change from PbO_2 to Pb_3O_4 (Pb_2PbO_4) as the oxidizing agent is quite remarkable, with the former acting as a $1e^-$ oxidizing agent and the latter as a $2e^-$ oxidizing agent. In terms of the ideas that have been discussed, the change in chemistry would perhaps be expected when the solid changes from a situation as in PbO_2 where the Pb(IV) ions are close together and share O^{-2} ions to one in which each Pb(IV) is completely surrounded by O^{-2}, none of which is shared by adjacent Pb(IV) ions. But it is astonishing to find that only a slight increase in the ratio of O^{-2}:Pb(IV), as when PbO_2 is converted to α-PbO_2, suffices to change the mechanism of the oxidation process, and it is clear that the general explanation we have advanced will need to be refined to understand the great sensitivity of the process to the O^{-2}:Pb(IV) ratio.

Many features of the interpretation of our observations are serviceable in explaining other dissolution reactions brought about by electron transfer, among them the Cr^{+2}-catalyzed dissolution of $CrCl_3$ in water.[1] It is significant that the process is catalyzed by reducing agents but not oxidizing agents such as Ce(IV). Chromium(IV) appears to be substitution-labile, but this fact is not sufficient to ensure catalytic dissolution.

It is necessary in addition that there be lattice damage on electron transfer. When Cr^{+3} absorbs an electron, the electron enters a $d\gamma$ orbital and produces a strong tetragonal distortion of the coordination sphere; but when Cr(III) loses an electron, the resulting Cr(IV) ion ($d\epsilon^2$) still requires an almost perfectly octahedral coordination sphere, and so it presumably fits well into the lattice. The point made here is borne out also by observations which have been made with VCl_2. This solid is very slow to dissolve, and it has been found[14] that V^{+3} does not noticeably catalyze the dissolution of the solid, although V^{+3} is substitution-labile. It should be noted that the V^{+2}–V^{+3} adn Cr^{+3}–Cr^{+4} systems are isoelectronic.

(14) Observations made by T. E. Rogers in the course of trying to prepare methanolic solutions containing V^{+2}.

Kinetics and Mechanism of the Aquation of Iodopentaaquochromium(III) Ion and of Oxidation of Coordinated Iodide Ion in Acidic Solution[1]

By JAMES H. ESPENSON

The rates of aquation of iodochromium(III) ion have been determined in acidic solution as a function of reactant concentration, acidity, and temperature. The rate law is of the form $-d \ln [CrI^{2+}]/dt = k_0 + k_{-1}/[H^+]$; values of the rate constants were determined for hydrogen ion concentrations 0.20–1.0 M, at 15–32° and unit ionic strength. Activation parameters associated with these paths are $\Delta H_0^* = 28.0$ kcal., $\Delta S_0^* = 16.4$ e.u.; $\Delta H_{-1}^* = 20.6$ kcal., $\Delta S_{-1}^* = -9.4$ e.u. Oxidation of bound iodide ion by iodate ion proceeds according to a rate law $-d[CrI^{2+}]/dt = k_{ox}[CrI^{2+}][I_2]$, independent of IO_3^-, a reactant, and accelerated by I_2, a product. At 20.0° and unit ionic strength, $k_{ox} = 7.8$ M^{-1} sec.$^{-1}$; alternative mechanisms are presented and discussed. Iodine does not catalyze aquation of CrI^{2+}. When either hydrogen peroxide or aquoiron(III) ion reacts with iodochromium(III) ion, oxidation proceeds no more rapidly than consistent with prior aquation of the complex, followed by oxidation of free iodide ion.

