Multielectron Processes Involving Structural Changes.[†] The Two-Electron Reduction of Os$_6$(CO)$_{18}$

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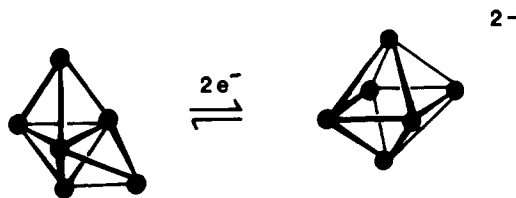
Abstract: The reduction of the hexaosmium carbonyl cluster, Os$_6$(CO)$_{18}$, has been studied by polarography, cyclic voltammetry, chronoamperometry, and controlled potential coulometry in tetrahydrofuran solutions. At either platinum or gold electrodes the reduction ($E° = 0.0$ V) proceeds in a chemically reversible, two-electron wave to the cluster dianion. Cyclic voltammetry results are consistent with a redox model involving stepwise one-electron transfers ($E_0^2 > E_0^1$) in which structural rearrangement from the bicapped tetrahedron of Os$_6$(CO)$_{18}$ to an octahedron occurs during the first electron-transfer step. At 298 K, the charge-transfer process has *apparent* values of $n = 2$, $\alpha = 0.36$, $k_s = 5 \times 10^{-4}$ cm/s at platinum or gold electrodes, as measured by cyclic voltammetry. Analysis of wave shape and peak potential shifts vs. scan rate shows that these parameters arise from the fact that $n = 1$, $\alpha = 0.72$ for the first, rate-determining, electron-transfer step. From the temperature dependence of the electron-transfer rate, a $\Delta H^{\ddagger}$ of about 8 kcal/mol for the cluster reorganization energy was estimated, making the energetics of this electron-induced change competitive with activation barriers to ligand scrambling in other clusters. A second two-electron reduction of the compound at –2.15 generated a transient product which might be the tetraanion Os$_6$(CO)$_{18}$$^{4-}$.

Relationships between the structure and redox state[1] of a molecule impact on a variety of chemical, physical, and biological phenomena. There is a need for more studies on the interconversion of *structurally characterized* pairs, especially from the viewpoint of charge-transfer kinetics. This need arises in part from the difficulty of determining structures of reduction or oxidation products, which are often quite reactive. Additionally, structural changes are often minor in chemically reversible redox couples, so that the electron-transfer kinetics are more affected by reorganization of the solvent medium than by the inner-sphere reorganizational energy of the compound.[2]

Thus there is increasing interest in redox processes involving more drastic, yet reversible, molecular changes during charge-transfer reactions.[3,4] Most often, it has been shown that the structural changes (e.g., isomerizations) occur prior to or subsequent to the actual charge-transfer step.[5] In other cases, the structural changes appear to be concomitant with electron transfer, or at least so rapid that they are experimentally indistinguishable from the charge-transfer step.[6] Then the electron-transfer rate is slowed due to the contribution made to the activation barrier by the inner-sphere reorganizational energy.[2] Measurement of the activation barrier gives information about the energetics of charge-transfer processes and increases our understanding of the mechanisms of electron-transfer reactions.

The hexaosmium metal cluster Os$_6$(CO)$_{18}$ is particularly interesting from this point of view. The neutral cluster Os$_6$(CO)$_{18}$ has a bicapped tetrahedral structure[8] (Scheme I). Reduction by iodide ion, Zn, sodium,[9] or other reductants[10] yields the corresponding dianion Os$_6$(CO)$_{18}$$^{2-}$, in which the osmium atoms form a nearly perfect octahedron.[11] Since the neutral compound is formally electron deficient, containing n bonding pairs of electrons (n = number of vertex atoms in the cluster), and the dianion is an ($n + 1$) electron pair system which has the expected *closo* structure, these two compounds stand as a paradigm for the structure/electron count predictions of the polyhedral skeletal electron pair theory.[12] Since the two-electron couple (Scheme I) was strongly implied by the synthetic results, we set out to study this system under electrochemical conditions, with the following questions in mind: (1) Does the reduction occur in a concerted two-electron step, or does it involve a stepwise process (two single one-electron transfers) with a detectable monoanion intermediate? (2) Can it be specified whether the structure change occurs before, during, or after the electron-transfer processes? For example, can thermodynamically disfavored species like octahedral neutral

Scheme I. Redox Interconversion of Os$_6$(CO)$_{18}$ and Os$_6$(CO)$_{18}$$^{2-}$ (Each Circle Stands for a Os(CO)$_3$ Group)

Os$_6$(CO)$_{18}$ or bicapped tetrahedral Os$_6$(CO)$_{18}$$^{2-}$ be detected prior to their isomerization? (3) If the structure change occurs during the charge-transfer step, what is the activation barrier to electron transfer, and how does it compare with the known energetics of metal–ligand and metal–metal deformations of cluster compounds?

(1) We use the term "redox state" to denote the electron count of a molecule, that is, the number of electrons it possesses, in preference to the term oxidation state, which necessarily assumes something about the nature of the orbital involved in the electron-transfer process.

(2) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(3) Geiger, W. E. In "Progress in Inorganic Chemistry"; Lippard, S. J., Ed.; J. Wiley: New York, 1985; Vol. 33, in press.

(4) Evans, D. H.; O'Connell, K. M. In "Electroanalytical Chemistry"; Bard, A. J., Ed.; M. Dekker: New York; in press.

(5) Reviewed in ref 3 and 4. For representative papers, see: (a) Yeh, L.-S. R.; Bard, A. J. *J. Electrochem. Soc.* **1977**, *124*, 189. (b) Bond, A. M.; Oldham, K. B. *J. Phys. Chem.* **1983**, *87*, 2492. (c) Bond, A. M.; Grabaric, B. S.; Jackowski, J. J. *Inorg. Chem.* **1978**, *17*, 2153. (d) Bond, A. M.; Darensbourg, D. J.; Mocellin, E.; Stewart, J. *J. Am. Chem. Soc.* **1981**, *103*, 6827. (e) Rieke, R. D.; Kojima, H.; Öfele, K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 538. (f) Ilan, Y.; Taube, H. *Inorg. Chem.* **1983**, *22*, 1655. (g) Olsen, B. A.; Evans, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 839. (h) Ahlberg, E.; Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1981**, *103*, 844.

(6) Many of the more reliable examples come from the literature of homogeneous electron-transfer processes. See, e.g.: Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. P. In "Progress in Inorganic Chemistry"; Lippard, S. J., ed.; J. Wiley: New York, 1983; Vol. 30. Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

(7) (a) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1972**, *37*, C39. (b) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. (Dalton) Trans.* **1975**, 2606. (c) Eady, C. R.; Jackson, W. G.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Chem. Commun.* **1975**, 958.

(8) Mason, R.; Thomas, K. M.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802.

(9) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1976**, 302.

(10) John, G. R.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1979**, *181*, 143.

(11) McPartlin, M.; Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1976**, 883.

(12) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Wade, K. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; J. Wiley: New York, 1980; Chapter 3.

