

REDUCTION OF SOME ACIDOPENTAQUOCHROMIUM(III) COMPLEXES AT THE MERCURY ELECTRODE

EFFECT OF MAXIMUM SUPPRESSORS AND FREE LIGAND

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Abstract—The complexes $[\text{CrNCS}(\text{H}_2\text{O})_5]^{2+}$, $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$, $[\text{CrF}(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ were studied by polarography and cyclic voltammetry in aqueous solution. It is shown that Triton X-100 and gelatine shift the polarographic waves to more negative potentials. In 1M $\text{NaClO}_4\text{-HClO}_4$ the half-wave potentials in the absence of maximum suppressor are (in Volts vs. SCE): CrNCS^{2+} : -0.675 ; CrCl^{2+} : -0.62 ; CrF^{2+} : -1.105 ; Cr^{3+} : -0.90 (water omitted in the formula). All reductions are irreversible. Replacement of NaClO_4 by NaSCN makes the reduction of CrNCS^{2+} and CrCl^{2+} more reversible and shifts $E_{1/2}$ 50 mV per log $[\text{SCN}^-]$ unit to more negative potentials for CrNCS^{2+} and 66 mV for CrCl^{2+} . It is suggested that CrNCS^{2+} and CrCl^{2+} may be reduced via a mechanism analogous to the inner-sphere mechanism in homogeneous reductions.

INTRODUCTION

THE AIM of this study is to obtain more information about the factors which influence the reduction of acidopentaquo chromium(III) complexes at the mercury electrode.

Preparation, stability and rates of homogeneous substitution reactions of a number of these complexes have been described in the literature[1-3].

The polarographic behaviour, however, is much less understood and contradictory statements are found in the literature.

Walsh and Early [4] report a reversible wave for CrNCS^{2+} with $E_{1/2} = -0.88$ V vs. SCE in 0.1 M NaClO_4 with 0.002% gelatine. Replacement of NaClO_4 by NaSCN did not affect the reduction wave. For CrF^{2+} these authors report deviation of reversibility and $E_{1/2} = -1.05$ V.

Bustin and Early [5] report an irreversible reduction of CrNCS^{2+} in 1.0 M NaClO_4 with $E_{1/2} = -0.65$ V. In 1.0 M NaSCN $E_{1/2} = -0.685$ V. They report the occurrence of maxima which could be easily suppressed by Triton X-100. These authors do not state, however, whether they actually used this maximum suppressor. Gomba and Early (to be published, cited by Bustin and Early) report $E_{1/2} = -0.54$ V for CrCl^{2+} . Watanabe *et al.* [6] report an irreversible reduction

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with $E_{1/2} = -0.65$ V for CrCl^{2+} in $\text{HClO}_4\text{-HCl}$ and $\text{HClO}_4\text{-HBr}$ solutions ($\mu = 2.0$).

For this study we chose the complex ions $[\text{CrNCS}(\text{H}_2\text{O})_5]^{2+}$, $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$, $[\text{CrF}(\text{H}_2\text{O})_5]^{2+}$ and for comparison of results $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. These complexes are fairly stable and inert. They will be written as CrNCS^{2+} , CrCl^{2+} , CrF^{2+} and Cr^{3+} .

EXPERIMENTAL

Preparation[1, 2]

Only analytical grade chemicals were used. Both demineralized and double distilled water was used, but no difference in polarographic behaviour was found. Chromium(III) perchlorate solutions were prepared by precipitation of chromium hydroxide from chromium sulfate solution with sodium hydroxide, filtration and redissolution in perchloric acid. The complexes CrNCS^{2+} , CrCl^{2+} and CrF^{2+} were prepared by heating equimolar amounts of chromium(III) perchlorate and potassium thiocyanate, chloride or fluoride in dilute perchloric acid.

After cooling and filtration of the precipitated potassium perchlorate, the complex was isolated by cation exchange separation on Dowex 50W with perchloric acid as eluting agent.

Conventional analytical procedures were used to determine the concentration and to confirm the 1:1 composition of the complexes. Spectra were in accordance with literature. Solutions of CrNCS^{2+} and CrF^{2+} in dilute HClO_4 remained unchanged for several months. CrCl^{2+} solutions had to be stored at low temperatures and experiments had to be done within a few days.

