$Ru_2(O_2CCF_3)_4Cl$ would be initially reduced at close to +0.6 V, generating an extremely stable Ru(II) dimer.

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Registry No. $Ru_2(HNOCCF_3)_4Cl$, 86846-89-1; $[Ru_2(HNOCCF_3)_4(Cl)_2]^-$, 86846-90-4; $Ru_2(O_2CC_3H_7)_4Cl$, 86846-91-5; $Ru_2(O_2CC_3H_7)_4$, 86846-92-6; $Ru_2(HNOCCF_3)_4$, 86846-93-7; $Ru_2(O_2CCH_3)_4Cl$, 38833-34-0; Ru, 7440-18-8; TBAP, 1923-70-2; (TBA)Cl, 1112-67-0.

Contribution from the Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide,
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Electrochemical Reduction of Uranium(IV) Acetylacetonate in Aprotic Media

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The electrochemical reduction of $U^{IV}(acac)_4$ has been investigated in propylene carbonate and acetonitrile solvents on mercury electrodes. The overall monoelectronic reduction of $U^{IV}(acac)_4$ to $[U^{III}(acac)_4]^-$ occurs in two distinct steps. Electrochemical measurements associated with temperature and/or drop-time changes show the presence of an intermediate chemical reaction following the first electrochemical step. Addition of basic molecules clearly demonstrates that the intermediate chemical step corresponds to the intermolecular exchange of one acac ligand between the oxidized and reduced forms of the acetylacetonate uranium complex, leading to the formation of the $[U^{IV}(acac)_5]^-$ complex. An interpretation resting on the nonoccupied ninth coordination position of uranium is given for this behavior.

Introduction

Redox properties of uranium in aqueous solutions have been studied by many investigators.[1-5] In aqueous media, hexavalent uranium UO_2^{2+} is reduced in two[1-3] or three steps,[4] depending on the pH and the nature of the supporting electrolyte. On the time scale of polarographic methods, the reduction of UO_2^{2+} occurs in three steps: the first is a reversible one-electron step resulting in the formation of quinquevalent uranium UO_2^+; this is followed by a second wave corresponding to the irreversible reduction of uranium(V) to uranium(IV); the third step corresponds to the reversible reduction of U^{IV} to U^{III}.[4] Direct reduction of U^V to U^{III} was also observed.[3,5]

On the other hand, electrochemical studies on U^{IV} solutions have shown that the system U^{IV}/U^{III} is reversible, with a half-wave potential close to that of the third polarographic wave of uranyl ion,[6] but it was noticed that the generated U^{III} species undergo fast chemical oxidation, probably due to the reduction of protons by U^{III}.

Such a chemical reduction of protons by electrochemically generated species may be prevented and, consequently, low oxidation states of uranium may be stabilized in solution, when appropriate organic solvents are used in electrochemical investigations.

In organic solvents the electrochemical reduction of U^{VI} and U^{IV} species to trivalent uranium has been previously reported[6-9a] but generally without mechanistic details. Also, obtention of zerovalent amalgamated uranium is not unambiguously established.[9b]

The present paper provides the first report of a study devoted to the redox behavior of tetrakis(acetylacetonato)uranium(IV) ($U^{IV}(acac)_4$). Previous studies on the reduction of acetylacetonates of several transition metals[10-12] have revealed that these reductions may trigger significant changes in the coordination of the metals and also that the coordinating acac ligands alter the redox reactivity of the central metal, and this is actually the basis of the current study.

Table I. Half-Wave Potentials of $U^{IV}(acac)_4$ (V/SCE at 20 °C) at a Dropping-Mercury Electrode[a]

	$E_{1/2}{}^1$	$E_{1/2}{}^2$
PC/TEAP	−0.780	−1.180
PC/TBAP	−0.800	−1.200
CH_3CN/TEAP	−0.780	−1.200
CH_3CN/TBAP	−0.780	−1.160

[a] Drop time 2 s; scan rate 2 $mV{\cdot}s^{-1}$.