The mechanism of the homogeneous reduction of $Os_6(CO)_{18}$ by iodide ion has been reported.[13] The reduction was found to proceed by an inner-sphere mechanism involving association between the osmium cluster and iodide, followed by slower attack by a second iodide ion. Because the iodide reduction was by an inner-sphere mechanism, the previous study could not directly address the questions raised above.

Our electrochemical data show that the reduction occurs in two one-electron steps (EE mechanism)[14] in which the $E°$ for the second process is positive of that of the first. Furthermore, the heterogeneous electron-transfer rate of the first process is slow compared to the second and is the rate-determining step. This suggests that the one-electron reduction of $Os_6(CO)_{18}$ yields thermodynamically unstable octahedral $Os_6(CO)_{18}^-$, which cannot be directly observed because it is reduced to the dianion by the electrode at a diffusion-controlled rate.

Experimental Section

Compounds. An original sample of $Os_6(CO)_{18}$ was provided by Dr. B. F. G. Johnson. Later samples were prepared by the literature method[7] involving pyrolysis of $Os_3(CO)_{12}$ (Strem Chemical Co.) and were recrystallized from hexane. A sample of $Ru_6(CO)_{18}^{2-}$ was also provided by Dr. Johnson.

Electrochemical Procedures. Tetrahydrofuran (Aldrich anhydrous) was stirred over lithium aluminum hydride and then flash distilled in vacuo into a storage flask containing sodium and benzophenone. It was distilled in a bulb-to-bulb vacuum distillation just prior to each electrochemical experiment. Methylene chloride (Aldrich) was distilled from calcium hydride and acetonitrile (Aldrich Spectrograde) was used as received. The supporting electrolyte for all solvents was 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6). The electrolyte was prepared by methathesis of Bu_4NI (Eastman) and ammonium hexafluorophosphate (Ozark-Mahoning) in acetone, followed by filtration of NH_4I and precipitation of the desired salt by addition of water. It was recrystallized several times from 95% ethanol and vacuum dried.

Most of the electrochemical measurements were accomplished by using bench top techniques and a nitrogen purge to exclude oxygen. Bulk coulometry and some low-temperature measurements were performed inside a Vacuum Atmosphere drybox. Voltammetric experiments were performed with a Princeton Applied Research (PAR) Model 173 potentiostat, a PAR Model 179 digital coulometer, and a PAR Model 175 function generator. Slow sweep rate data were recorded on a Hewlett-Packard Model 70001A X–Y recorder and faster experiments were recorded on a Tektronix Model 564B storage oscilloscope. Potentials, all referred to the aqueous saturated calomel electrode (SCE), were checked with a digital voltmeter.

Experiments were performed at either mercury, platinum, or gold electrodes. Mercury was obtained as triply distilled from Bethlehem Apparatus Co. The gold electrode was a small flag purchased from Radiometer Electrodes. It was pretreated by successive polishings with finishing sandpaper, diamond polishing compound, and Gamal polishing fluid (Fisher), followed by a distilled water wash and drying with a soft tissue. The platinum electrode was a small button sealed through the end of a glass tube. It was pretreated by refluxing in concentrated nitric acid, washing with distilled water, and then soaking in a saturated solution of ferrous ammonium sulfate in 1 M H_2SO_4. It was inserted into solution after washing with water and wiping dry. With use of these methods, the observed current values and peak shapes for the $Os_6(CO)_{18}$ reduction were reproducible. Furthermore, no effect of electrode history was evident in successve scans on this compound.

Bulk coulometry was accomplished with use of a 2-compartment cell in which the cathodic and anodic compartments were separated by a 20-mm fine frit. The working electrode was either a mercury pool or a platinum gauze cylinder. A platinum basket was placed in the auxiliary electrode compartment, which was either parallel to the working electrode (in the case of a mercury pool working electrode) or inside of it (platinum gauze cylinder). Low-temperature cyclic voltammetry experiments were performed inside the drybox by passing nitrogen gas at a controlled rate through a coil cooled in liquid nitrogen and then through the jacket of the electrochemical cell. Temperatures thusly attained had a precision
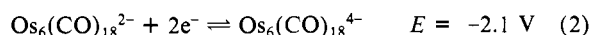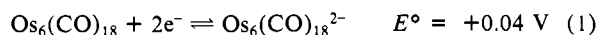
of ±2 °C. Temperature control for electron-transfer rate measurements was accomplished with use of a Masterline Forma-Temp Model 2095 system. These experiments performed external to the drybox were regulated to ±1 °C.

Maximum care was taken in cyclic voltammetry experiments to minimize the effects of solution resistance on the measurement of cathodic and anodic peak potentials. The use of moderately small electrodes and relatively dilute solutions [concentration of $Os_6(CO)_{18} \simeq 2.5 \times 10^{-4}$ M] kept currents below 5 μA. The reference electrode of the 3-electrode cell was placed very close to the working electrode by means of a luggin probe.[15] Finally, positive feedback iR compensation was employed by setting the feedback to just under the point of instability of the potentiostat under the measurement conditions.

Digital simulations of CV curves are based on the Feldberg method.[16] Computations were carried out on a DEC 2060 computer operating under TOPS-20. Plotting utilized a DISSPLA graphics software package.

Results and Discussion

The title compound displays two electrochemical reductions in THF, one close to 0 V (vs. SCE) and one negative of −2 V. It is first important to establish that each wave involves a transfer of two electrons and that the overall electron transfer at each wave is as given in eq 1 and 2

$$Os_6(CO)_{18} + 2e^- \rightleftharpoons Os_6(CO)_{18}^{2-} \qquad E° = +0.04 \text{ V} \quad (1)$$

$$Os_6(CO)_{18}^{2-} + 2e^- \rightleftharpoons Os_6(CO)_{18}^{4-} \qquad E = -2.1 \text{ V} \quad (2)$$

It will be shown that the first process is firmly established as a chemically reversible process and that the $E°$ value has thermodynamic significance. The assignment of the mechanism at the more negative wave [eq 2] is tentative since the tetraanion could not be isolated. Hence, the $E°$ potential for eq 2 may be considered as close to, but not necessarily, the value given.

I. The Reduction of $Os_6(CO)_{18}$ to $Os_6(CO)_{18}^{2-}$. A. Choice of Solvent, Electrodes. The neutral cluster reacts with strongly coordinating solvents and the structure of the bis(methylbenzonitrile) adduct has been reported.[9] Accordingly, in $CH_3CN/0.1$ M Bu_4NPF_6 no wave was seen near 0 V. Waves with $E_{1/2} = -1.02$ and −1.91 V were observed in which the plateau currents were in a 1:2 ratio. The first wave was reversible by cyclic voltammetry ($\Delta E_p = 60$ mV on Pt at $v = 50$ mV/s) and dc polarography (log slope = 60 mV) and probably represents a one-electron reduction of the acetonitrile adduct. The voltammetric behavior in CH_2Cl_2, in which the cluster is known to be stable, was identical with that seen in THF, establishing the integrity of the cluster compound in these two more weakly coordinating solvents. Since CH_2Cl_2 itself reduces positive of the process in eq 2, THF was settled on as the most appropriate electrochemical solvent.

