Monatshefte für Chemie 109, 1287—1294 (1978)

Monatshefte für Chemie

Ligand Exchange Reactions of Some Cr(III) Complexes Investigated by Cyclic Voltammetry

R. Landsberg[a,*], **P. Janietz**[a], and **M. Prügel**[b]

[a] Sektion Chemie, Humboldt-Universität zu Berlin,
DDR-108 Berlin, Deutsche Demokratische Republik
[b] Sektion NGW der Humboldt-Universität zu Berlin, Bereich Gärungstechnologie, DDR-104 Berlin, Deutsche Demokratische Republik

(Received 19 October 1977. Accepted 16 January 1978)

From cyclic linear sweep voltammograms of some Cr(III) complexes it is evident that after electron transfer ligand groups are expelled relatively slowly in *DMSO* and the tetra coordinated complex is formed. The rate constants could be determined in some cases by the methods of cyclic voltammetry. The following compounds were examined: $[Cr(en)_3]^{3+}$, $[Cr(acac)(en)_2]^{2+}$, $[Cr(acac)_3]$, $[Cr(dien)_2]^{3+}$, $[Cr(DMSO)_6]^{3+}$, $[Cr(ur)_6]^{3+}$. For $[Cr(en)_3]^{3+}$ the energy of activation could be determined as well.

The dependence of the velocity of ligand elimination on complex structure is discussed.

Untersuchung von Ligandenaustauschreaktionen einiger Cr(III)*-Komplexe mittels cyclischer Voltammetrie*

Bei der Reduktion einiger der folgenden Cr(III)-Komplexe in *DMSO* läßt sich auf Grund der Voltammogramme auf eine Ligandenabspaltung und Bildung der vierfach koordinierten Cr(II)-Komplexe schließen: $[Cr(en)_3]^{3+}$, $[Cr(acac)(en)_2]^{2+}$, $[Cr(acac)_3]$, $[Cr(dien)_2]^{3+}$, $[Cr(DMSO)_6]^{3+}$, $[Cr(ur)_6]^{3+}$. Für das $[Cr(en)_3]^{3+}$ konnten Geschwindigkeitskonstante und Aktivierungsenergie dieser nachgelagerten Reaktion bestimmt werden.

Der Einfluß der Struktur des Komplexes auf die Zerfallsgeschwindigkeit wird diskutiert.

Introduction

The cyclic linear sweep voltammograms obtained for some Cr(III) complexes in *DMSO* showed some unusual features. Thus an additional anodic and an additional cathodic peak appeared in the voltammogram of the $[Cr(en)_3]^{3+}$ ion[†] in *DMSO* after several cycles had been run

---

[†] The following abbreviations are used: *en* = ethylenediamine; *acac* = acetyl acetonate; *dien* = diethylenetriaamine; *DMSO* = dimethylsulfoxide; *ur* = urea.

0026-9247/78/0109/1287/$ 01.60

(Fig. 1). We attribute this to a chemical reaction following the electron transfer which consists in the expulsion of a bidentate ligand group and the conversion of the octahedric complex into the tetracoordinated Cr(II) complex. This reaction is a very fast one in aqueous solutions[1] and is caused by the strain existing in the primary octahedric Cr(II) product. In *DMSO* on the other hand this reaction may be much slower as the experiments of *Maki*[2] on the complex $[Cr(en)_2(CN)_2]^+$ ion have shown[3].

We pursued this question by varying the ligands and examining its effect on the rate of ligand elimination in the Cr(II) complex. The method of cyclic voltammetry was employed.

Experimental

The potentiostat AMEL Mod. 552 was used. It is specially designed for use in non-aqueous solvents. The potentiostat was combined with a low frequency generator permitting a wide range of sweep rates. For registering the current signal the adapter AMEL Mod. 550 in conjunction with an *x*-*y*-recorder was employed.

The complex compounds were prepared according to the literature[4–10]. As supporting electrolyte we used $N(C_4H_9)_4 \cdot ClO_4$.

