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THE ANODIC OXIDATION OF URANOCENE. EVIDENCE FOR A REACTIVE DICATION

JARED A. BUTCHER, JR., RICHARD M. PAGNI *, and JAMES Q. CHAMBERS *
Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916 (U.S.A.)

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Summary

Cyclic voltammetric evidence is presented which indicates the existence of uranocene radical cation and dication intermediates in the electrochemical oxidation of uranocene in nonaqueous solvents.

Introduction

In keeping with the current interest in organouranium chemistry [1], we wish to report at this time further work on the anodic oxidation of uranocene [$U(COT)_2$] (I) which demonstrates the existence of both $U(COT)_2^+$ and $U(COT)_2^{2+}$ in solution. Under these conditions, $U(COT)_2^+$ is very easily oxidized and $U(COT)_2^{2+}$ has appreciable Lewis acidity. The only previous literature report of these cations concerns the gas phase where the uranocene dication has been observed by mass spectrometry [2].

Reported previously from our laboratory were the gross details of the anodic oxidation of I indicating the formation of uranium cluster cations in nonaqueous solvents [3]. As we reported, two oxidation waves (Ox1 and Ox2) are observed, with the first being quasi-reversible at low temperatures. A detailed investigation of the quasi-reversible couple obtained at various temperatures and sweep rates now permits the elucidation of mechanistic details of this chemistry.

Results and discussion

At room temperature uranocene can be electrochemically oxidized at platinum, glassy carbon, and mercury electrodes. Representative voltammetric data at a platinum disk electrode in several nonaqueous solvents are presented in Table 1. The voltammetric parameters, especially the peak potentials (E_p), are dependent on the choice of solvent/electrolyte, electrode material, and concen-

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TABLE 1

VOLTAMMETRIC PEAK POTENTIALS FOR THE OXIDATION OF URANOCENE IN NONAQUEOUS SOLVENTS AT ROOM TEMPERATURE

Solvent	Electrolyte	E_p (Ox1) [a]	E_p (Ox2) [a]
CH_2Cl_2	TBAP [b]	0.33	0.70
THF	TBAP	0.17	0.63
THF	$TBAPF_6$ [c]	0.33	0.57
CH_3CN	$TBAPF_6$	−0.27 [d]	0.07 [d]
C_6H_5CN	$TBAPF_6$	0.27 [e]	0.77 [e]

[a] Volts vs. SCE. sweep rate: 0.121 V/sec. [b] TBAP: Tetrabutylammonium perchlorate. [c] $TBAPF_6$: Tetrabutylammonium hexafluorophosphate. [d] $E_{1/2}$ values obtained by normal pulse voltammetry. [e] Obtained in the presence of suspended alumina.

tration. Significantly, the peak current for wave Ox1 is directly proportional to the uranocene concentration as shown in Table 2.

An unequivocal comment on the rather negative potentials observed in acetonitrile cannot be made since these are pulse voltammetric $E_{1/2}$ values obtained on a dilute saturated solution of $U(COT)_2$. However, it can be noted that solvation of an electrode product could shift Ox1 in this direction. Acetonitrile complexes to uranium containing species are well known and easily prepared [4].

Benzonitrile proved to be a more suitable solvent in terms of electrochemical characteristics and uranocene solubility, and it was employed for a detailed low temperature study of the quasi-reversible Ox1 wave. As seen in Fig. 1, the quasi-reversible couple has a decidedly irreversible form at 22°C and slow sweep rate (121 mV/sec). This couple consists of Ox1, a wave consistent with a one-electron oxidation (current function = 0.52 amp M^{-1} cm^{-2} sec^{-1} at 22°C) and two peaks, R1 and R2, on the reduction side. At faster sweep rates and lower temperatures, there is a pronounced buildup in the R1 peak at the expense of the R2 peak. At −10°C and 800 mV/sec, R2 has completely disappeared. It is clear that an intermediate is being intercepted by reduction at R1 before it can react to give a species which is reduced at R2.

Even at −10°C the couple remains quasi-reversible because: (1) $E_p - E_{p_{1/2}} =$ 85—90 mV, (2) peak separation ≈200 mV, and (3) $i_p^c/i_p^a = 0.6$. Furthermore, at −10°C $i_p/\sqrt{v}$ and i_p^c/i_p^a are independent of sweep rate ($v = 0.8$ to 20 V/sec).

TABLE 2

CONCENTRATION DEPENDENCE OF THE FIRST OXIDATION WAVE OF URACENE (Ox1) IN $THF/TBAPF_6$ AT ROOM TEMPERATURE

$[U(COT)_2]$ (mM)	E_p (Ox1) (V)	i_p (μA)
0.19	0.19 [a]	15.0 [b]
0.25	0.26	—
0.45	0.33	35.8
0.87	0.37	68.9
1.17	0.39	92.4

[a] Volts vs. SCE. [b] Sweep rate: 0.121 V/sec.

