2O)(NO_2)](ClO_4)$, 41371-82-8; $[Co(PnAO)(H_2O)_2](ClO_4)$, 253011-18-0.

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Temperature-Jump Study of the Rapid Complexing of Iodate with Aquometal Ions

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Received July 24, 1974 AIC40505C

The reactions of pentaammineaquochromium(III) and *cis*-diaquobis(ethylenediamine)cobalt(III) with iodate have been studied at 25°, $I = 1.0\ M$ ($NaClO_4$), by the temperature-jump technique. Equilibrium formation constants for the iodato complexes have been determined spectrophotometrically and are 11.0 ± 2.2 and 2.3 ± 0.2 l. mol^{-1}, respectively. No evidence was obtained for the formation of the bis-iodato complex with *cis*-$Co(en)_2(H_2O)_2^{3+}$. The rapid rates observed suggest that substitution at the iodate is occurring rather than displacement of H_2O on the metal. Reciprocal relaxation times, τ^{-1}, give a first-order dependence on $[H^+]$, which suggests a mechanism for complex formation involving HIO_3 and not IO_3^-. Values for outer- to inner-sphere interchange rate constants k_2, involving HIO_3 and the aquo complexes, were calculated using estimates for the outer-sphere association constants. The rate constants obtained, *ca.* 5×10^4 sec^{-1}, are similar to but greater than those for water exchange with HIO_3. Possible mechanisms for substitution at iodine(V) are considered.

Oxy anions sometimes complex rapidly with substitution-inert complexes having aquo ligands. Thus the reactions of nitrite[1] and sulfite[2] with hexaaquochromium(III) fall within this category. All oxy anions participating in such processes undergo rapid oxygen exchange with solvent water,[3] (1). A similar exchange process can also occur with a water

$$H_2O^* + OXO_x^{n-} \rightleftharpoons H_2O + O^*XO_x^{n-} \tag{1}$$

molecule already coordinated to a metal, (2). Studies on the

$$(H_2O)_5MO^*H_2^{3+} + OXO_x^{n-} \rightleftharpoons (H_2O)_5MO^*XO_x^{(3-n)+} + H_2O \tag{2}$$

rapid complexing of iodate to substitution-inert chromium(III) and cobalt(III) complexes are reported in this paper. Oxygen exchange at iodate is known to be rapid,[4,5] but no other information is available and it is not clear whether an associative or dissociative process is involved. The investigations reported therefore provide further information on substitution at iodine(V).

The reactions of iodate with $Cr(NH_3)_5OH_2^{3+}$ and *cis*-$Co(en)_2(OH_2)_2^{3+}$ have been studied in full using the temperature-jump technique. With $Co(NH_3)_5OH_2^{3+}$ complexing was not sufficiently extensive for precise measurements, and with $Cr(OH_2)_6^{3+}$ formation of a diiodato complex has been reported,[6] with possible complications because the data obtained suggest that the formation constant for addition of the second iodate is greater than the first.

Results

Spectrophotometric Determination of Formation Constants. On addition of 0.1 M iodate to $Cr(NH_3)_5OH_2^{3+}$, $[HClO_4] = 0.1\ M$, an instantaneous orange to red color change, indicative of complex formation, was observed. Scan spectra, 300–600 nm, of solutions with $[Cr(NH_3)_5OH_2^{3+}]$ constant, $[H^+] = 0.1\ M$, and $I = 1.0\ M$ ($NaClO_4$) but with varying concentrations of iodate 0.04–0.25 M gave well-defined isosbestic points at 315 (ϵ 5.5), 356 (ϵ 26.8), 423 (ϵ 11.8), and 486 nm (ϵ 30.8 l. mol^{-1} cm^{-1}). At wavelengths <300 nm the charge-transfer spectrum of iodate predominates. The formation constant K(Cr) for (3) is defined in (4), where $[IO_3^-]_f$

$$Cr(NH_3)_5OH_2^{3+} + IO_3^- \rightleftharpoons Cr(NH_3)_5OIO_2^{2+} + H_2O \tag{3}$$

$$K(\mathrm{Cr}) = \frac{[Cr(NH_3)_5OIO_2^{2+}]}{[Cr(NH_3)_5OH_2^{3+}][IO_3^-]_f} \tag{4}$$

represents the concentration of free iodate, which was calculated knowing the protonation constant for iodate (a value 1.94 l. mol^{-1} was used; see below). The free hydrogen ion

