

Electrochemical Study of Triscyclopentadienyluranium Complexes

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(Received December 22, 1987)

Abstract

The electrochemical behaviour of Cp_3UBH_4 and Cp_3UNEt_2 in THF has been studied using cyclic voltammetry and chronoamperometry. Cp_3UBH_4 undergoes a simple one-electron quasi-reversible reduction, while chemical reactions between the product of the charge-transfer reaction and the starting electroactive species occur both after oxidation and reduction of Cp_3UNEt_2 .

Introduction

A limited number of investigations have been published concerning the electrochemistry of the cyclopentadienyluranium complexes [1–4] even though, in principle, the electrochemical approach seems particularly useful to produce and characterize new organouranium compounds with unusual oxidation states.

Such a scarcity of literature reports can be explained by taking into account the high reactivity of these compounds, which, in some cases, makes it difficult to obtain quantitative and reproducible electrochemical results, mainly when techniques operating on a time-scale comparable to the lifetime of the electroactive species are applied (e.g. bulk electrolysis method).

In the present paper we report the results of an investigation on the electrochemical behaviour of Cp_3UBH_4 [5] and Cp_3UNEt_2 [6, 7] based on cyclic voltammetric and chronoamperometric measurements, which are electroanalytical techniques able to operate on a sufficiently short time-scale and which, combined together, can be used as an alternative to coulometry in order to determine the number of electrons involved in reversible electrochemical processes [8].

Experimental

All operations and electrochemical experiments were carried out with rigorous exclusion of oxygen and moisture in a dinitrogen-filled recirculating glove-box. Tetrahydrofuran was distilled from K/benzophenone under N_2 . Cp_3UBH_4 [5a], Cp_3UNEt_2 [7]* and $\text{Cp}_3\text{U}\cdot\text{THF}$ [9] were synthesized according to the published procedures.

The supporting electrolyte, tetrabutylammonium tetraphenylborate ($\text{Bu}_4\text{N}^+\text{BPh}_4^-$; Fluka), was purified according to the literature method [10] and used at the maximum concentration available in THF before precipitation took place (0.07 M).

An Amel 553 potentiostat with IR compensation, an Amel model 568 digital logic function generator, a conventional three-electrode cell equipped with a Luggin capillary, a spherical Pt electrode and an Ag wire quasi-reference electrode with cobaltocene as an internal reference [11] were used.

The redox couple cobaltocene/cobalticinium (Coc/Coc^+) ($E_{1/2} \approx -0.45$ V versus Ag wire in our experiments) was chosen as internal reference instead of the more widely used ferrocene/ferricinium system because in our solutions the oxidation of ferrocene took place in the proximity of the oxidation of the electroactive species.

Results and Discussion

Figure 1 shows the cyclic voltammetric behaviour of Cp_3UBH_4 recorded immediately after the dissolution of this compound in 0.07 M THF/ $\text{Bu}_4\text{N}^+\text{BPh}_4^-$ solution (full line). No oxidation peak is detectable, while in the forward cathodic scan one reduction peak is observed with which one oxidation peak is

*For the synthesis of Cp_3UNEt_2 the method (b) was followed.

