The Reduction of Hexakis(urea)chromium(III) Ions at the Dropping Mercury Electrodes

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The polarographic reduction of hexakis(urea)chromium(III) ions at the dropping mercury electrode has been studied in various supporting electrolyte solutions. This complex exhibits two irreversible reduction waves; the first corresponds to Cr(III)→Cr(II), and the second, to Cr(II)→Cr(0). The kinetic parameters of the electrode reactions were determined in various supporting electrolyte solutions and at varied ionic strengths by means of Tast polarography. The differential-pulse polarographic characteristics of this complex are also given.

The cyclic voltammetry of hexakis(urea)chromium(III) ions (abbreviated hereafter as $[Cr(urea)_6]^{3+}$) has been briefly reported in dimethyl sulfoxide solutions.[1] This complex exhibits two irreversible reduction waves; the first corresponds to Cr(III)→Cr(II), and the second, to Cr(II)→Cr(0). The present investigation was undertaken to ascertain the electrochemical behavior in aqueous solutions in the hope of gaining further insight into the mechanism of the electroreduction of $[Cr(urea)_6]^{3+}$ ions. The kinetic parameters of the electrode reaction of $[Cr(urea)_6]^{3+}$ ions were also examined by means of Tast polarography.

Experimental

The Tast polarograms were recorded by a Yanagimoto voltammetric analyzer, P-1000. A National digital tester, Model VP-2521A, was used; the current and the the potential were thus measured precisely. A three-electrode cell equipped with a saturated calomel electrode (Yanagimoto MR-P_2-05-1) and a platinum-wire electrode was employed. The DME with a flow rate of 1.10 mg s^{-1} and a drop time of 2.99 s in 0.4 M (1 M=1 mol dm^{-3}) of NaCl containing a 0.1 M acetate buffer solution and 20 μM LEO was used. Poly(oxyethylene) dodecyl ether (LEO: mean molecular weight, 862) was used as the maximum suppressor.

The complex, $[Cr(urea)_6]Cl_3$, was prepared according to the literature[2] and converted to perchlorate salt. This complex is stable in aqueous solutions.[3] All the other chemicals used were of a guaranteed reagent-grade.

The dissolved oxygen was removed by bubbling purified nitrogen gas through the solution. All the measurements were made at 25 °C unless otherwise stated.

Results

Effects of Surface-active Substances. In the polarographic measurements, the $[Cr(urea)_6]^{3+}$ ions were found not to give a well-defined polarographic wave, but to give two well-defined waves in the presence of a small amount of surface-active substances. The effects of the surface-active substances on the Tast polarogram were examined; the results are shown in Fig. 1.

The addition of 20 μM of LEO to a solution containing 1 mM of complex ions gave satisfactory results; the maximum was suppressed without causing a decrease in the diffusion current. The addition of other surface-active substances, such as 0.0015% Triton X-100, 0.015% PAA (polyacrylamide) and 0.005% gelatin, caused a distortion of the Tast polarogram. The

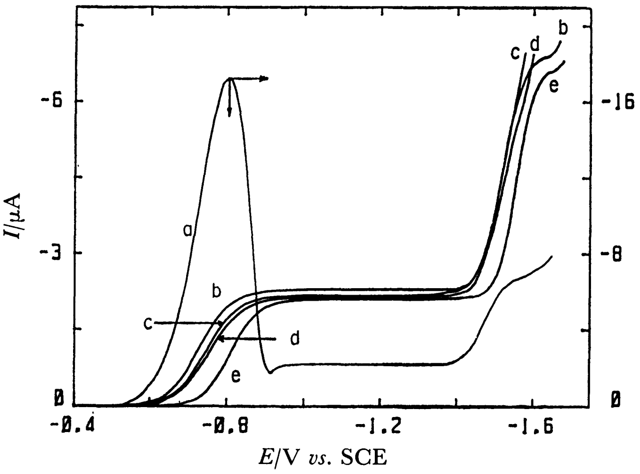

Fig. 1. Effects of surface active substances on the Tast polarogram of 1 mM $[Cr(urea)_6](ClO_4)_3$ in 0.4 M NaCl containing 0.1 M acetate buffer (pH 4.6).
(a) without maximum suppressor, with (b) 20 μM LEO, (c) 0.005% gelatin, (d) 0.015% polyacrylamide and (e) 0.0015% Triton X-100.