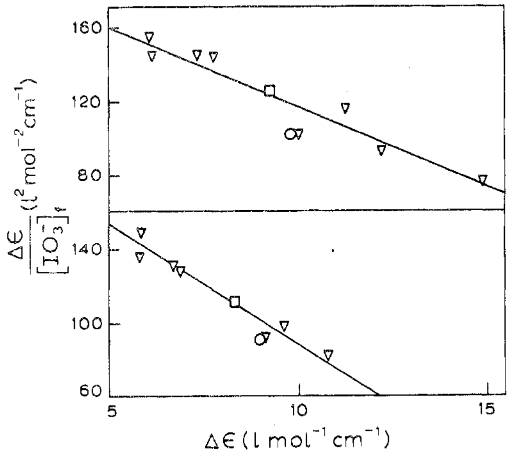


Figure 1. Equilibrium constant determinations for the formation of iodatopentaamminechromium(III) at 25°, $I = 1.0$ M ($NaClO_4$), λ 380 nm (upper scale) and 250 nm (lower scale), and $[H^+]_T = 0.002$ M (○), 0.01 M (▽), 0.2 M (□).

concentration, $[H^+]_f$, was determined from pH measurements. For the range of conditions investigated it could be assumed that $[IO_3^-]_f \gg [Cr(NH_3)_5OIO_2^{2+}]$. Absorption coefficients for equilibrated solutions, ϵ_{obsd}, were found to be independent of $[H^+]_f$ at constant $[IO_3^-]_f$, and (5) applies, where C_M is the

$$\epsilon_{obsd} = \frac{\epsilon_M[M]}{C_M} + \frac{\epsilon_{ML}[ML]}{C_M} \tag{5}$$

total concentration of complex, [M] and [ML] are the concentrations of aquo and iodato complex, and ϵ_M and ϵ_{ML} are their respective absorption coefficients. From (4) and (5), eq 6 is obtained. Plots of the left-hand side of (6) against (ϵ_{obsd}

$$\frac{\epsilon_{obsd} - \epsilon_M}{[IO_3^-]_f} = K(\epsilon_{ML} - \epsilon_M) - K(\epsilon_{obsd} - \epsilon_M) \tag{6}$$

$- \epsilon_M$) are linear, Figure 1. An unweighted least-squares treatment of data at 380 and 520 nm gave a mean K(Cr) = 11.0 ± 2.2 l. mol^{-1}.

On addition of iodate to *cis*-$Co(en)_2(OH_2)_2^{3+}$ a rapid red to purple color change was observed. Scan spectra at 300–600 nm for solutions with varying iodate revealed isosbestic points at 350 (ϵ 69), 431 (ϵ 29) and 491 nm (ϵ 79) consistent with the presence of only two species, one of which is the diaquo complex. Formation constants (see below) are consistent with 1:1 complex formation, (7), and no evidence was obtained for

$$Co(en)_2(OH_2)_2^{3+} + IO_3^- \rightleftharpoons Co(en)_2(OH_2)(OIO_2)^{2+} + H_2O \tag{7}$$

complexing with a second iodate. Plots of absorbance (OD) changes, $\Delta OD/[IO_3^-]_f$ against ΔOD, a relationship based on eq 6, where ΔOD is $OD_{obsd} - OD_M$, are shown in Figure 2. A least-squares treatment of data at 390 and 530 nm gave K(Co) = 2.3 ± 0.2 l. mol^{-1}.

Kinetic Studies. Although only one measureable absorbance change was observed in the temperature-jump studies, a fast (unresolvable) initial change was apparent in both cases (λ 520 and 546 nm for $Cr(NH_3)_5H_2O^{3+}$ and 530 nm for *cis*-$Co(en)_2(H_2O)_2^{3+}$). Since both complexes contain aquo ligands with $pK_a > 5$, this effect is not readily explained by deprotonation to give hydroxo forms over the pH range covered.[7,8] The initial fast absorbance change (but not the subsequent relaxation process) was also observed for runs under identical conditions with substitution-inert bromate and perchlorate ions in place of iodate and cannot therefore be ascribed to a chemical process involving that species. Ion-pairing effects are not expected to be manifest in the visible region of the spectrum, and the fast initial absorbance change is best ascribed to the temperature dependence of ϵ values of complexes involved. Similar effects have previously been noted for a number of complexes of first-row transition metals.[9] For temperature jumps of 5.9° initial changes of *ca.* 1.5% (Cr) and *ca.* 0.6% (Co) in ϵ values were observed. Changes of this magnitude were also observed by conventional spectrophotometry.

