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Electrochemical Investigations of Triphenylsilyl-Chromate(VI) in Acetonitrile Solutions

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Introduction

Electrochemical investigations of chromium compounds in non-aqueous solvents [1–7] have up to now been carried preferably to formal oxidation states III, II, I and 0. Practically no data are known concerning the cathodic reduction of chromium(VI) in non-aqueous media.

In the framework of our investigations on organometallic chromates [8] we have been interested in the electrochemical behaviour of chromates(VI). In order to distinguish between triphenylsilyl-, stannyl- and germanylchromates in their redox behaviour, an electrochemical study of chromates in non-aqueous solvents seemed to be of interest.

The results reported in this paper are based on triphenylsilylchromate reduction, but they also compare the electrochemistry of ionic chromium(VI) compounds.

Experimental

Chemicals

The solvents acetonitrile (AN) and dimethylsulphoxide (DMSO) were purified by fractional distillation according to standard procedures [9]. The water content was checked by Karl-Fischer titration, being lower than 0.1%.

All measurements were done in 0.1 *M* tetraethylammonium perchlorate (TEAP) prepared from tetraethylammoniumhydroxide/perchloric acid and recrystallized from acetonitrile. The hydroxide was obtained from commercial tetraethylammonium chloride by ion exchange on a strong basic anion exchanger (Wofatit SBK, VEB Chemiekombinat Bitterfeld, G.D.R.). Traces of chloride were removed by passing the hydroxide several times through the column. Potassium bichromate was dissolved by 18-crown-6 (Riedel-de Haen). The preparation of triphenylsilyl-, germanyl- and stannylchromate was described elsewhere [10].

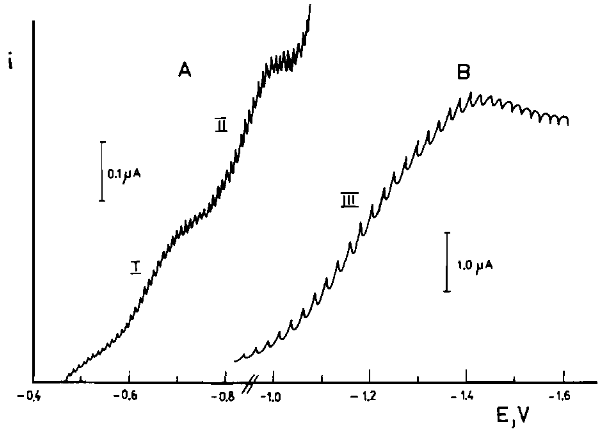

Fig. 1. Polarogram of 5 × 10^{-4} *M* triphenylsilyl chromate in AN/0.1 *M* TEAP recorded at different current sensitivities.

Apparatus and Methods

Polarogramms were recorded with a three electrode system by use of the polarographic instrument OH 105 (Radelkis Budapest) at 25 °C under argon atmosphere. The saturated calomel reference electrode was separated from the measuring solution by a frit filled with agar gel. A platinum wire served as auxiliary electrode, the working electrode being a conventional dropping mercury electrode (DME).

For cyclic voltammetric measurements a Beckman-Electroscan 30 equipped with a three electrode compartment was used. The working electrode was glassy carbon (VEB Elektrokohle, Berlin-Lichtenberg, G.D.R.) or was prepared from gold wire sealed with epoxy in a glass tube.

In the Karl-Fischer titration a double platinum electrode combined with a pH-meter MV 85 (VEB Präzitronic, G.D.R.) was used for dead stop monitoring.

All measurements were carried out in a dark room with green light in order to avoid photochemical reduction of chromates. However, during investigations it became evident that day light did not show any significant influence on the electrochemical behaviour of the solutions tested.

Results

Polarography

Electrochemical reduction of triphenylsilylchromate(VI) in AN at DME gave the polarogram outlined in Fig. 1. After appearance of a small anodic current at about –0.25 V, cathodic waves were observed at –0.64 V (I), at about –0.85 V (II) (Fig. 1, curve A) and at about –1.2 V (III) (Fig. 1, curve B). The initial anodic current was caused by

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chloride impurities of the supporting electrolyte favouring anodic dissolution of mercury. This effect could be avoided by careful purification of the tetraethylammonium perchlorate. In the extended potential range of up to +0.5 V however no additional waves were obtained. A study of the three reduction waves in more detail revealed a diffusion controlled process only in the case of the first one (I) (Fig. 1): the current depends linearly on chromate(VI) concentration and on the square root of the height of the mercury reservoir.

The logarithmic analysis (E *vs.* log (i/(i_d – i) of the wave gave a straight line with a slope of 0.060 V, indicating a one-electron reaction step.

The shape of the second reduction wave (II) depends in a non-reproducible manner on concentration and on the dropping time. The wave is observable only at dropping times lower than 3 seconds (5×10^{-4} *M* Cr(VI)), and its shape changes with the chromate (VI) concentration. The wave is associated with a maximum at 10^{-3} *M* concentrations, its quantitative characterization was thus impossible.

