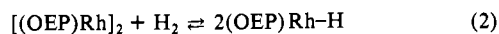
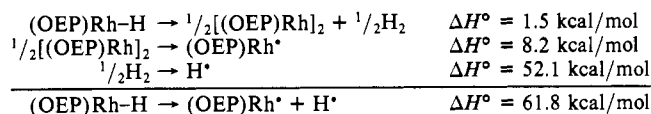


Availability of a value for the (Rh-Rh)BDE permits extraction of the (Rh-H)BDE from thermodynamic data for reaction 2 ($\Delta H_2^\circ = -3.0 \pm 1$ kcal/mol; $\Delta S_2^\circ = 0.8 \pm 2$ eu).¹⁴ Evaluation



thermodynamic cycle I (Rh-H) BDE

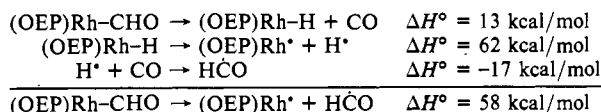


of thermodynamic cycle I results in a (Rh-H)BDE of approximately 62 kcal/mol. Calorimetric methods were used by Drago to obtain an average Rh-H bond energy of 57.6 kcal/mol in $\text{Rh}(\text{Cl})(\text{P}(4\text{-tolyl})_3)_3(\text{H})_2$,¹⁵ and the $\nu_{\text{Rh-H}}$ stretching frequencies for (OEP)Rh-H (2220 cm^{-1}) and $\text{Rh}(\text{Cl})(\text{P}(4\text{-tolyl})_3)_3(\text{H})_2$ (2034 cm^{-1}) qualitatively correlate with the Rh-H bond energies. A (Rh-H)BDE of 62 kcal/mol for (OEP)Rh-H is clearly in the range expected for a second-row transition-metal hydride,¹⁶ and judging from the unusually high Rh-H stretching frequency for (OEP)Rh-H, the (Rh-H)BDE of 62 kcal/mol is probably at the high end of the range of Rh-H bond energies.

The (Rh-H)BDE of 62 kcal/mol can be subsequently used in deriving a (Rh-C)BDE in (OEP)Rh-CHO from thermodynamic data for reaction 3 ($\Delta H_3^\circ = -13 \pm 1$ kcal/mol; $\Delta S_3^\circ = -29 \pm 3$ eu)⁶ and the formyl radical.^{17,18} The relatively large (Rh-



thermodynamic cycle II (Rh-C)BDE



C)BDE (~ 58 kcal/mol) and small difference in Rh-H and Rh-C bond energies (~ 4 kcal/mol) provides an operational explanation for the range of unusual organometallic chemistry associated with rhodium porphyrins, which is not observed for cobalt porphyrins.¹⁻⁶ A (Rh-C)BDE of 58 kcal/mol in (OEP)Rh-CHO is approximately twice the Co-C bond energy (Co-C ~ 28 kcal/mol) recently reported for a (OEP)Co-alkyl complex.¹³ Rh-C bonds are expected to be stronger than Co-C bonds due to improved overlap of the 4d orbitals, but differences of the magnitude observed for the (OEP)M complexes must be predominantly of steric origin.¹⁹

NMR line broadening is potentially a useful method for estimating M-M bond energies in the range 8-25 kcal/mol when NMR experiments in the temperature range 170-470 K are feasible. $[(\text{OEP})\text{Rh}]_2$ is an ideal case for use of this method because bond homolysis is the only pathway for a chemical exchange process to contribute to the line width. The primary criteria for using this method to estimate M-M bond energies are that bond homolysis occur at a rate of 2-100 events/s in an accessible temperature range and that a magnetic nucleus in the compound be coupled significantly with the unpaired electron on the paramagnetic monomer. Complexes that have M-M single bonds where the ligands have large steric requirements are potentially good candidates for application of this method.

Acknowledgment. This work was supported by the National Science Foundation and the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences (Grant DE-FG02-86ER13615).

Registry No. $[(\text{OEP})\text{Rh}]_2$, 63439-10-1.