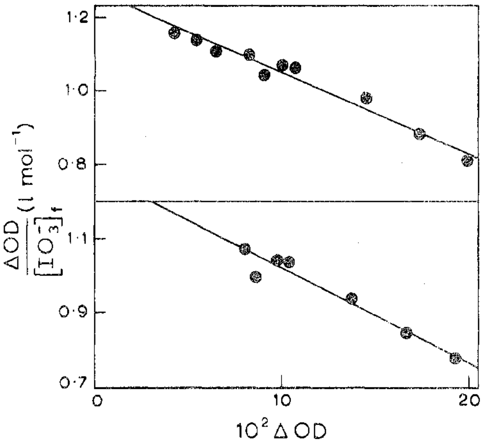


Figure 2. Equilibrium constant determinations for the formation of *cis*-iodatoaquobis(ethylenediamine)cobalt(III) at 25°, $I = 1.0$ M ($NaClO_4$), λ 390 nm (upper scale) and 530 nm (lower scale), and $[H^+]_f$ = 0.0016–0.16 M.

Table I. Reciprocal Relaxation Times (λ 520 or 546 nm As Indicated) for the Reaction of Iodate with Aquopentaamminechromium(III) at 25° and $I = 1.0$ M ($NaClO_4$)

$[Complex]_T$,[a] M	$[IO_3^-]_T$,[b] M	$[H^+]_f$,[c] M	τ^{-1},[d] sec^{-1}
0.04	0.03	0.006	38.5 (4)[e]
0.04	0.03	0.0083	54.8 (4)[e]
0.04	0.03	0.0256	145 (6)[e]
0.04	0.03	0.0515	298 (4)[e]
0.04	0.03	0.0791	446 (4)[e]
0.04	0.03	0.109	590 (4)[e]
0.02	0.01	0.02	107 (2)
0.02	0.03	0.02	103 (3)
0.02	0.05	0.02	108 (4)
0.02	0.07	0.02	119 (3)
0.02	0.01	0.0189	102 (2)
0.02	0.03	0.0196	100 (3)
0.02	0.05	0.0185	99 (4)
0.02	0.07	0.0165	99 (3)
0.02	0.01	0.10	586 (3)
0.02	0.03	0.10	620 (3)
0.02	0.05	0.10	556 (4)
0.02	0.07	0.10	600 (4)
0.02	0.01	0.0948	526 (3)
0.02	0.03	0.0894	535 (3)
0.02	0.05	0.0881	491 (4)
0.02	0.07	0.0816	470 (4)

[a] $[Complex]_T$ represents the total concentration of complex in the reactant solutions. [b] $[IO_3^-]_T$ represents the total iodate concentration. [c] $[H^+]_f$ represents the free hydrogen ion concentration as obtained from pH measurements. [d] Numbers in parentheses denote the number of experiments averaged. [e] λ 546 nm.

Reciprocal relaxation times, Tables I and II, give no discernible dependence on the concentration of reactants at constant $[H^+]_f$, which is somewhat surprising for $Cr(NH_3)_5OH_2^{3+}$ at least in view of the formation constant of 11.0 l. mol^{-1}. In both cases however the τ^{-1} values are linearly dependent on $[H^+]_f$, Figures 3 and 4 and a least-squares analysis reveal no evidence for an $[H^+]_f$-independent path. Thus eq 8 applies, where in the case of $Cr(NH_3)_5OH_2^{3+}$, a

$$\tau^{-1} = a[H^+]_f \tag{8}$$

= (5.82 ± 0.11) × 10^3 l. mol^{-1} sec^{-1}, and for *cis*-$Co(en)_2(OH_2)_2^{3+}$, a = (2.32 ± 0.04) × 10^4 l. mol^{-1} sec^{-1}. Contributions from $[H^+]$-independent paths, −7 ± 8 and −2.4 ± 13 sec^{-1}, respectively, are of no significance.

