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(7) By comparison with the spectrum of an authentic sample recorded by the authors in pH 1.0 DCl–D$_2$O and 1.0 M NaCl.

(8) In the presence of O$_2$, Sn^{II} will slowly dealkylate B$_{12,Me}$ without added B$_{12a}$ or Fe^{III}. An induction period observed preceeding this cleavage implicates a catalytic cycle where the slight B$_{12a}$ impurity, always present in alkyl-cobalamins, is reduced by Sn^{II}, reoxidized by O$_2$, and reduced by more Sn^{II}, etc.

(9) The excess Fe^{III} very rapidly oxidizes the product B$_{12r}$ to B$_{12a}$.

(10) Linear plots for reactions of both methyl- and ethylcobalamin could be obtained only for 7 to 10 min after mixing. A sudden dramatic decrease in the rate of cleavage after this time indicates complete or nearly complete depletion of one of the reactants, Sn^{II} or Fe^{III}, by competing side reactions (eq 4–6).

(11) The Fe^{III} was found to dealkylate B$_{12,Me}$ but at a rate too slow to interfere in the kinetic determinations.

(12) The HO–C$_{10}$H$_4$(NO)(SO$_3$Na)$_2$ salt has been used as a complexing reagent for a number of metal ions: E. B. Sandell, "Chemical Analysis", Vol. III, Interscience, New York, N.Y., 1959, p 208. Also the nitroso salts have been found to be effective scavengers for both organic and inorganic free radicals: E. G. Janzen, *Acc. Chem. Res.*, **4**, 31 (1971); P. T. Krusic, P. T. Fagan, and T. San Filippo. Jr., *J. Am. Chem. Soc.*, **99**, 250 (1977).

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(14) The rate expression for eq 5 is

$$-d[B_{12,alkyl}]/dt = k_5[Sn^{III}][B_{12,alkyl}]$$

$$-d[Sn^{III}]/dt = k_{-4}[Sn^{III}][Fe^{II}] + k_5[Sn^{III}][B_{12,alkyl}] + k_6[Sn^{III}][Fe^{III}] - k_4[Sn^{II}][Fe^{III}] = 0$$

$$[Sn^{III}] = \frac{k_4[Sn^{II}][Fe^{III}]}{k_{-4}[Fe^{II}] + k_5[B_{12,alkyl}] + k_6[Fe^{III}]}$$

so

$$-d[B_{12,alkyl}]/dt = k_5k_4/k_6[Sn^{II}][B_{12,alkyl}]$$

(15) With 1 M NaCl, Sn^{II} in solution exists largely as SnCl$_3$$^-$ and SnCl$_2$: K. G. Moodley and M. J. Nicol, *J. Chem. Soc., Dalton Trans.*, 239 (1977).

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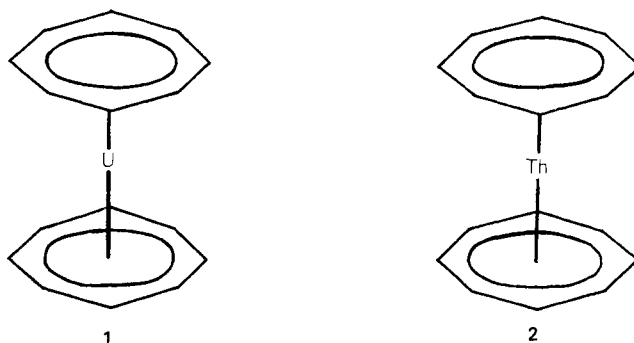*Received October 5, 1977*

Anodic Oxidation of Uranocene. Evidence for New Organouranium Cations in Solution

Sir:

The synthesis of uranocene (di-π-cyclooctatetraenyluranium(IV)) (1) by Streitwieser and Müller-Westerhoff in 1968[1] opened an exciting new era in organoactinide and lanthanide chemistry. We have extended this area by investigating the existence and properties of the uranocene mono- and possibly dication, and present evidence for formation of a diuranium cluster complex.

In spite of the fact that numerous related actinide and lanthanide complexes have been prepared,[2] uranocene is the most interesting. It, for example, has remarkable thermal stability and is resistant to attack by water and weak acids.[3] Streitwieser has proposed an ingeneous bonding scheme for uranocene[3] in which 5f orbitals on the metal and molecular orbitals (MOs) on the ligand, both having the proper energy and symmetry, interact to form a covalent bond.[4] The model also predicts that 1 should have two unpaired electrons in nonbonding orbitals which are largely 5f in character.

