sponding aquo complexes.[16] In this context, it is necessary to note that the reaction of *cis*-$Co(en)_2NH_3Br^{+2}$ with HOCl does *not* proceed *via* formation of a *cis*-$Co(en)_2NH_3Cl^{+2}$ intermediate, which then reacts with HOCl to yield the observed aquo product. A solution of *cis*-$Co(en)_2NH_3Cl^{+2}$ treated with HOCl under the same conditions as *cis*-$Co(en)_2NH_3Br^{+2}$ showed no detectable change in light absorption over a period of 30 min.[17]

TABLE III

POLARIMETRIC DATA FOR THE REACTIONS OF *d-cis*-$Co(en)_2NH_3Br^{+2}$ WITH CHLORINE AND HYPOCHLOROUS ACID (ROOM TEMPERATURE)[a]

Oxidant	$[M]_D$, reactant	$[M]_D$, product	$[M]_D$, calcd.[b]	% retention
Cl_2	+273[c]	+328[c]	+327	100
Cl_2	+412[d]	+487[d]	+495	98
Cl_2	+460[c]	+543[c]	+552	98
HOCl[e]	+438[f]	+377[f]	. . .	92[g]

[a] Hydrochloric acid (0.12 *M*) unless otherwise stated. [b] Calculated using the values $[M]_D = +500$ for *d-cis*-$Co(en)_2NH_3Br^{+2}$ (ref. 12), $[M]_D = +600$ for *d-cis*-$Co(en)_2NH_3Cl^{+2}$ (ref. 12) and J. G. Brushmiller, E. L. Amma, and B. E. Douglas, *J. Am. Chem. Soc.*, **84,** 3227 (1962), and $[M]_D = +432$ for *d-cis*-$Co(en)_2NH_3OH_2^{+3}$ (ref. 18). [c] Single experiment; $[Co(III)] = 1.11 \times 10^{-3}$ *M*. [d] Average for two experiments; $[Co(III)] = 8.14 \times 10^{-4}$ *M* and 1.11×10^{-3} *M*. [e] Perchloric acid (0.015 *M*). [f] Average for three experiments; [Co(III)] varied from 1.11 to 1.78×10^{-3} *M*. [g] Calculated for the reaction which results in the formation of *cis*-$Co(en)_2NH_3OH_2^{+3}$; see text.

The polarimetric studies carried out with *d-cis*-$Co(en)_2NH_3Br^{+2}$ are summarized in Table III and provide the most conclusive evidence for the retention of both geometry and optical configuration in the reaction with Cl_2. Within experimental error the retention of optical activity is 100%, a result which provides further support for the rearrangement mechanism postulated to account for the quantitative formation of $Co(NH_3)_4Cl^{+2}$ by the reaction of $Co(NH_3)_5Br^{+2}$ with Cl_2.[2]

Polarimetric studies of the reaction between *d-cis*-$Co(en)_2NH_3Br^{+2}$ (bromide salt) and HOCl were also carried out. A comparison of columns 3 and 4 of Table III shows that retention of optical activity is a major feature of the reaction. However, the quantitative interpretation of the results is complicated because of the formation of mixtures of chloro and aquo products. If it is assumed that the chloro product is formed with retention of optical activity, it is possible to calculate from the observed value of $[M]_D$ (+377), the known product distribution (18% *cis*-$Co(en)_2NH_3Cl^{+2}$ and 82% *cis*-$Co(en)_3NH_3OH_2^{+3}$), and the value of $[M]_D$ for *d-cis*-$Co(en)_2NH_3OH_2^{+3}$ (+432)[18] that the reaction which results in the formation of *cis*-$Co(en)_2NH_3OH_2^{+3}$ proceeds with 92% retention of optical activity. In view of the complications in this system, and of the accumulation of experimental errors in the calculation, it is reasonable to conclude that this reaction also proceeds with complete retention of optical activity.

If the retention of geometry and optical configuration proves to be a general feature of reactions of the present type, it is possible that such reactions will be useful in syntheses and in the determination of geometries and optical configurations of related complexes.

Acknowledgment.—A. H. is indebted to Dr. A. M. Sargeson for helpful discussions regarding the optical activity of *cis*-$Co(en)_2NH_3OH_2^{+3}$ and for the measurement of the value of $[M]_D$ for this complex.