The choice of electrode material had no important influence on the observed voltammetry. Consistent results were obtained on platinum, gold, and mercury. Cyclic voltammetry (CV) on mercury was judged not to be as clean as on the two solid electrodes, and the latter were used for most CV experiments. As will be shown below, only slight differences in apparent heterogeneous charge-transfer rates were seen when changing from Pt to Au.

The fact that the electrochemical results are essentially independent of both solvent (CH_2Cl_2 and THF) and electrode material (Hg, Pt, Au) argues strongly that the slow electron-transfer kinetics arise from factors inherent to structure changes in the reactant molecule, and are not due to an interfacial effect at the electrode surface. The importance of establishing this fact with regard to quasireversible electrode processes has been recently discussed.[3]

B. Establishment of the Two-Electron Wave for $Os_6(CO)_{18}^{0/2-}$. In dc polarography experiments, 3×10^{-4} M $Os_6(CO)_{18}$ in THF showed two waves (Figure 1) of approximately equal heights, each diffusion controlled, having half-wave potentials of +0.04 and −2.15 V. A diffusion current constant, I, of 4.10 was measured for the first wave, about twice that measured (2.25) for the

(13) John, G. R.; Johnson, B. F. G.; Lewis, J.; Mann, A. L. *J. Organomet. Chem.* **1979**, *171*. C9.
(14) We employ the nomenclature that E represents a heterogeneous electron transfer and C represents a homogeneous chemical reaction. Therefore, for example, the symbol ECE represents a stepwise process in which a redox system undergoes two electron-transfer reactions with an intervening chemical reaction coupling the two electron-transfer steps. We allow for the possibility that C may represent an intramolecular rearrangement.

(15) Sawyer, D. T., Roberts, J. L. "Experimental Electrochemistry for Chemists"; Wiley-Interscience: New York, 1974; pp 118ff.
(16) Feldberg, S. W., "Electroanalytical chemistry"; Bard, A. J., Ed.; Marcel Dekker: New York, 1968; Vol. 3.
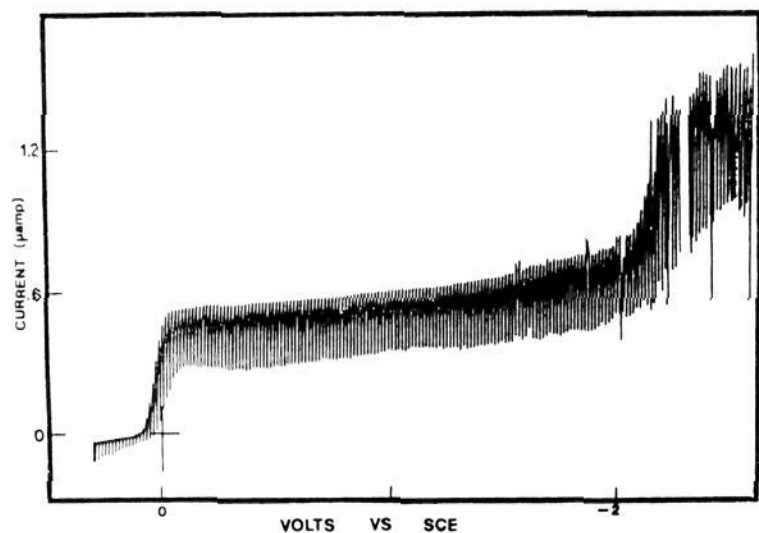
Figure 1. Dc polarograms of 3×10^{-4} M $Os_6(CO)_{18}$ in THF/0.1 M Bu_4NPF_6; drop time (controlled) = 2 s, scan rate ≈ 2 mV/s.
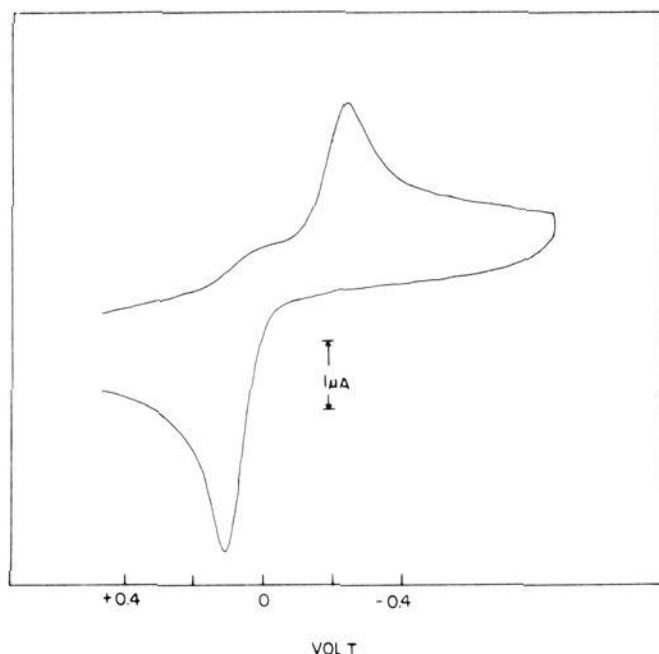
Figure 2. Cyclic voltammetry scan after exhaustive cathodic electrolysis of 3×10^{-4} M $Os_6(CO)_{18}$ in THF/0.1 M Bu_4NPF_6, scan rate 100 mV/s, Pt bead electrode. *The solution has been converted to $Os_6(CO)_{18}^{2-}$ in the* electrolysis.

one-electron standard $Co_3(CO)_9C(CH_3)$, which is known to be reduced reversibly to a stable monoanion.[17] The tricobalt cluster was chosen as a one-electron standard since it is likely that its diffusion coefficient is similar to that of the osmium cluster compound. Bulk electrolysis of the osmium compound confirmed that the reduction product was $Os_6(CO)_{18}^{2-}$. Reduction at a platinum gauze or mercury pool electrode at −0.4 V consumed 1.8 faradays as the solution went from dark brown to yellow. The polarogram of the electrolyzed solution was identical with that of the starting solution, except that the current at the first wave was anodic rather than cathodic. Cyclic voltammograms after bulk electrolysis (Figure 2) were the complement of those prior to electrolysis. That is, the peaks were at the same position, but *now the anodic portion was somewhat larger than the cathodic* portion. This effect will be discussed later. Re-oxidation of this solution at +0.2 V released 1.8 faradays and reestablished the original polarogram of $Os_6(CO)_{18}$.

Cathodic peak currents in CV scans of the first reduction of $Os_6(CO)_{18}$ *were also indicative of a two-electron wave. At a scan* rate, v, of 35 mV/s, peaks were observed at −0.19 V (cathodic) and +0.09 V (anodic). The cathodic current function (peak current divided by square root of scan rate) was independent of scan rate over the range $v = 20$–650 mV/s and was about twice that of the one-electron standard $Co_3(CO)_9C(CH_3)$. For example, at $v = 650$ mV/s, the ratio of peak currents of the osmium and cobalt compounds was 1.93.

