A Comparative Electrochemical Study of Thorium(IV) and Uranium(IV) Acetylacetonates

Alain Vallat
Laboratoire de Chimie Analytique et Appliquée, Faculté des Sciences Mirande, 21004 Dijon Cédex, France
Etienne Laviron and Alain Dormond
Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (UA 33), Faculté des Sciences, 6 bd Gabriel 21000 Dijon, France

---

The electrochemical behaviour of the Thorium(IV) and Uranium(IV) acetylacetonates $[Th(acac)_4]$ and $[U(acac)_4]$ (acac = acetylacetonate ion) has been investigated by cyclic voltammetry in tetrahydrofuran and acetonitrile. The complexes are reduced in two one-electron steps. The first electron uptake leads to the $[M^{III}(acac)_4]^-$ (M = Th or U) ion, which slowly loses an acetylacetonate ion $acac^-$, with formation of $[M^{III}(acac)_3]$. The second step is more complex and is due to the reduction of $[M^{III}(acac)_4]^-$ and/or $acac^-$.

Stable uranium(III) complexes are easily obtained by electroreduction of uranium(IV) organometallic derivatives in aprotic media.[1–4] Few studies dealing with the electrochemical behaviour of thorium(IV) derivatives have hitherto appeared; the electrochemical reduction of $ThCl_4$ directly leads to the metal,[5] whereas the tricyclopentadienyl or bis(pentamethylcyclopentadienyl) derivatives undergo a one-electron reduction, followed by the loss of a cyclopentadienyl anion.[6] A few thorium(III) complexes have been synthesized chemically or photochemically from the corresponding thorium(IV) precursors.[7–9]

We report in this paper the results of a comparative study of the electrochemical reduction of the complexes $[Th(acac)_4]$ and $[U(acac)_4]$ (acac = acetylacetonate ion).

Experimental

The complexes $[Th(acac)_4]$ and $[U(acac)_4]$ were prepared by treating $ThCl_4$ or UCl_4 with Na(acac) in tetrahydrofuran (thf); they were recrystallized from toluene.[10] The compound $NBu^t{}_4(acac)$ was prepared according to Burnett *et al.*[11] and $[Mn(acac)_3]$ was a commercial product (Merck).

The electrochemical experiments were carried out on thf or acetonitrile solutions of $[M(acac)_4]$ (M = Th or U) (2×10^{-3} mol dm^{-3}) with tetrabutylammonium hexafluorophosphate (*ca.* 0.1 mol dm^{-3}) as the supporting electrolyte under an argon atmosphere on a vacuum line. Tetrahydrofuran was first dried and deoxygenated over the benzophenone–sodium complex and then distilled under argon. Acetonitrile was dried over P_2O_5, distilled, and kept over P_2O_5 until it was used, when it was distilled again. The salt $[NBu_4]PF_6$ was recrystallized twice from ethanol, oven-dried, then deoxygenated and dehydrated under vacuum at 80 °C.

Potentials were recorded with respect to an Ag–AgClO$_4$ reference electrode (0.01 mol dm^{-3}) [respectively +0.39 and +0.35 V *vs.* an aqueous saturated calomel electrode (s.c.e.) in thf and acetonitrile] and the working electrode was in all cases a platinum disc (diameter = 1 mm). Voltammograms were obtained with the help of a Tacussel UAP4 unit, equipped with a Nicolet 3091 digital oscilloscope and an X-Y recorder.

Results and Discussion

Results obtained in thf and acetonitrile are very similar and we will report here only those obtained in thf. A compound described as $[U(acac)_4]$ was studied on mercury by Graf *et al.*[12] and we will compare their results with ours.