Iodochromium(III) ion[2] has been established as the dominant chromium(III) product, despite its very slight thermodynamic stability, of several reactions involving oxidations of substitution-labile chromium(II) ion. These include reaction with iodine,[3] with iodopentaamminecobalt(III) ion,[3] and with iron(III) in the presence of iodide ion.[4] This complex, least stable of the monohalochromium(III) ions,[5,6] is also the least stable of the series in the kinetic sense.[7,8]

This work presents results on the kinetics of aquation of CrI^{2+} in acidic solution

$$Cr(OH_2)_5I^{2+} + H_2O = Cr(OH_2)_6^{3+} + I^- \qquad (1)$$
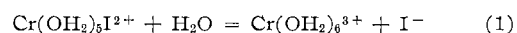
Reaction of ligands coordinated to substitution-

(4) This reaction, analogous to that found for iron(III) and chromium(II) in the presence of chloride ion, must be carried out shortly after mixing to avoid reduction of iron(III) by iodide ion, although quantitative conversion to CrI^{2+} nonetheless results, since iodine is also effective. Qualitative observation that CrI^{2+} forms essentially instantly upon mixing establishes that this reaction occurs *via* an iodide-bridged transition state, rather than by formation of iron(II) and iodine followed by reaction of iodine with chromium(II), since the iron(III)–iodide ion reaction occurs at a rate substantially lower than those involved here.

(1) This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) Iodopentaaquochromium(III); in general, the water molecules in the first coordination sphere of chromium(III) will not be indicated in the names or formulas of this and of similar ions.

(3) H Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

(5) H. S. Gates and E. L. King, *J. Am. Chem. Soc.*, **80**, 5011 (1958).

(6) J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960).

(7) F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

(8) (a) R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795 (1964); (b) N. Bjerrum, *Z. physik. Chem.*, **59**, 336, 581 (1907).

inert metal ions has been the subject of some recent investigations.[9-11] A quantitative study has been made of the kinetics of the oxidation–reduction reaction of CrI^{2+} and iodate ion in acidic solution. Observations were also made on reactions of other oxidizing agents with iodochromium(III).

Experimental

Reagents.—Prior to reduction, chromium(VI) solutions for preparation of hydrated chromium(III) perchlorate were freed of potassium perchlorate by filtration at $-30°$ of a saturated solution of reagent grade potassium dichromate in *ca.* 5 *F* perchloric acid. A slight excess of formic acid was used to reduce chromium(VI). Hydrated chromium(III) perchlorate was crystallized from this solution and recrystallized once from dilute perchloric acid; the solid prepared in this manner contains an approximately equimolar amount of perchloric acid. Electrolytic reduction of solutions of chromium(III) perchlorate at a mercury cathode generated chromium(II) perchlorate[12] stock solutions. Electrolysis was carried out under a stream of deoxygenated nitrogen gas, and chromium(II) stock solutions were stored under nitrogen in bottles equipped with self-sealing Buna-N rubber disks, from which aliquots were removed by a nitrogen-flushed hypodermic needle and syringe. Analysis of chromium(II) perchlorate stock solutions for chromium(II) was accomplished in either or both of two ways: titration of standard potassium iodate solution to the disappearance of iodine (starch indicator), and titration of standard iron(III) perchlorate solution (thiocyanate ion indicator). In each case titration was carried out under a stream of purified nitrogen with the chromium(II) titrant contained in a 1-ml. tuberculin syringe and needle calibrated to deliver. Total chromium was determined spectrophotometrically at 3720 Å. after oxidation of an aliquot to chromate with alkaline hydrogen peroxide.[13] Values for total chromium and for chromium(II) generally agreed to within 0.5%. The perchloric acid concentration in a chromium(II) perchlorate stock solution was determined as the difference between total cation normality in an air-oxidized aliquot (determined by titration of the perchloric acid solution obtained from the aliquot passed through a cation-exchange column in hydrogen ion form) and the concentration of dimeric chromium(III) (Cr_2O^{4+}) formed[14] by air oxidation of chromium(II). Solid hydrated lithium perchlorate was prepared from lithium carbonate and perchloric acid and was recrystallized twice. Stock solutions 2 *F* in lithium perchlorate contained no detectable perchloric acid and were standardized by cation exchange. Aquoiron(III) perchlorate was prepared from the chloride by prolonged fuming with perchloric acid until chloride ion was not detectable. The solid was recrystallized twice from perchloric acid.