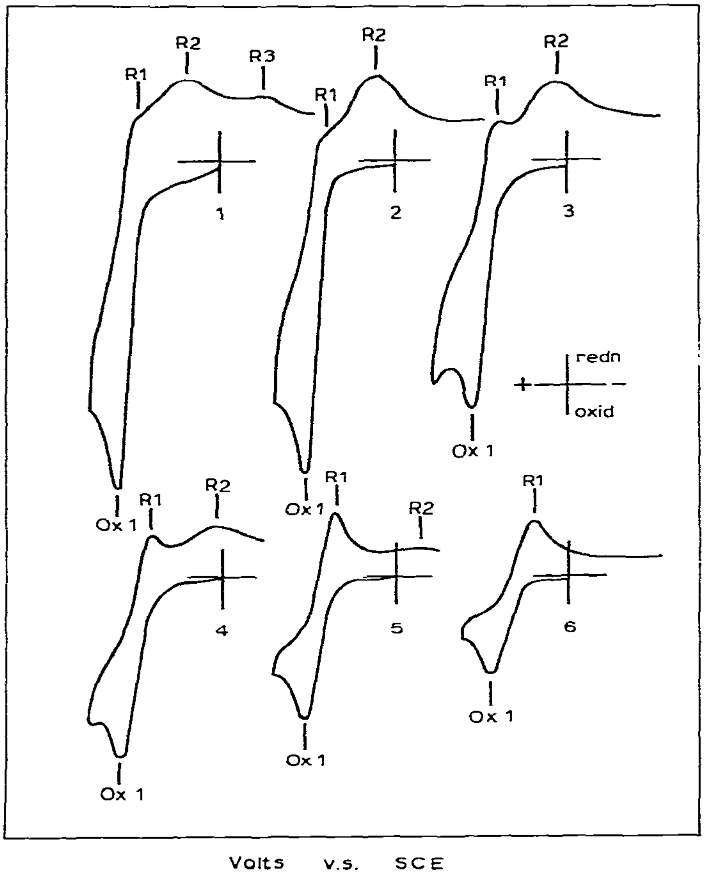

Fig. 1. The uranocene quasi-reversible couple in $C_6H_5CN/TBAPF_6$ under varying conditions of concentration, sweep rate, and temperature. Effect of concentration: (1) Typical behavior, 22° C, 121 mV/sec; (2) concentration doubled (note that the current scale has also been doubled). Effect of sweep rate: (2) 121 mV/sec; (3) 400 mV/sec; (4) 800 mV/sec. Effect of temperature: (4) +22° C; (5) +6° C; (6) —10° C. Initial potential: —0.5 V vs. SCE, switching potential: ca. 0.5 V vs SCE.

These results rule out simple EC (loss of electron followed by chemical transformation) and ECE (EC followed by loss of another electron) mechanisms at this temperature.

The mechanism shown below in eq. 1—4 accomodates all these data and the earlier observations [3] nicely. Here $U(COT)_2^{2+}$ is formed in two successive one-electron steps which cannot be separated under the experimental conditions. The first oxidation is irreversible, presumably because the initially formed uranocene monocation (indicated by brackets) undergoes a geometric and/or solvation change to yield a new uranocene monocation which is more easily oxidized than uranocene itself. Irreversible processes of this type for metallocene electrode reactions have precedent in the work of Geiger and coworkers [5].

$$U(COT)_2 \rightleftharpoons [U(COT)_2^+] + e^- \qquad (1)$$

$$[U(COT)_2^+] \xrightarrow{\text{fast}} U(COT)_2^+ \qquad (2)$$

$$U(COT)_2^{+} \rightleftharpoons U(COT)_2^{2+} + e^- \quad (3)$$

$$U(COT)_2^{2+} + U(COT)_2 \xrightarrow{slow} U_2(COT)_4^{2+} \quad (4)$$

At room temperature and slow sweep rates (ca. 0.1 V/s) the Ox1 wave consists of steps 1—4 to yield an apparent voltammetric n-value of unity. At low temperatures the slow fourth step is suppressed by the increased solvent viscosity and inherent activation energy for the bimolecular process (~11.5 kcal/mol). Thus, at fast sweep rates the electrophilic attack of the dication on $U(COT)_2$ can be outrun to yield curve 6 in Fig. 1 in which Ox1 can be interpreted as consisting of only the unimolecular steps (eq. 1—3) and R1 as the reduction of the dication $U(COT)_2^{2+}$ (eq. 5). Unfortunately, under these conditions, the current function (0.212 amp M^{-1} cm^{-2} sec^{-1}) cannot be adequately assessed owing the uncertainty introduced by changes in the diffusion coefficient for $U(COT)_2$ at this temperature in C_6H_5CN/TBAPF$_6$.