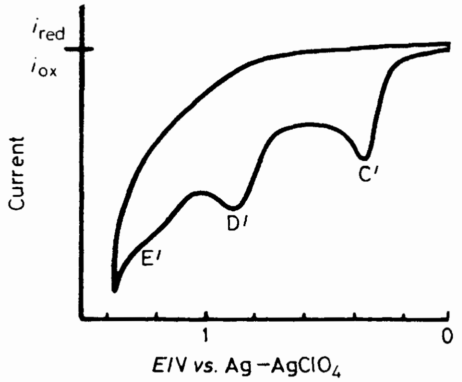

Figure 1. Cyclic voltammogram of $[U(acac)_4]$ in thf at a stationary platinum electrode between 0 and 1.4 V; scan rate 200 mV s^{-1}

Rotating Disc Electrode (R.D.E.) Voltammetry.—The complex $[Th(acac)_4]$ shows a first reduction wave A at −2.55, followed at −3.10 V by a second wave B, rather ill defined because of its proximity to the reduction 'wall.' The reduction of $[U(acac)_4]$ proceeds similarly with waves at −2.50 and −3.10 V. A comparison of the limiting currents with those obtained for $[Mn(acac)_3]$[13] under the same experimental conditions shows that for each of the waves A and B the reduction occurs *via* a one-electron process.

On oxidation, $[Th(acac)_4]$ shows no wave, whereas for $[U(acac)_4]$ a first wave C′ (0.5 F) appears at 0.35 V, followed by two waves D′ and E′ at 0.9 and 1.2 V.

Cyclic Voltammetry on a Stationary Electrode.—For the complex $[U(acac)_4]$, the three peaks C′, D′, and E′, corresponding to the r.d.e. waves, appear when the potentials are scanned anodically (Figure 1). Two reduction peaks A and B are observed for $[Th(acac)_4]$ (E_p = −2.68 and −3.1 V at 200 mV s^{-1}) (Figure 2). If the potential scan is switched before peak B, a reversible system A–A′ is seen. The ratio of the anodic peak height to that of the cathodic peak i_{p_a}/i_{p_c} is equal to 1 when the scan rate v is larger than 50 V s^{-1}, but it decreases for smaller values of v (Figure 2). If peak B is included in the cyclic scan,

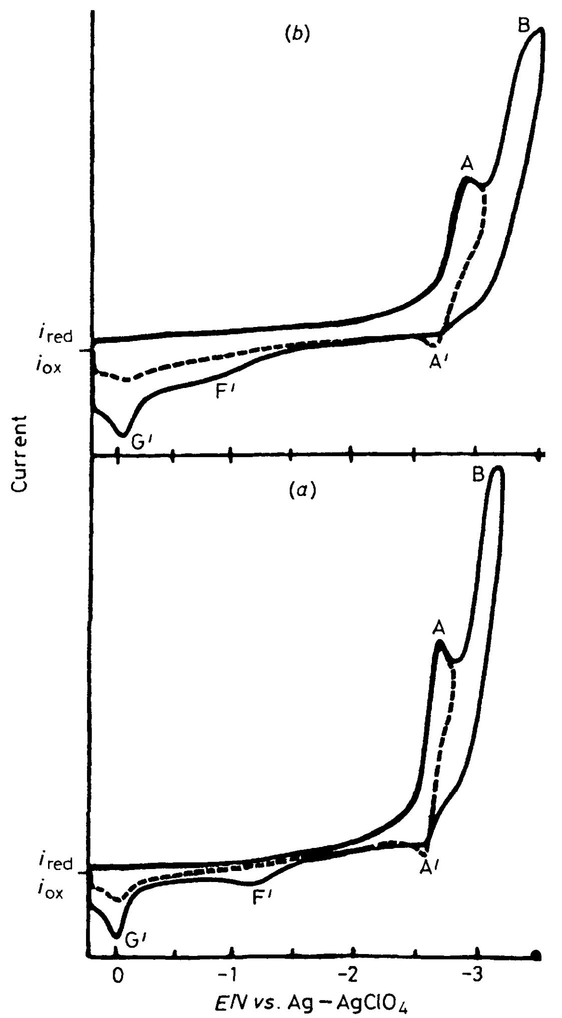

Figure 2. Cyclic voltammogram of $[Th(acac)_4]$ in thf at a stationary platinum electrode; scan rates (*a*) 200 mV s^{-1} and (*b*) 10 V s^{-1}

i_{p_a}/i_{p_c} decreases (Figure 2). When $i_{p_a}/i_{p_c} < 1$ (either because of the slow sweep rate or because peak B is reached), two oxidation peaks F′ and G′ appear on the reverse scan. Peak G′ corresponds to the oxidation of the anion $acac^-$; the same peak is obtained with a solution of t-butylammonium acetylacetonate.