Reaction Sequence and Interpretation. Possible reaction steps

Table II. Reciprocal Relaxation Times (λ 530 nm) for the Reaction of Iodate with *cis*-Diaquobis(ethylenediamine)cobalt(III) at 25° and $I = 1.0\ M$ ($NaClO_4$)[a]

$[IO_3^-]_T$,[b] M	$[H^+]_f$,[c] M	τ^{-1},[d] sec^{-1}	$[IO_3^-]_T$,[b] M	$[H^+]_f$,[c] M	τ^{-1},[d] sec^{-1}
0.03	0.010	240 (3)	0.10	0.0115	278 (6)[f]
0.03	0.012	283 (3)	0.10	0.0178	440 (3)
0.03	0.0292	690 (4)	0.10	0.0251	599 (3)
0.03	0.030	628 (4)	0.10	0.030	700 (3)
0.06	0.010	217 (4)	0.10	0.0434	943 (4)
0.06	0.0108	227 (4)	0.10	0.0597	1370 (4)
0.06	0.0275	571 (3)	0.10	0.0819	1960 (3)
0.06	0.030	710 (3)	0.15	0.00836	226 (2)
0.10	0.0055	106 (5)	0.15	0.010	285 (2)
0.10	0.0093	227 (3)	0.15	0.0225	513 (4)
0.10	0.010	247 (3)	0.15	0.030	683 (4)
0.10	0.0104	280 (7)[e]			

[a] The concentration of the complex in all runs was $9.4 \times 10^{-3}\ M$ except where stated. [b] $[IO_3^-]_T$ represents total iodate concentration. [c] $[H^+]_f$ represents the free hydrogen ion concentration as obtained by pH measurements. [d] Numbers in parentheses denote number of experiments averaged. [e] Concentration of complex $3.0 \times 10^{-2}\ M$. [f] Concentration of complex $4.0 \times 10^{-2}\ M$.

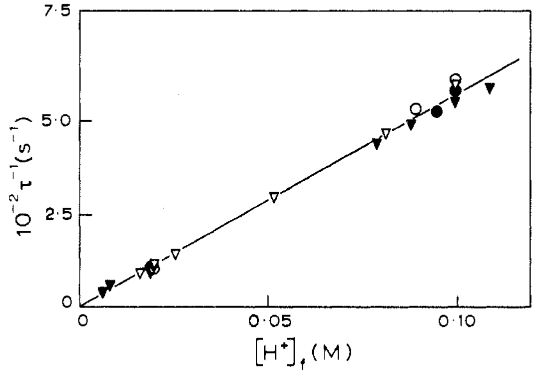


Figure 3. Dependence of reciprocal relaxation times on free hydrogen ion concentration for the reaction of aquopentaamminechromium(III) with iodate at 25°, $I = 1.0\ M$ ($NaClO_4$), and $[IO_3^-]_T$ + $[Cr(III)]_T = 0.03\ M$ (●), $0.05\ M$ (○), $0.07\ M$ (▼), $0.09\ M$ (▽).

for the complexing of iodate with $Cr(NH_3)_5OH_2^{3+}$ and *cis*-$Co(en)_2(OH_2)_2^{3+}$ ($\equiv M^{3+}$) are as shown in (9) where K_{HL},

$$\begin{tikzcd}
M^{3+} + H^+ + IO_3^- \arrow[r, shift left, "K_O"] \arrow[d, shift left, "K_{HL}"] & M,IO_3^{2+} + H^+ \arrow[l, shift left] \arrow[r, shift left, "k_1"] \arrow[d, shift left, "K_{HO}"] & MOIO_2^{2+} + H_2O + H^+ \arrow[l, shift left, "k_{-1}"] \arrow[d, shift left, "K_{HI}"] \\
M^{3+} + HIO_3 \arrow[u, shift left] \arrow[r, shift left, "K_O'"] & M,HIO_3^{3+} \arrow[u, shift left] \arrow[l, shift left] \arrow[r, shift left, "k_2"] & MOIO_2H^{3+} + H_2O \arrow[u, shift left] \arrow[l, shift left, "k_{-2}"]
\end{tikzcd} \qquad (9)$$

K_{HO}, and K_{HI} are protonation constants, K_O and K_O' are outer-sphere formation constants for M,IO_3^{2+} and M,HIO_3^{3+}, and K_1 ($=k_1/k_{-1}$) and K_2 ($=k_2/k_{-2}$) are constants for outer- to inner-sphere interconversions.