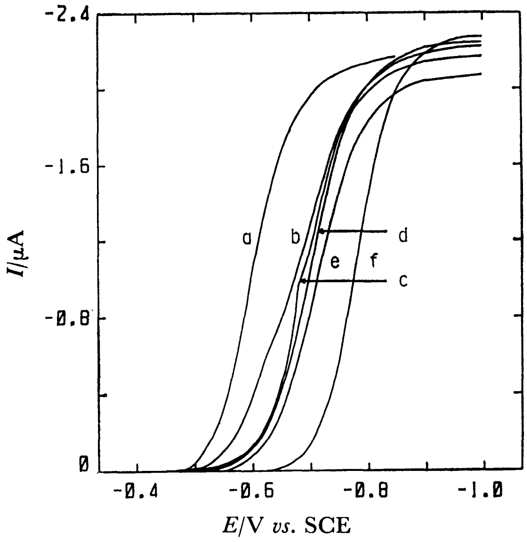

Fig. 2. Tast polarograms for the first wave of 1 mM $[Cr(urea)_6](ClO_4)_3$ obtained in various supporting electrolyte solutions containing 0.1 M acetate buffer and 20 μM LEO (μ=0.5) at 25 °C.
(a) NaI, (b) NaBr, (c) $NaNO_3$, (d) NaCl, (e) Na_2SO_4, (f) NaSCN.

current-potential curves were shifted to more negative potentials by the presence of Triton X-100. Also, the Tast polarogram in the presence of PAA and gelatin did not exhibit a second wave.

Effects of the Supporting Electrolytes. Measurements were made in various supporting electrolyte solutions. Figure 2 shows a Tast polarogram of the first waves of the 1 mM $[Cr(urea)_6]^{3+}$ ions obtained in various supporting electrolyte solutions (ionic strength $\mu=0.5$) containing 0.1 M of an acetate buffer and 20 μM of LEO at 25 °C. The Tast polarogram obtained in the solution containing NaSCN or $NaNO_3$ did not exhibit a second wave.

Conventional polarographic log-plots[4] were tested for the current-potential curves of the $[Cr(urea)_6]^{3+}$ ions. The value of the log-plot slope was found to be far different from the one predicted for a reversible electrode process indicating that the electrode reaction proceeds irreversibly.

The modified log-plots for an irreversible electrode process proposed by Oldham and Parry[5] were examined.

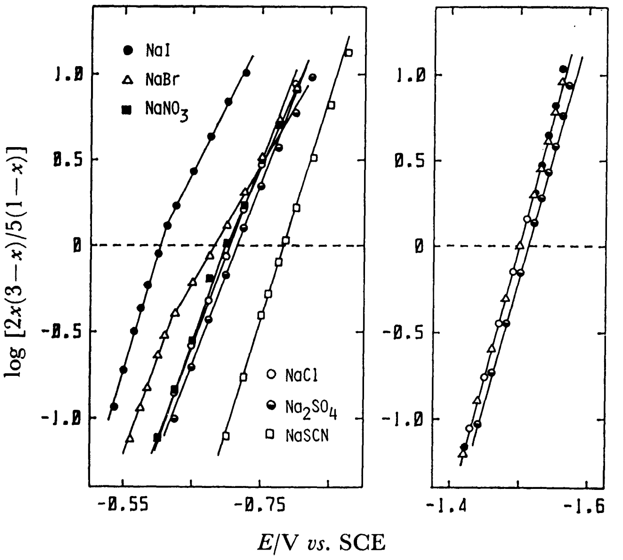

Fig. 3. Log-plots for the first (left) and the second (right) waves of 1 mM $[Cr(urea)_6](ClO_4)_3$ obtained in various supporting electrolyte solutions containing 0.1 M acetate buffer and 20 μM LEO at 25 °C.
(●) NaI, (△) NaBr, (■) $NaNO_3$, (○) NaCl, (◒) Na_2SO_4, (□) NaSCN.

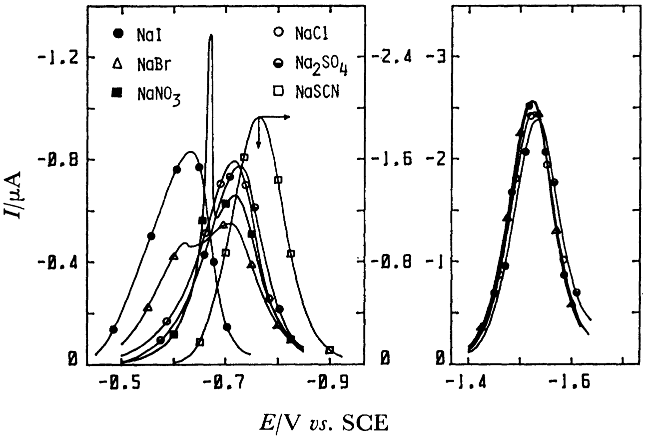

Fig. 4. Differential pulse polarograms of 1 mM $[Cr(urea)_6](ClO_4)_3$ in various supporting electrolyte solutions containing 0.1 M acetate buffer and 20 μM LEO (pH 4.6, $\mu=0.5$) at 25 °C.
(●) NaI, (△) NaBr, (■) $NaNO_3$, (○) NaCl, (◒) Na_2SO_4, (□) NaSCN.