The behaviour of $[U(acac)_4]$ is quite similar (Figure 3) (E_p at -2.61 and -3.1 V for A and B respectively), except that the system A–A′ is reversible when $v > 10$ V s^{-1}, and that peaks F′ and G′ are not so well defined.

The decrease in height of peak A′ when v decreases indicates that the first electron uptake is followed by a chemical reaction, whose rate is larger for the thorium than for the uranium complex. The reaction yields in particular the ion $acac^-$. These results can be accounted for by the mechanism shown in equations (1)—(3) (M = Th or U), equation (2) being a probable intermediate step. The uptake of the electron by the metal would be followed by its transfer to one of the ligands with opening of the metal–acetylacetonate ring.

$$[M^{IV}(acac)_4] + e^- \rightleftharpoons [M^{III}(acac)_4]^- \quad (1)$$

$$[M^{III}(acac)_4]^- \rightleftharpoons [M^{III}(acac)_3(acac)^-] \quad (2)$$

$$[M^{III}(acac)_4]^- \rightleftharpoons [M^{III}(acac)_3] + acac^- \quad (3)$$

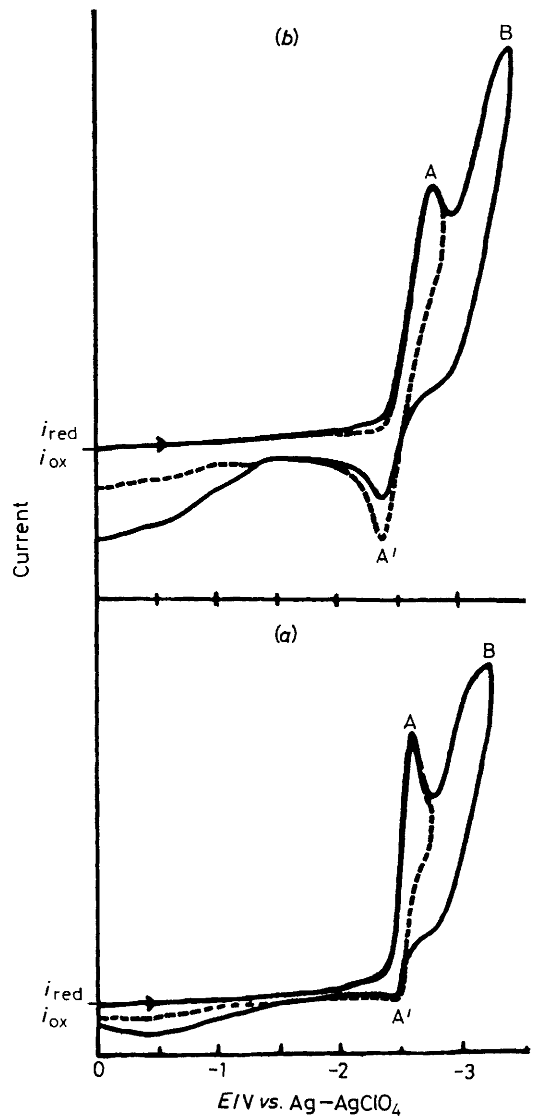

Figure 3. Cyclic voltammogram of $[U(acac)_4]$ in thf at a stationary platinum electrode; scan rates (*a*) 200 mV s^{-1} and (*b*) 10 V s^{-1}

