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Equilibrium Constants of Chromium(III) and Chromium(II) Inner- and Outer-Sphere Complexes with Chloride, Bromide, and Iodide Ions

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The electrochemical method was found to be very easy and relatively rapid in determining the equilibrium contants of outer-sphere complexes (ion pairs) of Cr(III) ions. (The terms "ion pairs" and "outer-sphere complexes" are used as synonyms.) It has been found that in halogen solutions ($X = Cl^-, Br^-, I^-$) only outer-sphere complexes of the type $Cr^{III}Cl$ are formed, having an equilibrium constant equal to 4.0 M^{-1}, and formation of other Cr(III) and Cr(II) complexes is negligibly small. Inner-sphere complexes of Cr(III) ions with X are easily formed during oxidation of Cr(II) ions at the mercury electrodes. From the formal potentials of the reaction $Cr(II) + X = Cr^{III}X + e^-$ and the formal potentials of the reaction $Cr(II) = Cr(III) + e^-$ measured in the presence of X, the inner-sphere equilibrium constants for $Cr^{III}X$ complexes were calculated. They were equal to 0.086, 2.1×10^{-3}, and 1.1×10^{-5} M^{-1} for chloride, bromide, and iodide complexes, respectively.

Introduction

Equilibrium constants of the chromium(III) inner-sphere complexes of the type $Cr^{III}X$ ($X = Cl^-, Br^-, I^-$) have been investigated for a long time. Most of these works have been carried out by spectrophotometric methods.[1-6] Due to inertness of Cr(III) ions[7] in most of these works long-lasting equilibration procedures have been used, accompanied by an ion-exchange separation of the inner-sphere complexes, followed by spectrophotometric analysis of the products. Particularly in the case of CrI^{2+} the whole experiment[6] should be carried out very carefully due to a rather high lability of this complex, absorbance of iodide ion itself, and possible oxidation of iodide to iodine.

Chromium(III) inner-sphere complexes with halogen ions have also been investigated by electrochemical methods.[8-13] It has been shown that the halogen ions enhance the rate of oxidation of Cr(II) ions at the mercury electrodes by a ligand-bridging mechanism[8-10] and the inner-sphere complexes of the type $Cr^{III}X$ are the products of Cr(II) ion electrooxidation.[11,12]

The formal potentials of the electrode process

$$Cr(II) + X = Cr^{III}X + e^- \qquad (1)$$

calculated from CV curves are more positive than the standard potential of the Cr(III)/Cr(II) couple, which indicates the thermodynamic instability of the $Cr^{III}X$ complexes. From the experimental point of view electrochemical investigations on the Cr(III)/Cr(II) couple are simple. However, the inner- and outer-sphere equilibrium constants have not been calculated from the results of electrochemical experiments, since equilibrium constants for Cr(II) ions were not known.

The aim of this work has therefore been to project such electrochemical experiments and a method of analysis of experimental data that would enable us to use electrochemical data for calculation of both inner- and outer-sphere equilibrium constants of Cr(III) and Cr(II) ions with halogen ions. The results obtained could be interpreted in a simple way, and the values of the equilibrium constants showed very good agreement with those obtained previously by spectrophotometric methods.

Experimental Section

Apparatus. A three-compartment cell was employed in which the reference electrode was isolated from the hanging-mercury-drop electrode (HMDE, Brinkman Instruments, Inc.), the Kemula–Kublik type homemade electrode, or the dropping-mercury electrode (DME). The mercury flow rate for the DME was 0.090 mg s^{-1}.

In polarographic and cyclic voltammetry (CV) experiments, a Pt wire served as the auxiliary electrode. This electrode was separated from the solution studied by two sintered-glass frits.

Cr(III) solution was reduced electrolytically at the mercury pool. In these experiments the auxiliary electrode (Pt wire) was isolated from the mercury pool by two sintered-glass frits.

Polarographic and CV curves were recorded by using an appropriate combination of instruments from PAR (Models 173–175), E.G. & G. Inc. (Model 179), Textronix (oscilloscope), and Radelkis (polarograph OH-105). In the latter case the $Tl^+/Tl/Hg/$ electrode process was used as a standard reversible reaction. The anodic and cathodic peak potentials for chromium electrode processes were corrected in relation to CV curves obtained for this process.

