The Formation of a Perchloratochromium(III) Complex in Strong Perchloric Acid Solutions

KENNETH M. JONES and JANNIK BJERRUM

Chemistry Department I, Inorganic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

It has been shown spectrophotometrically that a new chromium (III) species is formed slowly in solutions of the hexaquo ion in concentrated perchloric acid. The formation and dissociation of this complex at constant perchloric acid concentration followed the scheme for reciprocal first order reactions, and the apparent first order rate constant was found to vary linearly with the water activity in 5 to 10 M perchloric acid solutions.

The kinetic data have been interpreted in terms of the formation of a monoperchlorato complex. It has been hypothetically assumed that the hexaquo ion mainly exists as ion-pairs in concentrated perchloric acid, and under this supposition the rate constants for the reactions

$$[Cr(H_2O)_6]^{3+} \cdot ClO_4^- \rightleftharpoons [Cr(H_2O)_5ClO_4]^{2+} + H_2O$$
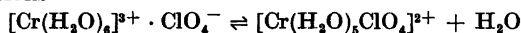
were estimated. The time of half-completion was approximately 70 min for the formation reaction at 20°, and $2.4/a_{H_2O}$ minutes for the dissociation reaction. The activation energies for the forward and reverse reactions (estimated from the rate constants at 9.8°C and 20°C) were 22.7 and 15.3 kcal/mole, respectively.

The absorption spectrum of the monoperchloratochromium(III) ion was estimated. Compared to the spectrum of the hexaquo ion the first band is shifted approximately 200 cm⁻¹, and the second band 300 cm⁻¹ towards red. The extinction coefficients for the complex differed essentially from those of the aquo ion only in the region < 250 mμ.

The question as to whether or no perchlorate ion forms metal complexes in aqueuos solution is of considerable interest because this ion is extensively used to regulate the ionic media in studies of complexes in solution. Many papers have appeared on the topic.[1-11] In 1932 Duval[1] reported the preparation of the complex [Co(NH₃)₅ClO₄] (ClO₄)₂. Subsequently other workers[2-8] who have studied the complexing properties of the perchlorate ion in solution have failed to distinguish conclusively between "outer" and "inner" sphere complexation. Infrared measurements[9,10] have been used to show that, in some anhydrous and partly hydrated transition metal perchlorates, the perchlorate

ion is covalently bound to the metal ion. However, this does not prove that such complexes exist in aqueous solution. Harris and coworkers [11] concluded from spectroscopic and conductivity measurements in nitrobenzene that the perchlorate ion is complexed to the metal ion in anhydrous bis (2,2'-dipyridyl) copper(II) perchlorate. This study is again in a different environment and cannot be taken as conclusive evidence for the formation of perchlorato-metal complexes in aqueous solution.

Linhard [12] has demonstrated that the presence of certain anions in solution can cause marked changes in the absorption spectra of tripositive Co(III) and Cr(III) complex ions in the wavelength region of the strong ultraviolet band. These changes occur immediately, and this phenomenon was first used by Posey and Taube,[13] and more recently by Fogel et al.[14] to distinguish between "outer" and "inner" sphere complex formation. If in the study of the hexaquochromium(III) perchlorate system one makes similar assumptions (that an immediate change in the ultraviolet spectrum is due to "outer" sphere complexation, whilst a time dependent change is due to "inner" sphere complexation) then it should be possible to distinguish between the two kinds of associations and to conclude whether or no true perchlorato complexes are formed. In the present study, slow changes in the ultraviolet spectrum of the hexaquochromium(III) ion in concentrated perchloric acid solutions have been found to occur, and this phenomenon has been interpreted as being due to the formation of a perchlorato complex.