This series of reactions is reversible. This was demonstrated with $[U(acac)_4]$ by scanning anodically the potential at different rates after maintaining the potential for 10 s at -2.7 V (first reduction stage) (Figure 4). The curves are compared in each case to those obtained without previous reduction. In all cases, peak A′ is very small. At slow sweep rates, only peaks C′ and D′ are observed; they have the same height as those due to the direct oxidation of $[U(acac)_4]$ [Figure 4(*a*)]. This indicates that $[U(acac)_4]$ is regenerated during the anodic scan. When the sweep rate increases [Figure 4(*b*) and (*c*)], peaks C′ and D′ decrease, while F′ and G′ appear. In view of these results, peak F′ can be attributed to a slow electrochemical oxidation of $[M^{III}(acac)_3]$.

The second reduction step (peak B) of $[Th(acac)_4]$ and $[U(acac)_4]$ does not actually correspond to a single reaction but to the reactions shown by equations (4)—(6). A reaction

$$acac^- + e^- \rightleftharpoons acac^{\bullet 2-} \quad \text{(peak B1)} \quad (4)$$

$$[M^{III}(acac)_4]^- + e^- \rightleftharpoons [M^{III}(acac)_3] + acac^{\bullet 2-} \quad \text{(peak B2)} \quad (5)$$

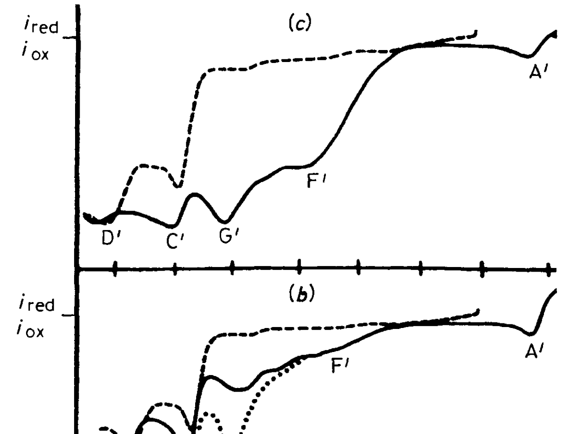

Figure 4. Anodic scan of [U(acac)$_4$] in thf at a stationary platinum electrode after initial polarization at −2.7 V for 10 s (——); after initial polarization at −2 V without previous reduction (– – – –); after additional introduction of NBu$_4$(acac) (· · · ·); scan rates (*a*) 200 mV s^{-1}, (*b*) 1 and (*c*) 10 V s^{-1}

$$\mathrm{acac}^{\bullet 2-} + \text{solvent} \longrightarrow \text{solvent}^{\bullet -} + \mathrm{acac}^{-} \qquad (6)$$

analogous to (4) has been described by Buchta and Evans[14] in the case of the enolate of 1,3-diphenyl-1,3-propanedione which is also reducible by NaH in thf.[15] The values of the reduction potentials of acac$^-$ and [M(acac)$_4$]$^-$ are little different, so that peaks B1 and B2 have a tendency to merge, forming only one peak B. On the other hand the height of peak B, which is the sum of those of B1 and B2, remains practically constant since the species acac$^-$ and [M(acac)$_4$]$^-$ both come from the reduction of [M(acac)$_4$] [*cf.* equations (1)—(3)]. At high sweep rates there is not enough time for reaction (3) to occur [the reaction stops at equation (1) or (2)], so that [M(acac)$_4$]$^-$ is reduced during the second stage [peak B2, equation (5)]. For slow potential scans, in contrast, [M(acac)$_4$]$^-$ completely dissociates [equation (2)], and the second stage corresponds entirely to the reduction of acac$^-$ [peak B1, equation (3)]. The transition depends on the metal. For thorium, for example, when $v > 50$ V s^{-1}, only peak B2 is observed. In the case of uranium, the rate needs to be only 10 V s^{-1}.