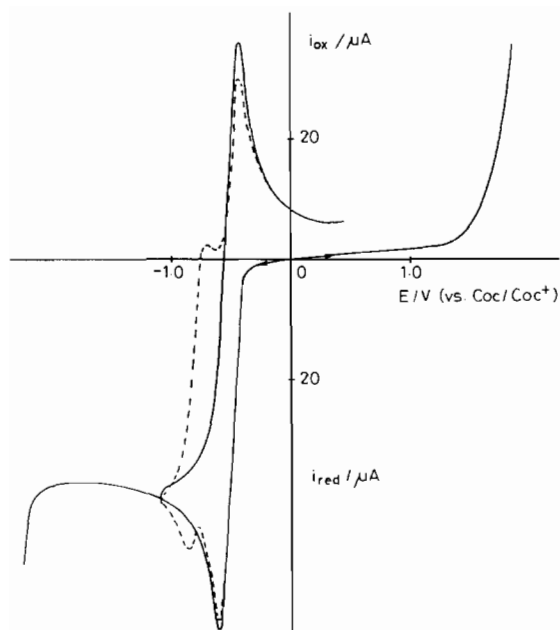


Fig. 1. Cyclic voltammograms of 2.5 mM Cp_3UBH_4 recorded in 0.07 M $\text{THF}/\text{Bu}_4\text{N}^+\text{BPh}_4^-$ solution at a platinum electrode; scan rate 0.1 V s^{-1} : (—) immediately after dissolution, (---) 30 min after dissolution.

directly associated. The value of the $i_p(v^{-1/2})$ product is independent of the scan rate as well as the i_p^b/i_p^f ratio (where i_p^f and i_p^b are the peak currents in the forward and backward scan, respectively, this last quantity being equal to 0.93 ± 0.05 in the range $0.05\text{--}0.50 \text{ V s}^{-1}$). The half-wave potential $E_{1/2} = (E_p^f + E_p^b)/2$ is -0.55 V at any scan rate explored, while the separation between the associated reduction and oxidation peaks is slightly dependent on the scan rate, being, for instance, 0.07 V at 0.05 V s^{-1} and 0.14 V at 0.50 V s^{-1} . These findings indicate that the reduction process is not perfectly reversible [12] and involves a transfer coefficient α , within the range 0.3 to 0.7, that allows one to evaluate the half-wave potential by the above simple relation [12].

The cyclic voltammetric pattern described above slowly changes with time due to reactions of Cp_3UBH_4 with the electrolytic solution: at first a new reduction peak gradually appears (Fig. 1, dotted line, recorded 30 min after Cp_3UBH_4 dissolution), while after a longer time other broad reduction peaks also emerge, further complicating the voltammetric pattern. All the data presented in this article concern only freshly prepared solution because only in this way was it possible to get reproducible results.

Attempts to carry out controlled potential electrolyses were unsuccessful because of fouling of the platinum gauze working electrode during the experiments. It is worth noting that coulometry

cannot give conclusive results on both the number of electrons involved and the identification of the species generated by the studied reduction process because the time-scale of these experiments is comparable to the lifetime of the starting electroactive substance in the electrolytic solution, also when no reduction process is taking place.

In order to determine the number of electrons involved on a shorter time-scale, an alternative to coulometry was used [8] that gives n from the combination of voltammetric and chronoamperometric responses according to:

$$n = \left[\frac{i_p(v^{-1/2})}{i_c(t^{1/2})} \frac{F}{K} \right]^2 \frac{1}{\pi} \quad (\text{A})$$

where K is the Randles–Sevcik constant, i_c is the chronoamperometric current at time t and all the other symbols have their usual meanings. It is noteworthy that eqn. (A) does not require knowledge of the electrode area nor the concentration of electroactive substance if both these parameters are kept constant in the voltammetric and chronoamperometric measurements. By substituting in eqn. (A) cyclic voltammetric and chronoamperometric data relevant to the reduction of Cp_3UBH_4 , an n value of 0.93 is obtained; it is worth noting that chronoamperometric measurements alone gave i_c versus $t^{-1/2}$ linear plots ($r = 0.98$) with an intercept of zero.

All the above reported results indicate that Cp_3UBH_4 undergoes a quasi-reversible one-electron reduction process generating a rather stable anion:



The formation of such an anionic species in solution agrees with the experimental evidence showing that some cyclopentadienyluranium(IV) complexes can undergo chemical or electrochemical one-electron reduction giving a stable anion in which the added electron presumably occupies a vacant 5f orbital of the metal [1, 2, 13, 14].