Electrochemical measurements

All electrochemical measurements were carried out with the Beckmann "Electroscan 30" electro-analytical system, using a three-electrodes system. Mainly Metrohm vessels and electrodes were used. The saturated calomel electrode which was used as reference-electrode, was separated from the electrolysis solution by a salt bridge of 1M NaClO_4 in 3 per cent Agar. The SCE dipped in a 1M NaCl solution. When the SCE dipped in a 1M NaClO_4 solution, a potential difference of up to 40 mV was formed at the KCl-NaClO_4 interface, due to the precipitation of KClO_4 . This effect shifts $E_{1/2}$ and E_p towards more positive potentials. The platinum auxiliary electrode dipped in 1M NaClO_4 and was separated from the electrolysis solution by a $\text{NaClO}_4\text{-Agar}$ plug.

The dropping mercury electrode had a regulated droptime of 2.90 sec and a flow rate of 1.50 mg. sec^{-1} . For current-time measurements a flow rate of 0.75 mg. sec^{-1} was chosen. Cyclic voltammetry was carried out both using a Metrohm BM 5-03 hanging drop electrode (surface 2.2 mm^2) and a slow dropping electrode (flow rate 0.50 mg. sec^{-1} , drop time *ca.* 18 sec). Scan rates of 200, 100, 40 and 20 mV. sec^{-1} were used in cyclic voltammetry.

All peak potentials reported in this study were obtained at a scan rate of 100 mV. sec^{-1} . Half-wave potentials were reproducible within some millivolts, peak potentials within about 10–20 mV.

All solutions to be electrolysed had a concentration of 1 mM complex ion and a total ionic strength of 1M, produced by $\text{NaClO}_4 + \text{HClO}_4$ mixtures. In most experiments NaClO_4 was partially replaced by NaSCN , NaCl or NaF .

In most experiments the pH value was between 1 and 3. The temperature of the solutions was kept constant at $25 \pm 0.1^\circ\text{C}$. Solutions were deoxygenated with a stream of purified argon.

RESULTS

Influence of maximum suppressors

The shift of $E_{1/2}$ for the reduction of CrNCS^{2+} and CrF^{2+} with increasing concentration Triton X-100 or gelatine is shown in Fig. 1.

Not only $E_{1/2}$, but also the shape of the polarogram is affected, becoming irregular and more drawn out.

The best way to show the effect of these additions is the shape of current-time curves at constant potential (Fig. 2).

Peak potentials in cyclic voltammetry are also strongly affected. At the free surface $E_{p,c}$ for the reduction of CrNCS^{2+} is -0.77 V, at the fully Triton covered

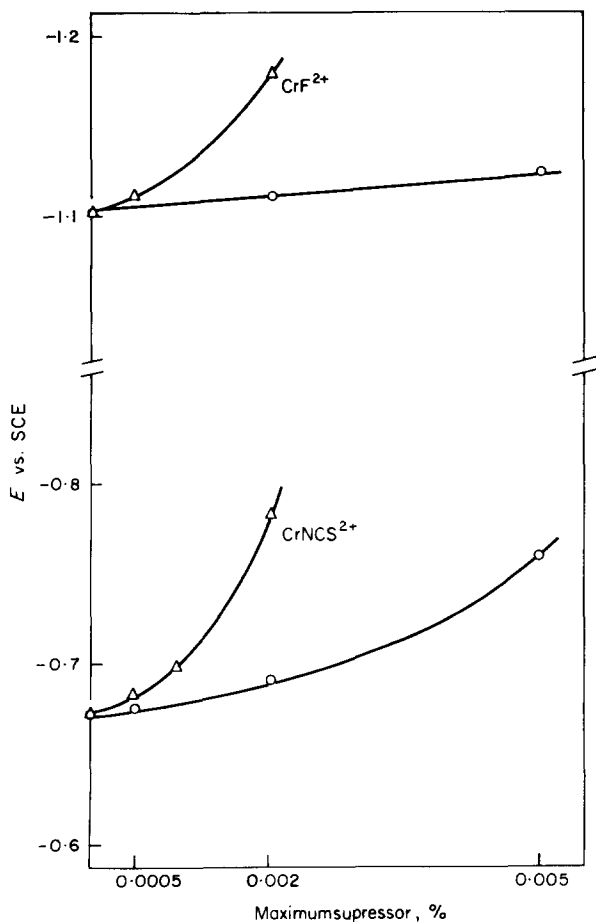


Fig. 1. Shift of $E_{1/2}$ with increasing concentration of Triton X-100 (Δ) and gelatine (o).