X-ray data in the solid state and several consistent arguments[13] indicate that tetrakis(acetylacetonato)uranium(IV) has the D_2 square antiprism as the ground-state coordination polyhedron. In solution, ^1H NMR indicates a less symmetrical structure, and the experimental observations can be rationalized only by assuming two (or more) nonequivalent sites for this 8-coordinated chelate.

Also, it is generally accepted that the ring-shaped β-diketone ligand is a conjugated system, and it is demonstrated that unpaired spin density is transferred from the paramagnetic transition metal to the ligand, in β-diketonates of uranium(IV).[14]

In this work, the redox behavior of $U^{IV}(acac)_4$ will be discussed and a reduction mechanism will be proposed.

Experimental Section

The studied compound $U^{IV}(acac)_4$ was purchased from Pfaltz and Bauer, Inc. $[N(CH_3)_4]$acac salts were prepared according to known procedures.[15] Sodium methanolate was a commercial product (Merck).

Electrochemical measurements were carried out under argon at controlled temperatures (20 or −25 °C) on dropping-mercury electrodes. All measurements were performed with a classical three-

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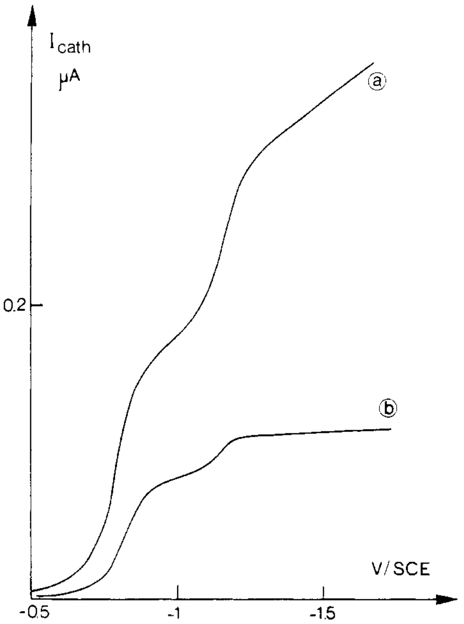

Figure 1. Dc polarograms of 1.0×10^{-3} M $U^{IV}(acac)_4$, in PC/0.1 M TBAP (drop time 2 s): (a) 20 °C; (b) -25 °C.

electrode potentiostatic device (Solea-Tacussel), involving a potentiostat (PRT 20-2X), a voltage pilot unit (Servovit 2), a millivoltmeter with high-impedance input (S 6B), and a potentiometric recorder (EPL 2). For cyclic voltammetric experiments, a signal generator (GSATP from Solea-Tacussel) was associated with the above units, through the potentiostat.

Coulometric measurements were performed on mercury-pool electrode (area 6 cm^2).

The solvent (propylene carbonate, PC) was purified by distillation under reduced pressure (0.1 torr) through a column (length 1 m) filled with glass rings. Traces of an unidentified impurity were eliminated by slowly percolating the solvent on molecular sieves (Merck, 0.5 nm, length of the column 1.20 m). Acetonitrile (CH_3CN) was used without further purification (Merck).

Tetra-*n*-butylammonium perchlorate (TBAP)—background electrolyte—was purified by dissolution in a small volume of methanol, then precipitated in a large volume of distilled water, and finally dried at least 48 h at 60 °C under reduced pressure (10^{-2} torr). Tetra-*n*-ethylammonium perchlorate (TEAP) was purified according to an earlier reported method.[16]

Throughout all measurements, the reference electrode was a calomel electrode in a saturated aqueous solution of KCl (SCE) electrically connected to the studied solution by a junction bridge filled with the studied solution without electroactive species.