The results for the first and the second waves are given in Fig. 3 (see also Discussion). The log-plots for the first wave in NaBr, NaI, and $NaNO_3$ did not give a straight line.

Differential Pulse Polarogram. Figure 4 shows the differential pulse polarograms of the 1 mM $[Cr(urea)_6]^{3+}$ ions obtained in several media at 25 °C. Much as in the results of the Tast polarography, the first waves appeared over a wide range of potentials, while the second waves appeared in a rather narrow potential range. The peak current for NaSCN was about twice as large as in the other cases.

The peak potential(E_p), the half-width(ΔW), and the peak current(I_p) of the differential pulse polarogram, which were obtained in several media, are given in Table 1. These results suggest that the electroreduction of $[Cr(urea)_6]^{3+}$ to the Cr(II) species proceeds irreversibly.

Measurements were also made at varied ionic strengths. Various parameters which characterize a differential pulse polarogram were obtained; they are shown in Table 2. The peak currents for the first and the second waves decreased with an increase in the ionic strength. The half-width of the first wave increased

TABLE 1. DIFFERENTIAL-PULSE POLAROGRAPHIC CHARACTERISTICS OF 1 mM $[Cr(urea)_6](ClO_4)_3$ IN VARIOUS SUPPORTING ELECTROLYTE SOLUTIONS CONTAINING 0.1 M OF AN ACETATE BUFFER AND 20 μM OF LEO AT 25 °C

Medium	First wave			Second wave		
	E_p / V vs. SCE	ΔW / mV	I_p / μA	E_p / V vs. SCE	ΔW / mV	I_p / μA
0.4 M NaCl	−0.717	125	−0.792	−1.528	90	−2.500
0.4 M NaBr	−0.705	206	−0.547	−1.525	90	−2.580
0.4 M NaI	−0.632	134	−0.836	−1.526	88	−2.590
0.4 M $NaNO_3$	−0.717 (−0.672)[a]		−0.644 (−1.260)[a]	—	—	—
0.4 M NaSCN	−0.764	115	−1.880	—	—	—
0.13 M Na_2SO_4	−0.727	128	−0.755	−1.536	94	−2.340

a) Corresponds to the prewave.

Table 2. Differential-pulse polarographic characteristics of 1 mM $[Cr(urea)_6](ClO_4)_3$ in varied ionic strengths in solutions containing sodium chloride, 0.1 M of an acetate buffer and 20 μM of LEO at 25 °C.

Ionic strength	First wave E_p V *vs.* SCE	ΔW mV	I_p μA	Second wave E_p V *vs.* SCE	ΔW mV	I_p μA
0.1	−0.702	93	−0.904	−1.489	88	−2.700
0.3	−0.715	110	−0.842	−1.516	89	−2.600
0.5	−0.717	125	−0.792	−1.528	90	−2.500
1.0	−0.730	143	−0.673	−1.548	92	−2.460
2.0	−0.690	190	−0.615	−1.560	94	−2.270

with an increase in the ionic strength, while that of the second wave scarcely changed. The shifts in $E_{1/2}$ and E_p were rather complicated.

Discussion

The hexakis(urea)chromium(III) ions gave two well-defined current-potential curves, as may be seen in Fig. 1. The limiting currents of both the first and second waves were diffusion-controlled and were proportional to the concentration of the complex. The limiting current of the second wave was twice that of the first one. The first wave corresponds to the reduction of $[Cr(urea)_6]^{3+}$ to $[Cr(urea)_6]^{2+}$ species.[1] The tervalent chromium species is stable,[3] but the divalent one, produced on the surface of the electrode, is unstable and may undergo hydrolysis. The overall electrode reaction was considered by a comparison of its electrode reaction with that of other chromium(III) complexes.[6-11] Thus,

$$[Cr(urea)_6]^{3+} + e \longrightarrow [Cr(urea)_6]^{2+}, \qquad (1)$$

$$[Cr(urea)_6]^{2+} + pH_2O \longrightarrow [Cr(urea)_{6-p}(H_2O)_p]^{2+} + p\text{urea}, \qquad (2)$$

for the first wave, and

$$[Cr(urea)_{6-p}(H_2O)_p]^{2+} + 2e \longrightarrow Cr(0) + (6-p)\text{urea} + pH_2O, \qquad (3)$$

for the second wave.