The third wave also showed some unexpected features: the intensity is nearly 10 times higher than that measured for the currents of the first and second reduction waves. In spite of the fact that wave three is raised at increasing concentrations, no reliable data for a diffusion-controlled reversible electrode process could be detected. The logarithmic analysis of the wave gave values between 0.130 and 0.182 V, depending on dropping time and concentration values which are far from the theoretical for any reversible redox reaction. In addition, at high concentrations the wave shape is at a maximum shaped, probably caused by overlapping of two reduction processes. This assumption was confirmed by ac-polarographic measurements where peaks at –1.17 V and at –1.42 V have been observed, the second peak having an intensity of about one tenth of the peak at –1.17 V. Attempts to evaluate the number of transferred electrons by controlled potential coulometry gave no reproducible results. From the experimental findings mentioned the following processes can be deduced: in AN, triphenylsilylchromate is initially reduced in a formally reversible one-electron step giving a species whose further reduction occurs (at sufficient concentrations) in an irreversible manner. The reduction at about –1.2 V is to be ascribed to formation of Cr(II) for the following reasons: the potential is similar to half wave potentials for the Cr(III)/Cr(II) couple at DME in DMSO or DMF (both –0.92 V *vs.* SCE 2), and the high intensity of the wave can be explained by a catalytic process connected with the participation of Cr(II). The electrochemically generated Cr(II) symproportionates with excess of chromate (VI), forming Cr(III) which is reduced again at the electrode to give Cr(II).

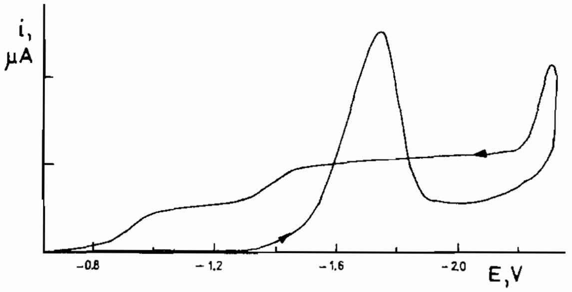

Fig. 2. Voltammetric profiles for the rotating gold electrode recorded on a 7×10^{-4} *M* triphenylsilyl chromate solution of AN in 0.1 *M* TEAP.

Such a behaviour is already known from studies with Cr(VI) in aqueous solution [11]. Furthermore, the formation of Cr(II) under our experimental conditions is favoured by its stability in non-aqueous solvents, a stability which is known to be much higher than that found in water [6]. Reduction of Cr(II) to Cr(0) occurs at a potential of –1.42 V, coinciding with half wave potentials measured for reduction of Cr(III)-species in DMF (–1.58 V) [2] and in AN (–1.43 V *vs.* SCE) [4].

In the potential range studied from 0 to –1.6 V the reduction of the organometallic group has not to be taken into consideration because it was shown to occur at potentials lower than –2 V [12].

The polarography of other organo-metallic chromates (VI), as tested for triphenylstannyl- and triphenylgermanylchromate, did not provide any difference compared to the behaviour of silylchromate.

Voltammetry at solid electrodes

In order to evaluate the electrochemistry of triphenylsilylchromate(VI) we examined its behaviour at both rotating and stationary solid electrodes.

By reduction of chromates (VI) at a rotating gold electrode whose surface was cleaned by hot nitric and sulfuric acid, no current signals were obtained in the range from 0 to –2 V. Only by use of untreated or cathodically (at –2 V) pretreated electrodes could voltammograms be obtained, as outlined in Fig. 2. After cathodic reduction at –1.7 V two waves at –1.42 V and –0.93 V were observable if the potential scan was reversed to positive potentials. As a result of the electrochemical processes the electrode is covered with a black layer, from irreversibly formed reduction products. The waves which appear just at potentials for the couples Cr(II)/Cr(0) and Cr(III)/Cr(II) respectively did not show any correlation with diffusion-controlled electron steps. Most probably, the waves are produced from reduction of species in the adsorbed material. This is supported by the fact that at further scans the heights of the waves decrease and the potentials are shifted

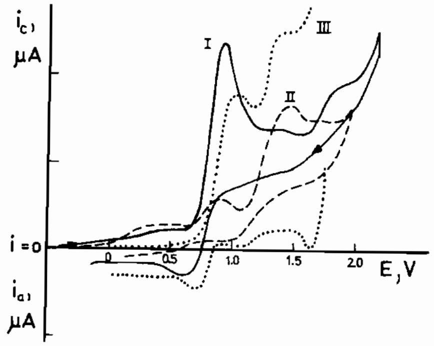

Fig. 3. Cyclic voltammograms recorded on 7 × 10^{-4} *M* triphenylsilyl chromate in AN solution at solid electrodes. I first and II second scan at Au-electrode; III glassy carbon electrode; scan rate 50 mV s^{-1}; 0.1 *M* TEAP.

to more negative values, presumably by progressive reduction of the species in the layer by formation of a completely passivated electrode surface.