These experiments establish that the wave near 0 V is due to a two electron process resulting in $Os_6(CO)_{18}^{2-}$, which can be

Table I. Observed Peak Separations in Cyclic Voltammetry Scans of 3×10^{-4} M $Os_6(CO)_{18}$ in 0.1 M Bu_4NPF_6/THF at a Gold Electrode for $Os_6(CO)_{18}^{0/2-}$ Couple

scan rate, mV/s	ΔE_p(meas), mV	ΔE_p(theor)^a, mV	$10^4 k_s$, cm/s
20	255	248	4.2
81	307	323	5.0
102	330	338	4.6
122	334	346	4.8
162	347	359	5.0
305	384	392	4.7
405	399	403	4.6
509	415	412	4.3
609	429	421	4.0

^{a} Theoretical value is that calculated for an electron-transfer rate of 4.5×10^{-4} cm/s, the average k_s value computed from the values in the last column.

anodically oxidized back to the starting material. These results are consistent with the previously established stability of both the neutral and dianionic forms of the cluster.[8-10]

C. Quasi-Reversible Charge-Transfer Kinetics for $Os_6(CO)_{18}^{0/2-}$. A plot of potential vs. minus log $[i/(i_d - i)]$ from the dc polarogram was linear with a slope of 45 mV. This value is intermediate between the theoretical values for electrochemically reversible (Nernstian) one-electron and two-electron waves (59 and 29.5 mV, respectively). Since the experiments above established that $n = 2$ for this wave, the slope indicates that the electron transfer is quasi-reversible, that is, subject to kinetic constraints.

The quasi-reversibility of the reduction was better demonstrated by cyclic voltammetry measurements, which showed that peak separations, ΔE_p, for the redox couple $Os_6(CO)_{18}^{0/2-}$ varied between about 250 and 450 mV as the scan rate was increased from $v = 20$ to 1000 mV/s. One must be concerned with the influence of solution resistance in THF since major errors may occur in fast *charge-transfer rates measured from CV peak separations.* This was not found to be an important obstacle in our experiments since test systems with highly reversible couples like cobaltocenium/ cobaltocene[18] gave ΔE_p values (65–70 mV) close to Nernstian behavior. Thus, resistive losses were too small to qualitatively affect *electron-transfer rate measurements on the osmium* compound. Table I gives the observed ΔE_p values for a series of scans at a gold electrode at 298 K.

The shape of the CV curve and the variation of ΔE_p with scan rate were consistent with that of an overall two-electron quasi-reversible charge-transfer reaction. Theoretical curves computed by the Feldburg method[16] matched very well with experimental data when $n(\text{app}) = 2$ and $\alpha(\text{app})$ and $k_s(\text{app})$ were in the range 0.38 ± 0.02 and $5.5 \ (\pm 1.5) \times 10^{-4}$ cm/s, respectively. It is important to note that since this is a multi-electron charge-transfer reaction, the values of n, α (the charge-transfer coefficient), and k_s (the heterogeneous charge-transfer rate) refer to the overall (or apparent) properties of the process and not necessarily to either (assumed) one-electron step. This is discussed in detail later. Figure 3 shows the excellent agreement between theory and experiment at a scan rate of 40 mV/s.[19]

The apparent value of αn was initially calculated from the difference between the cathodic peak potential, E_{pc}, and the half-peak potential, $E_{pc/2}$. For a system undergoing irreversible charge-transfer kinetics, it has been shown that $|E_{pc} - E_{pc/2}|$ is related to the α value by[20,21]
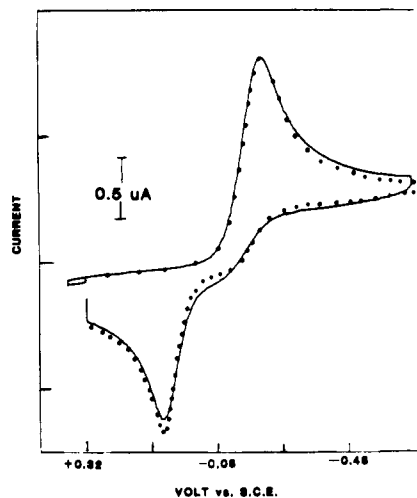
$$\alpha n = 0.048 \text{ V} / |E_{pc} - E_{pc/2}| \qquad (3)$$

(17) Bond, A. M.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 410.

(18) Geiger, W. E.; Smith, D. E. *J. Electroanal. Chem.* **1973**, *50*, 31.

(19) Because we employed fairly low concentrations of electroactive species to minimize errors due to uncompensated iR loss, experimental curves contained an observable amount of charging current. The fit between theoretical and experimental curves had to be adjusted for this charging current. The procedure used was to obtain the charging current slope from the linear extrapolation of the experimental current–potential curve in the region prior to (positive of) the reduction wave and to assume the opposite slope on the positive-going half of the CV curve. The charging currents thus obtained were *added to the computer-generated Faradaic curves to serve as the theoretical* points in Figure 3.

(20) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

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Figure 3. Cyclic voltammogram (solid line) of 3×10^{-4} M $Os_6(CO)_{18}$ in THF/0.1 M Bu_4NPF_6 at a platinum bead electrode. Theoretically calculated values ($\alpha = 0.38$, $n = 2$, $E^\circ = -0.03$ V, $k_s = 6.8 \times 10^{-4}$ cm/s) shown as circles. Scan rate 40 mV/s. The theoretical points contain a charging current component obtained by the method described in footnote 19.

Although the present system is not strictly irreversible, the charge-transfer step is slow enough that this equation is approximately correct for our use. This conclusion is based on consideration of the more general treatment of the quasi-reversible process by Matsuda and Ayabe,[22] who computed wave shapes for a broad range of electron-transfer parameters. With the values of k_s, $D_0^{1/2}$, and v found in our work, eq 3 should hold to within a few percent. In several voltammograms over the scan range 35 to 200 mV/s, an αn value of 0.72 ± 0.03 was calculated, quite consistent with the values used in the theoretical simulations (Figure 3).

The k_s(app) value was conveniently calculated over a range of scan rates by measurement of ΔE_p at each scan rate and use of eq 4:[23]

$$k_s = \frac{\psi(\pi a D_0)^{1/2}}{\lambda^\alpha} \qquad (4)$$

in which $\lambda = (D_0/D_R)^{1/2}$, D_0 is the diffusion coefficient of $Os_6(CO)_{18}$, D_R is the diffusion coefficient of $Os_6(CO)_{18}^{2-}$, and $a = nFv/RT$, in which n = apparent number of electrons transferred (2 in this case) and the other parameters have their usual significance. ψ is a dimensionless parameter related to the value of ΔE_p. The working curve of ψ vs. ΔE_p published earlier by Nicholson[23] did not specifically contain ψ (and ΔE_p) values in the range required for this study, so an extended working curve was calculated using ΔE_p values as large as 700 mV. Consistent with the suggestion in the earlier paper,[23] the curve of ΔE_p vs. log ψ was linear for ΔE_p values larger than about 170 mV.[24] These calculations yielded values for k_s(app) at 298 K of $4.5 \pm 0.7 \times 10^{-4}$ cm/s for the reduction at a gold electrode and $6.0 \pm 1.0 \times 10^{-4}$ cm/s at a platinum electrode. The diffusion coefficient needed for this calculation (2.97×10^{-5} cm²/s) was obtained from the polarographic I value and the Lkovic equation.[25]