Equilibrium potentials were measured with a V533 digital multimeter (Meratronik). Potentials were measured and are quoted with respect to a sodium chloride SCE. All experiments were made at room temperature (25 ± 2 °C).

Solutions were deaerated with argon purified by passage through two bubbling washers containing V(II) ions.

Spectra were recorded with a SPECORD UV–vis spectrophotometer.

Materials. Chromium(III) perchlorate was prepared by a reaction between CrO_3 and H_2O_2 and a threefold crystallization from $HClO_4$. After the third crystallization the absorbance ratio at 230 and 260 nm was equal to ca. 0.26. According to Altman and King,[19] this corresponds to a negligible quantity of polymeric Cr(III) species in the stock solution. According to these authors, the solution is free from polymeric species when this ratio is close to 0.22.

Solutions of halogen ions were prepared from sodium salts of p.a. chemicals (POCh) crystallized from triply distilled water. Triply

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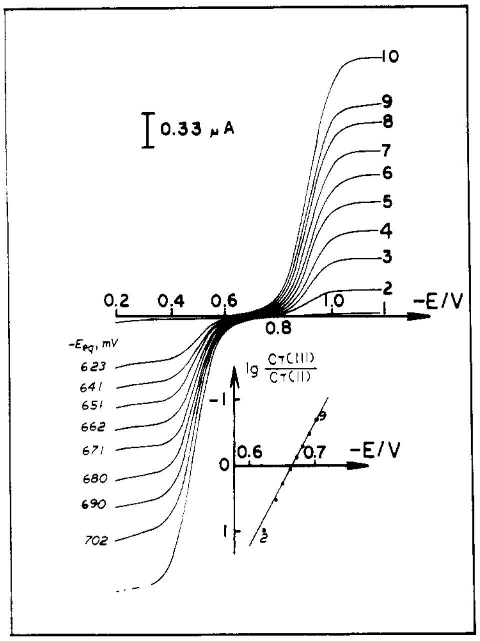

Figure 1. Polarographic anodic–cathodic curves obtained after step-by-step reduction of Cr(III) ions in 0.2 M solution of NaCl (μ = 1.0 M). At each anodic curve the equilibrium potentials are given. Dependence of this potential on log [[Cr(III)]/[Cr(II)]] is given in the lower part of this figure. Curve 1 corresponds to a background current. Supporting electrolyte: 0.2 M NaCl + 0.1 M $HClO_4$ + 0.7 M $NaClO_4$.

distilled mercury was used. Supporting electrolyte solutions were prepared from water distilled three times. The third distillation was carried out from an all-quartz still.

The procedure of synthesizing the $CrBr^{2+}$ complex was essentially the same as that described[27] by Moore and Basolo.

The content of Cr(III) was determined spectrophotometrically as chromate (ϵ 4815 at λ 375 nm). Perchlorate solutions were prepared by neutralizing Na_2CO_3 with $HClO_4$.

Results

Measurements of the Equilibrium Potentials of the Electrode Reaction Cr(III)/Cr(II) in Solutions of Cl^-, Br^-, and I^- Ions. Measurements of the equilibrium potentials of the electrode reaction Cr(III)/Cr(II) were carried out in solutions of 0.1 M $HClO_4$ having a constant ionic strength of 1.0 M ($NaClO_4$). The concentration of halogen ions was changed from 0.01 to 0.9 M. Concentration of Cr(III) ions was kept constant and was equal to about 7 mM. The solutions under study were carefully deaerated. In solutions of more concentrated iodides (0.5 and 0.9 M), usually small cathodic currents were recorded that were probably derived from the traces of free iodine. In such cases, deaeration was accompanied by electrolysis at −1.0 V, at the mercury pool, for at least 1 h. After the electrolysis no cathodic current was found. To such solution was added a known quantity of Cr(III), and deaeration was carried out without any electrolysis.