At stationary electrodes this passivation effect is seen more clearly. From the cyclic voltammogram in Fig. 3 it is evident that in the first scan typical reduction peaks are observed at –0.9 V (formation of Cr(II)) and at –1.45 V Cr(II) → Cr(0), as well as anodic oxydation of Cr(II) to Cr(III) at –0.7 V. At the second scan (Fig. 3) the intensities of the reduction peaks are markedly changed and at further scans passivation leads to complete depression of any electrode processes. From the high intensity of the reduction peak at –0.9 V the chemical generation of Cr(III) by the mentioned reaction of electrochemically formed Cr(II) with Cr(VI) diffusing towards the electrode is again verified. By use of glassy carbon instead of gold as the working electrode the chemical generation of Cr(III) leads to an anodic minimum at the reverse scan (Fig. 3), showing permanent reduction of Cr(III) to Cr(II) even at the anodic scan. Such an anodic minimum was also found for cyclic voltammograms of chromates(VI) in aqueous solution on a hanging mercury drop [13].

In the present case the appearance of an anodic minimum only at the carbon electrodes gives evidence for a lower passivation effect at the electrode compared to the gold electrode. In general, the investigation at solid electrodes supports the findings estimated polarographically. The initial one-electron step at –0.64 V observed at DME, however, can not be reproduced at solid electrodes, because only poor reduction waves or peaks at about –0.25 V are obtained (Fig. 3).

Discussion

From the results the following conclusions can be drawn:

i. Except for the polarographically-obtained one-electron reduction at –0.64 V, which seems to be a reversible-electron transfer, all reduction processes are irreversible in nature giving mainly Cr(II) and Cr(0). There is no direct evidence for stabilization of intermediate oxidation states as Cr(V), Cr(IV) and Cr(III).

ii. In the potential range from 0 to –2 V the electrochemical behaviour of triphenylsilylchromate(VI) is determined mainly by its chromate character. The same behaviour can also be observed with other organo-metallic chromates and with ionic chromates, *e.g.* potassium dichromate dissolved with 18-crown-6 or [pyH]CrO_3Cl.

iii. The similar behaviour of even ionic and organometallic chromates (VI) and the low reproducibility of the reduction waves suggest that no discrimination between different organo-metallic chromates (VI) is possible (based on electrochemical measurements). Differences in $E_{1/2}$ potentials found for various triorganohalo-silanes and -germanes [12] at –1.9 V to –2.2 V and –1.6 V to –1.85 V, respectively, have no corresponding case in esters of chromates(VI) from triphenylsilyl, germanyl- and stannylhalogens.

iv. The reactivity of organo-metallic chromates with electrochemically generated Cr(II) is slower than that of the ionic chromates (VI). Thus with ionic Cr(VI) species no anodic oxydation of formed Cr(II) is found, even by applying rapid scan voltammetry.

v. Passivation of metallic electrodes by chromium, as known from corrosion studies in aqueous solution [14], also occurs with chromates(VI) in nonaqueous solvents. In addition organo-metallic chromates(VI) show a stronger tendency for passivation of the electrode than ionic chromates do, most probably due to the formation of decomposed organic material.

The electrochemical behaviour of triphenylsilylchromates (VI) can be described by the following scheme (potentials refer to measurements at DME)

$$\begin{tikzcd}
{[R_3Si]_2CrO_4} \arrow[r, "-1.2\text{V}", "+4e"'] \arrow[d, shift right, "+e"'] & \text{Cr(II)} \arrow[r, "-1.42\text{ V}", "+2e"'] \arrow[d, shift right, "-1.17\text{ V}"'] & \text{Cr(0)} \\
{[[R_3Si]_2CrO_4]^-} \arrow[u, shift right, "-0.64\text{ V}"'] \arrow[r, dashed, "-0.85\text{ V}"'] & \text{Cr(III)} \arrow[u, shift right, "\text{Cr(II)} + R_3Si_2CrO_4 \text{ or } -0.75\text{ V}"'] &
\end{tikzcd}$$

The formulation of the species formed at –0.64 V in the scheme correlating formally with a one-electron step is only hypothetical. For its further reduction to Cr(III) because up to now no product analysis was successful.

The present investigation shows conventional electrochemistry to be a rather limited approach for characterization of chromium (VI) species according to their redox behaviour, unlike other very informative studies (*e.g.* with uranium(VI) complexes in non-aqueous media [15]) which have been reported.

A comparison of the electrochemically-determined reduction potentials of chromate(VI) with the redox potentials determined by other techniques is not possible, as at present no such data are known for chromium [16].

In order to overcome the hindered electron-transfer reaction between chromates(VI) and the electrodes, further efforts are necessary in finding suitable mediators [17] for the transfer of electrons from the electrode to the chromium species in reversible electron steps.

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