Triply-distilled conductivity water, prepared by distillation from alkaline permanganate in a Barnstead still, was used for all solutions. Reagent grade chemicals were used elsewhere without further purification.

Aquation Reaction.—Iodochromium(III) ion was prepared at 0.01 *M* concentration by reaction of chromium(II) and iodine,[3] the latter generated immediately before use from equivalent quantities of iodide and iodate ions. Iodine thus prepared reacts

essentially instantly with chromium(II). The required volumes of potassium iodide, perchloric acid, and lithium perchlorate stock solutions were mixed and flushed with purified nitrogen in a rubber-capped vessel (a 5-cm. spectrophotometer cell or a 150-ml. screw-cap bottle, as appropriate) and brought to reaction temperature. Standard potassium iodate just equivalent to the iodide present was added, quickly followed by the appropriate volume of chromium(II) perchlorate. The latter solutions were also at the reaction temperature and were added through the rubber cap by hypodermic syringes. Air was excluded even after preparation of iodochromium(III) to prevent oxidation of iodide ion.

The rate of aquation of iodochromium(III) ion was followed by three independent methods: (1) direct spectrophotometric measurement on a reacting solution, (2) analysis of the product, free iodide ion, separated from the quenched reaction solution by absorbing the chromium cations on a 30-cm. cation-exchange column and washing through iodide ion with ice-cold perchloric acid, and (3) analysis of iodochromium(III) ion separated from hexaaquochromium(III) ion by cation-exchange resin.

Procedure (1) was carried out at either of two wave lengths at which the absorbancy index difference between iodo- and aquo-chromium(III) is a maximum: 4750 Å. (iodo 31.9, aquo 3.7) and 6500 Å. (iodo 35, aquo 3.8 M^{-1} cm.$^{-1}$). Reaction solutions were prepared in a 5-cm. spectrophotometer cell supported in a constant temperature bath, immersed up to the rubber-capped filling neck. At periodic intervals the cell was removed, quickly dried, and its absorbance measured on a Cary Model 14 spectrophotometer. The time required for this procedure was generally $\sim$40 sec., and it has been assumed that temperature effects on the aquation rate caused by this exposure to room temperature air are negligible. Absorbance measurements were taken at equal time intervals over $\sim$4–5 half-times for aquation.

For procedures (2) and (3), 5-ml. aliquots were taken by calibrated syringe quickly into $\sim$5 ml. of water or perchloric acid at $0°$, such that the final acid concentration was 0.5 *F*. Procedures (2) and (3) were used only at the reaction temperature of 25.0° and were often carried out on the same 5-ml. aliquot of reaction solution: after collection of free iodide ion with $\sim$40 ml. of 0.5 *F* $HClO_4$ at $0°$, iodochromium(III) ion was eluted by $\sim$90 ml. of 1 *F* $HClO_4$ also at $0°$. Iodide was determined spectrophotometrically after oxidation to iodine with excess iodate ion.[15] Iodochromium(III) was determined spectrophotometrically as chromate in alkaline solution, after oxidation with peroxide.[13] In iodide analyses, "infinite time" aliquots were taken in duplicate and were generally within experimental error of one another, as well as in satisfactory agreement with the expected value.

Oxidation Reactions.—The general technique for studying the various oxidizing agents investigated was to monitor spectrophotometrically the growth of the 4650 Å. peak due to iodine.[15] Generally, a solution of iodochromium(III) complex was prepared at 20.0° in a rubber-capped spectrophotometer cell of appropriate path length (2 or 5 cm.) by reaction under purified nitrogen of iodide ion with the stoichiometric amounts of iodate ion followed by chromium(II). To this solution, which contained at that point CrI^{2+}, $HClO_4$, and $LiClO_4$,[16] an aliquot of oxidizing agent was added, and a continuous recording of absorbance of iodine at 4650 Å. *vs.* time was made.[17]

(9) P. Saffir and H. Taube, *J. Am. Chem. Soc.*, **82**, 13 (1960).