In order to have an independent measurement of k_s(app), the redox couple was also studied by double potential step chronoamperometry. The chronoamperogram was obtained by stepping, for 5 s, from +0.5 V to a potential, E, sufficient to allow the reduction of $Os_6(CO)_{18}$ to $Os_6(CO)_{18}^{2-}$ for 5 s and then back

Table II. Calculated Electron Transfer Rates for the Redox Couple $Os_6(CO)_{18}^{0/2-}$

method	electrode material	apparent k_s (cm/s)
cyclic voltammetry	gold	$4.5 (\pm 0.7) \times 10^{-4}$
cyclic voltammetry	platinum	$6.0 (\pm 1.0) \times 10^{-4}$
chronoamperometry	platinum	8×10^{-4}
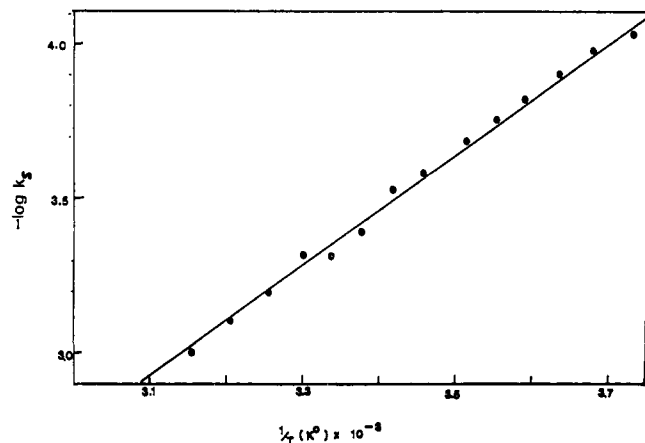
Figure 4. A plot of $-\log k_s$ vs. T^{-1} for the process $Os_6(CO)_{18}^{0}/Os_6(CO)_{18}^{2-}$ at a platinum electrode, as measured by cyclic voltammetry.

to +0.5 V [reoxidation of $Os_6(CO)_{18}^{2-}$]. The k_s(app) value was found from data generated in a set of cathodic steps, using the method of Schwarz and Shain.[26] A series of chronoamperograms was generated in which the step potential, E, was made successively closer to the E° value of the system, essentially stepping the potential out onto the reduction wave. For each current–time curve a plot of i vs. $t^{1/2}$ was made which upon extrapolation to $t = 0$ yielded i_0, the cathodic exchange current, which is defined in eq 5.

$$i_0 = nFk_sC_0 \exp[-\alpha nF(E - E^\circ)/RT] \qquad (5)$$

Plotting $\ln i_0$ against $(E - E^\circ)$ gave a straight line, and from the intercept (equal to $\ln nFk_sC_0$), a k_s value of 8×10^{-4} cm/s was calculated at 298 K at platinum. This is in reasonable agreement with the k_s value of $6 \pm 1 \times 10^{-4}$ cm/s calculated from CV measurements at a platinum electrode and serves to further verify the quasi-reversible nature of the electrode reaction. The results are summarized in Table II.

D. Temperature Dependence of k_s(app). The heterogeneous electron-transfer rate was evaluated over a range of temperatures at gold and platinum electrodes with use of cyclic voltammetry measurements as outlined above. A new value of D_0 was calculated at each new temperature from the cathodic peak height in the CV scan. Changes in D_0 roughly followed the rule of thumb of Meites[27] that a decrease of 1.3% for $D_0^{1/2}$ occurs with every 1 deg decrease in temperature. A plot of $\ln k_s$ vs. $1/T$ over the temperature range 269 to 317 K at a platinum electrode is shown in Figure 4. A similar curve was obtained with data at the gold electrode. The slope of these lines is the quantity $-\Delta H^\ddagger$, the enthalpy of activation of the electron-transfer reaction. The measured values were $\Delta H^\ddagger = -8.1$ kcal/mol (Pt electrode) and -7.6 kcal/mol (Au electrode).

II. Mechanism of the Reduction: Consideration of the Sequence of Electron Transfers and Structural Changes. The redox reaction in eq 1 is deceptively simple. The transfer of two electrons is involved, as well as a structural change from a bicapped tetrahedral cluster to an octahedral one. In considering the sequence of these changes, we begin by assuming that the two electrons are transferred in sequential one-electron steps (an EE mechanism) rather than in a simultaneous two-electron step. The one-electron nature of electron transfers is widely assumed, and we know of

(21) Adams, R. "Electrochemistry at Solid Electrodes"; Marcel Dekker, Inc.: New York, 1969; p 156.

(22) Matsuda, H.; Ayabe, Y. *Z. Elektrochem.* **1955**, *59*, 494.

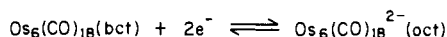(23) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

(24) A copy of the calculated ψ vs. ΔE_p curve is available from the authors upon request.

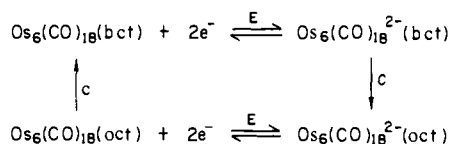(25) Heyrosvky, J.; Kuta, J. "Principles of Polarography"; Academic Press: New York, 1965; Chapter 6.

(26) Schwarz, W. M.; Shain, I. *J. Phys. Chem.* **1965**, *69*, 30.

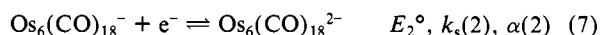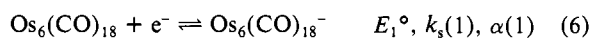(27) Meites, L. "Polarographic Techniques", 2nd ed.; Interscience: New York, 1965; p 139.

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Scheme II

$$Os_6(CO)_{18}(bct) + 2e^- \rightleftharpoons Os_6(CO)_{18}^{2-}(oct)$$

Scheme III

$$Os_6(CO)_{18}(bct) + 2e^- \xrightarrow{E} Os_6(CO)_{18}^{2-}(bct)$$

$$\Big\downarrow c \qquad\qquad \Big\downarrow c$$

$$Os_6(CO)_{18}(oct) + 2e^- \xrightarrow{E} Os_6(CO)_{18}^{2-}(oct)$$

no confirmed example of a simultaneous two-electron process.