Cr(III) ions were reduced at the mercury pool at potentials close to −1.0 V. After a charge of approximately 2 C was passed, the electrolysis was stopped and the anodic–cathodic polarographic waves were recorded. Then, the equilibrium potential was measured with an HMDE. In solutions free of halogen ions, the potential reached a constant and reproducible value within 1–3 min. In solutions containing halogen ions, the potential reached a constant value much faster, in some cases almost instantaneously.

Measurements of the equilibrium potential were carried out at least three times, and they were reasonably reproducible (±2 mV).

Table I. Formal Potentials of the Electrode Process Cr(III) + e^- = Cr(II) in Solutions Containing Halides

anion	C ([X]), M	$-E_f°$, V	slope,[a] mV
		0.650	64
Cl^-	0.01	0.651	64
	0.1	0.661	60
	0.2	0.668	52
	0.5	0.677	45
	0.7	0.684	46
	0.9	0.690	40
Br^-	0.01	0.641	60
	0.1	0.645	67
	0.2	0.641	60
	0.4	0.644	68
	0.5	0.647	62
	0.9	0.638	51
I^-	0.01	0.650	62
	0.1	0.652	62
	0.5	0.652	67
	0.9	0.648	66

[a] Slope of dependence of log [[Cr(III)]/[Cr(II)]] on E.

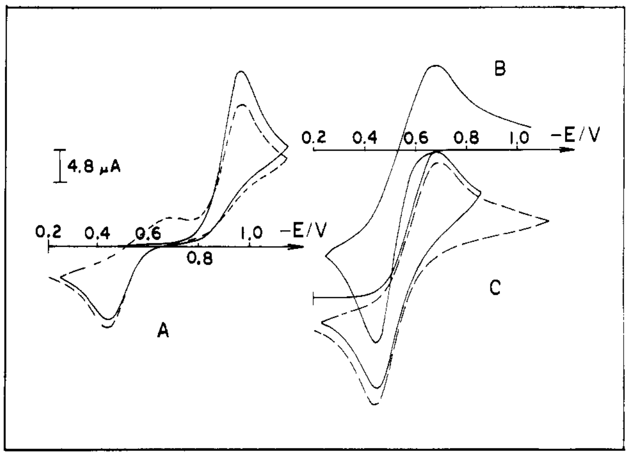

Figure 2. Cyclic voltammetry (0.2 M NaCl; μ = 1.0 M; scan rate 2 V/min): (A) ~7 mM Cr(III); (B) solution after a complete reduction of Cr(III) to Cr(II); (C) solution B after oxidation of Cr(II) ions at the mercury pool at −0.2 V.

Then, Cr(III) solution was reduced step-by-step, and 6–8 equilibrium potentials were measured for every solution. As a measure of concentrations of Cr(III) and Cr(II) ions, the limiting maximum cathodic and anodic currents were used. The ratio of diffusion coefficients of those ions was estimated to be close to 0.9; thus, the error connected with this procedure was not higher than 1.5 mV. An example of such a procedure is shown in Figure 1.

In solutions of NaI the concentration of Cr(II) ions was calculated from cathodic currents of Cr(III) reduction only, since the determination of anodic current was not certain.

Table I contains all values of formal potentials together with slopes of dependences of log [[Cr(III)][Cr(II)]] on E.

These slopes are varied from 40 to 68 mV/log unit, and the average values are equal to 50, 61, and 62 mV/log unit for Cl^-, Br^-, and I^- solutions, respectively, i.e. close to the theoretical value of 59 mV/log unit.

Measurements of Formal Potentials of the Electrode Process Cr(II) + X = $Cr^{III}X$ + e^-. The formal potentials of reaction 1 were determined in two ways: from CV measurements and from measurements of the equilibrium potentials.

