Polarographic reduction of cis- and trans-diisothiocyanatochromium(III) ions in acid solution of sodium perchlorate and sodium perchlorate–thiocyanate

Introduction

In a recent paper in this journal Yamaoka[1] describes the polarographic reduction of hexaaquo- and mono- and diisothiocyanatochromium(III) complex ions in aqueous acidic perchlorate solution at the mercury surface free from adsorbed SCN^- ions.

We studied the polarographic and cyclic voltammetric behaviour of some chromium(III) complexes in aqueous solutions containing free ligand. The results for $[Cr(H_2O)_6]^{3+}$, $[CrF(H_2O)_5]^{2+}$, $[CrCl(H_2O)_5]^{2+}$ and $[CrNCS(H_2O)_5]^{2+}$ have been described elsewhere[2]. We found that the successive replacement of $NaClO_4$ by $NaSCN$ shifts the waves of $[CrNCS(H_2O)_5]^{2+}$ and $[CrCl(H_2O)_5]^{2+}$ to more negative potentials and makes the reduction wave more reversible.

In this communication the results are given for the trans- and cis-$[Cr(NCS)_2-(H_2O)_4]^+$ complex ions.

Experimental

Most experimental details have been described elsewhere[2]. The complex ions were prepared and separated according to Hougen et al.[3]. The chromium content of the solutions was determined spectrophotometrically after oxidation to CrO_4^{2-} in alkaline medium. The thiocyanate content was determined by destruction of the complex in alkaline solution, reacidification to pH 4 and titration with $Hg(NO_3)_2$, using diphenylcarbazone as indicator. The $SCN^-:Cr^{3+}$ ratios were found to be 1.995 ± 0.04 for the cis-isomer and 2.007 ± 0.016 for the trans-isomer.

In all polarographic experiments the concentration of complex ion was 1 mM and the total ionic strength 1 M. The pH value was between 1.5 and 2. The dropping mercury electrode had a regulated drop time of 2.90 s and a flow rate of 1.50 mg s^{-1}. The temperature was $25 \pm 0.1°C$.

Results and discussion

Some polarographic and cyclic voltammetric results are given in Table 1. From Table 1 we see that in 1.0 M $NaClO_4$ electrolyte all polarographic reductions are irreversible ($\theta = \alpha < 1$, n_a being 1). The cis-$[Cr(NCS)_2(H_2O)_4]^+$ complex showed a strong maximum, which could be fully suppressed by 0.0005% Triton X-100. This maximum disappeared if the concentration of free SCN^- in the electrolyte was greater than 20 mM.

The successive replacement of $NaClO_4$ by $NaSCN$ in the electrolyte has two effects on the polarographic reduction of the isothiocyanatochromium(III) complexes: it shifts the reduction waves to more negative potentials and increases the θ value, which means that the reduction becomes more reversible.

This may be explained as follows: from Table 1 we see that the replacement of $NaClO_4$ by $NaSCN$ in the electrolyte causes a much greater shift to more negative potentials of $E_{p,a}$ than of $E_{p,c}$. This means that the presence of SCN^- ions in the electrolyte (and thus at the mercury surface) facilitates the oxidation of chromium(II) ions, as was also found and explained by Barclay et al.[4]. The reoxidation of chro-

TABLE 1

POLAROGRAPHIC AND CYCLIC VOLTAMMETRIC DATA FOR CHROMIUM(III)–ISOTHIOCYANATO COMPLEXES

Complex ion	$E_{\frac{1}{2}}/V$(vs. SCE)		θ		$E_{p,c}/V$(vs. SCE)		$E_{p,a}/V$(vs. SCE)		$\dfrac{\Delta E_{\frac{1}{2}}}{\Delta \log[SCN]}/n$
	a	b	a	b	a	b	a	b	
$[Cr(H_2O)_6]^{3+}$ (ref. 2)	−0.90	−0.895	0.60	0.60	−0.99	−0.98	−0.17	−067	0
$[CrNCS(H_2O)_5]^{2+}$ (ref. 2)	−0.675	−0.76	$\begin{cases} 0.50 \\ 0.40 \end{cases}$	$\begin{matrix} 0.9 \\ 0.4 \end{matrix}$	−0.77	−0.83	−0.43	−0.67	50
$trans$-$[Cr(NCS)_2(H_2O)_4]^+$	−061	−0.75	0.50	0.8	−073	−0.81	−0.44	−0.67	65
cis-$[Cr(NCS)_2(H_2O)_4]^+$	−0.55	−0.74	0.49	$\begin{matrix} 1.0 \\ 0.6 \end{matrix}$	−070	−0.80	−040	−0.66	70