Results

Dc Polarography at Controlled Drop Time. In PC/0.1 M TBAP, $U^{IV}(acac)_4$ exhibits (Figure 1) two well-defined reduction waves at -0.80 and -1.20 V/SCE. For drop times (t_d) greater than 2 s, both waves have limiting currents proportional to the analytical concentration of $U^{IV}(acac)_4$ at 20 °C. A third, ill-defined signal is also present at -2.2 V/SCE. For drop times smaller than 2 s the recorded polarograms are shown in Figure 2. The cathodic limiting current of the second reduction step diminishes faster than the first one and almost vanishes at $t_d < 0.1$ s. In addition, the temperature decrease from +20 to -25 °C influences drastically the relative heights of the first two cathodic waves: The limiting currents of these two waves are equal at 20 °C, whereas at -25 °C the limiting current of the second wave is only one-fourth of the first (Figure 1).

These results lead to the hypothesis that the first reduction step is followed by a chemical step that generates a new species whose reduction corresponds to the second reduction wave. For $t_d < 0.1$ s, the second reduction step almost vanishes (Figure 2).

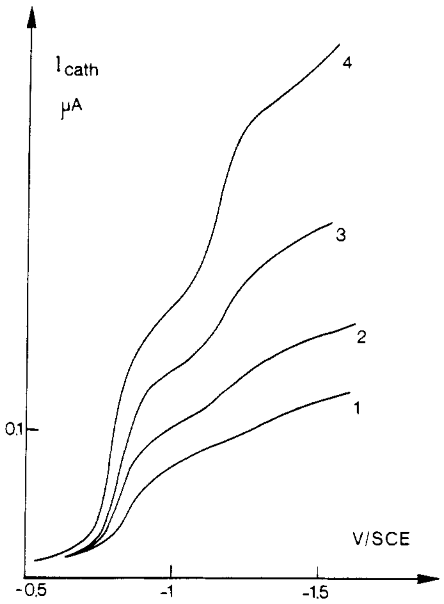

Figure 2. Drop-time effects on polarograms of 10^{-3} M $U^{IV}(acac)_4$, in PC/0.1 M TBAP, at 20 °C. Drop time: (1) 0.1, (2) 0.2, (3) 0.6, and (4) 2 s.

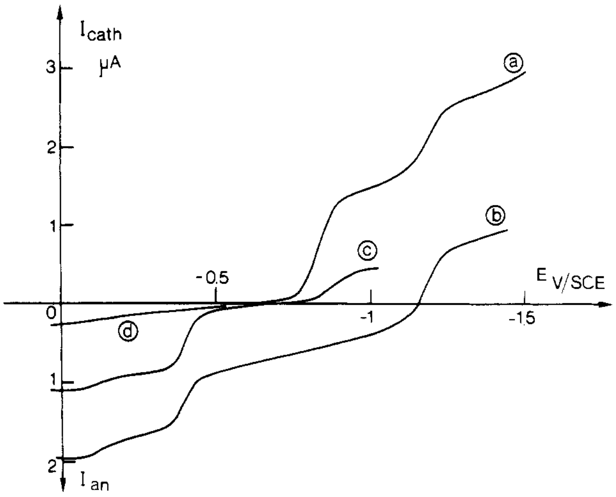

Figure 3. Direct (a) and reverse (b–d) normal-pulse polarograms of 1.1×10^{-3} M $U^{IV}(acac)_4$, in PC/0.1 M TBAP (drop time 2 s, delay 1.90 s, pulse duration 40 ms, sampling 80–90%, temperature 20 °C). Initial potential on the scans: (a) 0, (b) -1.5, (c) -1.0, and (d) -0.5 V/SCE.

Pulse Polarography. As already observed in dc polarography, normal-pulse polarography from 0 to -2 V/SCE exhibits two reduction waves (Figure 3a). Criteria based on the shift of the sampling time window on the pulse[17] indicate that the limiting currents are diffusion controlled for the first wave and under control of chemical kinetics for the second wave. Moreover, reversed-pulse polarograms (RPP) (i.e., scanning toward anodic potentials) from -1.5 to 0 V/SCE (Figure 3b) and from -1.0 to 0 V/SCE (Figure 3c) reveal that only the second wave has a reversible character whereas the first wave corresponds to an irreversible electron transfer.