- (14) Farnos, M. D. Ph.D. Thesis, University of Pennsylvania, 1987 [$K_2(294) = 116 \pm 8$; $K_2(335) = 60 \pm 10$].
 (15) Drago, R. S.; Miller, J. G.; Hoselton, M. A.; Farris, R. D.; Desmond, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 444.
 (16) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.
 (17) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.
 (18) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.
 (19) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.* **1987**, *109*, 1351.

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, Department of Chemistry and Biochemistry, Illinois Benedictine College, Lisle, Illinois 60532, and Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Cyclic Voltammetric Study of Organoactinide Compounds of Uranium(IV) and Neptunium(IV). Ligand Effects on the M(IV)/M(III) Couple

David C. Sonnenberger*^{1a,b} and John G. Gaudiello*^{1c}

Received October 15, 1987

The physical and chemical properties of organoactinides vary greatly with the nature of the ligands about the actinide center.² The effects of ligand environment on the bonding and chemical behavior of organoactinide systems have been studied by a number of techniques, including magnetic susceptibility,³ Mössbauer spectroscopy,⁴ photoelectron spectroscopy,⁵ and solution calorimetry.⁶

Electrochemical methods have provided a considerable amount of information on the nature of the ligand-metal interaction in transition-metal complexes.^{7,8} This tool has been utilized less frequently in organoactinide systems.⁹⁻¹¹ Herein, we report the results of a cyclic voltammetric study of a series of uranium(IV) and neptunium(IV) organometallics. Our objective is to gain insight into the sensitivity of the M(IV)/M(III) couple to ligand environment.

Experimental Section

Synthetic Methods. The organometallics were prepared and handled in Schlenk glassware on a dual-manifold Schlenk line or interfaced to a high-vacuum system. Solid transfers were accomplished under nitrogen in a Vacuum Atmospheres Corp. inert-atmosphere box. Solvents were purified and dried as previously described.^{6b}

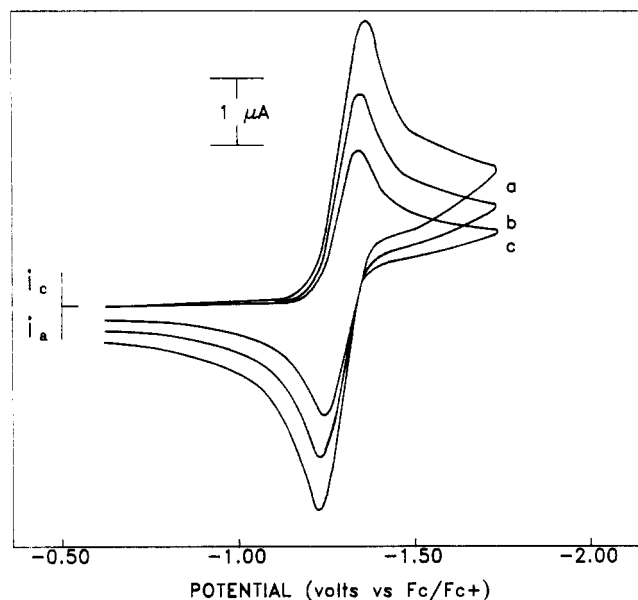
The compounds Cp_4U^{12} ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), Cp_3UCl ,¹³ Cp^*UCl_2 ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), Cp_4Np ,¹⁵ Cp_3NpCl ,¹⁶ and Cp^*NpCl_2 ¹¹ were prepared by literature procedures.

