ELECTROCHEMICAL REDUCTION OF RARE-EARTH CHELATES
WITH CERTAIN β-DIKETONES

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UDC 541.138.3:541.49:546.65/66:547.442

Chelates of a number of lanthanides (Pr, Eu, Tb, Dy, Er, Tm, Yb) and certain other metals (Cu, Ni, Co, Ti) with the β-diketones dipivaloylmethane and trifluoroacetylcamphor are reduced electrochemically for the first time in an aprotic medium (DMF). The nature of the lowest unoccupied molecular orbital, into which the first electron enters, is demonstrated to be centered on the ligand and not the metal. A difference is observed in the polarographic behavior of the cerium subgroup complexes (Pr, Eu), which are reduced in one step, and those of the yttrium subgroup, which exhibit two waves (Tb, Er, Yb) of a distinctly doubled wave (Tm, Dy).

Of all the organic reagents used to separate and determine various metals, β-diketones are used extensively. This group of compounds includes 2,2,6,6-tetramethylheptane-3,5-dione, or dipivaloylmethane (DPM), and 3-trifluoroacetylcamphor (TFAC).

![Structure of DPM and TFAC](image)

The structure and properties of these diketones and their chelates with many metals have been studied and described in [1]. However, their electrochemical behavior, which is interesting regarding their oxidative and reductive properties, the oxidation state of the central metal atom, the interaction of the metal and ligand, and other structural features have not yet been studied. Although the structure of a number of diketones and their electrochemical reduction have been described in sufficient detail, the electrochemical behavior of DPM and TFAC in nonaqueous solvents have not been studied before.

The goal of the present work is to study the electrochemical reduction of dipivaloylmethanates and trifluoroacetylcamphorates of several metals, primarily lanthanides, that have not been studied earlier in nonaqueous media. The polarography of certain other β-di-

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ketones, mainly Eu in aqueous medium, is reported in [2, 3]. The first waves in the polarograms as a rule are assigned to electrochemical reduction (ECR) of the metal cation. However, an exception was observed for the Eu complex with thienylacetone in aqueous-ethanol where only a ligand wave was found [4]. Dimethylformamide (DMF) was used as solvent since aprotic media not only ensure sufficient solubility but also enable the complexes to be studied at negative potentials not attainable in aqueous media.

EXPERIMENTAL

Classical voltammograms were recorded using a GWP-673 (GDR) polarograph in DMF with supporting electrolyte 0.1 M Et₄NClO₄ at a potential scan rate 0.5 V/min in a thermostated bath at 25 ± 0.1°C using a two-electrode cell. The capillary parameters of the polarized dropping mercury electrode (DME) in DMF solution were: \( \tau = 0.75 \text{ sec}^{-1} \) and \( m = 2.23 \text{ mg/sec} \) (\( h_{\text{Hg}} = 45 \text{ cm} \)). A mercury pool was used as reference electrode and anode. Cyclic voltammograms at a stationary mercury electrode were recorded over a wide potential-scan-rate range (0.1-25 V/min) using a triangular potential.

RESULTS AND DISCUSSION

Complexes of the trivalent lanthanides Pr, Eu, Tb, Dy, Er, Tm, and Yb of composition 1:3 (metal:deprotonated ligand), divalent Cu, Ni, and Co (1:2), and monovalent Tl (1:1) with the diketones were synthesized in the structure and reactivity laboratory of the A. E. Arbuzov IOPC, Academy of Sciences of the USSR. They were assigned the following structure on the basis of physicochemical data:

![Chemical Structure](image)

Ligands in these chelates exist in the enol form.

Certain polarographic characteristics of the chelates, the starting \( \beta \)-diketones, and the model compounds are presented in Table 1. Analysis of the data presented shows that TFAC (1) is irreversibly reduced in DMF solutions (as seen from the cyclic voltammograms). The activation energy of the limiting current of the first wave \( (Q_{\text{lim}}) \) was calculated from the dependence of the limiting current \( (i_{\text{lim}}) \) on temperature between 10-70°C. It is close to that characteristic of a purely diffusional process \( (1.5-2 \text{ kcal/mole}) \) but slightly elevated (small kinetic limitations). Since it was demonstrated by PMR that TFAC (1) exists as a mixture of the ketone and enol \( (3:1) \) in DMF, in contrast to DPM (9), which is practically totally in the enol form, it is most likely that the first wave of TFAC (1) \( (at -1.53 \text{ V}) \) is due to ECR of the ketone and the second \( (at -2.30 \text{ V}) \) to ECR of the enol form. The half-wave potential \( E_{1/2} \) of the enol form of DPM (9) is \(-2.30 \text{ V} \). This agrees with the hypothesis. Benzophenone (17) is known to be reduced in the ketone form, giving two waves at \(-1.63 \text{ and } -2.00 \text{ V} \) under our conditions. However, camphor itself, for which the fraction of enol is only \(-0.14\% \) in water containing a little methanol [5], gives a wave at rather negative potentials (with a height indicative of one electron). There are no data in the literature for ECR of camphor in nonaqueous media. It is usually studied in electrochemical processes in aqueous-organic mixtures since it is a surfactant and inhibits ECR processes of other substances by forming a film on the electrode. There are many reports of chemical reduction of camphor to the enantiomeric alcohols. Reduction of camphor by chemical reagents has been well studied. For example, a SET mechanism (with homogeneous electron transfer in solution) with intermediate formation of an anion-radical in the first step of the process of borneol formation has been proposed [6]. It can be presumed that ECR follows an analogous path. In ethanol containing H₂SO₄, at a mercury cathode, camphor is also reduced to borneol [7]. Data have been obtained only for oscilopolarographic quantitative determination of camphor at Pt, Cu, and Ag amalgamated electrodes [8]. The polargraphically active fragment in TFAC (1) is probably the C=O group of the trifluoroacetyl substituent. Reduction of this moiety is facilitated since it is an electron-acceptor.

The single irreversible wave of DPM (9) \( at -2.10 \text{ V} \) \(-600 \text{ mV more negative than } E_{1/2} \text{ of TFAC (1)} \) is probably due to ECR of the enol form. The reduction mechanism in aprotic solvents...