The concentration $[H^+]_f$ can be shown to be effectively constant during the relaxation process, for which (10) can be derived.

$$\tau^{-1} = \frac{(k_1K_O + k_2K_O'K_{HL}[H^+]_f)([M^{3+}]_f + [IO_3^-]_f + [HIO_3]_f)}{1 + K_{HL}[H^+]_f + (K_O + K_O'K_{HL}[H^+]_f)([M^{3+}]_f + [IO_3^-]_f + [HIO_3]_f)} + \frac{k_{-1} + k_{-2}K_{HI}[H^+]_f}{1 + K_{HI}[H^+]_f} \qquad (10)$$

From spectrophotometric studies no evidence was obtained for a protonated iodato complex even though, from (8), only the pathway involving k_2 and k_{-2} is kinetically important. Furthermore since the concentration of the outer-sphere complex involving HIO_3 is very much less than that involving IO_3^-, over the $[H^+]$ range investigated, eq 10 may be simplified to (11). The equilibrium constant K can be expressed as in (12). To obtain an expression for the overall

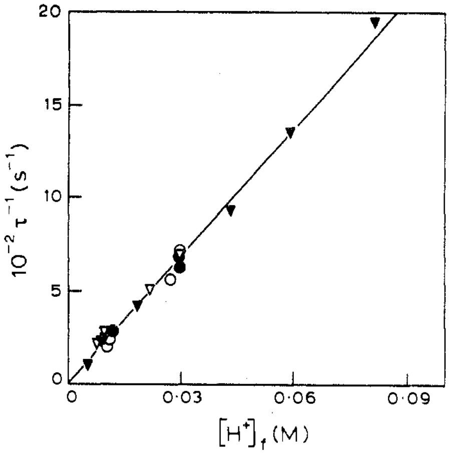


Figure 4. Dependence of reciprocal relaxation times on free hydrogen ion concentration for the reaction of *cis*-diaquobis(ethylenediamine)cobalt(III) and iodate at 25°, $I = 1.0\ M$ ($NaClO_4$), $[Co(III)]_T = 9.4 \times 10^{-3}\ M$, and $[IO_3^-]_T = 0.03\ M$ (●), $0.06\ M$ (○), $0.10\ M$ (▼), $0.15\ M$ (▽).

$$\tau^{-1} = \frac{k_2K_O'K_{HL}[H^+]_f([M^{3+}]_f + [IO_3^-]_f + [HIO_3]_f)}{1 + K_{HL}[H^+]_f + K_O([M^{3+}]_f + [IO_3^-]_f + [HIO_3]_f)} + k_{-2}K_{HI}[H^+]_f \qquad (11)$$

$$K = \frac{[M,IO_3^{2+}] + [MOIO_2^{2+}]}{[M^{3+}]_f[IO_3^-]_f} = K_O + K_2K_{HL}K_O'/K_{HI} \qquad (12)$$

formation rate constant, $k_2K_{HL}K_O'$ from (12) is substituted into (11) to give

$$\tau^{-1} = \frac{k_2K_{HL}K_O'}{Q(K - K_O)}[H^+] \qquad (13)$$

where

$$Q = \frac{1 + K_{HL}[H^+]_f + K_O([M^{3+}]_f + [IO_3^-]_f + [HIO_3]_f)}{1 + K_{HL}[H^+]_f + K([M^{3+}]_f + [IO_3^-]_f + [HIO_3]_f)} \qquad (14)$$

No dependence of τ^{-1} on reactant concentrations was observed, Figures 3 and 4, and Q must remain constant over the range of concentrations investigated. Values of a in (8) therefore correspond to $k_2K_{HL}K_O'/Q(K - K_O)$. An extrapolation of data by Ramette gives K_{HL} = 1.94 l. mol^{-1} at $I = 1.0\ M$ ($NaClO_4$),[10] and values of K for (3) and (7) are as determined above. Estimates of outer-sphere formation constants K_O' and K_O are now considered.