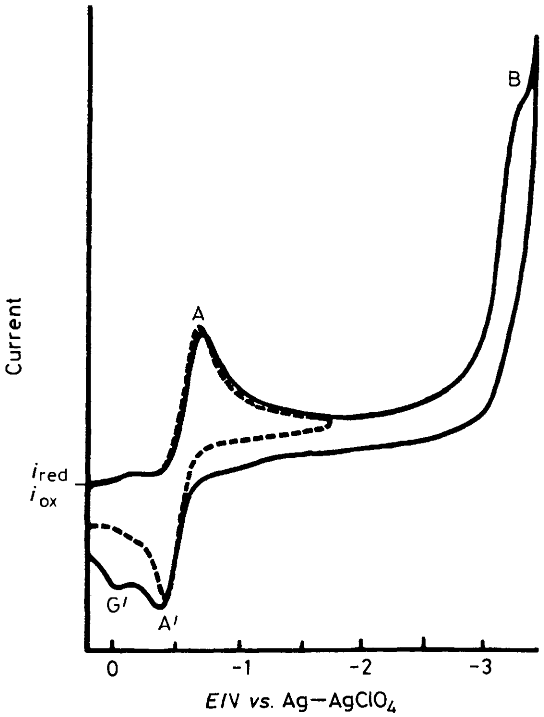

Figure 5. Cyclic voltammogram of [Mn(acac)$_3$] in thf at a stationary platinum electrode; scan rate 1 V s^{-1}

Our interpretation is confirmed by the following experiments and observations.

(*i*) At 5 V s^{-1}, for example, only one broad peak B is observed for [U(acac)$_4$]. Addition of NBu$_4$(acac) causes peak B1 to appear at −3.25 V, whereas peak B2 is seen at −3.4 V.

(*ii*) Sock *et al.*[13] have established that the monoelectronic reduction of [Mn(acac)$_3$] leads reversibly to the stable anion [Mn(acac)$_3$]$^-$. We have re-examined the reduction of this compound (Figure 5) and it shows indeed a first reversible stage, followed by a second stage which must under these conditions correspond to the reduction of [Mn(acac)$_3$]$^-$ (peak B2 at − 3.2 V). Upon addition of NBu$_4$(acac), peak B is shifted to − 3.1 V.

(*iii*) On the backward scan, when the sweep direction is reversed after peak B (Figures 2, 3, and 5), the oxidation peak G′ of the acac$^-$ anion always appears. This confirms that acac$^-$ is formed and justifies reaction (6).

(*iv*) When reaction (3) does not occur or occurs incompletely (A′ is observed if the scan is reversed after A), a decrease of peak A′ and an increase of peak G′ are observed if the potential is scanned up to peak B (compare the curves of Figures 2 and 3). This shows that a ligand separates [reaction (5)].

The oxidation processes in the case of [U(acac)$_4$] appear as complex. During stage C′, 0.5 F mol^{-1} is consumed; the reaction mechanism is probably that shown by equations (7) and (8). We are currently investigating these reactions.

$$[\mathrm{U^{IV}(acac)_4}] \rightleftharpoons [\mathrm{U^{V}(acac)_4}]^+ + e^- \qquad (7)$$

$$[\mathrm{U^{V}(acac)_4}]^+ + [\mathrm{U^{IV}(acac)_4}] \longrightarrow [\mathrm{U_2(acac)_8}]^+ \qquad (8)$$

At first sight, our results are at variance with those of Graf *et al.*[12] who observed with a sample of [U(acac)$_4$], supplied by Pfaltz and Bauer, two reduction peaks at −0.8 and −1.2 V *vs.* s.c.e. Their work was carried out on a mercury electrode in propylene carbonate or acetonitrile. They attributed these