Cyclic Voltammetry Measurements. In the first case the CV curves were recorded (Figure 2). A new cathodic peak present in the second scan of curve A corresponds to reduction of the inner-sphere complex $CrCl^{2+}$. This complex is formed during oxidation of Cr(II) ions in the presence of halogen and pseudohalogen ions. The formation efficiency of this complex

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Table II. Cyclic Voltammetry, Polarographic, and Equilibrium Data for the Cr(II) + X = $Cr^{III}X$ + e^- Electrode Process

						$-E_f°$			
anion	C ([X]), M	$-E_{pa}$, V	$-E_{pc}$, V	β[a]	α[a]	CV, V	equil pot., V	slope,[b] mV	$-E_{1/2}$,[c] V
				ν = 2 V/min					
Cl^-	0.01	0.310	0.690	0.45	0.38	0.485	0.490	76	0.360
	0.1	0.420	0.690	0.53	0.40	0.535	0.540	67	0.455
	0.2	0.450	0.690	0.58	0.40	0.550	0.550	61	0.485
	0.5	0.490	0.690	0.59	0.40	0.570	0.570	62	0.520
	0.7	0.500	0.690	0.60	0.40	0.575	0.575	58	0.535
	0.9	0.520	0.690	0.60	0.40	0.590	0.585	60	0.545
Br^-	0.01	0.340	0.400			0.370			0.345
	0.1	0.400	0.460			0.430	0.460	77	0.425
	0.2	0.415	0.475			0.445			0.440
	0.4	0.440	0.500			0.470	0.520	96	0.465
	0.5	0.440	0.510			0.475	0.520	80	0.465
	0.9	0.460	0.515			0.490	0.530	87	0.475
$CrBr^{2+}$	0.5	0.445	0.510			0.480	0.500	63	0.475[d]
				ν = 5 V/s					
I^-	2.8[e]	0.200	0.290			0.245			
	6.4[e]	0.205	0.305			0.255			
	10.0[e]	0.230	0.300			0.265			
	14.0[e]	0.240	0.325			0.280			
	21.0[e]	0.250	0.305			0.280			
	50.0[e]	0.260	0.340			0.300			

[a] Taken from ref 20. [b] Slope of dependence of log [[$Cr^{III}X$]/[Cr(II)]] on E. [c] Anodic $E_{1/2}$. [d] Cathodic $E_{1/2}$. [e] Concentration in units of mM.

is equal to 100%, when the ratio of chloride to Cr(III) ions concentrations is higher[10,11,14] than one. This condition was fulfilled for all experiments.

Figure 2 shows the CV curves recorded in this solution after the complete reduction of Cr(III) ions (curve B) and after oxidation of Cr(II) ions at the mercury pool at potentials corresponding to the limiting currents of Cr(II) (curve C). The potentials at which the oxidation of Cr(II) ions was carried out was usually by at least 0.1–0.2 V more positive than the anodic peak potential.

In all cases the cathodic E_{pc} and anodic E_{pa} peak potentials corresponding to reduction and oxidation of $Cr^{III}X$ complexes are within limits of experimental error (±5 mV). The values of these potentials are collected in Table II.

For bromide ions the difference $\Delta E_p = E_{pa} - E_{pc}$ is constant and equal to about 60 mV for all concentrations of Br^-. As follows from the data presented in Table II, for bromide ions there is good agreement between the average of anodic and cathodic peak potentials and the half-wave potentials of Cr(II) ions oxidation and reduction of $CrBr^{2+}$ complex. Thus, the electrode process (1) in the presence of bromide ions should be regarded as a reversible one.

In the presence or iodide ions the CV curves were recorded for smaller concentrations of I^- within the range from 2.8 to 50 mM. These curves were quite similar to those presented[10] by Ulrich and Anson.

A typical CV curve redrawn from the oscilloscope screen for a 6.4 mM solution of iodide ions is presented in Figure 3A. As the reverse potential is made more positive, one observes the anodic peak of mercury oxidation (curve B). In this solution, the difference between the anodic peak potentials of Cr(II) and mercury oxidation is on the order of 0.12 V. At concentrations of iodide higher than 50 mM, oxidation of Hg caused difficulties in determining the anodic and cathodic peak potentials with tolerable precision. In all these cases the concentration of Cr(III) ions was on the order of 1 mM. CV curves were recorded at scan rates of 0.5–10 V/s. At lower scan rates the ratio i_{pc}/i_{pa} is lower than 1.[14]

The accuracy of the determined peak potentials was in this case lower and equal to ±15 mV. The differences between the peak potentials did not depend on the scan rate (1–5 V/s) and were equal to 60–80 mV. Thus, the electrode process (1) in the presence of iodide is very fast.