At low ionic strengths ($I \leq 0.1\ M$) ion-pair constants K_O and K_O' can be estimated using the Eigen–Fuoss treatment,[11,12] with activity coefficients as suggested by Davies.[13] Several assumptions are made however, the most important being that activity coefficients for all ions of like charge are the same, an approximation which is no longer valid at higher ionic strengths. At ionic strengths $\geq 1.0\ M$ ion-pairing constants would be expected to be very approximate, but in some cases agreement between experiment and theory is reasonable.[14] Values of K_O and K_O' obtained in this way, $I = 1.0\ M$, are *ca.* 3 and 0.3 l mol^{-1}, respectively. Diebler[15] has used a value K_O of 1 l. mol^{-1} in the reaction of titanium(III) with thiocyanate based on experimentally determined values for other 3+, 1− charged species. A value of 0.15 l. mol^{-1} has been used by Wilkins[16] for K_O' for the reaction of nickel(II) with neutral ligands. For *cis*-$Co(en)_2(OH_2)_2^{3+}$ at least, K_O cannot be >2.3 l. mol^{-1} since this is the value of $K(Co) = K_O + K_2K_{HL}K_O'/K_{HI}$. For $Cr(NH_3)_5OH_2^{3+}$ an outer-sphere as-

Table III. Composite Rate Constants, k_2K_{HL}, for Reactions of Aquometal Ions with Iodate in Acid Solution at 1.0 *M* Ionic Strength ($NaClO_4$)

Nucleophile	10^4a, l. mol^{-1} sec^{-1}	K, l. mol^{-1}	K_O, l. mol^{-1}	Q_{av}	$10^{-4}k_2K_{HL}$,[a] l. mol^{-1} sec^{-1}
$[Cr(NH_3)_5H_2O]^{3+}$	0.58	11	1	0.71	13.7
			3	0.77	12.0
			5	0.82	9.5
			8	0.91	5.3
$[Co(en)_2(H_2O)_2]^{3+}$	2.32	2.3	1	0.91	9.3

[a] Evaluated with $K_O' = 0.3$ l. mol^{-1}.

sociation constant $K_O \geq 5$ l. mol^{-1} would give a better fit to the data, bearing in mind the apparent lack of dependence of τ^{-1} on reactant concentrations. Values of 1, 3, 5, and 8 l. mol^{-1} for K_O in the case of $Cr(NH_3)_5OH_2^{3+}$ and 1 l. mol^{-1} for *cis*-$Co(en)_2(OH_2)_2^{3+}$ cover all these possibilities, Table III.

Finally with the various measured and estimated equilibrium constants it is possible to comment further on the magnitude of Q, (14), which should remain approximately constant for the range of reactant concentrations investigated. This is certainly true for $Cr(NH_3)_5OH_2^{3+}$ if $K_O \geq 5$ l. mol^{-1}, when values of Q agree to within ±10%. If $K_O = 1$ l. mol^{-1}, the variation in Q is >±15% which is clearly less satisfactory. For *cis*-$Co(en)_2(OH_2)_2^{3+}$ a value of 5 l. mol^{-1} for K_O is not consistent with the relatively small overall stability constant $K(Co) = 2.3$ l. mol^{-1}. However, $K_O = 1$ l. mol^{-1} gives a reasonable fit in this case with Q varying by less than ±10%.

Discussion

The reactions of $Cr(NH_3)_5OH_2^{3+}$ and *cis*-$Co(en)_2(OH_2)_2^{3+}$ with iodate occur exclusively by a pathway first order in $[H^+]_f$, (8), over the range $[H^+]_f = 0.005$–0.11 *M*. Rates observed for the equilibration processes (3) and (7) are independent of concentrations of complex and iodate used. Moreover they are much faster than those expected for substitution at the metal center,[17] and values of k_2K_{HL} are similar to those observed for the rate of oxygen exchange between iodate and solvent water,[4] which exhibits a first-order dependence on $[H^+]$, $[H^+]_f < 0.1$ *M*. It is concluded that formation of iodato complexes in the two systems studied occurs by substitution at the iodine(V) center.

The kinetics described provide information on the magnitude of a, eq 8, which corresponds to $k_2K_{HL}K_O'/Q(K - K_O)$, (13). Of the quantities in this expression, K has been measured for both complexes. Estimates of the outer-sphere formation constants K_O and K_O' have already been considered, as well as the magnitude of Q, eq 14. Hence values of k_2K_{HL} have been deduced, Table III. For reasons already given K_O values of 5 l. mol^{-1} for $Cr(NH_3)_5OH_2^{3+}$ and 1 l. mol^{-1} for *cis*-$Co(en)_2(OH_2)_2^{3+}$ are preferred and these give k_2K_{HL} values of 9.5×10^4 and 9.3×10^4 l. mol^{-1} sec^{-1}, respectively. Using the estimated value of $K_{HL} = 1.94$ l. mol^{-1}, both $k_2(25°)$ values may be considered to be 4.8×10^4 sec^{-1} at $I = 1.0$ *M* ($NaClO_4$). It should however be borne in mind that if significantly higher values of K_O are used, k_2 is decreased.