In addition, an oxidation wave is observed at -0.4 V/SCE on both reverse polarograms (Figure 3b,c). Also, it should be noticed that the assisted oxidation of the mercury electrode

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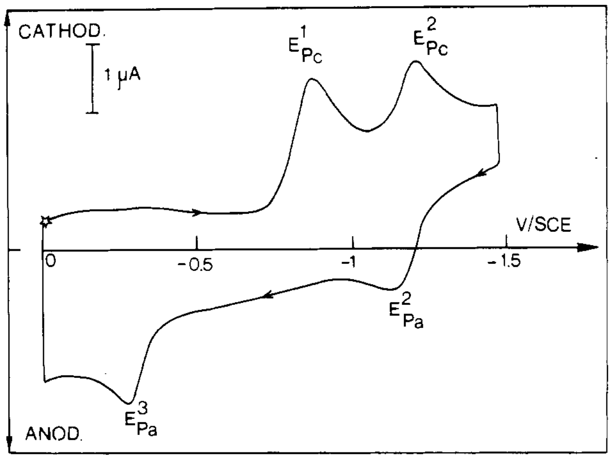

Figure 4. Cyclic voltammetry of 3×10^{-3} M $U^{IV}(acac)_4$, in PC/0.1 M TEAP [$v = 5$ V·s^{-1}, scan between 0 and −2 V/SCE (initial potential 0 V/SCE), electrode Hg, temperature 20 °C].

in the presence of acac ions[15] was not observed on the reverse polarograms.

The above results thus indicate that the first reduction of $U^{IV}(acac)_4$ is irreversible, whereas the second reduction is reversible and kinetically controlled by a chemical step. Also, none of these reduction steps results in the decoordination of acac ions from the complexes in the solution.

Cyclic Voltammetry. A typical voltammogram is given in Figure 4. The reduction peak potentials E_{pc}^1 and E_{pc}^2 correspond to the two reduction waves analyzed in polarography. On the backward scan, two anodic peaks (E_{pa}^2 and E_{pa}^3) are observed at all scan rates (1–100 V·s^{-1}), and a weak anodic peak E_{pa}^1 is associated to the cathodic peak E_{pc}^1 only at high scan rates (≥50 V·s^{-1}).

The peak E_{pa}^2 corresponds to the reduction peak E_{pc}^2, the difference $\Delta E_p = E_{pa}^2 - E_{pc}^2$ being about 70 mV at low scan rates (500 mV·s^{-1}). These results indicate that only the second reduction is reversible, and they support the hypothesis that a chemical step is interposed between the two observed electrochemical reduction steps of $U^{IV}(acac)_4$.

The third oxidation peak E_{pa}^3 at −0.4 V/SCE corresponds to the wave observed at the same potential in reverse-pulse polarography (Figure 3b,c).

Coulometry. Coulometric electrolyses at constant potential have been carried out on $U^{IV}(acac)_4$ for each of the two observed reduction steps. In each of the two steps, it is found that only 0.5 faraday/mol of $U^{IV}(acac)_4$ introduced in the solution is exchanged. Also, electrolyses performed at −1.4 V/SCE on $U^{IV}(acac)_4$ solutions give 1 faraday exchanged for the overall double reduction. This result is confirmed by comparison of the cathodic limiting currents in dc polarography of $U^{IV}(acac)_4$ with the cathodic limiting current of $Mn^{III}(acac)_3$ under the same experimental conditions and at the same analytical concentration. $Mn^{III}(acac)_3$ is known[11,18] to be reducible at −0.07 V/SCE in a one-electron diffusion-controlled process. If the diffusion coefficients of the electroactive complexes $Mn^{III}(acac)_3$ and $U^{IV}(acac)_4$ are assumed to be about equal, intercomparison of the above reduction waves again leads to 0.5 faraday exchanged in each reduction step of $U^{IV}(acac)_4$.