$$U(COT)_2^{2+} + e^- \overset{R1}{\rightleftharpoons} U(COT)_2^{+} \quad (5)$$

The final step in the overall electrode process, which gives rise to wave Ox2, must be the loss of COT and the further oxidation of the dimer dication (eq. 6) in order to be consistent with reported coulometric data. This occurs on the coulometric time scale to yield an n-value of 1.5 as reported previously [3].

$$U_2(COT)_4^{2+} \rightarrow U_2(COT)_3^{3+} + COT + e^- \quad (6)$$

In terms of the above mechanism the dication is reduced in wave R1. Further reduction to uranocene does not take place in the potential range of Fig. 1 owing to the irreversible nature of the geometric and/or solvation change associated with eq. 2. Thus a peak current ratio (i_p^c/i_p^a) of approximately 0.5 at low temperatures is predicted by eq. 1—3 and 5. This mechanism finds analogy in the electrochemical reduction of 3,8-dimethyl-2-methoxyazocene [6]. The literature computer-simulated cyclic voltammograms of Jensen et al. show remarkable similarity to the behavior of $U(COT)_2$.

Wave R2 is assigned to reduction of the dication dimer, $U_2(COT)_4^{2+}$, which is produced in the diffusion layer via eq. 4. Significantly, doubling the concentration of $U(COT)_2$ (see Fig. 1) markedly increases the height of R2 relative to R1, which is consistent with this bimolecular process.

The significance of this mechanistic interpretation of the uranocene voltammetry is two-fold. Firstly, it is evident that the uranocene cations $U(COT)_2^{+}$ and $U(COT)_2^{2+}$ can be made in solution by electrochemical means. Secondly, removal of the 5*f* electrons has weakened the metal—ligand bonds leading to different structural and chemical properties of the uranocene sandwich. In particular $U(COT)_2^{2+}$ exhibits appreciable Lewis acidity because it reacts with $U(COT)_2$ to yield $U_2(COT)_4^{2+}$.

Experimental

Materials

Uranocene was prepared by literature procedures using COT (Aldrich) and UCl_4 [7]. UCl_4 was either prepared from UO_3 (Ventron) by the method of Hermann and Suttle [8] using hexachloropropene (Aldrich), or purchased from Ventron and used without purification.

THF and CH_2Cl_2 (Fisher) were dried over $LiAlH_4$ and CaH_2, respectively, and distilled under N_2. Benzonitrile (Eastman), dried by passing through a 4 ft by 3 in alumina column (Activity 1, Fisher), was found to contain trace quantities of a reducible species (presumably $C_6H_4(CN)_2$). Spectroscopic grade C_6H_5CN and CH_3CN (Gold-Label, Aldrich) were used without purification.

The supporting electrolytes were crystallized twice from methanol and dried in vacuum at 60°C for at least 4 h immediately prior to use. Tetrabutylammonium hexafluorophosphate, $TBAPF_6$, was prepared by titrating tetrabutylammonium hydroxide (40% in CH_3OH Aldrich) with HPF_6 (Ventron); tetrabutylammonium perchlorate, TBAP (Eastman) was crystallized and used without further purification.

Procedure

Voltammetry was conducted primarily at a platinum disk electrode (Beckman): area 0.21 cm^2. Other electrodes employed included a hanging Hg drop and a glassy carbon electrode embedded in glass and contacted via a column of Hg. The platinum electrodes were polished using a Buehler polishing cloth and lapping compound immediately prior to recording each voltammogram. Solutions were purged of O_2 by bubbling Ar through the solution for 10—15 min. Uranocene was introduced via dome break-seal vials in bench-top experiments [9].

Potentials were measured against an aqueous saturated calomel electrode which was immersed in a fritted glass tube containing the electrolyte/solvent. Peak potentials were difficult to reproduce better than ±30 mV, especially in the THF/TBAP solution. Experiments at subambient temperatures were performed by immersing the entire cell in a dewar flask, containing CO_2/EtOH except for the reference electrode which was maintained at room temperature. The temperature was measured in the electrolyte directly.

Slow sweep cyclic voltammetry ($V < 0.8$ volt/sec) was performed using a three-electrode potentiostat of conventional design. Positive feedback techniques were used to minimize uncompensated IR drop effects in the fast sweep studies (1—20 V/sec).

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