(10) A. Haim and H. Taube, *ibid.*, **85**, 495, 3108 (1963).

(11) "Reactions of Coordinated Ligands and Homogeneous Catalysis," Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963.

(12) In some early preparations substantial concentrations of chloride ion were found; redesign of the electrolysis setup to require a lower voltage provided chromium(II) solutions containing no detectable chloride ion.

(13) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(14) M. Ardon and R. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959). Since the chromium(II) solutions contributed 5% at most to the final [H$^+$] in any reaction solution, uncertainties in perchloric acid concentration of chromium(II) stock solutions are negligible in all final reaction solutions.

(15) These dilute iodine solutions with excess iodate obey Beer's law at 4650 Å., a maximum, over the range 5 × 10^{-5} to 1.1 × 10^{-3} *M* I_2, with absorbancy index of I_2 733 M^{-1} cm.$^{-1}$.

(16) Plus any I_2, IO_3^-, Cr^{2+}, Cr_2O^{4+}, Cr^{3+}, and/or I^- present due to slight stoichiometric inequalities and/or air oxidation. Such small adventitious quantities are of no consequence here and are rapidly converted, by the oxidizing agent subsequently added, to chromium(III), which is without effect, or to iodine, which is quantitatively measured.

(17) During these measurements the spectrophotometer cell remains in the cell compartment through which constant temperature water is circulating. Temperature control is not precisely achieved by this method but in the interval required for a run (5–12 min. for all experiments from which quantitative data were obtained) fluctuations probably do not exceed $\pm0.2°$. This temperature uncertainty may contribute appreciably, however, to scatter between different runs.

Inorganic Chemistry

Results and Discussion

Aquation Reaction.—The rate of aquation of iodochromium(III) ion at hydrogen ion concentrations in the range 0.20–0.95 M and temperatures 15–32° at ionic strength 1.00 F follows the rate law

$$-d[CrI^{2+}]/dt = k_{aq}[CrI^{2+}] \qquad (2)$$

which describes the kinetic behavior during a run at constant [H⁺]. Spectrophotometric data were treated by the method of Guggenheim[18] for first-order reactions, so that neither the infinite-time reading nor the value of the absorbancy index difference enter the computation. A constant time interval τ was chosen as $\sim$ two half-lives, and plots of log $(A_t - A_{t+\tau})$ vs. time are linear with slopes related to the desired first-order rate constant. For runs involving analyses of iodide ion or iodochromium(III) ion, rate constants were obtained from slopes of plots of log $(A_t - A_\infty)$ vs. time. Table I presents values of the pseudo first-order rate constant, k_{aq}, under the conditions investigated. The relation

$$k_{aq} = k_0 + k_{-1}[H^+]^{-1} \qquad (3)$$

describes the dependence of the rate on hydrogen ion concentration. Values of the activation parameters ΔS^* and ΔH^* for each of the two paths are presented in Table II. Since an individual k_{aq} value has associated with it an uncertainty estimated at 4%, it is not surprising that four adjustable parameters can fit these data—there are likely other sets that would do as well.

TABLE I

EXPERIMENTAL[a] (AND CALCULATED)[b] RATE CONSTANTS FOR THE FIRST-ORDER AQUATION OF IODOCHROMIUM(III) ION

Ionic strength 1.00 F

	0.200 M H⁺	0.333 M H⁺	0.590 M H⁺	0.948 M H⁺
15.0°	0.77 (0.71)	0.47 (0.48)	0.335 (0.324)	0.26 (0.25)
20.0°	1.44 (1.43)	1.01 (0.97)	0.73 (0.68)	0.57 (0.53)
25.0°	2.88 (2.79)	2.03 (1.96)	1.50 (1.42)	1.21 (1.16)
32.0°	6.87 (7.02)	5.01 (5.00)	3.30 (3.82)	3.20 (3.20)

(10⁴k_{aq}, sec.⁻¹)

[a] Estimated uncertainty in an individual k_{aq} is $\sim$4%. [b] Calculated from parameters given in Table II.