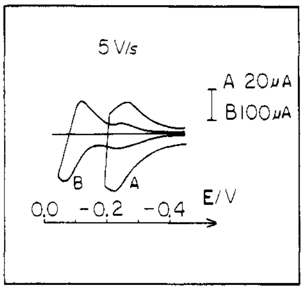

Figure 3. CV curves for 1 mM Cr(III) in 6.4 mM solution of iodides redrawn from an oscilloscope screen (μ = 1.0 M; starting potential -1.1 V/30 s; scan rate 5 V/s).

The formal potentials of the electrode process (1) in bromide and iodide solutions were calculated as an average of anodic and cathodic peak potentials. In chloride solutions the equation[28]

$$E_f° = (\beta E_{pa} + \alpha E_{pc})/(\alpha + \beta)$$

was used, where α stands for cathodic and β for anodic transfer coefficients (Table II).

The dependences of formal potentials on the logarithms of concentrations of halides are linear, along with the slopes not far distant from the slope of 59 mV for a 10-fold change in concentration of X, i.e. the value expected if the electrode processes were Nernstian ones and a single X ion were in-

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(28) This equation is a sum of two equations describing the peak potentials for irreversible processes (n = 1): cathodic, $(E_{pc} - E°)\alpha + (RT/F)[\ln((\pi D_{Ox}b_{Ox})^{1/2}(k_s))] = -0.005\,34$; anodic, $(E_{pa} - E°)\,\beta - (RT/F)[\ln((\pi D_R b_R)^{1/2}(k_s))] = 0.005\,34$, where $b_{Ox} = \alpha FV/RT$ and $b_R = \beta FV/RT$. This equation obtains on the assumption that $D_{Ox} = D_R$ and $\ln((\alpha/\beta)^{1/2}) \sim 0$. For $\alpha = \beta = 0.5$, we obtain $E° = (E_{pc} + E_{pa})/2$. Values of anodic transfer coefficients (β) were determined from the slopes of log k_{bh} vs. E (Koutecky's method). These dependences were linear over the whole region of potentials. β values were also calculated from the equation $\beta = (E_{pa} - E_{pa/2})/0.048$. Both methods gave almost the same results. Values of cathodic transfer coefficients (α) were determined from the equation $\alpha = (E_{pc/2} - E_{pc})/0.048$ and were, in practice, independent on Cl^- ions concentration. The same and constant values were obtained from the slope of log k_{fh} vs. E (impedance method) for higher Cl^- concentrations. Also in this case linear plots were obtained.

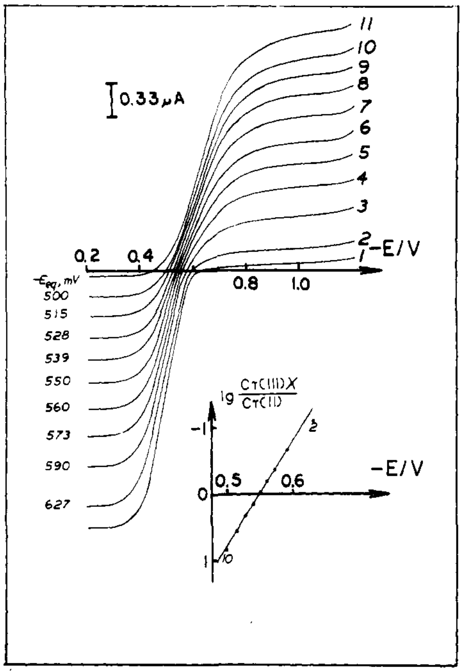

Figure 4. Polarographic anodic–cathodic curves obtained after step-by-step oxidation of Cr(II) ions at the mercury pool at −0.2 V. At each anodic curve the equilibrium potential is given. Dependence of log [[$Cr^{III}X$]/[Cr(II)]] on this potential is given in the lower part of the Figure (0.2 M NaCl; μ = 1.0 M).

corporated in the Cr(III) product but released while reduced. These slopes were equal to 51, 62, and 45 mV for Cl^-, Br^-, and I^- ions, respectively.