[16] For *trans*-$Co(en)_2NH_3Br^{+2}$ the reaction with HOCl yields, apparently, only *trans*-$Co(en)_2NH_3OH_2^{+3}$. However, for the corresponding reaction of the *cis* complex some *cis*-$Co(en)_2NH_3Cl^{+2}$ is detected in addition to the principal product *cis*-$Co(en)_2NH_3OH_2^{+3}$. Part of the *cis*-$Co(en)_2NH_3Cl^{+2}$ may arise from the reaction of *cis*-$Co(en)_2NH_3Br^{+2}$ with the Cl_2 generated in the system by Br^- (inner and outer sphere) reduction of HOCl to Cl^-, followed by HOCl oxidation of Cl^-. Some attempts were made to investigate this point further, but the situation appears to be complicated. A solution of *cis*-$[Co(en)_2NH_3Br](ClO_4)_2$ was prepared from the corresponding Br^- salt by an ion-exchange technique, and aliquots were treated with a 5-fold excess of HOCl in the presence of 0.015 or 0.96 *M* $HClO_4$. The yields of *cis*-$Co(en)_2NH_3OH_2$ were 91 and 85%, respectively. Furthermore, visual observation indicated that the rate of the reaction increases markedly with increasing $[H^+]$.

[17] A similar observation was made previously. $Co(NH_3)_5Cl^{+2}$ does not react with HOCl within 10 min. at room temperature.[2]

[18] A. M. Sargeson, private communication.

CONTRIBUTION NO. 1770 FROM THE INSTITUTE FOR ATOMIC
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A Kinetic Study of the Reaction of Iodine and Iodochromium(III) Ion in Acidic Solution[1]

BY JAMES H. ESPENSON

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In the course of a previous kinetic study[2] of the formation of iodine in the reaction of iodate ion with iodide ion in an inert metal ion complex, $Cr(H_2O)_5I^{2+}$, the rate equation suggested that the oxidation reaction might proceed through a mechanism where iodine catalyzed the removal of iodide ion from the primary coordination sphere of chromium(III), followed by rapid oxidation of the liberated iodide ion. The present work constitutes a kinetic study of the reaction of iodine and iodopentaaquochromium(III) ion

$$Cr(H_2O)_5I^{2+} + I_2 + H_2O = Cr(H_2O)_6^{3+} + I_3^- \qquad (1)$$

and an examination of its role in the mechanism of oxidation of coordinated iodide ion.

Experimental

Reagents.—Iodochromium(III) ion was prepared by reaction of solutions of chromium(II) perchlorate and iodine and was isolated and purified by ion exchange on Dowex 50W-X8 cation-exchange resin as described by Swaddle and King.[3] During this procedure, water at 0° was circulated through the column jacket to prevent aquation of the complex

$$Cr(H_2O)_5I^{2+} + H_2O = Cr(H_2O)_6^{3+} + I^- \qquad (2)$$

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[1] This work was performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission.

[2] J. H. Espenson, *Inorg. Chem.*, **3**, 968 (1964).

[3] T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).

which is fairly rapid at room temperature ($t_{1/2}$ = 40 min. at 25° and 0.2 M H^+). The resin column was washed with cold 0.2 F perchloric acid to remove iodide ion, and the complex was then slowly eluted with cold 1 F perchloric acid. The solution of CrI^{2+} was frozen in acetone–Dry Ice upon elution; these solutions were stored at Dry Ice temperature except for brief intervals of thawing when samples were removed for analysis or kinetics experiments. The preparations, elutions, and subsequent analyses of the complex were always carried out in a semi-darkened room, and the solutions were stored in opaque vessels. The complex was identified as CrI^{2+} on the basis of the known visible and ultraviolet spectrum[2,3] and by direct analysis for chromium and iodine. In analysis of solutions of the complex, chromium was determined spectrophotometrically at 3720 Å. after oxidation to chromium(VI) by hydrogen peroxide in basic solution. Iodide was oxidized by excess iodate ion to iodine, which was analyzed spectrophotometrically at 4650 Å., a wave length of maximum light absorption of iodine, where its absorbancy index is 733 M^{-1} cm.$^{-1}$. Values of the (chromium)/(iodide) ratio determined for three separate preparations of CrI^{2+} were 0.965, 1.018, and 1.040.