Rather more complex electrochemical behaviour is displayed by Cp_3UNEt_2 which, as shown in Fig. 2, can be both oxidized and reduced directly. Analogously to Cp_3UBH_4 , Cp_3UNEt_2 also reacts with the electrolytic solution giving in a few minutes a more complicated voltammetric picture (dotted line in Fig. 2). In the forward anodic scan an oxidation peak approaching reversible behaviour is observed at $E_{1/2} = +1.030 \text{ V}$ ($\Delta E_p = 0.09 \text{ V}$ at 0.05 V s^{-1} , 0.18 V at 0.5 V s^{-1} , $n = 0.46$ calculated by eqn. (A) using $i_p(v^{-1/2})$ at $v \geq 0.1 \text{ V s}^{-1}$ and $i_c(t^{-1/2})$ at $t \leq 2 \text{ s}$, see later). The involvement of about one-half of an electron per molecule suggests that a fast chemical reaction between the oxidation product and the starting electroactive species follows the charge-transfer reaction.

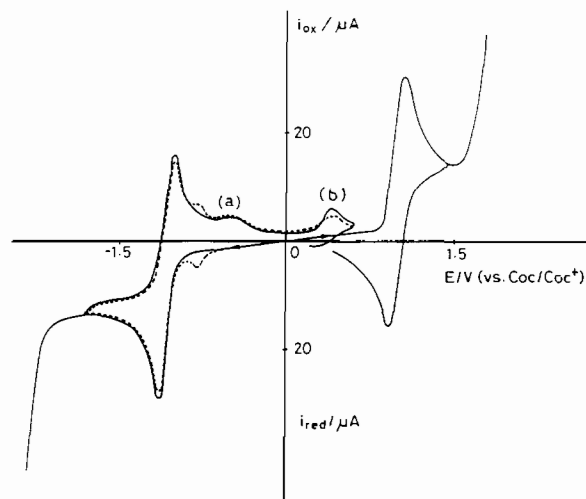
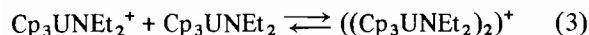
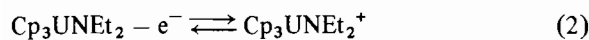


Fig. 2. Cyclic voltammograms of 2.5 mM Cp_3UNEt_2 recorded in 0.07 M $\text{THF}/\text{Bu}_4\text{N}^+\text{BPh}_4^-$ solution at a platinum electrode; scan rate = 0.1 V s^{-1} : (---) immediately after dissolution, (—) 7 min after dissolution.

On the other hand, it is reasonable to postulate that the U(V) product generated at the electrode is an unstable species (five is a very unusual oxidation state for organouranium derivatives). This species can be involved in equilibrium reactions generating a more stable dimeric species according to the scheme:



The positive charge produced in the electrochemical reaction (2) on the uranium atom could be stabilized by the lone-pair of an NEt_2 group nitrogen of a second molecule of Cp_3UNEt_2 via the formation of U-N-U bridging bonds between the two uranium atoms; the formation of such a bimolecular complex is encouraged by the easy possibility of an increase in the coordination number of the actinides [15–17].

Furthermore, the dependence of $i_{\text{pc}}/i_{\text{pa}}$ on the scan rate (Fig. 3) indicates that this dimeric species is also rather unstable and that an irreversible decomposition reaction occurs, causing the progressive decrease of the associated cathodic peak by lowering the scan rate. Owing to this decomposition reaction, chronoamperometric and voltammetric data to be inserted in eqn. (A) must be obtained at low chronoamperometric time and at a relatively high scan rate, i.e. in a time-scale where this decomposition is not operative.

Cathodic cyclic voltammetry shows a reversible wave at $E_{1/2} = -1.070 \text{ V}$ ($\Delta E_p = 0.08 \text{ V}$ at 0.05 V

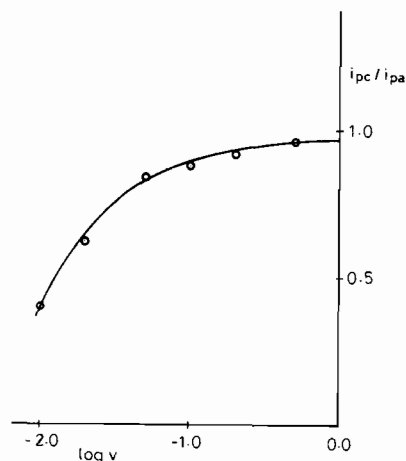
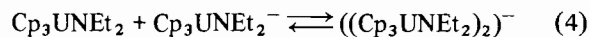