The voltammetric and chemical behavior of EE systems depends on the relative $E°$ values of the one-electron-transfer reactions. Specifically, for our cluster system, we can assign $E_1°$ to the first reduction of $Os_6(CO)_{18}$ (eq 6) and $E_2°$ to the second reduction. Each process would also have its own heterogeneous rate constant

$$Os_6(CO)_{18} + e^- \rightleftharpoons Os_6(CO)_{18}^- \qquad E_1°, k_s(1), \alpha(1) \quad (6)$$

$$Os_6(CO)_{18}^- + e^- \rightleftharpoons Os_6(CO)_{18}^{2-} \qquad E_2°, k_s(2), \alpha(2) \quad (7)$$

and α value. Of course, if $E_2° \ll E_1°$, i.e., $E_2°$ more negative, two separate waves would be observed, but if $E_2° \gg E_1°$, a single two-electron wave is seen. The third possibility that $E_2° = E_1°$ is unlikely in this system, since that situation usually arises when a molecule has two essentially noninteracting redox sites.[28-30] Hence, we assume that $E_2° \gg E_1°$, i.e., that the monoanion $Os_6(CO)_{18}^-$ is thermodynamically unstable.

Quite distinct from the question of relative $E°$ values is that of defining when the structural rearrangement actually occurs. The two most obvious possibilities are during a charge-transfer step or subsequent to it. If the structure change occurs during (*concomitant with*) the electron transfer, the energy barrier to electron transfer contains the free energy needed to bring about the structural transformation, as required by the Marcus theory.[2] This leads to a retardation of the charge-transfer rate and the possibility of quasi-reversible or irreversible kinetics. Scheme II details this two-component mechanism for the cluster compound, using (bct) to denote the bicapped tetrahedron and (oct) to denote the octahedron. Note that we have not yet specified whether the rearrangement occurs in the first or second electron-transfer step. We will do this later. For purposes of discussion we will refer to Scheme II as the "quasi-reversible" model. An alternate "four-component" model can also be considered (Scheme III) in which the structural rearrangements occur after electron transfer (once again, for purposes of clarity of the model, we do not separate the individual EE steps in the two-electron process). This is a more general scheme than is Scheme II and basically views the structural changes as isomerizations *after* electron transfer. It is essentially an ECEC scheme. There is ample precident for the four-component scheme in other systems. For example, Bond and co-workers have studied the oxidative interconversions of a series of cis and trans isomers of metal carbonyl compounds of the Cr group.[31,32] Other organometallic examples include *cis*- and *trans*-Mo(CO)$_4$ carbene compounds and their cations[4e,33] and metal–polyolefin isomerizations.[34] A variety of conformational effects or organic compounds have also been studied.[35] One factor
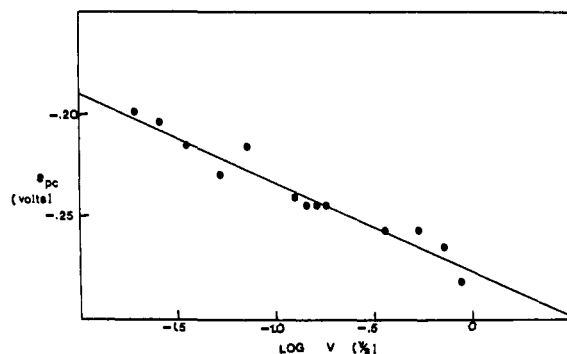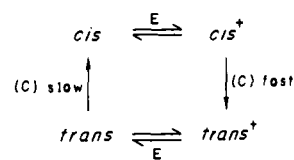
Scheme IV

Figure 5. A plot of cathodic peak potential vs. log scan rate for the reduction of $Os_6(CO)_{18}$ in THF/Bu_4NPF_6 at a platinum electrode. Potentials were taken from linear scan voltammograms.

the quoted studies have in common is that at least 3 of the 4 possible components of the square mechanism have been detected. When this is so, the "four-component" ECEC scheme is unquestionably the appropriate one. For example,[32] Bond and co-workers showed that *cis*-Cr(CO)$_2$(dpm) [dpm = bis(diphenylphosphino)methane] undergoes oxidation to a cis cation of limited stability, forming *trans*-Cr(CO)$_2$(dpm)$^+$ during a slow CV scan. A reduction wave for *trans*-Cr(CO)$_2$(dpm)$^+$ was observed in the CV scan about 650 mV negative of the oxidation wave. At increased scan rates or at lower temperatures both couples (cis/cis$^+$ and trans/trans$^+$) were chemically reversible. This established that both isomers had measurable lifetimes after each electron-transfer step, and the problem was properly interpreted in terms of independent electron-transfer and isomerization steps (Scheme IV).

If the structural isomerizations coupled to electron transfer were to become so rapid that the "un-isomerized" form of the couple could not be detected, then ambiguity arises as to whether the four-component or two-component scheme should be used to interpret the results. The reduction of cyclooctatetraene[36] (COT) provides an example in which the structure change (neutral tub to planar anion) appears to occur *during* the charge-transfer step and the process $COT^{0/-}$ has been treated as a "two-component" reaction. Electron-transfer rate measurements for this quasi-reversible couple have been used to estimate the energy barrier to flattening of the COT ring during the electron-transfer step.[36]

The $Os_6(CO)_{18}$ reduction is analogous to that of the COT reduction, in that only two structural forms are detected in the redox process. Hence, we favor the quasi-reversible model or the two-component scheme for this process. Experimental tests which also come out in favor of the two-component model involve the scan rate dependence of the cathodic peak potential, E_{pc}, and the ΔE_p values. In the limit of very fast follow-up reactions (structural changes) which would be needed to reconcile the four-component model to our experimental observations on the $Os_6(CO)_{18}$ reduction, both the reduction wave of $Os_6(CO)_{18}(bct)$ and the oxidation wave of $Os_6(CO)_{18}^{2-}(oct)$ would be viewed as EC processes in which both the electron-transfer step E and the following

(28) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

(29) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(30) There are exceptions to this generalization. For example, a study of stepwise oxidation of tetrakis(amino)ethylene compounds is reported in which $\Delta E°$ values of essentially zero were achieved by taking advantage of unequal changes in solvation energies in the two redox couples: Phelps, J.; Bard, A. J. *J. Electroanal. Chem.* **1976**, *68*, 313.

(31) Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617.

(32) Bond, A. M.; Colton, R.; Jackowski, J. *Inorg. Chem.* **1975**, *14*, 274, 2526.

(33) Rieke, R. D.; Kojima, H.; Ofele, K. *J. Am. Chem. Soc.* **1976**, *98*, 6735.

(34) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 4779.

(35) See, for example: Nelson, S. F.; Clennan, E. L.; Evans, D. H. *J. Am. Chem. Soc.* **1978**, *100*, 4012 and ref 4a,g,h.

(36) (a) Allendoerfer, R. A.; Rieger, P. H. *J. Am. Chem. Soc.* **1965**, *87*, 2336. (b) Huebert, B. J.; Smith, D. E. *J. Electroanal. Chem.* **1971**, *31*, 333. (c) Thielen, D. R.; Anderson, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 2521. (d) Kojima, H.; Bard, A. J.; Wong, H. N. C.; Sondheimer, F. *J. Am. Chem. Soc.* **1976**, *98*, 5560. (e) Fry, A. J.; Hutchins, C. S.; Chung, L. L. *J. Am. Chem. Soc.* **1975**, *97*, 591. (f) Paquette, L. A.; Gardlik, J. M.; Johnson, L. K.; McCullough, K. J. *J. Am. Chem. Soc.* **1980**, *102*, 5026.