EXPERIMENTAL

A stock solution of spectroscopically pure hexaquochromium(III) perchlorate was prepared from *pro analysi* chemicals (Riedel-de Haën) by reduction of a weighed amount of chromium trioxide (40 g) in 4 M perchloric acid (500 ml) with 30 % hydrogen peroxide. The excess peroxide and intermediate products were destroyed by refluxing the solution for 24 h. The solution was then made up to one litre. The composition of the solution was according to the preparation: $C_{Cr(ClO_4)_3} = 0.40$ M, $C_{HClO_4} = 0.80$ M. The chromium concentration was determined to be 0.3994 M spectrophotometrically after oxidation with alkaline hydrogen peroxide. The spectrum (given in Fig. 2) agreed well with those published in the literature for the hexaquo ion.[14-16]

A selected one litre sample of 70 % perchloric acid (Merck's *pro analysi*) which was shown to be sufficiently optically clean in the ultraviolet region down to 220 mμ (optical density in a 1 cm cell < 0.07) was used in the experiments.

The spectrophotometric data were recorded on a "Cary 14" recording spectrophoto-meter, fitted with a thermostated cell holder. Temperatures were regulated to $\pm 0.1°$ by means of a Lauda ultra-thermostat (Messgeräte-Werk Lauda), and for temperatures below 15° by means of a Lauda ultracryostat.
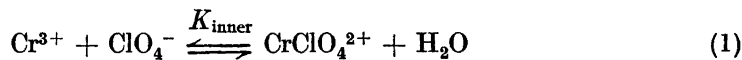
The solutions to be measured were made in the following manner:

(a) In the study of the formation of perchlorato complexes, 2 ml of the standard stock solution of hexaquochromium(III) perchlorate was diluted with the concentrated perchloric acid (70 %) to 20 ml (care being taken in the initial stages to eliminate the heat of mixing, by cooling the solutions in a salt-ice bath). A similar solution was used as a blank, but with 2 ml 2.0 M perchloric acid substituted for the chromium(III) per-chlorate solution. The concentration of the perchloric acid in the blank solution was determined by titration with a standard base. This concentration was taken to be the total perchlorate ion concentration in the studied solution.
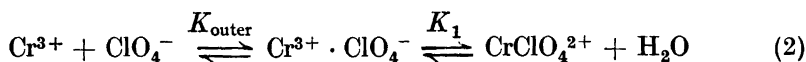
(b) For the study of the decomposition of the perchlorato complex a certain known volume of the above solution (after equilibrium had been attained) was transferred to a 10 ml standard volumetric flask, and made up to the mark with distilled water. Care was again taken with regard to the heat of dilution. A similar solution, but without the chromium(III) species, was used as a blank.

TREATMENT OF DATA AND RESULTS

The reaction between the hexaquochromium(III) ion and a perchlorate ion can be written as a one step reaction

$$Cr^{3+} + ClO_4^- \overset{K_{inner}}{\rightleftharpoons} CrClO_4^{2+} + H_2O \tag{1}$$

or as a two step reaction

$$Cr^{3+} + ClO_4^- \overset{K_{outer}}{\rightleftharpoons} Cr^{3+} \cdot ClO_4^- \overset{K_1}{\rightleftharpoons} CrClO_4^{2+} + H_2O \tag{2}$$

where K_{inner}, K_{outer}, and K_1 are the equilibrium constants for the reactions in question (complexed water has been excluded for simplicity). The expression,

$$K_1 = [CrClO_4^{2+}] \, a_{H_2O}/[Cr^{3+} \cdot ClO_4^-]$$

is assumed to be valid (a_{H_2O} is the activity of water).

In the light of more recent studies on the mechanism of complex formation, the second scheme appears to be the more reasonable.[13,14,17] Assuming, as is usual for such a reaction scheme, that the "outer" sphere equilibrium is established instantaneously, and that the second equilibrium is the rate determining step, it is suggested that the kinetic expression for the formation of the monoperchlorato complex is given by

$$\frac{d[CrClO_4^{2+}]}{dt} = k_1 \, [Cr^{3+} \cdot ClO_4^-] - k_{-1} \, [CrClO_4^{2+}]a_{H_2O}$$