A saturated Ag/AgCl (aq) electrode served as reference electrode to which the potentials in this paper refer. Its potential against SCE amounted to —25 mV. The bottom of the shaft of this electrode was closed by a glass frit with small pores, so that effectively no water could penetrate; this bottom was filled with saturated NaCl solution in order to avoid $KClO_4$ precipitation.

Two methods were used to determine the reaction rates. First method: after reaching the first reduction peak corresponding to the reduction of the Cr(III) complex the potential was kept constant for a time τ and then the linear sweep was reversed. A new peak is then observed in the anodic half cycle which increases with τ (e.g. Figs. 1 and 2). The latter one is due to the oxidation of the product formed in the chemical reaction after charge transfer, the former mentioned peak is due to the unchanged primary product. In case of stationary conditions during the period τ and the height (i_{pa}) of the first peak being proportional to the concentration of the primary unconverted octahedral product, a concentration—time dependence may be obtained. It was found to be logarithmic, corresponding to a first-order decomposition reaction (e.g. Fig. 3).

The second method consists in determining the ratio of the anodic (i_{pa}) to cathodic (i_{pc}) peak currents[11,12]; this ratio is directly proportional to the rate constant of the succeeding chemical reaction, provided certain conditions are fulfilled[11]. k_s—the heterogeneous rate constant of charge transfer—was found by *Nicholson*'s method for quasi-reversible processes[13]; k_f is the rate constant of the following chemical reaction.

Results

The complex $[Cr(en)_3]$ $(ClO_4)_3$ was examined by both methods. Cyclic voltammograms are shown in Fig. 1, the anodic peaks after different halting periods τ in Fig. 2; Fig. 3 shows first order reaction

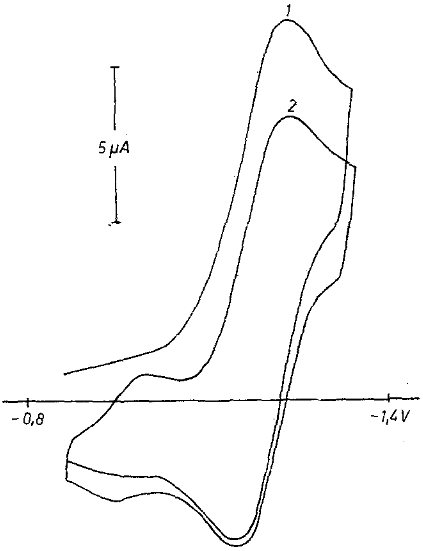

Fig. 1. Cyclic voltammogram for $5 \cdot 10^{-4} M$ [Cr(*en*)$_3$] (ClO$_4$)$_3$; 25 °C; *1* first cycle; *2* tenth cycle

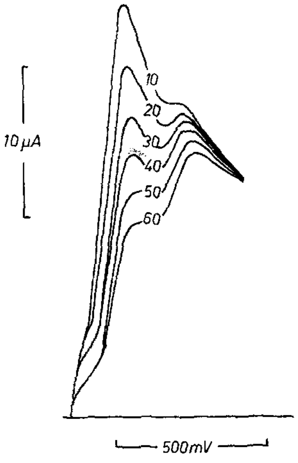

Fig. 2. Anodic half-cycle for $1 \cdot 10^{-3} M$ [Cr(*en*)$_3$] (ClO$_4$)$_3$ with different halting periods (in seconds)

plots according to the first method for various temperatures; at 25 °C we found $k_f = 3.3 \cdot 10^{-2}\,\mathrm{s}^{-1}$ at a Cr(III) concentration of $1 \cdot 10^{-3} M$. We applied the second method for the same conditions varying the sweep rates and obtained a mean value: $k_f = (3.42 \pm 0.03) \cdot 10^{-2}\,\mathrm{s}^{-1}$, so both methods agree well. The temperature dependence of k_f was determined by the first method and is shown in Table 1 and Fig. 4. It leads to an activation energy $E_A = 21\,\mathrm{kcal\,mol}^{-1}$. This value is of the usual order of magnitude for ligand exchange reactions[14].