Measurements of the Equilibrium Potentials of Reaction 1. (1) Chloride Solutions. As Anson et al. have shown,[10,11] the only product of oxidation of Cr(II) ions at the mercury electrodes in presence of Cl^- ions is $CrCl^{2+}$ ions as long as the ratio [Cl^-]/[Cr(II)] is higher than one. This result was the basis for determination of the equilibrium potentials of reaction 1 and finally enabled us to determine the formal potentials of this reaction.

In this case, the solution of Cr(II) ions was oxidized step-by-step at the mercury pool kept at potentials 0.1–0.2 V more positive than the anodic peak potential. After every step the equilibrium potential was measured. An example of such a procedure is shown in Figure 4. As follows from the results presented in this figure, oxidation of Cr(II) results in small quantities of Cr_{aq}^{3+} ions.

At higher concentrations of $CrCl^{2+}$ the polarographic waves of $CrCl^{2+}$ and Cr_{aq}^{3+} reduction were not well separated. Thus, the determination of concentration of this ion was not very accurate. Cathodic currents were measured at potential equal to −0.8 V at which the Cr_{aq}^{3+} reduction current is small (cf. Figure 1). As follows from the results presented in Figure 4 for smaller $CrCl^{2+}$ concentrations, the cathodic current at this potential is not very much different from those measured at more negative values. Measurements of the current at different cathodic potentials did not much change the value of the formal potentials. For example, in a 0.2 M solution of chloride, the $E_f°$ value determined with the use of currents measured at −0.8 and −1.1 V were equal to −0.551 (slope 61 mV) and −0.555 V (slope 62 mV), respectively.

An important question arises how this small concentration of Cr_{aq}^{3+} ions may influence the measured equilibrium potential. To answer this question, oxidation of Cr(II) ions was carried out in the solution in which ca. 75% of Cr(III) ions were reduced. The formal potential determined in this case was by 2 mV more negative than that in the solution in which complete Cr(III) reduction was carried out. This result strongly suggests that Cr_{aq}^{3+} ions do not influence, to any large extent, the measured equilibrium potential. Due to the presence of Cr_{aq}^{3+} ions the equilbrium potentials are mixed. However, since the standard rate constants of reaction 1 are by almost 2 orders of magnitude higher than that of reaction 2, for $C_{Cl^-} > 0.1$ M the influence of Cr_{aq}^{3+} ions should not exceed 20 mV and decreases with a rise in Cl^- concentration. (I am grateful to one of the reviewers for drawing my attention to this problem.)

(2) Bromide Solutions. A procedure described above was used in solutions containing bromide ions. However, in this case after oxidation of Cr(II) ions at the mercury pool, the solution became cloudy. A detailed analysis of this suspension was not carried out, but it resembled rather small particles of mercury. The formal potential determined from the equilibrium potentials measured with the use of the HMDE was by 30–50 mV more negative than that calculated from the CV curves. Although the differences between the formal potentials determined by both of the methods were not far apart, we have decided to carry out measurements of the equilibrium potentials of reaction 1 using the synthesized $CrBr^{2+}$ complex. The formal potential was only 20 mV more negative.

(3) Iodide Solutions. In iodide solutions it was, in practice, impossible to observe formation of CrI^{2+} complexes during oxidation of Cr(II) ions at the mercury-pool electrode due to pronounced oxidation of mercury. Since aquation of this complex is much faster[23-25] than aquation of the $CrBr^{2+}$ ion, no attempts at measurement of the equilibrium potential of the system CrI^{2+}/Cr(II) have been carried out. Aquation of the CrI^{2+} complex is also catalyzed by Cr(II)[22] ions; therefore, attempts like that would be, probably, not successful.

Interpretation of Results and Discussion

Outer-Sphere (Ion-Pairing) Equilibrium Constants. The formal potentials of the system Cr(III)/Cr(II) presented in Table I may be explained in a rather simple way. Since no formation of the inner-sphere complexes of Cr(III) ions was observed, the determined formal potentials may be entirely ascribed to the outer-sphere fast interaction of Cr(III) ion with halogen ions and formation of halogen complexes of Cr(II) ions. The rate of water molecule exchange in the Cr(II) ion is high,[26] and it is difficult to distinguish between outer- and inner-sphere complexes of this ion.