Many laboratories have conducted experiments on 1 designed to test the Streitwieser model.[5] One interesting approach has been to study the photoelectron spectrum of 1.[6] Although these spectra are largely in agreement with the bonding model, much information is lost because little is learned about the ions, particularly the ground-state ion, formed by photoejection.[7] However, problems with the model remain. Is the covalency ascribed to 1, which is based on its stability to water, due to the 5f electrons on the uranium, or

1   2

are they truly nonbonding as the model suggests? Loss of these electrons would form the uranocene dication, a species which is isoelectronic with thoracene (2), the latter being largely ionic in nature[8] and highly sensitive to water. Thus we anticipated that solution oxidation of uranocene would lead to simple cation species, making further tests of the uranocene bonding scheme possible via comparison to the known properties of 2.

Because chemical oxidants proved unsatisfactory in the controlled oxidation of uranocene,[9] anodic oxidation was investigated. Owing to the extreme air sensitivity of 1, cyclic voltammograms were obtained under argon in an inert atmosphere box using a Pt disk working electrode with (n-Bu)$_4$N$^+$PF$_6$$^-$ as the supporting electrolyte.[10] Figure 1 shows cyclic voltammograms of 1 in benzonitrile, a solvent which showed good electrochemical characteristics and in which 1 was reasonably soluble.[11] Simple reversible faradaic processes are not observed at sweep rates up to 20 V/s, and only at subambient temperatures is a quasi-reversible ($E_p^a - E_p^c = 200$ mV) one-electron oxidation wave obtained at 0.06 V vs. SCE.[12] Added cyclooctatetraene (COT) in THF at room temperature had no effect on the general appearance of the voltammogram and the position of the uranocene oxidation wave. This result implies that COT is not lost reversibly by the uranocene cation formed in the initial electron-transfer process. Based on the known ionization potential of uranocene,[13] an $E_{1/2}$ value may be calculated by Miller's formula[14a] which corresponds very closely to the experimental value.[14b] It would appear that a uranocene cation is being generated but that it is unstable under our reaction conditions.

$$U(COT)_2 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} U(COT)_2{}^+ \xrightarrow{U(COT)_2} \longrightarrow \text{products}$$
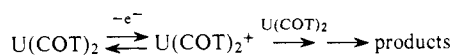
If the potential is swept past the first wave, a broad poorly defined oxidation process is observed which consists of at least two waves (+0.445 and +0.679 V). The best resolution of these two waves was observed when the voltammograms were obtained in the presence of suspended alumina.[15,16] The position of the third wave corresponds very closely to that observed in cyclic voltammograms of exhaustive electrolysis solutions.

Coulometric electrolyses were carried out on ~25-mg samples of uranocene in THF/(n-Bu)$_4$N$^+$PF$_6$$^-$ using a reticulated vitreous carbon working electrode (100 pores per inch, Chemitronics).[17] The oxidation proceeded smoothly at potentials up to 0.85 V vs. SCE with continuous argon flushing of the working electrode compartment.[18] After all of the uranocene had reacted (20–35 min), an *air-stable*, yellow-green solution was produced.

Although the separation of this green material from the supporting electrolyte defied our best efforts,[19a] the evidence below leaves little doubt that it is an organouranium cation possessing two or more uranium atoms. An n value of 1.42 ± 0.08 was obtained from 12 coulometry experiments indicating 3e$^-$ were lost per 2 molecules of uranocene. Cyclic voltammograms of the oxidized solution demonstrated that COT was liberated during the electrolysis. By FT NMR it could be
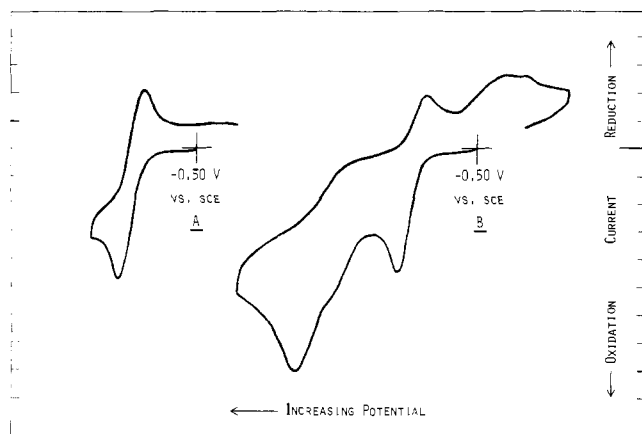
Figure 1. Cyclic voltammograms of uranocene in C_6H_5CN, 0.1 M (*n*-Bu)$_4$N$^+$PF$_6^-$, at a Pt disk electrode (area = 0.21 cm^2). Conditions: sweep rate, 0.8 V/s; 6 °C; switching potentials,0.232 (A),1.167(B). Abscissa: 20 μA/division.