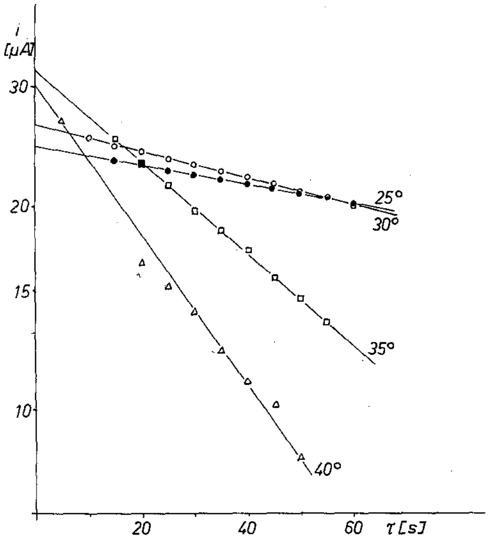

Fig. 3. Dependence of the anodic peak current on τ for various temperatures, semilogarithmic plot; $1 \cdot 10^{-3} M$ $[\mathrm{Cr}(en)_3]\,(\mathrm{ClO}_4)_3$

The following elementary steps may represent the overall reduction process.

$$[\mathrm{Cr}(en)_3]^{3+} + \mathrm{e}^- \underset{}{\overset{k_s}{\rightleftharpoons}} [\mathrm{Cr}(en)_3]^{2+} \qquad (1\mathrm{a})$$

$$[\mathrm{Cr}(en)_3]^{2+} \xrightarrow{k_f} [\mathrm{Cr}(en)_2]^{2+} + en \qquad (1\mathrm{b})$$

$k_s = 4.5 \cdot 10^{-4}\,\mathrm{cm\,s}^{-1}$; $k_f = 3.4 \cdot 10^{-2}\,\mathrm{s}^{-1}$ (at 25 °C).

The $[\mathrm{Cr}(en)_2(acac)]^+$ decomposes in a similar way once it is formed by reduction of the Cr(III) complex. The rate constant was determined by the method of *Nicholson* and *Shain*[11] and found to be $k_f = 4 \cdot 10^{-2}\,\mathrm{s}^{-1}$.

Table 1. *Temperature dependence of k_f, the rate constant of the succeeding homogeneous chemical reaction;* $1 \cdot 10^{-3} M$ $[Cr(en)_3]^{2+}$

$T/°C$	$10^2 k_f/s^{-1}$
25	3.3
30	5.0
35	15.3
40	18.4

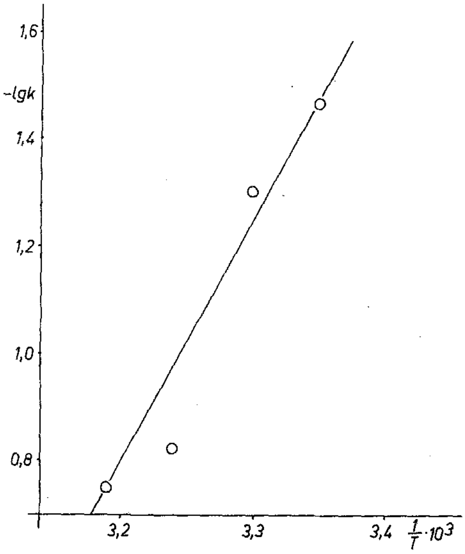

Fig. 4. Arrhenius plot for the rate constant of ligand elimination: $[Cr(en)_3]^{2+} \rightarrow [Cr(en)_2]^{2+} + en$

The introduction of yet another *acac* ligand into the complex ion reduces the rate constant of ligand elimination considerably. For the $[Cr(en)(acac)_2]^+$ complex only a weak shoulder could be detected in the anodic half-cycle. Poisoning effects occur in this case and did not allow a quantitative determination of the rate constant. The reaction rate seems to be very low.