Table III. Comparison of Experimental Values with Diagnostic Criteria[48] for EE Mechanisms

	predicted relationship			calculated[a]	
diagnostic	$E_{irrev}E_{rev}$	$E_{rev}E_{irrev}$	measured	$E_{irrev}E_{rev}$	$E_{rev}E_{irrev}$
$\lvert E_{pc} - E_{pc/2}\rvert$	47.7 mV/α_1	47.7 mV/(1 + α_2)	66 mV	66 mV	40–27 mV
$d[(E_{pc}/d(\log v)]$	30 mV/α_1	1 + (30 mV/α_2)	45 mV	42 mV	25–17 mV
i_a/i_c	$[(2 - \alpha_1)/\alpha_1]^{1/2}$	$[(1 - \alpha_2)(1 + \alpha_2)]^{1/2}$	1.2	1.32	0.98–0.60

[a] For the $E_{irrev}E_{rev}$ case, α_1 = 0.72 in calculations. For the $E_{rev}E_{irrev}$ case, values for diagnostic criteria are calculated over the range of α_2 values 0.2 to 0.8, all of which are shown to be inconsistent with the measured value.
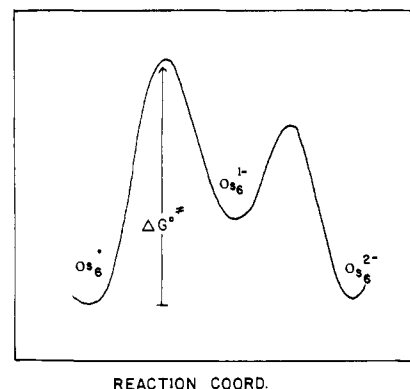
reaction C are extremely rapid. It has been shown[20,37] that for this mechanism, the peak current potential shifts negative (for a reduction process) by 30/n mV per decade increase in scan rate. Thus, a slope of 15 mV per decade in the E_{pc} vs. log v curve would be expected if the Os$_6$(CO)$_{18}$ reduction were an EC process with n = 2, or a 30 mV shift if n = 1. On the other hand, if the structural change is viewed as occuring concomitant with charge transfer (2-component model), the process is viewed simply as a slow charge transfer, being either quasi-reversible or irreversible, depending on the magnitude of k_s. In the irreversible limit, the slope of E_{pc} vs. log v would be 30/αn mV (predicted 42 mV for the Os$_6$(CO)$_{18}$ reduction, αn = 0.72). Experimentally, a slope of 45 mV (Figure 5) was found, supporting the model of concomitant electron transfer and structural rearrangement. Furthermore, as already discussed, the ΔE_p values measured were consistent with the quasi-reversible, 2-component, model over a range of scan rates. In Table I, the measured ΔE_p values are compared with those calculated theoretically (from eq 4) for k_s of 4.5 × 10^{-4} cm/s.

III. Diagnosis of the First Electron Transfer as the Slow Step.

Given that the cluster appears to behave as an EE system in which $E_2°$ ≫ $E_1°$, with at least one of the steps involving a slow heterogeneous charge transfer, we now turn to the questions of which is the rate-determining step and of what chemical significance are the measured barriers to electron transfer.

Multi-electron-transfer reactions have long been recognized as difficult to disect into their component parts.[2,38–41] Each electron-transfer reaction has its own $E°$, k_s, and α values. The case in which $E_2°$ < $E_1°$ can be fairly easily treated because (for a reduction) there is observed either a broadened wave if $E_2°$ is close to $E_1°$ or two distinct waves if $E_2°$ ≪ $E_1°$.[42] Theoretical values of wave breadth have been calculated for Nernstian charge-transfer systems with close $E°$ values,[29,43] and in principle all systems with $E_2°$ < $E_1°$ are subject to accurate theoretical analysis. This matches our intuitive expectations, since the one-electron intermediate has thermodynamic stability and may even be monitored by spectroscopic or other techniques.

The more difficult case is that in which $E_2°$ > $E_1°$, i.e., the one-electron intermediate is thermodynamically unstable. If both electron transfers are fast (the $E_{rev}E_{rev}$ case), a single wave is seen and the voltammetry is characteristic of the *overall* two-electron transformation, and not of either of the individual steps. The observed $E°$ value is the average of the $E°$ values of the individual steps $[E_{obsd}° = (E_1° + E_2°)/2]$[20,40,44] and the wave shape and its response to changes of experimental variables is governed by an *effective*, or apparent, α value, which we designate α(app), and a k_s value, k_s(app), of similar significance.[45] However, when one of the two electron transfers is slow ($E_{rev}E_{irrev}$ or $E_{irrev}E_{rev}$), then there is opportunity for analysis of the stepwise processes.

(37) Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem.* **1973**, *48*, 113.
(38) Vetter. K. J. "Electrochemische Kinetik"; Springer: Berlin, 1961; pp 129–133. Vetter, K. J. "Electrochemical Kinetics"; Academic Press: New York, 1967; pp 149–154 and references therein.
(39) Bockris, J. O'M.; Reddy, A. K. N. "Modern Electrochemistry"; Plenum Press: New York, 1970; Vol. 2, pp 991–1008.
(40) Polcyn, D. S.; Shain, I. *Anal. Chem.* **1966**, *38*, 370.
(41) Parsons, R. *Faraday Soc. Trans.* **1951**, *47*, 1332.
(42) This is true in all cases if k_s^1 is large (first reduction reversible) and in cases of lower k_s^1 (quasi-reversible or irreversible first reduction) if $E_2°$ is sufficiently negative of $E_1°$.
(43) Myers, R. L.; Shain, I. *Anal. Chem.* **1969**, *41*, 980.
(44) Ruzic, I. *J. Electroanal. Chem.* **1974**, *52*, 331.
(45) Mohilner, D. M. *J. Phys. Chem.* **1964**, *68*, 623.
(46) If both electron transfers are slow, analysis is extremely difficult. See section V of Results and Discussion and ref 48.

Figure 6. Schematic representation of the changes in standard free energy as the neutral Os$_6$(CO)$_{18}$ cluster undergoes stepwise reduction to the thermodynamically unstable monoanion and then to the dianion. The curves are depicted for an electrode potential close to the $E°$ value.

Two limiting cases may be considered, in which either the first or second electron transfer is the rate-determining step. Mohilner has shown that in a multielectron-transfer reaction the effective α value, α(app), is given by eq 8

$$\alpha(\text{app}) = (\alpha n_a + n_p)/n \qquad (8)$$

when one electron-transfer step is slow and the other is fast.[45] In this equation, n_a is the number of electrons transferred in the rate-determining step (rds) (essentially always one),[47] n_p is the number of electrons transferred in steps preceding the rds, and n is the overall number of electrons transferred. In the case of a rate-determining first step ($E_{irrev}E_{rev}$) in an overall two-electron process, α(app) = $\alpha_1/2$, that is, the observed α value is one-half that of the α value for the first charge transfer. When the second transfer is rate determining ($E_{rev}E_{irrev}$), α(app) = (1 + α_2)/2. Since the charge-transfer coefficient strongly affects the shapes of cyclic voltammetry curves,[20,22] the α(app) values are of primary importance in diagnosing the rate-determining step.