The formal potential $E_f°$ of the system

$$\mathrm{Cr(III)} + e^- = \mathrm{Cr(II)} \tag{2}$$

in the presence of halogen ions may be described as follows (25 °C):

$$E_f° = E°[\mathrm{Cr(III)/Cr(II)}] + 0.059 \log \frac{1 + K_2\mathrm{X}}{1 + K_3°\mathrm{X}} \tag{3}$$

where

$$K_2 = \frac{[\mathrm{Cr^{II}X}]}{[\mathrm{Cr(II)}][\mathrm{X}]} \tag{4}$$

$$K_3° = \frac{[\mathrm{Cr^{III}X°}]}{[\mathrm{Cr(III)}][\mathrm{X}]} \tag{5}$$

K_2 is the equilibrium constant for Cr(II) complexes and $K_3°$ is the outer-sphere equilibrium constant for Cr(III) complexes.

Chloride Solutions. The formal potentials of reaction 2 are more negative than the standard potential of this reaction in the absence of halogen ions (Figure 5). A straight line drawn through the experimental points may be described by the equation $Y = 1.05 + 3.99[\mathrm{X}]$ (where $\log Y = -(E_f° - E°)/0.059$) with a correlation coefficient of $R = 0.996$. Thus, the $K_3°$ value may be estimated as equal to $K_3° = 4.0 \pm 0.4$ M^{-1}

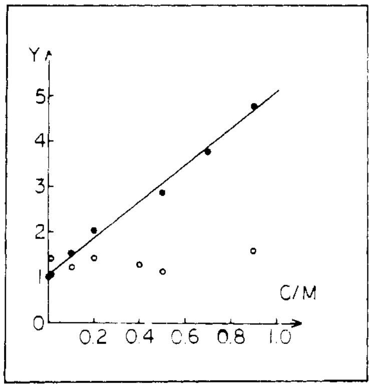

Figure 5. Dependence of $(1 + K_3{}^{o}X)/(1 + K_2X)$ (chlorides) or the reciprocal of this function (bromides) on concentration of X: chlorides, ●; bromides ○.

Table III. Outer-Sphere Equilibrium Constants for the $Cr^{III}Cl$ Complex

$K_3{}^{o}$, M^{-1}	μ, M	temp, °C	ref
0.30	4.4	25	1
0.88	1.0	25	2
1.5	1.0	25	16
4.0	1.0	25 ± 2	this work
13			17

(SD = 0.156, student distribution $t_{0.05,5} = 2.571$). Since the linear correlation between Y and [X] is highly probable (student test for correlation coefficient $t = 24.92 > t_{0.001,5} = 6.859$) and $Y = 1.05 \pm 0.14$ for [X] = 0 (SD = 0.53, same confidence level), one may conclude that the term $1 + K_2X$ is close to 1. Thus, K_2 should not be greater than 0.1 M^{-1}.

The value of $K_3{}^{o}$ obtained in this work is in fairly good agreement with earlier data (Table III).

Bromide and Iodide Solutions. The formal potentials of reaction 2 determined in bromide and iodide solutions are close to standard potentials of the Cr(III)/Cr(II) couple. In bromide solutions, the formal potentials are a bit more positive and deviations from the standard potential are higher than the experimental error. Experimental points (Figure 5) show a very poor correlation ($R = 0.504$) and, in practice, no dependence on Br^- ($Y = 1.20 + 0.31[Br^-]$). In our opinion this result shows that interactions of Br^- ions with both Cr(II) and Cr(III) ions may be neglected.

Similar conclusions may be drawn from the data obtained in iodide solutions.