The $[Cr(acac)_3]^-$ ion is stable as far as we could find; voltammetrically, no elimination of ligand could be detected.

For $[Cr(ur)_6](ClO_4)_3$ we observed a very fast ligand elimination.

After the second cycle an additional cathodic wave appears in the cyclic voltammogram. After about 15 cycles there was no further change in the cyclic voltammograms (see Fig. 5).

The observations may be explained by the following mechanism.

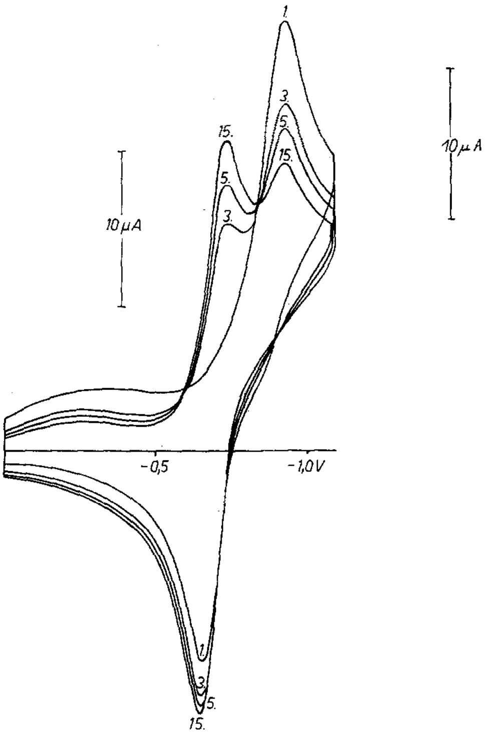

Fig. 5. Cyclic voltammograms for $1.5 \cdot 10^{-3} M$ [Cr(*ur*)$_6$] (ClO$_4$)$_3$; the number of the consecutive cycle is shown in the diagram

During the first cathodic half-cycle the Cr(II) complex ion is formed, ligand elimination taking place almost simultaneously. The tetracoordinated complex ion formed is oxidized during the following second anodic half-cycle and is then slowly reconverted into the original hexacoordinated ion by incorporating two ligand groups. This reaction is so slow, that the tetracoordinated complex ion also shows up during the next, the third (cathodic) half-cycle, when it is reduced to the tetracoordinated Cr(II) complex.

Half-cycle 1 (cathodic):

$$[\mathrm{Cr}(ur)_6]^{3+} + e^- \rightleftharpoons [\mathrm{Cr}(ur)_6]^{2+} \tag{2a}$$

$$[\mathrm{Cr}(ur)_6]^{2+} \xrightarrow{k_f} [\mathrm{Cr}(ur)_4]^{2+} + 2\,ur \tag{2b}$$

Half-cycle 2 (anodic):

$$[\mathrm{Cr}(ur)_4]^{2+} \rightleftharpoons [\mathrm{Cr}(ur)_4]^{3+} + e^- \tag{2c}$$

$$[\mathrm{Cr}(ur)_4]^{3+} + 2\,ur \xrightarrow{k_{f'}} [\mathrm{Cr}(ur)_6]^{3+} \tag{2d}$$

Half-cycle 3 (cathodic):

$$[\mathrm{Cr}(ur)_4]^{3+} + e^- \rightleftharpoons [\mathrm{Cr}(ur)_4]^{2+} \tag{2e}$$

$$[\mathrm{Cr}(ur)_6]^{3+} + e^- \rightleftharpoons [\mathrm{Cr}(ur)_6]^{2+} \tag{2f}$$

For constant sweep rate v, the stationary ratio of concentration of tetra- to hexacoordinated complex ion reached after several cycles is determined by $k_f/k_{f'}$.

An anodic peak indicating the oxidation of the octahedric Cr(II) complex could not be detected even at a scanning speed of 20 V s^{-1} showing that reaction (2b) is too fast.