The diffusion coefficient of the $[Cr(urea)_6]^{3+}$ ions was measured by means of a method previously reported[12] by using $[Co(NH_3)_6]^{3+}$ as the reference substance; the results are summarized in Table 3.

The reduction of $[Cr(urea)_6]^{3+}$ to chromium(II) species in an acid solution was considered to be irreversible from the facts described above (Fig. 3 and Table 1). For a totally irreversible electrode reaction, the following relations of the Tast polarography are derived:[5]

$$(RT/\alpha nF)\ln[2x(3-x)/5(1-x)] = E_{1/2} - E, \qquad (4)$$

with:

$$x = I/I_d, \qquad (5)$$

and:

$$E_{1/2} = (RT/\alpha nF)\ln[1.35k_c^\circ(t_d/D)^{1/2}], \qquad (6)$$

where I is the current at the potential, E; I_d, the diffusion-controlled current; D, the diffusion coefficient; t_d, the drop time; α, the transfer coefficient; k_c°, the cathodic rate constant at $E=0$; n, the number of electrons; R, the gas constant; F, the Faraday constant, and T the absolute temperature. According to Eq. 4, a plot of $\ln[2x(3-x)/5(1-x)]$ *vs.* E should be a straight line. The transfer coefficient, α, can be obtained from the slope, and the half-wave potential, $E_{1/2}$, from the intersection. The rate constant, k_c°, can be obtained from $E_{1/2}$ by applying Eq. 6. An example of the plots for Eq. 4 has been shown above (Fig. 3).

The kinetic parameters of the electrode reactions thus obtained are given in Table 3. These kinetic parameters obtained were checked by calculating the current according to this relation:

$$2x(3-x)/5(1-x) = 1.35k_c^\circ(t_d/D)^{1/2}\exp(-\alpha nFE/RT). \qquad (7)$$

The calculated currents were in agreement with the observed ones except for the cases of NaBr, NaI, and $NaNO_3$.

It has been reported that the interaction reaction between the reduced chromium(II) complex and the nitrate ions occurs to a considerable extent.[13,14] The abnormality of the current-potential curve in a nitrate medium may, therefore, be understood in termes of this effect.

Table 3. Kinetic parameters of electrode reactions of $[Cr(urea)_6](ClO_4)_3$ obtained in various supporting electrolyte solutions containing 0.1 M of an acetate buffer and 20 μM of LEO at 25 °C

Medium	D 10^{-6} cm² s⁻¹	First wave $E_{1/2}$ V *vs.* SCE	α	k_c° cm s⁻¹	Second wave $E_{1/2}$ V *vs.* SCE	α	k_c° cm s⁻¹
0.4 M NaCl	5.16	−0.705	0.62	3.78×10^{-11}	−1.500	0.44	7.11×10^{-26}
0.4 M NaBr	5.26	−0.685	0.72 (0.47)[a]	1.18×10^{-11} (3.79×10^{-9})[a]	−1.500	0.45	2.62×10^{-26}
0.4 M NaI	5.13	−0.600	0.86 (0.53)[a]	1.97×10^{-12} (1.28×10^{-8})[a]	−1.500	0.46	6.50×10^{-27}
0.4 M $NaNO_3$	5.07	−0.699	0.67 (0.53)[a]	1.34×10^{-11} (5.01×10^{-10})[a]	—	—	—
0.4 M NaSCN	5.11	−0.783	0.73	2.50×10^{-13}	—	—	—
0.13 M Na_2SO_4	4.40	−0.716	0.63	1.94×10^{-11}	−1.510	0.43	9.32×10^{-26}

a) The values in parentheses were obtained from the more negative potential range.