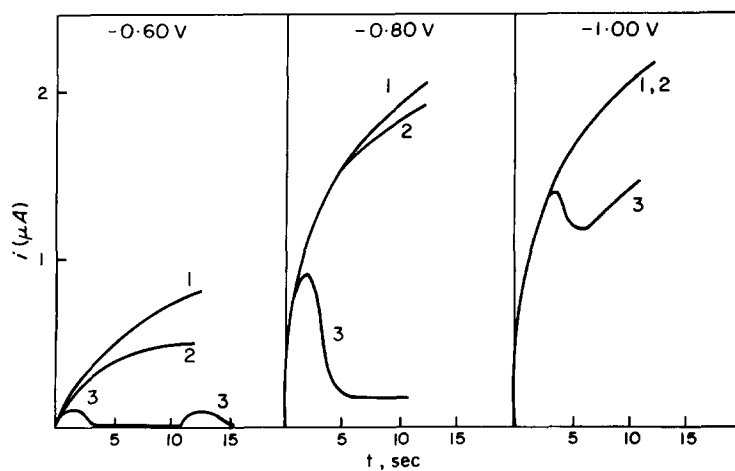


Fig. 2. Current-time curves for reduction of CrNCS^{2+} at the d.m.e. (flowrate $0.75 \text{ mg. sec}^{-1}$) at various potentials. Recorder undamped. Triton X-100: (1). 0; (2). 0.0005 per cent; (3). 0.002 per cent.

surface -1.10V and at the fully gelatine covered surface -1.05V . For the other complexes very similar effects were found, although they were not studied as extensively.

Half-wave potentials

In the absence of maximum suppressors the polarographic waves were regular and no maxima occurred. However, in 0.1M base electrolyte a small maximum was found. All limiting currents were diffusion controlled. In Table 1 some results are given. The values of α (transfer coefficient) were found by plotting $\log \{i/(\bar{i}_d - i)\}$ vs. E .

Table 1. Polarographic and spectrophotometric data[1, 2] of chromium(III) complexes in $1\text{M NaClO}_4\text{-HClO}_4$

Complex	λ_{max} ($\text{m}\mu$)	$E_{1/2}$ vs. SCE (V)	α	
			$i < \frac{1}{2}\bar{i}_d$	$i > \frac{1}{2}\bar{i}_d$
CrCl^{2+}	609	-0.62	0.46	0.38
CrF^{2+}	595	-1.105	0.66	0.66
Cr^{3+}	575	-0.90	0.60	0.60
CrNCS^{2+}	570	-0.675	0.50	0.40

The half-wave potential are independent of the pH value for CrNCS^{2+} and CrF^{2+} at pH 1–3. $E_{1/2}$ for CrCl^{2+} becomes slightly more negative with decreasing pH (a shift of 10 mV between pH 1–2). $E_{1/2}$ for Cr^{3+} is given at pH = 1.

Effect of free ligand

Replacement of the sodium perchlorate electrolyte by sodium thiocyanate has a large effect on the reduction of CrNCS^{2+} and CrCl^{2+} . The shift of $E_{1/2}$ which is shown in Fig. 3, is 50 and 66 mV per $\log [\text{SCN}^-]$ unit for CrNCS^{2+} and CrCl^{2+} respectively.

The steepness of the polarographic waves increases with increasing SCN^- concentration; the reductions are then best defined as quasi-reversible. The effect of free ligand on $E_{1/2}$ and cathodic and anodic peak potentials is shown in Table 2.

Using the multi-scan method CrNCS^{2+} gives a small second cathodic peak at -0.50V , probably due to an adsorbed product of the reoxidation reaction. CrF^{2+} and Cr^{3+} also give a second cathodic peak at -0.79V in a solution containing free thiocyanate and at -0.73V in a solution containing free chloride. These peaks could be due to the formation of chromium(III)-isothiocyanate and chloride complexes by the reoxidation of chromium(II). Adding free fluoride ion does not affect $E_{1/2}$, $E_{p,c}$ or $E_{p,a}$.