Reagent grade iodine, potassium iodide, sodium iodate, and perchloric acid were used without further purification. For use in the rate studies, iodine solutions were prepared at *ca.* 10^{-3} M in 1.00 F perchloric acid. The water used in all the preparations and reaction solutions was a double redistillation of laboratory distilled water from alkaline permanganate in a tin-lined Barnstead still.

Results

Rate Measurements.—The disappearance of CrI^{2+} was followed spectrophotometrically at its absorption maximum at 2600 Å., where its molar absorbancy index is 5.41 × 10^3 M^{-1} cm.$^{-1}$. The spectrophotometric measurements were made with a Cary Model 14 recording spectrophotometer; continuous readings were taken on a solution in a glass-stoppered 2-cm. quartz cell in a water-filled thermostated cell holder. The duration of such experiments was generally 10–60 min.

The extent to which the triiodide ion forms in these solutions must be taken into account in deriving concentrations from the absorbance data. In the present work a number of spectrophotometric experiments were carried out at 3500 Å. (an absorption maximum for triiodide ion) and at 2600 Å. These data agree with the spectral results of Awtrey and Connick.[4] The present data, expressed as apparent molar absorbancy indices of iodine(0) as a function of the formal iodide concentration, were used to derive instantaneous formal concentrations from absorbance readings during rate runs. Katzin and Gebert's value[5] of the equilibrium quotient, $Q = [I_3^-]/[I_2][I^-] = 787\ M^{-1}$ in 1.00 F perchloric acid at 25.0°, was used to calculate the instantaneous molar concentrations of the species I^-, I_2, and I_3^-, needed for interpretation of the present rate measurements. The ranges of initial concentrations over which the kinetics were studied are these: CrI^{2+}, 0.4–1.8 × 10^{-4} M; I_2, 0.13–1.2 × 10^{-3} F; and I^-, 0–1.5 × 10^{-4} F.

The concentration of iodine in these experiment was generally sufficiently large relative to that of CrI^{2+} that it was converted to triiodide ion to only a slight extent as iodine ion was released from the complex. In addition, the approximate constancy of $[I_2]$ in each experiment ensured that the fraction of the uncomplexed iodide ion converted to triiodide would also remain essentially constant. The errors introduced by the use of average values of $[I_2]$ and $[I^-]/([I^-] + [I_3^-])$ in computations in individual runs are relatively small in these experiments.

Form of the Rate Law.—Preliminary treatment of the kinetic data indicated a definite decrease of rate with increased concentration of iodide ion as was demonstrated in runs with and without added iodide ion. All the experiments performed here are consistent with the rate equation

$$-\mathrm{d}\ln [CrI^{2+}]/\mathrm{d}t = k_{aq} + k[I_2]/(\kappa + [I^-]) \qquad (3)$$

in which k_{aq} represents the known[2,3] specific rate of spontaneous aquation, reaction 2.

The treatment of the kinetic data to verify this rate law and evaluate the parameters k and κ was carried out using directly the measured extent of reaction.[6] Values of the slope $-\mathrm{d}\ln [CrI^{2+}]/\mathrm{d}t$ were evaluated graphically or by differences between adjacent points, the known[2,3] k_{aq} (1.20 × 10^{-4} sec.$^{-1}$) subtracted, and the results treated graphically. Rearrangement of eq. 3 leads to

$$[I_2]/(-\mathrm{d}\ln [CrI^{2+}]/\mathrm{d}t - k_{aq}) = \kappa/k + [I^-]/k \qquad (4)$$

Values of the quantity on the left side of eq. 4, using 6–15 values per run, were plotted *vs.* the instantaneous average $[I^-]$ at the place in the run where the average rate was evaluated. Data from 19 runs were plotted on the same graph. Although use of rate data in this form inevitably leads to considerable scatter, in this case it appeared quite random, and the data from all runs lay along a straight line from which were derived the parameters and their average deviations, k/κ = 2.9 ± 1.0 M^{-1} sec.$^{-1}$ and k = 5.0 ± 0.5 × 10^{-5} sec.$^{-1}$.