Fig. 3. Dependence of $i_{\text{pc}}/i_{\text{pa}}$ for the oxidation process of Cp_3UNEt_2 .

s^{-1} , 0.16 V at 0.5 V s^{-1} , $i_{\text{pa}}/i_{\text{pc}} = 0.92$, $i_{\text{pc}}(v^{-1/2}) = \text{const.}$, $n = 0.43$ calculated by (A)).

In the reverse scan the broad peaks (a) and (b) are also observed: the irreversible peak (b) corresponds to the oxidation of $\text{Cp}_3\text{U}\cdot\text{THF}$, as verified by comparison with the voltammetric behaviour of a pure sample of this compound (E_{pa} about $+0.320 \text{ V}$).

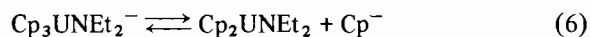
Also in this case an n value less than 1 can be explained by the occurrence of fast chemical reactions involving the starting Cp_3UNEt_2 compound. Possible reactions in agreement with the stoichiometry of the reduction process are a dimerization:



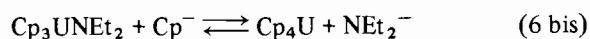
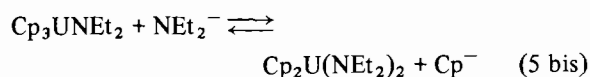
or a loss of ligands from the reduction product



or



followed by reaction of these ligands with the starting electroactive compound:



Our experimental results, i.e. the presence of peak (b) in Fig. 2 and the well-known possibility of a ligand exchange reaction between Cp and NEt_2 in Cp_3UNEt_2 [7], suggest the occurrence of the reaction pathway (5, 5 bis). Nevertheless, the low height of this peak as well as the appearance of

the unidentified peak (a) cannot exclude the possibility that all the reactions (4, 6, 6 bis) could occur simultaneously.

On the other hand, reactions analogous to (6, 6 bis) have been considered plausible for similar $\text{Cp}_3\text{U}^{(\text{IV})}\text{X}$ systems [1], and the formation of dimers (eqn. (4)) are in principle possible since uranium in these complexes is coordinatively unsaturated [15, 17].

Conclusions

According to what has been previously reported for other uranium(IV) organometallic derivatives [2, 3], our study concerning the electrochemical behaviour of Cp_3UBH_4 and Cp_3UNEt_2 has been greatly hampered by their reactivity towards the electrolytic solutions (Cp_3UNEt_2 and Cp_3UBH_4 are very sensitive to traces of impurities; moreover, a reaction with a BPh_4 anion of the supporting electrolyte is not excluded [18]; other supporting electrolytes containing PF_6 , AsF_6 , ClO_4 , BF_4 anions have been tested, but the lowest rate of decomposition occurred with $\text{Bu}_4\text{N}^+\text{BPh}_4^-$).

Nevertheless, such a study has been possible by avoiding the obstacle of determining the number of electrons involved in the electrochemical reaction by using a combination of voltammetric and chronoamperometric responses.

The results obtained show that while Cp_3UBH_4 exhibits a one-electron quasi-reversible reduction to Cp_3UBH_4 without ligand loss, Cp_3UNEt_2 is reduced at more negative potential than Cp_3UBH_4 , and also undergoes an oxidation process; the electrode charge-transfer of Cp_3UNEt_2 is followed by chemical reactions involving the starting species Cp_3UNEt_2 ; these reactions can be dimerization, loss and exchange of ligands.

Interestingly, the oxidation of Cp_3UNEt_2 gives rise to unstable species of uranium(V), a rather unusual oxidation state for cyclopentadienyluranium derivatives.

Acknowledgements

We thank Mr F. Braga and Mr D. Rudello for skilled technical assistance.

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