The above results are obtained in PC. The corresponding experiments repeated in CH_3CN are found to be very similar to those in PC.

Electrochemical Reduction of $U^{IV}(acac)_4$ in the Presence of Basic Potential Ligands. These results, as well as the specific characteristics in the chemistry of uranium, led us to examine the electrochemical behavior of $U^{IV}(acac)_4$ in the presence of basic species considered as potential ligands of uranium. The ligands examined here were acac, methanolate (CH_3O^-), and pyridine.

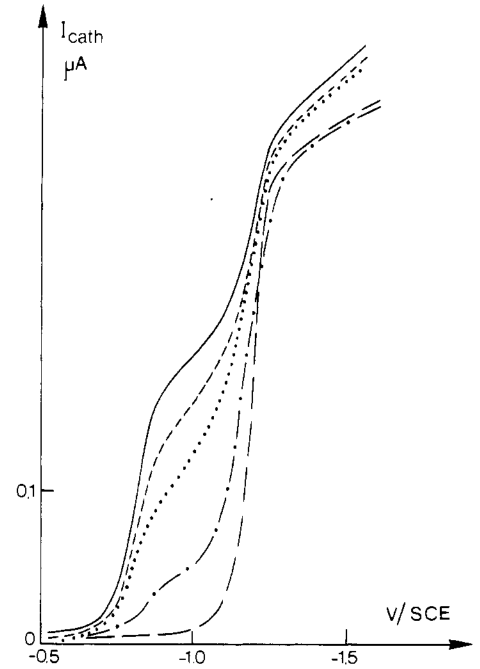

Figure 5. Dc polarograms of $U^{IV}(acac)_4$ in the presence of increasing amounts of added $[N(CH_3)_4]$acac (drop time 2 s, temperature 20 °C). Initial solution: 10 mL of PC (+0.1 M TBAP) containing 6.5 mg of $U^{IV}(acac)_4$. Solution of $[N(CH_3)_4]$acac in PC: 16.8 mg/mL, added in aliquots of (—) 0, (- - -) 20, (···) 40, (-·-) 100, and (– –) 200 µL.

(a) Addition of $[N(CH_3)_4]$acac. Figure 5 illustrates the changes induced on a polarogram of $U^{IV}(acac)_4$ in PC (and 0.1 M TBAP) when increasing amounts of $[N(CH_3)_4]$acac are introduced in the studied solution: The second reduction wave ($E_{1/2} = -1.20$ V/SCE) increases at the expense of the first wave ($E_{1/2} = -0.80$ V/SCE), whereas the overall limiting current corresponding to the sum of the two waves remains unchanged. In these experiments, each polarogram (Figure 5) corresponds to addition of a solution containing 16.8 g/L of $[N(CH_3)_4]$acac in PC. The concentration of the added $[N(CH_3)_4]$acac solution is such that an equimolar (1/1) ratio of $[N(CH_3)_4]$acac/$U^{IV}(acac)_4$ is obtained after adding 100 µL of the solution containing $[N(CH_3)_4]$acac to the initial 10 mL of the $U^{IV}(acac)_4$ solution.

The limiting current of the first reduction wave is found to decrease linearly with the added amount of $[N(CH_3)_4]$acac, so that this wave almost vanishes as soon as the molar ratio $[N(CH_3)_4]$acac/$U^{IV}(acac)_4$ reaches unity, the limiting current corresponding to the second reduction ($E_{1/2} = -1.20$ V/SCE) being then twice its initial value (no $[N(CH_3)_4]$acac added). No further changes are observed after additional introduction of $[N(CH_3)_4]$acac.

Also, in the solutions where the polarograms of Figure 5 are recorded, the presence of uncomplexed acac anions is sought on the basis of the assisted oxidation of mercury at −0.18 V/SCE in the presence of free acac[15] and also through the UV band of acac at 270 nm.[19] The presence of free acac is only detected in the studied solutions where more than 100 µL of $[N(CH)_4]$acac has been added.