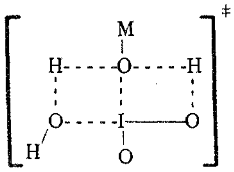
The possibility that the reaction $Cr(NH_3)_5OH^{2+} + H_2IO_3^+$ is effective has been considered since this gives an $[H^+]$ dependence of the same form as the above. If it is assumed that the constant for protonation of HIO_3 to $H_2IO_3^+$ is <1 l. mol^{-1} and the pK_a for $Cr(NH_3)_5H_2O^{3+}$ is *ca.* 5.2,[7] then the rate constant for such a path is in excess of the diffusion-controlled limit for 2+, 1+ reactants. Thus it is unlikely that this pathway makes a major contribution to the reaction observed.

A comparison of k_2 values obtained in the present study with the related value for oxygen exchange is highly relevant to any discussion of the mechanism of substitution at iodine(V). A precise and straightforward comparison is not possible since neither of the two studies of the oxygen exchange between iodate and solvent water were carried out at the same ionic strength or over the same range of hydrogen ion concentrations. The study by Anbar and Guttmann[4] was at pH >4.5 where the oxygen exchange gives a first-order dependence on $[H^+]$. In their nmr investigation Dwek, *et al.*,[5] accepted the first-order dependence obtained by Anbar and Guttmann and, for a somewhat higher range of hydrogen ion concentrations, demonstrated the existence of an $[H^+]^2$ dependence. Although this term makes some contribution even with $[H^+] < 0.1$ *M*, no $[H^+]^2$-dependent pathway was detected in the present studies. The value of k_2K_{HL} obtained by Anbar and Guttmann, 3.24×10^4 l. mol^{-1} sec^{-1}, cannot be directly compared with our k_2K_{HL} values since the ionic strength was not held constant and (we estimate) varies over a range 0.002–0.050 *M*. At such ionic strengths a value of K_{HL} of 5.0 ± 0.5 l. mol^{-1} has been inferred from the data of Pethybridge and Prue,[18] yielding a value of $k_2 = 6.5 \times 10^3$ sec^{-1}. This is a factor of *ca.* 7 less than those for complexing of HIO_3 to $Cr(NH_3)_5OH_2^{3+}$ and *cis*-$Co(en)_2(OH_2)_2^{3+}$.

In view of the various approximations that have been made, this factor of *ca.* 7 is not too large as to exclude the possibility of a dissociative mechanism for the complexation reactions. This requires either that the leaving group is OH^- or that proton transfer occurs from the aquo ligand to HIO_3 within the outer-sphere complex. Although both of these may be perfectly feasible, a dissociative mechanism would have been more plausible if an $[H^+]^2$ dependence had been observed. Thus for reactions involving substitution at chromate and nitrite[19,20] a strong case has been put forward for an S_N1 mechanism with water loss from the chromium(VI) and nitrogen(III) centers rate determining. Nmr studies of iodate solutions[5] indicate that the inner-coordination sphere does not contain a bound solvent water molecule and there is therefore no possibility of a rate-determining loss of water without proton transfer within the outer-sphere complex. Since pK_a of the aquo ligand in the complex is >5,[7,8] this would seem prohibitive, especially since the species $H_2IO_3^+$ could be formed relatively easily by protonation from bulk solution, with a resultant $[H^+]^2$ dependence as observed in oxygen-exchange studies.[5]

For bromate, redox and exchange reactions often exhibit such an $[H^+]^2$ dependence but the oxygen-exchange studies[21] and studies of reactions involving anionic species[22-24] would seem to rule out formation of BrO_2^+. The reaction of iodate with iodide[25] shows a similar dependence and it seems that the nature of the hydrogen ion dependence for reactions of halate(V) species might be determined by electrostatic factors, positively charged $H_2XO_3^+$ being the preferred reactant species with negatively charged anions.