Experimental details:
(1) 1.0 M NaClO$_4$ base electrolyte for columns headed a, 0.1 M NaSCN+0.9 M NaClO$_4$ base electrolyte for columns headed b. (2) Cathodic and anodic peak potentials ($E_{p,c}$ and $E_{p,a}$) are given for a scan rate of 0.1 V s^{-1}. (3) Results for cis-$[Cr(NCS)_2(H_2O)_4]^+$ in 1.0 M NaClO$_4$ electrolyte are given in the presence of 0 0005% Triton X-100 (see text).
(4) $\theta = n$ (number of electrons transferred in the reduction of one complex ion), if the polarographic reduction is reversible or $\Theta = \alpha n_a$ if the polarographic reduction is irreversible, α being the transfer coefficient and n_a the number of electrons transferred in the rate determining step, according to the well known equation $E = E_{\frac{1}{2}} - (0 059/\theta) \log [i/(i_d - i)]$. Where two values of θ are given, the first refers to potentials where $i < \frac{1}{2}i_d$, and the second to potentials where $i > \frac{1}{2}i_d$.

mium(II) then partly falls in the potential range of the polarographic reduction of the chromium(III) complexes. The more this is the case, the stronger is the effect on the overall measured current, that is, the stronger is the shift of the polarogram to more negative potentials. Thus there is a correlation between the increasing value of $\Delta E_{\frac{1}{2}}/\Delta \log[SCN^-]$ and the more positive $E_{\frac{1}{2}}$ of the complex ions in the absence of free SCN^-. The slopes of $E_{\frac{1}{2}}$ vs. log $[SCN^-]$ are linear and are given in Table 1. This linearity seems to us to be quite fortuitous and thus the numerical values probably have no fundamental significance.

Our findings confirm the supposition made by Yamaoka[1]. that "in the presence of an appreciable amount of free ligand, the overall reversibility of the redox-system might increase. This may, however, be due mainly to the enhancement of the backward reaction".

It is known that the chromium(III)–isothiocyanato complexes are strongly adsorbed at the mercury surface[4]. We measured the drop time as a function of E of freshly prepared solutions of complexes, which are essentially SCN^- free, under the same experimental conditions as for the polarographic experiments. No significant adsorption was found for 1 mM $[Cr(NCS)(H_2O)_5]^{2+}$; $trans$-$[Cr(NCS)_2(H_2O)_4]^+$ was markedly adsorbed, but to a much smaller extent than cis-$[Cr(NCS)_2(H_2O)_4]^+$ which gave a drop time lowering of 0.05–0.10 s at $E = 0.00$ V (concentration 1 mM; droptime in the base electrolyte at this potential 4.90 s). The reproducibility of the electrocapillary curves was poor, probably due to varying quantities of polymer chromium(III) species, which can be strongly adsorbed. Treatment of the solutions with active carbon did not improve the reproducibility.

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Contributions to the study of heterocycles
XVII. Polarographic study of some 2-(aryl)-4-chloromethyl-thiazoles, 2-(anilino)-4-chloromethyl-thiazoles and 2-(anilino)-5-methyl-1,-3,4-thiodiazoles*

In connection with our studies[1-3] on compounds (I)–(III) we examined the polarographic reduction of the three nitro derivatives (IIIc) obtained by the nitration of (IIIa)[4]. In the present study the behaviour of the chloromethyl derivatives (Ia)–(Ic) and (IIa)–(IIc) has been investigated. No reduction waves corresponding to the cleavage of the C–Cl band were found, but catalytic hydrogen evolution waves were observed and compared with those obtained for (IIa) and (IIIb).
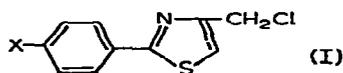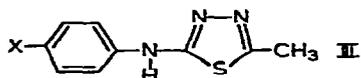

2-(p-X-phenyl)-4-chloromethyl-thiazoles

(Ia) X=H   (Ic) X = Br
(Ib) X=CH$_3$ (Id) X = NO$_2$
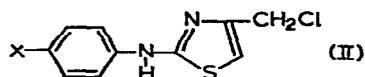
2-(p-X-anilino)-4-chloromethyl-thiazoles

(IIa) X = H   (IIb) X=CH$_3$
(IIc) X = Br

(IIIa) X = H   (IIIb) X=CH$_3$
(IIIc) X = NO$_2$

2-(p-X-anilino)-5-methyl-1,3,4-thiadiazoles

N B (Wave IIIc is reduction of NO$_2$ and is not included)