- (1) (a) Argonne National Laboratory. (b) Illinois Benedictine College. (c) Michigan State University.
 (2) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 21.
 (3) (a) Edelstein, N.; Streitwieser, A., Jr.; Morrell, D. G.; Walker, R. *Inorg. Chem.* **1976**, *15*, 1397. (b) Amberger, H. D.; Fischer, R. D.; Kanelakopoulos, B. *Theor. Chim. Acta* **1975**, *37*, 105.
 (4) Karraker, D. G. In *Recent Chemical Applications of the Mössbauer Effect*; Shenoy, G., Stevens, J. G., Eds.; Advances in Chemistry 194; American Chemical Society: Washington, DC, 1981; Chapter 15.
 (5) (a) Bursten, B. E.; Casarin, M.; DiBella, S.; Fang, A.; Fragala, I. L. *Inorg. Chem.* **1985**, *24*, 2169. (b) Green, J. C.; Payne, M. P.; Streitwieser, A., Jr. *Organometallics* **1983**, *2*, 1707. (c) Fragala, I. L.; Goffart, J.; Granozzi, G.; Ciliberto, E. *Inorg. Chem.* **1983**, *22*, 216. (d) Fragala, I.; Condorelli, G.; Zanella, P.; Tondello, E. *J. Organomet. Chem.* **1976**, *120*, C9.
 (6) (a) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275. (b) Sonnenberger, D. C.; Morss, L. R.; Marks, T. J. *Organometallics* **1985**, *4*, 352. (c) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824.
 (7) (a) Bursten, B. E.; Green, M. R.; Katovic, V.; Kirk, J. R.; Lightner, D., Jr. *Inorg. Chem.* **1986**, *25*, 831. (b) Bursten, B. E. *J. Am. Chem. Soc.* **1982**, *104*, 1299.
 (8) (a) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228. (b) Nagy, A. G.; Toma, S. *J. Organomet. Chem.* **1984**, *266*, 257. (c) Koelle, U.; Khouzami, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *91*, 640.
 (9) Butcher, J. A.; Pagni, R. M.; Chambers, J. A. *J. Organomet. Chem.* **1980**, *199*, 223.
 (10) Finke, R. G.; Gaughan, G.; Voegeli, R. *J. Organomet. Chem.* **1982**, *229*, 179.
 (11) Sonnenberger, D. C.; Gaudiello, J. G. *J. Less-Common. Met.* **1986**, *126*, 411.
 (12) Fischer, E. O.; Hristidu, Y. Z. *Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1962**, *17B*, 275.
 (13) Marks, T. J.; Seyam, A. M.; Wachter, W. A. *Inorg. Synth.* **1976**, *6*, 147.
 (14) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6550.
 (15) Baumgartner, F.; Fischer, E. O.; Kanelakopoulos, B.; Laubereau, P. *Angew. Chem., Int. Ed. Engl.* **1986**, *7*, 634.
 (16) Karraker, D. G.; Stone, J. A. *Inorg. Chem.* **1979**, *18*, 2205.

Table I. Cyclic Voltammetric Data for the Reduction of Organoactinide Compounds in Tetrahydrofuran

compd	$E_{1/2}^{a,b}$	compd	$E_{1/2}^{a,b}$
Cp ₄ U	-1.94	Cp ₃ NpCl	-1.29
Cp ₄ Np	-1.27	Cp* ₂ UCl ₂ ^c	-2.18
Cp ₃ UCl	-1.80	Cp* ₂ NpCl ₂	-1.38

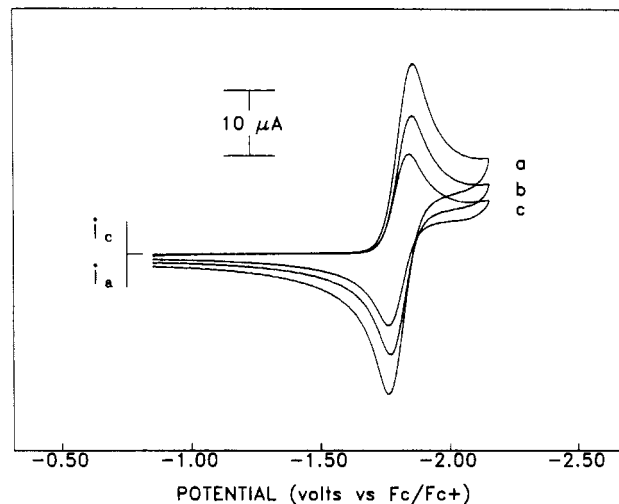
^aVolts vs ferrocene/ferrocenium. ^b $E_{1/2}$ = reversible half-wave potential. ^cThis compound has also been studied by Finke and co-workers¹⁰ using tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