where k_1 and k_{-1} are the rate constants for the forward and the reverse reactions, respectively. Since very high perchloric acid concentrations have been used, it is reasonable, as a first approximation, to try the simplifying assumption that the formation of the ion-pair is complete, so that

$$C_{Cr(ClO_4)_3} = [Cr^{3+} \cdot ClO_4^-] + [CrClO_4^{2+}].$$

Table 1. Kinetic data for the formation of the perchloratochromium(III) complex. The rate was followed spectrophotometrically, by measuring the change in the optical density (D_t) with time, at 235 mμ in a 2 cm quartz cell. First reading ($t = 0$), after 5 min temperature equilibration in the cell compartment.

$$C_{Cr(ClO_4)_3} = 0.040 \text{ M}, \ C_{HClO_4} = 10.63 \text{ M}, \ 9.8° \pm 0.1°.$$

t (min)	D_t	$\ln \dfrac{D\infty - D_0}{D\infty - D_t}$	$k_{app} \times 10^4$ (sec^{-1})
0	0.275		
40	0.320	0.1148	0.483
70	0.350	0.1994	0.485
130	0.420	0.4299	0.550
190	0.470	0.6357	0.550
357	0.555	1.1230	0.501
505	0.605	1.5857	0.501
4315 (∞)	0.690		
		Average	0.517 $\pm$ 0.027

Table 2. Kinetic data for the decomposition of the perchloratochromium(III) complex. The rate was followed spectrophotometrically at 230 mμ in a 2 cm quartz cell after dilution of the equilibrium solution from the experiment in Table 1 to the appropriate concentrations.

First reading ($t = 0$), after 5 min in the cell compartment.
$C_{Cr(ClO_4)_3} = 0.0328$ M, $C_{HClO_4} = 8.709$ M, $9.8° \pm 0.1°$.

t (min)	D_t	$\ln \dfrac{D\infty - D_0}{D\infty - D_t}$	$k_{app} \times 10^4$ (sec^{-1})
0	0.495		
10	0.430	0.1932	3.22
25	0.365	0.4329	2.89
40	0.320	0.6405	2.68
55	0.280	0.8701	2.49
75	0.240	1.1686	2.59
95	0.210	1.4709	2.58
125	0.175	2.0015	2.66
155	0.155	2.5123	2.69
1540 (∞)	0.125		
		Average	2.72 $\pm$ 0.16

In that case one has a system of reversible pseudo first order reactions for which

$$k_{app} = k_1 + k_{-1}a_{H_2O}$$

where k_{app} is the apparent rate constant which is measured experimentally for the formation reaction ($k_1[Cr^{3+} \cdot ClO_4^-] > k_{-1}[CrClO_4^{2+}]a_{H_2O}$) as well as for the decomposition reaction ($k_1[Cr^{3+} \cdot ClO_4^-] < k_{-1}[CrClO_4^{2+}]a_{H_2O}$).

Since the activity of water in perchloric acid solutions is known,[18] the validity of this reaction scheme can be demonstrated by a straight line plot of k_{app} against a_{H_2O}, if we assume that k_1 and k_{-1} remain constant in the medium range studied.

Table 3. Summary of the values of k_{app} obtained for various perchloric acid concentrations at two temperatures. The water activities (in the last column) were interpolated from the data given by Robinson and Baker [18] at 25°.*

$C_{Cr(ClO_4)_3}$ (M)	C_{HClO_4} (M)	Temp.	$k_{app} \times 10^4$	a_{H_2O}
0.0400	10.63	20	1.85	0.015
0.0360	9.57	20	5.02	0.063
0.0320	8.50	20	8.99	0.150
0.0257	6.82	20	18.0	0.340
0.0200	5.32	20	27.6	0.543
0.0400	10.63	9.8	0.52	0.015
0.0328	8.71	9.8	2.69	0.126
0.0265	7.04	9.8	6.52	0.316
0.0200	5.32	9.8	10.80	0.543