Inner-Sphere Equilibrium Constants of Cr(III) with X. The formal potential of reaction 1 may be easily related to the equilibrium constant of this reaction. A combination of the formal potential of reaction 1 with E^{o} gives

$$E_f{}^{o} - E^{o} = -0.059 \log \frac{[Cr^{III}X^{i}]}{[Cr(III)][X]} \qquad (6)$$

For [X] = 1 M the right hand side of eq 6 is equal to $-0.059 \log K_3{}^{i}$, where $K_3{}^{i}$ is the inner-sphere equilibrium constant of $Cr^{III}X$. The formal potential of reaction 1 should be shifted toward more negative values with an increase in X, with a slope close to 0.06 V/log unit. Both of these conditions are fulfilled (Figure 6).

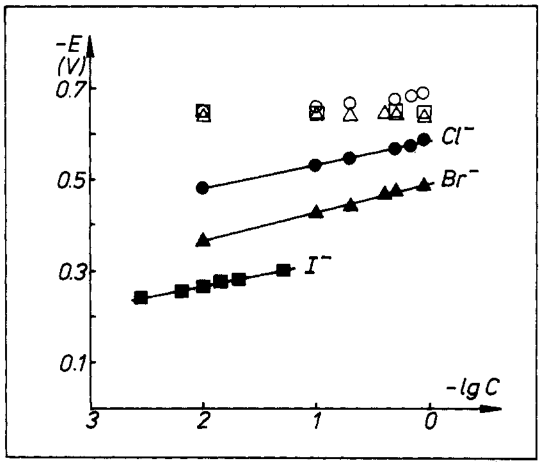

Figure 6. Dependence of formal potentials of reaction 2 (○, △, □) and reaction 1 (●, ▲, ■) on the logarithm of the concentration of halogen ions for solutions of chlorides (○, ●), bromides (△, ▲), and iodides (□, ■).

Table IV. Inner-Sphere Equilibrium Constants for Chromium(III) Halide Complexes

complex	$-E^{o}$, V	$K_3{}^{i}$, M^{-1}	μ, M	temp, °C	ref
$CrCl^{2+}$		0.105^{a}	4.44	25	1
		0.202^{b}	4.44	25	1
		0.22	1.0	40	2
		0.17	0.98	40	3
		0.09	0.96	30	4
	0.587	0.086^{c}	1.0	25 ± 2	this work
$CrBr^{2+}$		2.3×10^{-3}	2.0	25	5
	0.492	$2.1 \times 10^{-3\ c}$	1.0	25 ± 2	this work
CrI^{2+}		6.9×10^{-5}	4.2	25	6
		$1.0 \times 10^{-5\ d}$	1.0	25	6
	0.358	$1.1 \times 10^{-5\ c}$	1.0	25 ± 2	this work

[a] At $[Cl^-] = 4.4$ M. [b] At $[Cl^-] = 0$. [c] $K_3{}^{i}$ values were calculated directly from E^{o} values. The errors of E^{o} determination are equal to ±5, ±5, and ±15 mV for the chloride, bromide, and iodide ions, respectively. [d] Extrapolated.

The standard potentials of reaction 1 calculated for X = 1 M are presented in Table IV together with the calculated inner-sphere equilibrium constants. The values of these potentials are not very much different from those given[15] by Weaver and Anson, although these authors used not quite reliable equilibrium constants for Cr(II) ions and formally assumed equilibrium of Cr(III) ions with halogen ions. Only by using such an assumption can one get eq 13 in the paper by Weaver and Anson. Although eq 6 in this work and eq 13 in their paper are almost identical, one should remember that they were derived in different ways. Equation 6 has been obtained on the assumption that the inner-sphere complexes of Cr(III) are inert and when the CV curve is recorded they do not undergo any changes. Such an interpretation would be to some respect closer to that given by Watanabe et al.[13] These authors did not, however, interpret the equilibrium potential of their $CrBr^{2+/+}$ redox couple. In this work[13] appears also the equilibrium constant for Cr(II) with Br^- ions, which, as has been shown in the present work, may be neglected in practice.

As follows from a comparison of the results presented in Table IV the results obtained in the present work are in a very good agreement with the literature data. Good agreement between the results obtained in this paper and those obtained earlier seems to confirm the correctness of the method proposed.

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Registry No. Cr, 7440-47-3; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5.