In the study of the oxidation of coordinated iodide ion in CrI^{2+} by iodate ion[2]

$$5CrI^{2+} + IO_3^- + 6H^+ = 5Cr^{3+} + 3I_2 + 3H_2O \qquad (5)$$

the rate equation is $-\mathrm{d}[CrI^{2+}]/\mathrm{d}t = k_{ox}[CrI^{2+}][I_2]$ with the average value of k_{ox} = 7.8 M^{-1} sec.$^{-1}$ in 1.00 F perchloric acid at 20.0°. Since the present study was carried out at 25.0°, a few additional measurements were made here on the rate of this reaction at the higher temperature. These data are also consistent with the reported rate law, with k_{ox} = 10.7 ± 1.5 M^{-1} sec.$^{-1}$ at 25.0°.[7]

Interpretation and Discussion

The rate equation written in terms of the predominant forms of the substances involved has been pre-

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[4] A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842 (1951).

[5] L. I. Katzin and E. Gebert, *ibid.*, **77**, 5814 (1955).

[6] A tabulation of initial concentration conditions and of time and fraction of reaction has been deposited as Document No. 8599 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[7] Evidence has been advanced (ref. 3) that the solution of CrI^{2+} used in the earlier study (ref. 2) may have contained a catalyst for reaction 2, which was effective at low $[H^+]$. (The CrI^{2+} had not been isolated by the ion-exchange procedure in the earlier work.) The consistency of the results of the two studies of k_{ox} substantiates the earlier results on the reaction of CrI^{2+} with iodate ion.

sented (eq. 3). The two-term denominator, $\kappa + [\mathrm{I}^-]$, suggests the operation of a two-step-mechanism, either step of which may become rate-determining, depending upon the relative magnitudes of κ and $[\mathrm{I}^-]$; it also suggests that solvent and iodide ion compete for an intermediate present at its steady-state concentration. The rate law reveals the compositions of the activated complex in each step; these are $(\mathrm{CrI_3}^{2+})$ and $(\mathrm{CrI_2}^{3+})$, respectively.

A mechanism consistent with the observed kinetics of the reaction is given by the following reaction sequence (in which coordinated solvent molecules have been omitted)

$$\mathrm{CrI}^{2+} + \mathrm{I_2} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{CrI_2}^{3+} + \mathrm{I}^- \qquad (k_1 \ll k_2) \qquad (6)$$

$$\mathrm{CrI_2}^{3+} \xrightarrow{k_3} \mathrm{Cr}^{3+} + \mathrm{I_2} \qquad (7)$$

$$\mathrm{I_2} + \mathrm{I}^- \rightleftharpoons \mathrm{I_3}^- \qquad (\text{rapid; } Q = 787\ M^{-1})$$

The spontaneous aquation was also included and the steady-state procedure applied to the postulated unstable intermediate in this reaction, resulting in the equation

$$-\mathrm{d}\ln[\mathrm{CrI}^{2+}]/\mathrm{d}t = k_{\mathrm{aq}} + (k_1k_3/k_2)[\mathrm{I_2}]/(k_3/k_2 + [\mathrm{I}^-])$$

which is of the same form as the experimental rate law (eq. 3), with the empirical constants k and κ identified as k_1k_3/k_2 and k_3/k_2, respectively.

It is useful to compare these results with those obtained in the study of the CrI^{2+}–$\mathrm{IO_3}^-$ reaction (eq. 5), the rate law for which resembles that found in the present work under comparable circumstances, namely the limiting form with $[\mathrm{I}^-] = 0$.[8] Although it is tempting to interpret the identical form of the two rate laws as indicating a similarity of mechanism, this leads to quantitative difficulties. The present study has $k/\kappa = 2.9 \pm 0.1\ M^{-1}\ \mathrm{sec.}^{-1}$ at 25.0° and 1.00 F $\mathrm{HClO_4}$, whereas $k_{\mathrm{ox}} = 10.7\ M^{-1}\ \mathrm{sec.}^{-1}$ under the same conditions. It appears, therefore, that although the oxidation reaction proceeds necessarily in part by a path in which iodine catalyzes the decomposition of CrI^{2+}, this path cannot quantitatively account for the entire course of reaction.[9]