TABLE II

ACTIVATION PARAMETERS ASSOCIATED WITH THE RATE EQUATION FOR AQUATION OF IODOCHROMIUM(III) ION

	ΔH^*, kcal. mole⁻¹	ΔS^*, cal. mole⁻¹ deg.⁻¹
k_0 path	28.0 ± 1.5	16.4 ± 1.0
k_{-1} path	20.6 ± 1.4	−9.4 ± 1.0

Transition states for different pathways for aquation of iodochromium(III) ion involve different numbers of protons. This is analogous to the situation found with bromo-,[7] thiocyanato-,[19] and chlorochromium(III)[8b] complexes. The question of whether the observed k_{-1} term corresponds to a transition state $Cr(OH_2)_4(OH)X^+$ or $Cr(OH_2)_5X^{2+} \cdot OH^-$ has been

discussed by Guthrie and King.[7] The contribution of the k_{-1} term to the rate is not due to an appreciable fraction of complex existing in a basic form at these acidities, but to an aquation rate for this form $\sim$10⁵-fold higher than that of the pentaaquo complex. Perhaps all that is needed to explain this rate difference is the lowered net charge on the hydroxo species: loss of a negatively charged ligand would be aided by a less positive net charge on the reacting species.

Some significant differences set this system apart from some other $Cr(OH_2)_5X^{2+}$ aquation reactions.[7,19,20] Generally the acid-independent path has the lower activation enthalpy; the reverse situation was found in the present case ($\Delta H_0^* - \Delta H_{-1}^* = 7.4$ kcal.). Perhaps more striking is the magnitude of the activation entropy parameter. The value of ΔS_0^* found here is +16.2 e.u., compared with −3 to −7 for many related systems.[7,19,20] (An exception is X⁻ = azide ion[21] for which $\Delta S_0^* = +16$ e.u. In this instance a redistribution of protons in the transition state brought about by the strongly basic character of azide ion was invoked as the explanation for this large positive entropy of activation.) The more positive value of ΔS_0^* observed here for iodochromium(III) ion may be due to the lowered ability of the large iodide ion to create order in the solvent in the activation process, as compared with the smaller and less polarizable fluoride and bromide ions. The increase in aquation rate of CrX^{2+} with increasing atomic weight of the halide ion X⁻ parallels the decreasing stability of these ions. The higher rate of the iodo complex is due chiefly to the activation entropy term, rather than to the enthalpy term. (In fact, the value of ΔH_0^* is 4.2 kcal. less favorable for aquation of CrI^{2+} than $CrBr^{2+}$.)

Oxidation Reactions. Iodate Ion.—The stoichiometry of the reaction occurring here was established to be

$$5CrI^{2+} + IO_3^- + 6H^+ = 5Cr^{3+} + 3I_2 + 3H_2O \quad (4)$$
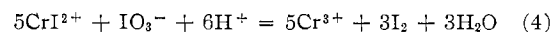
(with excess iodate ion, triiodide ion cannot exist at appreciable levels). Since reaction is substantially complete in 10–15 min. under the conditions studied here, this provides certain evidence that the mechanism is *not* the slow thermal aquation of iodochromium(III) ion (ca. 200 min. half-life at 20° and 0.95 M H⁺) followed by oxidation of the liberated iodide ion by iodate ion. In acidic solution formation of iodine from reaction of iodate and iodide ions is very rapid.[22]

A quantitative study of the kinetics of reaction 4 showed that its rate exhibits no dependence upon iodate ion over a 400-fold variation in concentration (8 × 10⁻⁵ to 3 × 10⁻² M). On the other hand, the reaction is autocatalytic, with the concentration of a product, iodine, entering the rate law expression raised to a positive power. Concentrations were chosen such that both [CrI^{2+}] and [I_2] changed appreciably in each run; [H⁺] was constant during each run and [IO_3^-] and [Cr^{3+}] (which were shown to exert no effect on the

(18) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).
(19) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1217 (1955).