**Figure 1.** Cyclic voltammograms of Cp₄Np in THF/0.2 M (TBA)BF₄. Scan rate: (a) 200 mV/s; (b) 100 mV/s; (c) 50 mV/s.

Cyclic Voltammetry. Electrochemical experiments were performed in a single-compartment three-electrode cell designed for highly air-sensitive compounds.¹⁷ Solutions were prepared by vacuum-transferring THF directly into the cell. A platinum-disk working electrode (area 0.020 cm²), a platinum-wire auxiliary electrode, and a silver-wire quasi-reference electrode were used. The potential of the reference electrode was determined by using the ferrocene/ferrocenium couple as an internal standard.¹⁸ All potentials are referenced to this couple. Electrochemical measurements were made with a Princeton Applied Research potentiostat-galvanostat (Model 173) and a Princeton Applied Research universal programmer (Model 175). Sample solutions were typically 2.5 mM in organoactinide and 0.2 M in tetrabutylammonium tetrafluoroborate.

Results and Discussion

The results of the electrochemical reduction of Cp₄M, Cp₃MCl, and Cp*₂MCl₂ (M = U, Np) are summarized in Table I, and representative cyclic voltammograms are shown in Figures 1 and 2. In each case, the cyclic voltammetry of these compounds shows a single reduction wave exhibiting the characteristics of a one-electron reversible process. No additional processes were observed down to a solvent limit of -2.5 V. Mono(cyclopentadienyl)ura-

**Figure 2.** Cyclic voltammograms of Cp₃UCl in THF/0.2 M (TBA)BF₄. Scan rate: (a) 200 mV/s; (b) 100 mV/s; (c) 50 mV/s.

anium complexes such as CpUCl₃·2THF, Cp*UCl₃·2THF, CpUCl₃·2OPPh₃, and Cp*UCl₃·2OPPh₃ as well as UCl₄ exhibited chemically irreversible reductions.

The potential of the M(IV)/M(III) couple is sensitive to the nature of the ligands about the metal center (see Table I). The order in ease of reduction (least to most difficult) of the compounds studied is Cp₃UCl < Cp₄U < Cp*₂UCl₂ and Cp₄Np ≈ Cp₃NpCl < Cp*₂NpCl₂. The more negative the M(IV)/M(III) couple, the greater the stability of the M(IV) state with respect to M(III).

From Cp₃UCl to Cp₄U, the $E_{1/2}$ value of the M(IV)/M(III) couple becomes more negative by 0.14 V. This is consistent with the Cp ligand being a better electron donor than chloride, thus stabilizing the M(IV) oxidation state. A greater shift is observed from Cp₃UCl to Cp*₂UCl₂ (0.38 V). The Cp* ligands place more electron density on the uranium center than either the chloride or Cp, which results in greater stability of the M(IV) state. Similar trends have been previously observed in substituted ferrocene⁸ and organolanthanide¹⁹ systems and suggest that the role played by a permethylated cyclopentadienyl ligand in organoactinide chemistry is electronic, as well as steric.²

Interestingly, the differences in the redox potentials between the M(IV)/M(III) couples in the Cp₄M, Cp₃MCl, and Cp*₂MCl₂ series are smaller for neptunium than for uranium. This observation suggests that the uranium center is more sensitive to its ligand environment and is consistent with it having a greater degree of covalency in its bonding.²⁰

Acknowledgment. This research was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under Contract No. W-31-109-ENG-38 at ANL. D.C.S. acknowledges the Research Corp. for partial support of this work.

Registry No. Cp₄U, 1298-76-6; Cp₄Np, 37216-56-1; Cp₃UCl, 1284-81-7; Cp₃NpCl, 1317-00-6; Cp*₂UCl₂, 67506-89-2; Cp*₂NpCl₂, 112312-05-7.

(17) Tokel, N. E.; Keszthelyi, C. P.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 4872.

(18) Gagne, R. R.; Koval, C. A.; Lisensky, B. C. *Inorg. Chem.* **1980**, *19*, 2854.

(19) Bond, A. M.; Deacon, G. B.; Newnham, R. H. *Organometallics* **1986**, *5*, 2312.

(20) Edelstein, N. In *Fundamental and Technological Aspects of Organof-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; Reidel: Dordrecht, Holland, 1985; p 229.