* The total perchlorate concentration ($C_{HClO_4} + 3\ C_{Cr(ClO_4)_3}$) was inserted for C_{HClO_4} when calculating a_{H_2O}, and for the most concentrated perchloric acid solution (10.63 M) the value given was obtained by linear extrapolation.
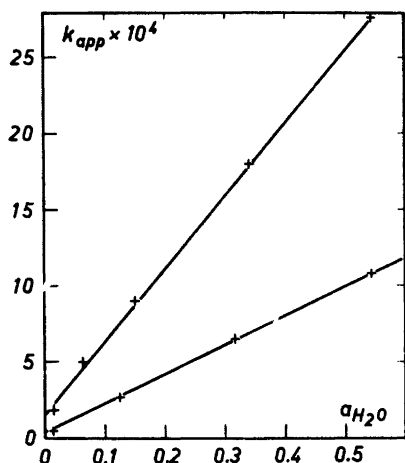
Fig. 1. Linear plots of the apparent rate constant (k_{app}) *versus* the water activity at 9.8° and 20°.

The experimental results are given in Table 1 for the formation of the perchlorato complex in 10.63 M perchloric acid solution at 9.8°. Table 2 gives the data obtained in the study of the decomposition in 8.71 M perchloric acid at the same temperature. In these, as well as in other experiments at 9.8° and 20°, k_{app} was found to be a constant (within experimental error) showing the reactions to be pseudo first order. A summary of all the experiments made for perchloric acid concentrations in the range 5 to 11 M is given in Table 3, and the plots of k_{app} *versus* a_{H_2O} are recorded in Fig. 1.

From the simple theory presented here the slopes of the straight lines obtained should give the rate constant of the decomposition, whilst the intercept should give the constant of the formation of the complex. In this way the following values were obtained for the rate constants (time in sec): $k_1 = 4.0 \times 10^{-5}$, $k_{-1} = 1.90 \times 10^{-3}$ at 9.8°, and $k_1 = 1.6 \times 10^{-4}$, $k_{-1} = 4.83 \times 10^{-3}$ at 20°.

DISCUSSION

It is generally assumed that the reactivity of an aquometal ion is dependent on the rate of exchange of its coordinated water molecules. [17],[19] From this point of view, the rate constants k_1 obtained for the formation of the per-chlorate complex seem to have rather high values for a reaction involving the hexaquochromium(III) ion. Thus, at 20° the half-time of formation of the monoperchlorato ion was 1.2 h compared to $t_{1/2} = 80$ h for the water exchange in a chromium(III) perchlorate solution ($C_{Cr(ClO_4)_3} = 1.1$ M, $C_{HClO_4} = 0.37$ M).[20] However, Plane and Taube [20] have measured the rate of water exchange for the hexaquochromium(III) ion at different perchlorate ion concentrations ($C_{ClO_4^-}$ varied from 1.8 M to 5.2 M) and found a more than threefold increase in the rate, on going to the concentrated solution. Since the rate of water exchange varies with the concentration of the salt media, it is not too surprising that a much faster rate of reaction is observed in 10.63 M perchloric acid solution. A similar fast rate of reaction was observed

in a concentrated sulphuric acid solution (13 M) with about the same water activity ($a_{H_2O} \sim 0.02$). The kinetics of this system were rather complicated, but equilibrium was established in two days (see equilibrium spectrum given in Fig. 2).