DISCUSSION

Influence of maximum suppressors

It is well known that the addition of surface-active substances, which are used

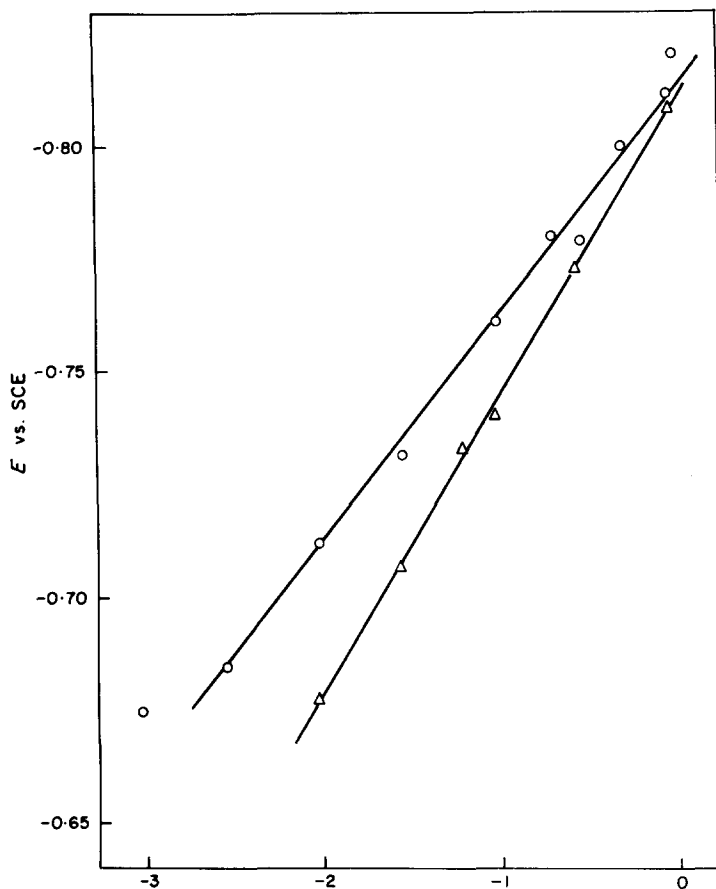


Fig. 3. $E_{1/2}$ for CrNCS^{2+} (O), pH = 1.85 and CrCl^{2+} (Δ), pH = 1.65, in NaSCN- NaClO_4 mixtures ($\mu = 1.0$). No maximum suppressor.

Table 2. Effect of 0.1M thiocyanate and chloride on the electrode reactions of chromium(III) complexes (potentials in Volts vs. SCE)

Complex	Free ligand	$E_{1/2}$	$E_{p.c}$	$E_{p.a}$
CrNCS^{2+}		-0.675	-0.77	-0.43
CrNCS^{2+}	NCS^-	-0.76	-0.83	-0.67
CrNCS^{2+}	Cl^-	-0.67	-0.79	-0.43
CrCl^{2+}		-0.62	-0.76	-0.14
CrCl^{2+}	NCS^-	-0.74	-0.81	-0.67
CrCl^{2+}	Cl^-	-0.62	-0.76	-0.38
CrF^{2+}		-1.105	-1.21	-0.14
CrF^{2+}	NCS^-	-1.10	-1.20	-0.67
CrF^{2+}	Cl^-	-1.09	-1.19	-0.39
Cr^{3+}		-0.90	-0.99	-0.17
Cr^{3+}	NCS^-	-0.895	-0.98	-0.67
Cr^{3+}	Cl^-	-0.90	-0.99	-0.41

as maximum suppressor, to an electrolyte can exert inhibitory effects[7–10]. The shape of the current–time curves (Fig. 2) indicates that in our case the rate of coverage of the electrode surface is diffusion controlled. The inhibitory effect is easily overlooked in polarography if the droptime is smaller than the time necessary for reaching the maximum instantaneous current. Under our experimental conditions (drop time 2.90 sec) for example, this maximum was reached only in the presence of 0.002% Triton (after 0.8 sec) and in the presence of 0.005% galatine (after 2.0 sec).

Half-wave potentials and effect of free ligand

The half-wave potentials (Table 1) are in fairly good agreement with literature, except the results of Walsh and Early for the reduction of CrNCS^{2+} [4]. There are some explanations possible for a shift of $E_{1/2}$ with increasing concentration free ligand (Fig. 3).

Watanabe *et al.* [6] derived the equation

$$E_{1/2} = E^\circ - 0.059 \log K_1 - 0.059 \log [L^-] \quad (1)$$

for the reversible reduction of an inert CrL^{2+} complex ion, CrL^+ being labile under the condition $K_1[L^-] \ll 1$.

Equation (1) predicts a shift of $E_{1/2}$ of 59 mV to more negative potentials with a tenfold increase of $[L^-]$.

If, on the other hand, only a specific adsorption effect was operative, the so called ψ -effect [9, 10], there should be an acceleration of the electrode reaction, resulting in a shift of the reduction wave to more positive potentials. This was not observed, however. The most important fact seems us to be that the presence of adsorbed SCN^- ions at the electrode surface facilitates the oxidation of chromium(II) ions, as was found already by Pecsok and Lingane [11] and more recently also for the oxidation of chromium(II) in the presence of halide ions [12].