The reactions of CrI^{2+} with $\mathrm{I_2}$ and $\mathrm{IO_3}^-$ constitute an example of a pair of reactions for which the activated complexes in the rate-determining steps at low $[\mathrm{I}^-]$ have the same composition, but are, in fact, not the same (presumably the geometry of the three iodine atoms is different in the two activated complexes). Another interesting feature of the CrI^{2+}–$\mathrm{I_2}$ reaction is the failure of the bimolecular path, forming directly Cr^{3+} and $\mathrm{I_3}^-$, to compete with the two-step sequence required by the rate equation.

The second step of the reaction represents aquation of an iodine–chromium(III) complex; these data allow only a lower limit to be set on its specific aquation rate, namely $k_3 = \kappa k_2 \gg 5.1 \times 10^{-5}\ \mathrm{sec.}^{-1}$ at 25.0°.

Acknowledgment.—The author is grateful to Prof. E. L. King for helpful comments concerning the kinetic data and some implications of the proposed reaction mechanism.

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[8] The circumstances are comparable for the reason that iodide ion cannot accumulate in the presence of $\mathrm{IO_3}^-$—it is rapidly and completely oxidized to iodine.

[9] It is worth commenting on a semiquantitative experiment on the CrI^{2+}–$\mathrm{I_2}$ reaction described in the earlier study (ref. 2) on the CrI^{2+}–$\mathrm{IO_3}$ reaction. This experiment involved ~0.005 M CrI^{2+} and ~0.001 F $\mathrm{I_2}$ in 1 F $\mathrm{HClO_4}$; it was observed that the iodine-catalyzed aquation occurred at a negligible rate relative to that of the CrI^{2+}–$\mathrm{IO_3}$ reaction. The apparent failure of iodine as a catalyst here is due to its concentration relative to that of CrI^{2+}: the so-called catalyst is largely converted to the inactive form $\mathrm{I_3}^-$ after only ~20% reaction.

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Complex Metal Oxides of the Type $\mathrm{AMMo^{IV}{}_3O_8}$

By Josephine DeBenedittis and Lewis Katz

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The preparation and structure of compounds of the type $\mathrm{A^{II}{}_2Mo^{IV}{}_3O_8}$, where $\mathrm{A^{II}}$ may be Mg, Mn, Fe, Co, Ni, Zn, or Cd, have been reported.[1] More recently, an apparently related lithium–scandium–molybdenum(IV) oxide has been reported.[2]

The $\mathrm{A_2Mo_3O_8}$ compounds were shown to have a hexagonal unit cell with four close-packed layers of oxygens. One of the divalent ions is in a tetrahedral hole, and the other is in an octahedral hole. The molybdenum ions are in octahedral holes and the octahedra share edges in such a way as to form rings of three molybdenums. Both the closeness of approach of the molybdenum atoms in the rings and the very low magnetic susceptibility of the compounds indicate Mo–Mo bonding.

From the starting reactant composition, the formula postulated for the lithium–scandium–molybdenum oxide was $\mathrm{LiScMo_3O_8}$, and the structure was assumed to be related to that of $\mathrm{A_2Mo_3O_8}$, with the monovalent lithium and the trivalent scandium substituted for the two divalent A cations. The c axis of the new compound is only half as long as that of the $\mathrm{A_2Mo_3O_8}$ compounds, so the structure was assumed to repeat after two layers of oxygens rather than four.

In this note we present chemical evidence for the formula $\mathrm{LiScMo_3O_8}$, evidence for the existence of additional compounds of the same type, in particular $\mathrm{LiYMo_3O_8}$ and $\mathrm{LiGaMo_3O_8}$, and X-ray powder data in support of the postulated structure. From the results of a least-squares treatment of the $\mathrm{LiYMo_3O_8}$ powder data, we are able to present proof of the distribution of Li and Y in the tetrahedral and octahedral sites and somewhat refined values of the position parameters.

Experimental

Preparations.—Two methods were used for the preparation of the scandium compound

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[1] W. H. McCarroll, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5410 (1957).

[2] P. C. Donohue and L. Katz, *Nature*, **201**, 180 (1964).