(20) E. L. King and T. W. Swaddle, private communication.
(21) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).
(22) O. E. Myers and J. W. Kennedy, *J. Am. Chem. Soc.*, **72**, 897 (1950).

rate) were relatively unchanged during some runs and varied appreciably in others. The rate law established over a 10-fold variation in iodochromium(III) ion concentration (2–20×10^{-4}) and a 7-fold variation in iodine concentration (1–7×10^{-4}) is

$$-d[CrI^{2+}]/dt = k_{ox}[CrI^{2+}][I_2] \qquad (5)$$

with the average value of $k_{ox} = 7.8\ M^{-1}\,\text{sec.}^{-1}$ at $20.0°$, ionic strength $1.00\ F$. Integration of eq. 4 leads to the result

$$\log\,[CrI^{2+}]/[I_2] = -(k_{ox}c_0/2.303)(t - t_0) + \log\,[CrI^{2+}]_0/[I_2]_0 \quad (6)$$

in which $c_0 = [I_2]_0 + \,^3/_5[CrI^{2+}]_0$ and subscript zero refers to concentration and time values at the first recorded point in a run. The value of k_{ox} for each run was calculated from slopes of plots of $\log\,[CrI^{2+}]/[I_2]$ *vs.* $t - t_0$. Figure 1 presents such plots for two typical runs, and Table III lists the value of k_{ox} obtained in each run and the appropriate initial concentration conditions. An apparently small effect due to hydrogen ion (last two entries in Table III) does not imply eq. 5 is incorrect. The small increase in k_{ox} in these circumstances is explained quantitatively by the effect on the oxidation rate of enhanced aquation at lower hydrogen ion concentration. A more complete form of eq. 5 takes into account both sources of iodine formation—oxidation of free and of bound iodide. The complete rate equation becomes

$$-d[CrI^{2+}]/dt = \{k_0 + k_{-1}/[H^+] + k_{ox}[I_2]\}[CrI^{2+}] \quad (7)$$

The first term is nearly negligible throughout, but the term $k_{-1}/[H^+]$ becomes appreciable at lower $[H^+]$. As an example, at $0.948\ M\ H^+$, aquation paths never contribute more than $\sim7\%$ to the rate (at the lowest $[I_2]$ studied), whereas this contribution can amount

TABLE III
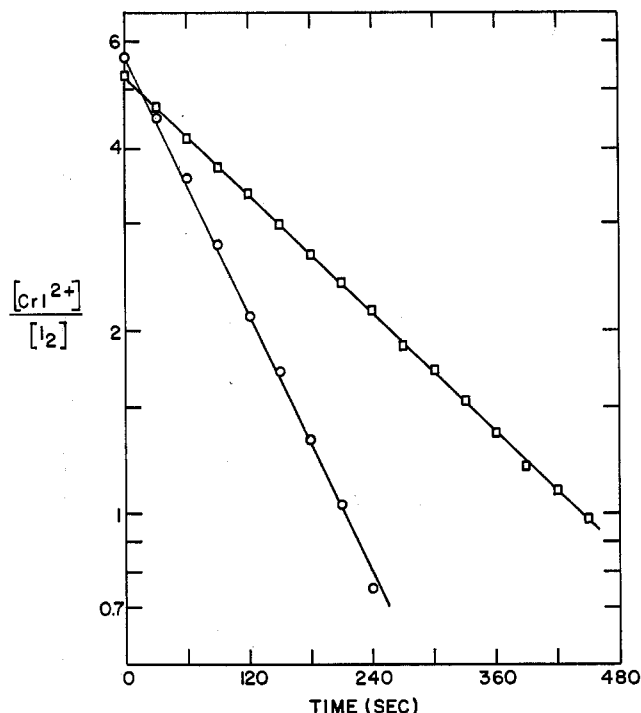#### RATE CONSTANTS[a] FOR THE REACTION OF IODATE ION AND IODOCHROMIUM(III) ION
$20.0°$, $0.948\ M\ H^+$, $I = 1.00\ F$