From the values of the rate constants obtained at 9.8° and 20°, the activation energy for the formation of the monoperchlorato ion was estimated to be 22.7 kcal/mole. This value seems to be of a reasonable order of magnitude, especially as Plane and Taube [20] have found 23—26 kcal for the activation energy for the exchange of water in the hexaquo ion. The activation energy for the dissociation of the perchlorato complex was calculated from the rate constants to be 15.3 kcal, and for the endothermic equilibrium reaction,
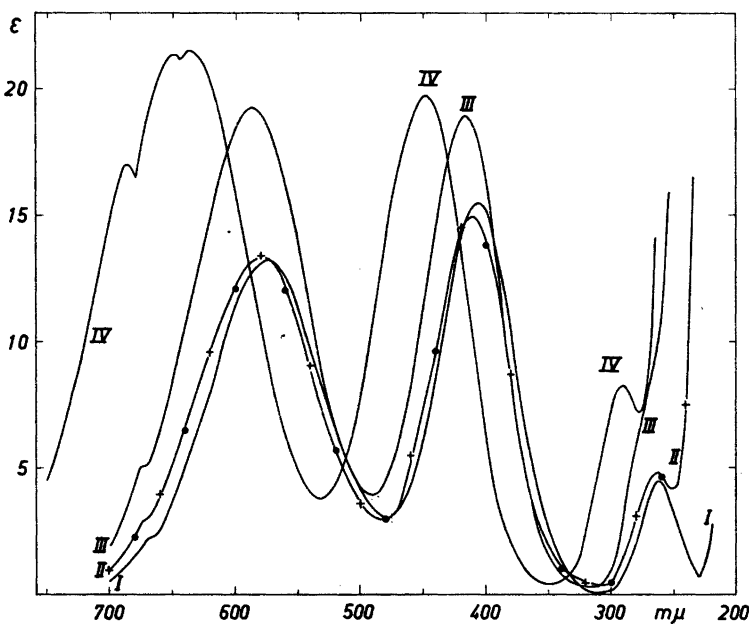
$$Cr^{3+} \cdot ClO_4^- \rightleftharpoons CrClO_4^{2+} + H_2O$$

Fig. 2. The absorption spectra of various chromium(III) species. Molar extinction coefficients *vs.* wavelength in mμ.
I. Spectrum of the hexaquochromium(III) ion: $C_{Cr(ClO_4)_3} = 0.040$ M, $C_{HClO_4} = 1$ M.
II. Calculated spectrum of the monoperchloratochromium(III) ion. The full-drawn curve is an average curve of values calculated at 9.8° (●-points), and 20° (+-points).
III. Spectrum of an analyzed sample of the monosulphatochromium(III) ion: $C_{CrSO_4^+} = 0.060$ M. A sample of $Cr_2(SO_4)_3 \cdot 18H_2O$ was heated to constant weight in a hygrostat at 80°. A portion of the resulting solid was dissolved in 0.1 M $HClO_4$, and the mono-sulphato complex was separated from the mixture on a cation exchange column using Amberlite CG—120, H⁺, and measured before any decomposition had taken place. The spectrum recorded agreed well with that given by Fogel *et al.*[14]
IV. Spectrum of an equilibrium solution of hexaquochromium(III) perchlorate in 13 M H_2SO_4: $C_{Cr(III)} = 0.040$ M.

the values $\Delta H = 22.7 - 15.3 = 7.4$ kcal/mole, and $\Delta S° = 19$ e.u. were estimated. The corresponding figures for the reaction

$$Cr^{3+} \cdot SO_4^{2-} \rightleftharpoons CrSO_4^+ + H_2O$$
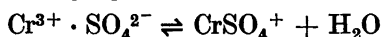
as given by Fogel et al.[14] are $\Delta H = 7.2$ kcal/mole, and $\Delta S° = 29$ e.u. From these figures it would appear that the entropy term is mainly responsible for the higher stability of the sulphato complex.

The spectrum of the monoperchloratochromium(III) complex given in Fig. 2 was calculated from the equilibrium spectrum in the most concentrated perchloric acid solution (10.63 M), in which more than half of the chromium is thought to be present as monoperchlorato complex. The following assumptions were made: (1) That ion-pair formation is complete so that the kinetically derived apparent equilibrium constants $K_1 = k_1/k_{-1} : K_1$ (9.8°) $= 2.1 \times 10^{-2}$, and K_1 (20°) $= 3.3 \times 10^{-2}$, could be used to calculate the concentration of the monoperchlorato complex. (2) That the spectrum of the "outer" sphere complex does not differ essentially from that of the hexaquo ion.