These results indicate that, in solution, acac becomes coordinated to $U^{IV}(acac)_4$ in the ratio 1/1, thus generating $[U^{IV}(acac)_5]^-$. It may therefore be reasonably assumed that the second reduction step observed corresponds indeed to the

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reduction of $[U^{IV}(acac)_5]^-$, the first wave being the reduction of the initial species $U^{IV}(acac)_4$.

(b) Addition of Sodium Methanolate ($NaCH_3O$) or Pyridine. When increasing amounts of sodium methanolate are added to an initial solution containing $U^{IV}(acac)_4$, the first reduction wave undergoes a negative shift toward the second wave until the two waves merge in a unique signal spread out between −0.9 and −1.5 V/SCE. The limiting current equals the sum of the limiting currents of the two waves obtained in the initial solution of $U^{IV}(acac)_4$.

Addition of pyridine to an initial solution of $U^{IV}(acac)_4$ in PC has effects much like those observed above in the presence of CH_3O^- anions.

Discussion

In the present study of $U^{IV}(acac)_4$, electrochemical results are obtained in CH_3CN or PC as solvents, in the absence and in the presence of basic coordinating species (acac, CH_3O^-, pyridine).

In the absence of coordinating species, the electrochemical reduction of U^{IV} to U^{III} occurs in two distinct steps. In the first step, the reduction of $U^{IV}(acac)_4$ requires only 0.5 faraday/mol of $U^{IV}(acac)_4$ introduced in the solution. As demonstrated by the characteristics of the cyclic and stationary voltammograms (Figures 1, 2, and 4) this first electrochemical step is followed by a chemical reaction that destroys the electrogenerated species, and it is necessary to reduce considerably the time scale of the electroreduction (i.e., scan rates beyond 100 $V \cdot s^{-1}$ in cyclic voltammetry) to observe the reoxidation of the reduced form of $U^{IV}(acac)_4$ on the backward scan. These results may be rationalized in Scheme I, in which the chemical step is a bimolecular reaction between the initial species $U^{IV}(acac)_4$ and $[U^{III}(acac)_4]^-$ electrogenerated in the electrochemical step. The second reduction step observed in $U^{IV}(acac)_4$ solution exhibits an overall kinetics controlled by a preceding chemical step while 0.5 faraday/mol of $U^{IV}(acac)_4$ initially introduced is exchanged. As no free acac is detectable in the solution after the reductions, it is reasonable to expect that $[U^{III}(acac)_4]^-$ is the final product of the two reduction steps. This conclusion is fully supported by the observation that, after exhaustive reduction of a solution of $U^{IV}(acac)_4$, a complete reoxidation of the solution, carried out at −0.5 V/SCE, regenerates the initial $U^{IV}(acac)_4$.

Scheme I

$$\text{(E)}\quad U^{IV}(acac)_4 + e^- \rightarrow [U^{III}(acac)_4]^-$$

$$\text{(C)}\quad U^{IV}(acac)_4 + [U^{III}(acac)_4]^- \rightarrow \text{products}$$

The above results lead us to Scheme II in which the chemical step (C) in Scheme I is the exchange of an acac ligand between the reduced and the oxidized forms of the redox couple $U^{IV}(acac)_4/[U^{III}(acac)_4]^-$. This ligand exchange is compatible with the known coordination properties of uranium: the eight oxygens from the four acac ligands linked to uranium indeed do not fill out the coordination sphere of uranium, and it has been shown[20] that basic species (alcohol, ketone, amine) coordinate through a ninth bond. The formation of this additional bond is clearly revealed in NMR spectra: the spectrum of the coordinated basic species undergoes a large chemical shift, owing to the increased interactions between the atoms of this species and the f electrons (paramagnetic) of uranium. As these spectral shifts may be interpreted in terms of coordination stereochemistry, they provide useful information on the geometry of the molecules and they allow one to demonstrate that intermolecular exchanges of ligands are possible in these compounds.[13]