Initial[b] concentrations, $M \times 10^3$		k_{ox},[a]
[CrI^{2+}]	[IO$_3^-$]	$M^{-1}\,\text{sec.}^{-1}$
0.74	0.15	7.4
0.74	0.57	9.2
0.74	0.57	6.8
0.74	1.67	6.8
0.74	3.33	9.7
0.74	3.33	8.8[d]
0.74	3.33	8.4[e]
0.74	6.67	9.2
1.86	33.3	6.8
1.86	33.3	6.6
1.86	33.3	7.6
1.86	33.3	6.6
0.74	3.33	11.[c]
0.74	3.33	15.[c]

Av. $k_{ox} = 7.8 \pm 1.0$[f]

[a] Rate constant defined by eq. 5. [b] Concentrations at true zero time. [c] Last two entries are for 0.51 and $0.22\ M\ H^+$, respectively, and are not included in average. These are not true k_{ox}, but apparent rate/[CrI^{2+}][I$_2$], which includes enhanced aquation at lower acid concentration. [d] [Cr^{3+}]$_0 = 3 \times 10^{-3}\ M$. [e] [Cr^{3+}]$_0 = 6 \times 10^{-3}\ M$. [f] Average deviation of individual values from the mean.

Fig. 1.—Linear plots of $\log\,[CrI^{2+}]/[I_2]$ *vs.* $t - t_0$ illustrating conformity of data to eq. 4 and 5. The two runs shown are the seventh (□) and the eleventh (○) entries in Table III.

to $\sim20\%$ at $0.22\ M\ H^+$ at this same $[I_2]$. In evaluating k_{ox} only values at $0.948\ M\ H^+$ were considered, and the contribution of aquation paths was ignored.

Further details on the reaction mechanism were obtained from experiments suggested by the form of the rate law. There can be visualized at least two paths in accord with facts presented up to this point: (1) slow formation of a species CrI$_3{}^{2+}$, followed by its rapid oxidation by iodate ion, or (2) iodine catalysis of iodochromium(III) aquation, followed by rapid oxidation of the liberated free iodide ion.

With regard to (1), spectrophotometric examination of solutions containing combinations of two or three of the species CrI^{2+}, Cr^{3+}, and I$_2$ provides no spectral evidence for any appreciable association, fast or slow, in such solutions. Thus if a species CrI$_3{}^{2+}$ does form, it does so to only a very small extent. Semiquantitative experiments were done to check on the plausibility of mechanism 2 by establishing directly whether iodine catalyzes aquation of CrI^{2+} at or near a rate which can account for the rate law observed for the oxidation reaction. Solutions were prepared, at $20 \pm 2°$, containing $\sim0.005\ M\ CrI^{2+}$ and $\sim0.001\ M\ I_2$ in $1\ F\ HClO_4$. (The concentrations of reactants were somewhat higher than in the oxidation experiments to make the chromium(III) species easily visible.) At ~5-min. intervals over a 30-min. period aliquots were taken and delivered into a solution containing a 2-fold excess of thiosulfate ion, and qualitative observation immediately was made of the chromium(III) color. (Appropriate blanks were run with a solution containing Cr^{3+}, I$^-$, and I$_2$.) Were reaction between iodochromium(III) ion and iodate ion occurring *via* mechanism 2, the parameters associated with eq. 5

would require the half-time of CrI^{2+} in 10^{-3} M I_2 to be ~90 sec.; it was observed here that less than 20% aquation had occurred after 30 min. Mechanism 2 is rejected on the basis of the conclusion that iodine does not catalyze the aquation of iodochromium(III) ion. In this regard the present system is similar to iodopentaamminecobalt(III) ion, toward which iodine does not act as an effective aquation catalyst,[10] and unlike iodopentacyanocobaltate(III) ion, toward which it does.[23]

A mechanism consistent with these several requirements consists of the rate-determining formation of CrI_3^{2+} at low concentration. This unstable species may then react with iodate ion in a relatively rapid step. This mechanism requires that intermediates formed in these subsequent steps (likely candidates are HIO_2 and HIO) react rapidly with iodochromium(III) ion and/or with CrI_3^{2+}, a reasonable hypothesis if it is accepted that iodate ion, a similar but less powerful oxidizing agent, does. That the association of CrI^{2+} and I_2 should proceed at a rate ~10^9-fold lower than the association of I^- and I_2[22] may be due to the more stringent steric requirements of the former reaction and to the altered electronic structure of the coordinated iodide ion.