Table 4. Kinetic parameters of electrode reactions of $[Cr(urea)_6](ClO_4)_3$ obtained at varied ionic strengths in solutions containing 0.1 M of an acetate buffer and 20 μM of LEO at 25 °C

Ionic strength	$\frac{D}{10^{-6}\,cm^2\,s^{-1}}$	First wave $\frac{E_{1/2}}{V\ vs.\ SCE}$	First wave α	First wave $\frac{k_c^\circ}{cm\ s^{-1}}$	Second wave $\frac{E_{1/2}}{V\ vs.\ SCE}$	Second wave α	Second wave $\frac{k_c^\circ}{cm\ s^{-1}}$
0.1	5.33	−0.681	0.77	1.34×10^{-12}	−1.463	0.50	1.73×10^{-28}
0.3	5.27	−0.696	0.69	7.62×10^{-12}	−1.488	0.46	1.18×10^{-26}
0.5	5.16	−0.705	0.62	3.78×10^{-11}	−1.500	0.44	7.11×10^{-26}
1.0	5.03	−0.718	0.56	1.54×10^{-10}	−1.516	0.43	1.37×10^{-25}
1.5	4.83	−0.693	0.52	8.59×10^{-10}	−1.519	0.42	3.77×10^{-25}
2.0	4.70	−0.682	0.49	2.41×10^{-9}	−1.525	0.41	4.82×10^{-25}
3.0	3.72	−0.663	0.40	2.74×10^{-8}	−1.526	0.39	6.14×10^{-24}

On the other hand, the distortion of the Tast polarogram obtained in solutions containing NaBr or NaI may be explained by the double-layer effect. It is a well-known fact that Br^- and I^- are specifically adsorbed on mercury and change the double-layer potentials.[15] The potential of PZC (point of zero charge) in the presence of Br^- and I^- lies[16] near the potential where the half-wave potential of the Tast polarogram appears. Therefore, the effect of the double layer on the current-potential curves may be more pronounced,[17] since the charge of $[Cu(urea)_6]^{3+}$ ions is high and its electroreduction process is irreversible. This causes a distortion of the current-potential curves. Such a double-layer effect has also been reported for the reduction of $[Cr(NH_3)_6]^{3+}$ ions in the presence of Br^- and I^-.[18]

Kinetic parameters are also obtained at varied ionic strengths in solutions containing 0.1 M of an acetate buffer and 20 μM of LEO at 25 °C. The results are shown in Table 4. The rate constants, k_c°, for the first and the second waves increased with an increase in the ionic strength. The transfer coefficient varied drastically, indicating the presence of a specific adsorption of the complex ions.

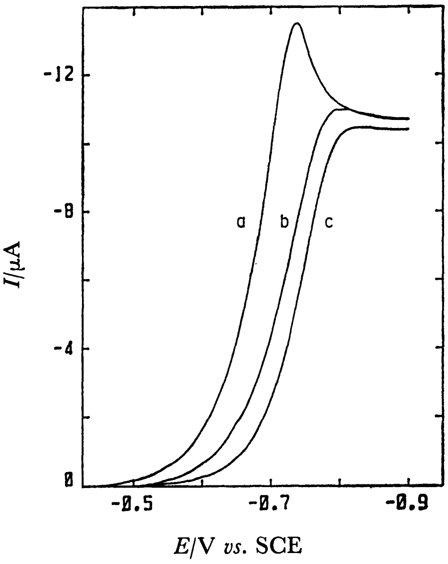

Fig. 5. Normal pulse polarograms of 1 mM $[Cr(urea)_6](ClO_4)_3$ in various halogenide solutions containing 0.1 M acetate buffer and 20 μM LEO (pH 4.6, $\mu=0.5$) at 25 °C.
(a) NaI, (b) NaBr, (c) NaCl.

Anion-induced adsorption[19–21] has been reported for the reduction of some cations, such as Pb(II), Cd(II), and Zn(II), in the presence of I^-, Br^-, Cl^-, *etc.* A similar situation will hold good for the reduction of $[Cr(urea)_6]^{3+}$ ions: the charge of the complex ions is tripositive, and, therefore, the extensive adsorption of $[Cr(urea)_6]^{3+}$ ions on mercury electrodes might be induced from iodide and bromide media. This prediction might be supported by the results of the normal-pulse polarography. Usually, the maximum diminishes at a longer sampling time of the current, but in the present case the maximum still appears at a shorter sampling time ($t_d=50$ ms), as is shown in Fig. 5. For the case of the anion-induced adsorption, the possibility that current-potential curves obtained at shorter sampling times shows a maximum at intermediate potentials has been suggested by Oka and Matsuda.[22]

The diffusion current in Na_2SO_4 was found lower by about 15% than those in other electrolytes. This is considered to be a result of the formation of ion pairs between $[Cr(urea)_6]^{3+}$ and SO_4^{2-}, by analogy with the electrode reactions of other tervalent complexes.[23,24]

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