shown that no more than $\frac{1}{3}$ of all the COT ligand is liberated as free COT. Subtraction of both the electrolyte and the solvent bands from the FT IR spectrum of the product solution left bands at 810 (w), 774–780 (m), 758 (w), 719 (w), 644–650 (m), and 608 (w) cm^{-1}, which are in the region characteristic for π-COT complexes to lanthanides and actinides.[19b] The solution is paramagnetic (Gouy balance) and no peaks in the NMR spectrum were observed which one might attribute to the product. The visible spectrum of a typical THF solution showed bands at 659 ($\epsilon \simeq 222$), 637 ($\epsilon \simeq 253$), 540 ($\epsilon \simeq 113$), 490 ($\epsilon \simeq 136$, sh), 478 ($\epsilon \simeq 149$), and 410 nm ($\epsilon \simeq 264$).[20] The same product is formed in both benzonitrile and tetrahydrofuran which appears to rule out solvent molecule incorporation in the structure.

Since at most $\frac{1}{3}$ of all COT is liberated in the oxidation and the *n* value is fractional, a dimeric or cluster product cation is indicated.[21] Strikingly, this substance is air stable, unlike most organouranium compounds, suggesting that the uranium atoms are effectively shielded from attack by O_2 as is the case for both tetra-π-cyclopentadienyluranium(IV)[22a] and di-π-tetraphenylcyclooctatetraenyluranium(IV).[22b]

In summary, the uranocene monocation has been shown to be a short-lived species, thus making a detailed test of Streitwieser's model impossible. It appears, however, that the removal of a 5f electron weakens the metal–ligand bond in uranocene, leading to structural changes and irreversible electrochemistry.[23] The electrochemistry of thoracene (both oxidation and reduction) should also be interesting, but, owing to its insolubility in most solvents, a direct comparison with the uranocene electrochemistry will be difficult.[24] It is clear that electrochemistry, and electrosynthesis in particular, has a valuable role to play in the area of organoactinide chemistry.[25]

References and Notes

(1) A. Streitwieser, Jr., and U. Müller-Westerhoff, *J. Am. Chem. Soc.*, **90**, 7364 (1968).
(2) (a) Thoracene: A. Streitwieser, Jr., and N. Yoshida, *J. Am. Chem. Soc.*, **91**, 7528 (1969). (b) Neptunacene and plutonacene: D. G. Karraker, J. A. Stone, E. R. Jones, Jr., and N. Edelstein, *ibid.*, **92**, 4841 (1970). (c) Ce, Pr, Nd, Sm, Tb COT complexes: F. Mares, K. O. Hodgson, and A. Streitwieser, Jr., *J. Organomet. Chem.*, **24**, C68 (1970). (d) Ce dimer with Cl bridges:

(3) F. Mares, K. O. Hodgson, and A. Streitwieser, Jr., *ibid.*, **28**, C24 (1971).
A. Streitwieser, Jr., U. Müller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson, and C. A. Harman, *J. Am. Chem. Soc.*, **95**, 8644 (1973).
(4) See R. G. Hays and N. Edelstein, *J. Am. Chem. Soc.*, **94**, 8688 (1972), for a molecular orbital calculation on uranocene and related species.
(5) The U(IV) character of the metal is established by its magnetic moment and by Mössbauer spectroscopy of the analogous neptunium compound.[3]
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(7) Positive and negative ions have been generated in the gas phase by mass spectrometry: A. D. Williamson, R. N. Compton, J. A. Butcher, Jr., J. E. Bloor, and R. M. Pagni, unpublished results.
(8) Of course, if the 5f orbitals on thorium are not sufficiently close in energy to the ligand orbitals, an ionic structure for **2** is certainly reasonable.
(9) Attempted oxidation with Ag$^+$, NO$^+$, Cu^{2+}, Cu$^+$, Sn^{2+}, Cd^{2+}, CH$_3$NO$_2$, TCNQ, (C$_6$H$_5$)$_3$C$^+$, and HFSO$_3$ resulted in disruption of the complex and the formation of inorganic products.
(10) There is some evidence that either (*n*-Bu)$_4$N$^+$ClO$_4^-$ or a trace impurity in it participates in the chemical reactions in this system as witnessed by a large and variable reduction wave observed in CVs in the presence of this electrolyte.
(11) Cyclic voltammograms in THF, CH$_2$Cl$_2$, and CH$_3$CN (pulse voltammogram) were qualitatively similar to those in benzonitrile.
(12) The current function of this wave ($i_p/\sqrt{v}$) is proportional to U(COT)$_2$ concentrations, independent of sweep rate, and corresponds approximately to a one-electron process. The peak current ratio, i_p^c/i_p^a, attains a maximum value of 0.6 at a sweep rate of 1 V/s.
(13) IP = 6.20,[6a,b] 6.15,[6c] and 6.20 eV.[7]
(14) (a) L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, **37**, 916 (1972); (b) E$_{1/2}$ vs. Ag = 0.89 IP − 6.04 leads to $E_{1/2}$ = −0.57 vs. Ag using IP = 6.2 eV, which is identical with the $E_{1/2}$ obtained in acetonitrile.
(15) O. Hammerlich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973).
(16) The uranocene appeared to react with the alumina and decreased in concentration rapidly. The alumina turned a yellow-brown color and a large COT wave appeared in the CV. This was in spite of vacuum drying the alumina at 150 °C overnight and breaking vacuum to Ar.
(17) A Pt gauze electrode passivated under these conditions. The RVC electrode was connected by a carbon rod above the solution level. If contact was made by either a Pt wire or carbon in the solution, the point of contact passivated as well. Other workers in this department have used RVC electrodes successfully. See V. E. Norvell and G. Mamantov, *Anal. Chem.*, **49**, 1470 (1977).
(18) Owing to the high solution resistance and porous nature of the working electrode, constant potential electrolysis conditions were not achieved with the potentiostat (P.A.R. Model 173)–cell configuration. The RVC electrode potential was initially at the foot of the oxidation wave and became more positive as the electrolyses proceeded.
(19) (a) Although the material was air stable, it was sensitive to water and changes in the polarity of the THF solution. Standard methods—chromatography, fractional crystallization, dialysis, adding nucleophyles, electrochemical reduction, and sublimation—were of no avail. Either no separation from the electrolyte was achieved or precipitation of an inorganic degradation product resulted. (b) 900 (m), 787 (w), 772 (w), 741 (m), 594 (s) cm^{-1} for uranocene from ref 3. See also ref 2c.
(20) These ϵ values are calculated for a diuranium cluster and are approximate. The uranocene concentration prior to electrolysis (visible spectrum using published ϵ values for uranocene[3]) was assumed to be equal to the total uranium concentration in the postelectrolysis solution.
(21) For example, the ion could be U$_2$COT$_3^{3+}$ if n = 1.5 and $\frac{1}{4}$ of all COT is liberated. See S. R. Ely, T. E. Hopkins, and C. W. DeKock, *J. Am. Chem. Soc.*, **98**, 1624 (1976), for a lanthanide example: Nd$_2$COT$_3$·2THF.
(22) (a) E. O. Fischer and Y. Hristidu, *Z. Naturforsch. B.*, **17**, 275 (1962); (b) A. Streitwieser, Jr., and R. Walker, *J. Organomet. Chem.*, **90**, C41 (1975).
(23) Structural changes leading to irreversible steps in metallocene electrochemistry have been observed: J. D. L. Holloway, W. L. Bowden, and W. E. Geiger, Jr., *J. Am. Chem. Soc.*, **99**, 7090 (1977).
(24) We have recently found that thoracene in HMPA yields a solution which exhibits cyclic voltammetry consistent with that expected for thoracene based on Miller's correlation:[14] E_p = 0.11 vs. SCE. Unfortunately corresponding measurements on uranocene cannot be made in this solvent since U(COT)$_2$ decomposes in HMPA, as reported in ref 3 and verified in this laboratory.
(25) Electron spin resonance and field ionization mass spectrometry experiments are now in progress on the product of the bulk electrolysis.

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Synthesis of Highly Conducting Films of Derivatives of Polyacetylene, (CH)$_x$

Sir:

We have recently reported[1-3] that, when flexible, crystalline, silvery films of the semiconducting *cis*-(CH)$_x$ (**1**) or *trans*-