Since bromate reactions seem to involve nucleophilic attack at $H_2BrO_3^+$ rather than BrO_2^+, it seems possible that for HIO_3 an associative mechanism is operative. However water is usually considered to be a weak nucleophile and when coordinated to a metal center will exhibit even weaker nucleophilic properties. A simple nucleophilic attack with k_2 greater for complexed water than for solvent water therefore seems unlikely. If some form of hydrogen bonding or partial transfer of protons from the aquo ligand to the HIO_3 occurs, then the mechanism might gain credibility since proton transfer should be more facile from a coordinated water molecule than from solvent. One way in which this could be achieved is by formation of an activated complex



A similar activated complex has been invoked by Beech, *et al.*,[26] for the complexing of arsenate(V) with $Co(NH_3)_5OH_2^{3+}$. Loss of water and a proton from such an activated complex gives the reaction product.

It is quite remarkable that k_2 values for oxygen exchange and for complex formation should be so similar if this mechanism applies. Two factors—(a) the weaker nucleophilicity of coordinated water compared to solvent water and (b) the stronger acidic nature of the coordinated water—must effectively balance out for this explanation to hold.

To summarize therefore, the mechanistic implications of this and other studies involving iodate are not at present entirely clear. Complexing to chromate[19] and nitrite[19,20] is believed to occur by a dissociative mechanism, whereas for arsenate[25] an associative process has been suggested. With iodate a dissociative mechanism is possible if OH^- is the leaving group. Rate constants k_2 for the complexing of HIO_3 with $Cr(NH_3)_5OH_2^{3+}$ and *cis*-$Co(en)_2(OH_2)_2^{3+}$, *ca.* 10^4 sec^{-1}, would certainly support such a process if our estimates of K_O and K_O' are too low. We cannot however feel confident about such an assignment, because with bromate, even when an $[H^+]^2$ dependence is observed, evidence obtained does not support a dissociative process.[22] An associative mechanism with hydrogen bonding is a plausible alternative.

Experimental Section

AnalaR grade sodium perchlorate and perchloric acid were used throughout this study. Fresh 0.4 *M* stock solutions of sodium iodate (Hopkin and Williams, GPR) were prepared at regular intervals. The preparations of $[Cr(NH_3)_5OH_2](ClO_4)_3$[27] and *cis*-$[Co(en)_2(OH_2)_2](ClO_4)_3$[28] were as described elsewhere.

Hydrogen ion concentrations were determined from pH measurements using a Radiometer pHM4 meter and glass and calomel electrodes. The calomel electrode was modified by replacing the standard potassium chloride solution in the electrode by a saturated solution of sodium chloride. This served to minimize junction effects arising from possible precipitation of potassium perchlorate when the electrode was used in perchlorate-containing media. Solutions of perchloric acid (0.1, 0.02, 0.01, and 0.002 *M*) made up to $I = 1.0$ *M* ($NaClO_4$) were used to standardize the pH meter at 25° prior to determination of the pH of temperature-jump solutions; the pH obtained was then a direct measure of the free hydrogen ion concentration. Free iodate concentrations were then determined using a value for the protonation constant of iodate of 1.94 l. mol^{-1} at 25° and 1.0 *M* ($NaClO_4$) extrapolated from the data of Ramette.[10] This value is in good agreement with the value 2.02 l. mol^{-1} calculated from data obtained by Gamsjager, *et al.*,[29] at 25° and 1.0 *M* ($LiClO_4$).

Scan spectra were recorded on a Unicam SP800 spectrophotometer and equilibrium constants were determined using an SP500 spectrophotometer thermostated at 25°. Kinetic experiments were carried out using a temperature-jump transient spectrometer[30] (Type SBA7, Messanlagen, Gottingen, West Germany). Using a tungsten lamp source various wavelengths were selected to follow the kinetics. A discharge of 40 kV, from a 0.05-μF condenser, corresponding to an increase in temperature of 5.9° was used in all experiments.

The preparation of the complex $Cr(NH_3)_5OIO_2^{2+}$ is described elsewhere.[31]

Acknowledgment. We are grateful to SRC for a research grant for the purchase of temperature-jump equipment. R. K. W. wishes to thank the University of Leeds for the award of a Henry Ellison Fellowship. The authors also wish to acknowledge personal communications from and discussions with Dr. Hartmut Diebler.

Registry No. $[Cr(NH_3)_5H_2O]^{3+}$, 15975-47-0; *cis*-$[Co(en)_2(H_2O)_2]^{3+}$, 21274-59-6; IO_3^-, 15454-31-6; $[Cr(NH_3)_5OIO_2]^{2+}$, 52843-02-4; *cis*-$[Co(en)_2(OH_2)(OIO_2)]^{2+}$, 52843-01-3.

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