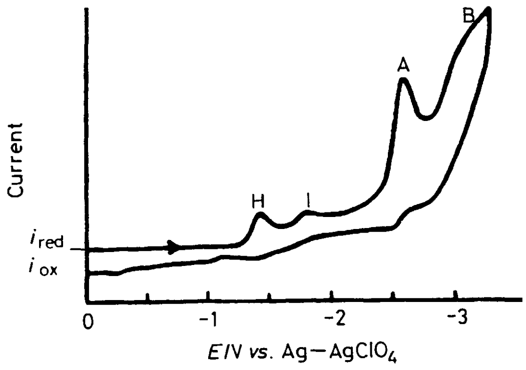

Figure 6. Cyclic voltammogram of [U(acac)$_4$] in thf after exposure to air for 10 d at a stationary platinum eletcrode; scan rate 1 V s^{-1}

peaks to the formation of uranium(III) species. The use of a mercury electrode did not allow them to see oxidation waves. We indeed found these peaks (H and I, Figure 6) under our experimental conditions at −1.3 and −1.7 V (−0.91 and −1.31 V *vs.* s.c.e.) in thf and −1.2 and −1.6 V (−0.85 and −1.25 V *vs.* s.c.e.) in acetonitrile either when the solution of [U(acac)$_4$] is exposed to air for several days, or when the potential is scanned slowly after being initially held for a few seconds at +1 V.

The n.m.r. spectrum of the sample from Pfaltz and Bauer is described as being complex, whereas the spectrum of freshly prepared [U(acac)$_4$] shows only two singlets of respective intensity 1 and 6 at δ 12.96 and −3.76, which corresponds to a highly symmetrical structure (archimedean square antiprism).[16] The sample from Pfaltz and Bauer appears in fact as an ill defined oxidation product of [U(acac)$_4$].

Acknowledgements

We are grateful to Mrs. E. Savrot for her technical assistance.

References

1 Y. Mugnier, A. Dormond, and E. Laviron, *J. Chem. Soc., Chem. Commun.*, 1982, 257.
2 P. Reeb, Y. Mugnier, A. Dormond, and E. Laviron, *J. Organomet. Chem.*, 1982, **239**, C1.
3 R. G. Finke, G. Gaughan, and B. Voegeli, *J. Organomet. Chem.*, 1982, **229**, 179.
4 S. Renaud, A. Dormond, L. Roullier, and Y. Mugnier, *J. Organomet. Chem.*, 1988, **347**, 71.
5 G. Duyckaerts and C. Degueldre, *J. Electroanal. Chem.*, 1981, **119**, 347.
6 A. M. Koulkes-Pujo, J. F. Lemaréchal, A. Dormond, and G. Folcher, *Inorg. Chem.*, 1987, **26**, 3171.
7 B. Kanellakopulos, E. Domberger, and F. Baumgartner, *Inorg. Nucl. Chem. Lett.*, 1974, **10**, 155.
8 D. G. Kalina, T. J. Marks, and W. A. Wachter, *J. Am. Chem. Soc.*, 1977, **99**, 3877.
9 J. W. Bruno, D. G. Kalina, E. A. Mintz, and T. J. Marks, *J. Am. Chem. Soc.*, 1982, **104**, 1860.
10 R. Guilard, A. Dormond, M. Belkalem, J. E. Anderson, Y. H. Liu, and K. M. Kadish, *Inorg. Chem.*, 1987, **26**, 1410.
11 J. N. Burnett, L. K. Hiller, and R. W. Murray, *J. Electrochem. Soc.*, 1970, **117**, 1028.
12 E. Graf, A. Giraudeau, and M. Gross, *Inorg. Chem.*, 1983, **22**, 3233.
13 O. Sock, P. Lemoine, and M. Gross, *Electrochim. Acta*, 1981, **26**, 99.
14 R. C. Buchta and D. H. Evans, *Anal. Chem.*, 1968, **40**, 2181.
15 N. L. Bauld, *J. Am. Chem. Soc.*, 1964, **86**, 2305.
16 W. L. Steffen and R. C. Fay, *Inorg. Chem.*, 1978, **17**, 779.

Received 22*nd May* 1989; *Paper* 9/02124H