This idea is supported by the shift of $E_{p,a}$ to more negative potentials (Table 2). Whereas the reducibility of CrNCS^{2+} and CrCl^{2+} increases with increasing negative potential at the raising part of the polarogram, the oxidizability of chromium(II) decreases. This results in the quasi-reversibility of the polarographic wave. Increasing reversibility is also demonstrated by the fact that the addition of SCN^- to the electrolyte brings $E_{p,c}$ and $E_{p,a}$ closer together. Cl^- additions have the same effect, but to a much smaller extent; the shape of the polarogram is not influenced.

It may seem possible that our results (Fig. 3) can be explained by a thermodynamic shift, as found by Watanabe *et al.* for the chromium–bromide system [6].

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The deviation of the theoretical slope of 59 mV per log $[\text{SCN}^-]$ may then be due to factors such as lack of full reversibility of the electrode reaction as a consequence of a decrease of the specific adsorption with increasing negative electrode potential and decreasing SCN^- concentration [13]. Homogeneous oxidation-reduction reactions in the double layer may also play a role. Although the reduction of CrNCS^{2+} and CrF^{2+} is slow and of CrCl^{2+} is fast [14], the reaction rates in solutions containing excess free ligand are not known. By such a reaction a complex which is faster or slower reduced at the mercury electrode can be formed.

The most serious objection to this explanation, however, is the fact that the condition $K_1[L^-] \ll 1$ is not fulfilled in our case. For CrNCS^+ $K_1 = 12.3$ and for $\text{Cr}(\text{NCS})_2$ $K_2 = 0.48$ [15]. So higher $\text{Cr}(\text{II})\text{-NCS}^-$ complexes will be formed in solutions containing excess free SCN^- . The increasing oxidation rate if the SCN^- concentration increases thus can be explained either by acceleration due to SCN^- adsorption (ψ -effect) or by better oxidizability of those higher complexes. Our experiments do not allow to choose between these two possibilities. However, for both cases a $\text{Cr}^{2+}\text{-NCS}^-$ -Hg intermediate in the oxidation mechanism is very probable at potentials more positive than the electrocapillary maximum, as was proposed by Ulrich and Anson for the oxidation of $\text{Cr}(\text{II})$ in halide solutions [12].

Relation between polarographic and spectrophotometric data

For a series of chromium(III) complexes Pamfilov *et al.* [16] report a linear relationship between increasing ligand-field strength Δ and increasing heterogeneous rate constant k^0 . As Δ increases from 15,750 to 19,500 cm^{-1} , $\log k^0$ increases from -4.2 to -3.3 cm sec^{-1} . These reductions are thus best qualified as quasi-reversible. Some care has to be taken, however, because these authors used 0.01% gelatine in their experiments [17]. A similar correlation was found by Walsh and Early [4] for a series of 1:1 chromium(III) complexes, which were, however, not very closely related.

On the other hand experimental correlation is found between the red shift of the first absorption band and more positive half-wave potential for closely related chromium(III) complexes which are reduced irreversibly [18] and also for CrI^{2+} , CrB^{2+} , CrSCN^{2+} , CrCl^{2+} , CrNCS^{2+} and CrCN^{2+} [5]. Such a simple correlation cannot be derived from our data. It may be possible, however, that the reduction mechanism is not the same for all complexes.

The Cr^{3+} ion may not have a specially favoured orientation to the electrode, but CrNCS^{2+} may be reduced quite well with the SCN^- ion oriented to the

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electrode. This idea is supported by the adsorbability of chromium(III) complexes, containing NCS^- as a ligand [19].

Therefore it is possible that CrNCS^{2+} is reduced by a mechanism in which the NCS^- ligand is a bridge for the electron transfer between chromium(III) ion and the electrode, analogous to the ligand bridging mechanism in the electrochemical oxidation of chromium(II) at mercury electrodes in the presence of (pseudo) halides and to the inner sphere mechanism of homogeneous reduction [14]. The same mechanism may hold for the reduction of CrCl^{2+} but not for CrF^{2+} , which is reduced at potentials far more negative than the electrocapillary maximum.

In a bridge mechanism the bridging (pseudo) halide ligand donates an electron to the metal ion to be reduced. Thus a correlation may be expected between reduction behaviour and charge transfer spectra.

Therefore it is interesting that CrNCS^{2+} shows a strong absorption at 270–295 $m\mu$ [3], whereas the other complexes do not show this. At 200–250 $m\mu$ CrCl^{2+} shows a much stronger absorption than CrF^{2+} and Cr^{3+} [2]. It should be kept in mind, however, that our data give no direct experimental proof for a bridge mechanism.

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