Reactions with Other Oxidizing Agents.—Also examined for their oxidizing properties on iodochromium(II) ion were hydrogen peroxide and aquoiron(III) ion. Each of these was examined under the following reaction conditions: 0.01–0.05 F oxidizing agent, 0.002 M iodochromium(III), 0.948 M H^+, at 20.0° and at ionic strength 1.00 F.

In the case of hydrogen peroxide slow formation of iodine occurs. A difficulty arising in the interpretation of these experiments is that oxidation of free iodide by peroxide is not instantaneous in these circumstances,

although it is rather rapid (the half-life of iodide ion under these conditions is ~3 min.).[24] The gross rate of production of I_2 estimated from the slope of absorbance *vs.* time, in four experiments with two values of $[H_2O_2]$, leads to the conclusion that the rate is approximately independent of $[H_2O_2]$, and is close to that ($\pm30\%$) predicted on the basis that the reaction occurs by slow aquation of the complex followed by the more rapid reaction of free iodide with hydrogen peroxide. This does not exclude the possibility that there may exist other reaction conditions where attack of peroxide upon coordinated iodide in iodochromium(III) dominates, as it does in the case of the reaction between hydrogen peroxide and iodopentaamminecobalt(III) ion,[10] but it does appear that such conditions may be inaccessible in this case, or nearly so.

Aquoiron(III) reacts only slowly with free iodide ion under these conditions (the first half-time of 10^{-3} M iodide ion in a solution 0.02 F in Fe(III) and 1 F in $HClO_4$ at 20° is ~40 min.).[25] No oxidation of iodide ion by iron(III) was observed in this study when iron(III) was added to iodochromium(III) ion under the conditions given above, even after enough time elapsed so that substantial aquation of the complex had taken place. Conclusions cannot be drawn with regard to the effectiveness of iron(III) in oxidizing bound iodide relative to free iodide; since the complex aquates under these particular conditions of concentration and temperature at a rate comparable to that of the iron(III)–I^- reaction, the direct iron(III)–CrI^{2+} process would be undetected. No evidence was obtained here on the direct oxidation of bound iodide by iron(III); if it can occur, it does so at a rate less than about twice the aquation rate under these conditions.

(23) R. J. Grassi and W. Wilmarth, Proceedings, International Conference on Coordination Chemistry, Uppsala, Sweden, 1962, p. 242.

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Cations and Oxy Cations of Iodine. II. Solutions of Iodosyl Sulfate, Iodine Dioxide, and Iodic Acid–Iodine Mixtures in Sulfuric Acid and Dilute Oleum

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Solutions in sulfuric acid of iodosyl sulfate, iodine dioxide, and mixtures of iodic acid and iodine having the mole ratio $HIO_3/I_2 = 3$ have been studied by means of cryoscopic and conductometric measurements. It is concluded that iodosyl hydrogen sulfate, $IO \cdot HSO_4$, which behaves as a weak electrolyte, is formed in each case. The results of similar measurements on solutions of the same solutes in dilute oleum lead to the conclusion that more sulfated species such as $(HSO_4)_2IOI(HSO_4)_2$ and $I(HSO_4)_3$ and related polymers are formed under these conditions.

Introduction

Chretien[1] obtained a yellow compound of trivalent

iodine, to which he assigned the composition $I_2O_3 \cdot SO_3 \cdot 0.5H_2O$, by heating iodic acid in the presence of concentrated sulfuric acid. The composition of this compound was the subject of a controversy that was mainly

(1) P. Chretien, *Compt. rend.*, **123**, 814 (1896); *Ann. Chim. Phys.*, **15**, 367 (1898).