Scheme II

step 1

$$U^{IV}(acac)_4 + e^- \rightarrow [U^{III}(acac)_4]^-$$

$$U^{IV}(acac)_4 + [U^{III}(acac)_4]^- \xrightarrow{\text{fast}} [U^{IV}(acac)_5]^- + U^{III}(acac)_3$$

step 2

$$[U^{IV}(acac)_5]^- + e^- \rightleftarrows [U^{III}(acac)_5]^{2-}$$

$$[U^{III}(acac)_5]^{2-} + U^{III}(acac)_3 \xrightarrow{\text{slow}} 2[U^{III}(acac)_4]^-$$

A critical examination of the above proposed reduction schemes is possible in light of the results obtained in the presence of basic molecules. Assuming that $U^{IV}(acac)_4$ may coordinate to a fifth acac ligand (when such a ligand is available in solution), it is reasonable to expect that such coordination would occur also with any similar moieties. The coordination of acac to $U^{IV}(acac)_4$ is indeed unambiguously demonstrated by the changes induced on the polarograms of $U^{IV}(acac)_4$ by increasing additions of $[N(CH_3)_4]$acac (Figure 5) and by the absence of the anodic signal at −0.18 V/SCE, which characterizes the assisted oxidation of mercury by acac anions.[15] This absence of a signal at −0.18 V/SCE after addition of acac to $U^{IV}(acac)_4$ solution indicates that the coordination step of the fifth acac is fast. Also, since the assisted oxidation of mercury at −0.18 V/SCE becomes observable as soon as the concentration ratio $[N(CH_3)_4]$acac/$U^{IV}(acac)_4$ is higher than unity, it is clear that only one more acac group is coordinated per molecule of $U^{IV}(acac)_4$. Moreover, similar coordinative properties were already observed[21] with $U^{IV}(tfa)_4$ in the presence of excess tfa anion (tfa = trifluoroacetate). In the same context, when the ninth coordination position of uranium is occupied by CH_3O^- or pyridine, a single, one-electron-reduction wave is observed in solutions containing $U^{IV}(acac)_4$ plus the basic ligand. This is consistent with the expected resulting hindrance to the intermolecular exchange of acac between $U^{IV}(acac)_4$ and $[U^{III}(acac)_4]^-$.

It is then quite clear that the overall reduction of $U^{IV}(acac)_4$ in PC or CH_3CN is a one-electron process leading to $[U^{III}(acac)_4]^-$. In contrast to the behavior of several acetylacetonates of transition metals, which decoordinate one or more acac groups during the reaction, the acac ligands remain coordinated to uranium(IV) and -(III) as well, which is indicative of strong metal–ligand interactions.

On the other hand, it is observed (Figure 1) that additional coordination of an acac to U^{IV} results in a negative shift of the reduction potential (U^{IV} to U^{III}) of about −0.4 V on the basis of the above reduction scheme involving the couples $U^{IV}(acac)_4/[U^{III}(acac)_4]^-$ (step 1) and $[U^{IV}(acac)_5]^-/[U^{III}(acac)_5]^{2-}$ (step 2). Thus, subtraction of an acac in such a complex is expected to bring a positive shift of about +0.4 V in the reduction potential, and thereby the observed anodic signal at −0.4 V/SCE is fully consistent with the oxidation of the triply coordinated species $U^{III}(acac)_3$ generated in the chemical reaction following the first reduction step.

Registry No. $U^{IV}(acac)_4$, 65137-03-3; $U^{IV}(acac)_5^-$, 87039-18-7; $[N(CH_3)_4]$acac, 64881-96-5; $NaCH_3O$, 124-41-4; TEAP, 2567-83-1; TBAP, 1923-70-2; pyridine, 110-86-1.

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