The stable $[\mathrm{Cr}(dien)_2]^{3+}$ ion does not decompose after reduction to the Cr(II) compound, it is stable even in aqueous solution[15]. Nor could any conversion be detected when $[\mathrm{Cr}(DMSO)_6]\ (\mathrm{ClO_4})_3$ was reduced.

Discussion

The experiments show that the speed of the decomposition reaction of the octahedric Cr(II) complex mainly depends on the nature of the ligand and less on differences in thermodynamic stability. Decomposition will take place if the octahedric Cr(II) complex is thermodynamically not sufficiently stable to compensate for the steric strain.

Ligand elimination may be suppressed or slowed down, if it is possible to relax steric strain by an alteration in electronic density within the complex or by some special influence of solvation.

The importance of solvation is known and demonstrated by the fact that $[\mathrm{Cr}(en)_3]^{2+}$ immediately decomposes in aqueous solution while the elimination reaction is markedly slower in *DMSO*.

In the series $[\mathrm{Cr}(en)_3]^{2+}$, $[\mathrm{Cr}(en)_2(acac)]^{+}$, $[\mathrm{Cr}(en)(acac)_2]^{\circ}$ and $[\mathrm{Cr}(acac)_3]^{-}$ the rate constant of ligand elimination after reduction decreases with rising number of *acac* groups in the ion. For the $[\mathrm{Cr}(acac)_3]^{-}$ we could not observe any ligand elimination. This is evidently due to the chelate rings which delocalize electron density. Electron delocalization is insufficient in $[\mathrm{Cr}(en)_2(acac)]^{\circ}$, in this case the lower symmetry and the probably less favourable solvation dominates and leads to a very slow decomposition as shown by the voltammograms which did not, however, allow quantitative evaluation.

The $[\mathrm{Cr}(DMSO)_6]^{2+}$ is a special case. Ligand exchange with the solvent should be easy but would lead to no change in composition, the free ligand is present in the maximum possible excess and will favour, of course, the hexacoordinated structure.

For $[\mathrm{Cr}(ur)_6]^{2+}$ the possible electron delocalization is insufficient.

References

[1] *A. Earnshaw*, J. Chem. Soc. **A 1969**, 1339.

[2] *N. Maki*, J. Inorg. Nucl. Chem. **37**, 1207 (1975).

[3] Compare also papers by *G. Hills* and *L. Peter* and by *Yu. M. Povarov* presented at the 28th meeting of ISE at Varna on Sept. 23, 1977.

[4] *M. Linhard*, Z. Electrochem. **50**, 224 (1944).

[5] *W. C. Fernelius* and *J. E. Blanche*, in: *T. Moeller*, Inorg. Synth. **5**, 130(1957).

[6] *M. Linhard* and *M. Weigel*, Z. anorg. allg. Chem. **271**, 351 (1930).

[7] *P. A. House* and *C. S. Garner*, Inorg. Chem. **5**, 840 (1966).

[8] *H. L. Schäfer* and *H. Opitz*, Z. anorg. allg. Chem. **313**, 178 (1961).

[9] *F. A. Cotton* and *R. Francis*, J. Amer. Chem. Soc. **82**, 2986 (1960).

[10] *E. Wilke-Dörfurth* and *K. Niederer*, Z. anorg. allg. Chem. **184**, 145 (1929).

[11] *R. S. Nicholson* and *I. Shain*, Anal. Chem. **36**, 706 (1964).

[12] *R. S. Nicholson*, Anal. Chem. **38**, 1406 (1966).

[13] *R. S. Nicholson*, Anal. Chem. **37**, 1351 (1965).

[14] *T. W. Swaddle*, Coord. Chem. Rev. **14**, 217 (1974).

[15] *A. Earnshaw, L. S. Arkworthy*, and *K. C. Patel*, J. Chem. Soc. **A 1969**, 2276.