The first assumption is reasonable for a 3−1 electrolyte, and the second assumption is supported by the fact that the spectra of the equilibrium solutions in 5 to 7 M perchloric acid had extinction coefficients in the far ultraviolet region which were only slightly different from those of the hexaquo ion in 1 M $HClO_4$ (see Table 4). It was also noteworthy that, immediately after mixing, the colour in 10.63 M perchloric acid was indistinguishable from that of the hexaquo ion, and then gradually became greenish.

The spectra of the monoperchlorato ion estimated in this way at 9.8° and 20° are seen to agree fairly well with each other. In order to check the validity of this spectrum we have tried to recalculate K_1 from the equilibrium spectra in 9 to 7 M $HClO_4$. This calculation showed that K_1 at 9.8° decreased from 2.1×10^{-2} in 10.63 M $HClO_4$ to 0.3×10^{-2} in 7.0 M $HClO_4$, and at 20° from 3.3×10^{-2} in 10.63 M $HClO_4$ to 0.4×10^{-2} in 6.8 M $HClO_4$. The reason for this drift is that the extinction coefficients of the equilibrium solutions (see Table 4) show a much too strong dependence on the water activity. However, it must be remembered that we have completely neglected any influence of the perchlorate ion activity, which changes markedly in the concentration range studied. The discrepancies must be ascribed to the defi-

Table 4. Equilibrium values for the molar extinction coefficients of chromium(III) perchlorate in strong perchloric acid solutions.

	Wavelength range $250-230$ mμ. Temp. 20°.					
C_{HClO_4}	10.63	9.57	8.50	6.82	5.32	1.00
$C_{Cr(ClO_4)_3}$	0.040	0.036	0.032	0.0257	0.020	0.040
a_{H_2O}	0.015	0.063	0.150	0.340	0.543	0.96
ε_{250}	3.86	3.12	3.26	3.23	3.25	3.12
ε_{240}	6.40	2.29	1.81	1.59	1.55	1.50
ε_{235}	12.5	3.19	1.68	1.09	1.05	0.91
ε_{230}	24.8	5.90	2.39	1.03	0.90	0.69

Table 5. Main transitions for some chromium(III) species estimated from Fig. 2.

	1st Band λ (mμ)	2nd Band λ (mμ)	3rd Band λ (mμ)
$Cr(H_2O)_6^{3+}$	574	407	263
$CrClO_4^{2+}$	580	412	266
$CrSO_4^+$	588	418	280 [b]
$Cr(HSO_4)_n^{3-n}$	648 [a]	449	291

[a] Midpoint of the band below the spin-forbidden structure.
[b] Shoulder.

ciencies in the very rough assumptions which underlie the treatment of the kinetic data in this paper.

In Fig. 2 the spectrum of the monoperchlorato ion is compared with that of the hexaquo ion, the monosulphato ion, and that of the chromium(III) complex in 13 M H_2SO_4. The locations of the three bands of interest in the above spectra are given in Table 5. The bathochromic shift accompanying the formation of the perchlorato complex ($\sim$ 200, and $\sim$ 300 cm^{-1} in the 1st and 2nd band, respectively) is seen to be about half of the shift caused by the sulphato group in the monosulphato complex, and many times smaller than that caused by the complex in 13 M H_2SO_4. The ratio of wavenumbers of the 2nd to the 1st band is somewhat higher for the last mentioned complex ($\nu_2'/ \nu_1' = 1.44$ compared to 1.41 for the monosulphato complex, which may be partly chelated [21]). As ν_2'/ ν_1' is assumed to increase with decreasing covalency of the bond,[22] this gives further support for the assumption that the complex in strong sulphuric acid solutions contains monodentate-bound hydrogensulphato groups: $Cr(HSO_4)_n^{3-n}$ with $n \rightarrow 6$. With regard to the perchlorate ion, which in some respects is comparable with the bisulphate ion, the linear relationship found between the apparent rate constant and the water activity strongly supports that this ligand is also monodentate-bound.

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