Ryan[48] has considered in detail cyclic voltammograms for both the $E_{irrev}E_{rev}$ and $E_{rev}E_{irrev}$ cases, expanding on earlier efforts.[40,49] A set of criteria were developed for distinguishing between these two models, and we now apply those criteria to our own data (Table III).

As discussed in section Ic, a value of (αn) app = 0.72 was calculated from the breadth of the cathodic wave, $E_{pc} - E_{pc/2}$ over a range of scan rates, the mean experimental value being 66 mV. This is consistent only with the *first electron transfer* being rate determining, since the prediction of the $E_{rev}E_{irrev}$ case would be for a much narrower cathodic peak. By using a generously wide range of possibilities for α_2 (0.2 to 0.8), $E_{pc} - E_{pc/2}$ values of 40 to 27 mV are predicted[48] for the $E_{rev}E_{irrev}$ case (Table III), considerably smaller than the observed value.

Similarly, the observed cathodic shift of E_{pc} with increasing scan rate, 45 mV per decade increase in v, is close to that predicted (42 mV) for $\alpha_1 n$ = 0.72 ($E_{irrev}E_{rev}$), and outside the range predicted for the $E_{rev}E_{irrev}$ case. Finally, the anodic-to-cathodic current ratios are predicted to be >1 if the the first step is rate determining and <1 if the second step is the slow one. In this last case the fit is

(47) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; John Wiley and Sons: New York, 1980; p 111.
(48) Ryan, M. R. *J. Electrochem. Soc.* **1978**, *125*, 547.
(49) Feldberg, S. W. In "Electrochemistry", Mattson, J. S., Mark, H. B., McDonald, Jr., H. C., Eds.; Marcel Dekker: New York, 1972; pp 185–215.

not unambiguous, since our relatively dilute solutions gave enough charging current that it was difficult to measure precisely the extrapolated value of the cathodic current branch, the most reliable procedure for such a measurement.[50] Our measured values consistently fell in the range $i_a/i_c = 1.0$ to 1.2, and multiple cycle (steady state) voltammograms gave 1.2 to 1.3. The predicted value for $\alpha_1 n = 0.72$ is 1.30. We certainly did not observe the significantly smaller reverse peak that would be expected if the second step were rate determining. Finally, on this point, CV scans after electrolysis gave a larger anodic peak (Figure 2), as expected. Taken together, these data argue strongly for the *first electron transfer* being the *rate-determining step* in the redox process.

IV. Significance of the Activation Barrier to Electron Transfer. In stepwise two-electron-transfer processes, there are two activation barriers, and if the first step is rate determining, the reaction coordinate diagram is qualitatively as depicted in Figure 6. In order for the first step to be the rds the free energy of the first activated complex must be the highest free energy of either activated state compared with the energy of the ground-state reactant.[39] Therefore, the measured activation parameters have relevance to the energetics of the initial one-electron process $Os_6(CO)_{18} \rightarrow Os_6(CO)_{18}^-$. According to the Marcus theory,[2] the activation barrier to electron transfer contains contributions from the energetics of solvation changes and structural reorganization of the cluster. $\Delta G^{\ddagger}$ can be calculated[51] from the standard heterogeneous electron-transfer rate through eq 9.

$$\Delta G^{\ddagger} = kT \ln (k_s/10^4) \qquad (9)$$

$\Delta G^{\ddagger}$ at 298 K was 11.6 kcal/mol when computed from the k_s value at a Pt electrode and 11.3 kcal/mol from the k_s value at Au. The temperature dependence of k_s was used to evaluate the activation enthalpy, $\Delta H^{\ddagger}_{meas}$, of the reduction. From the slopes of the ln k_s vs. $1/T$ plots (e.g., Figure 4), values of 8.1 and 7.6 kcal/mol were obtained for data at Pt and Au electrodes, respectively. These values of $\Delta H^{\ddagger}_{meas}$ actually contain a contribution from the activation enthalpy of diffusion, $\Delta H_D^{\ddagger}$, which is usually small.[36a] This latter quantity was evaluated for $Os_6(CO)_{18}$ in THF from the slope of log I_p vs. $1/T$ plots (I_p = cathodic peak current) derived from CV data. At both gold and platinum electrodes, the value of $\Delta H_D^{\ddagger} = 0.30$ kcal/mol was obtained. Then from eq 10 the actvation enthalpy of electron transfer was calculated:

$$\Delta H^{\ddagger} = \Delta H^{\ddagger}_{meas} + \tfrac{1}{2}\Delta H_D^{\ddagger} \qquad (10)$$

Thus, $\Delta H^{\ddagger}$ values of ca. 8.0 kcal/mol (average of gold and platinum data) are appropriate for this reorganization process.

This activation barrier can be compared to those measured for other kinds of metal cluster structure changes. Relatively little data are available on the energetics of metal cluster *framework* reorganizations,[52] although there are now several examples in which reversible making and breaking of M–M bonds have been demonstrated.[53–55] However, studies of processes in which *ligands* scramble over the metal cluster framework have been common. For example, NMR studies have shown that cluster carbonyl scrambling generally has an activation barrier in the range 5–20 kcal/mol, interpreted as being roughly the energy associated with interconversion of nonbridging and bridging carbonyls.[56] Osmium clusters tend not to form bridging carbonyls, and carbonyl migrations were not observed[56,57] in NMR spectra of clusters like $Os_6(CO)_{18}$, or $Os_6(CO)_{18}^{2-}$. Apparently, then, the 8-kcal activation barrier to cluster framework reorganization which we measure

for the change between bicapped tetrahedron and octahedron is lower than even the energy of carbonyl scrambling in this cluster. This seems to be a rare example of a cluster in which breaking and re-making metal–metal bonds is energetically more favorable than similar processes involving metal–ligand bonds. However, it must be kept in mind that this metal framework reorganization requires the electron-transfer step in order to take place. In that sense, *one-electron transfer activates the cluster to M–M bond cleavage*. Finally, we note that not even all of the 8 kcal goes into the metal framework deformation, for part of the activation enthalpy must involve the energy required to reorient solvent dipoles around the cluster as the charge is changed.[2] We are left with the conclusion that, when accompanied by electron transfer, the cluster structure change is remarkably facile. This observation is consistent with not only the redox chemistry but also the reaction chemistry of the osmium cluster. The addition of nucleophiles to $Os_6(CO)_{18}$ dominates its reaction chemistry, and the fission of metal–metal bonds which accompanies these reactions implies a degree of M–M bonding character to the cluster LUMO.[58] Acid–base reactions also result in facile changes between skeletal forms[11] (e.g., octahedral for $[Os_6(CO)_{18}^{2-}]$ and capped square-pyramidyl for $[H_2Os_6(CO)_{18}]$).

V. Assumptions and Limitations in the Analysis. It should be noted that we have explicitly assumed in analysis of the EE mechanism that one of the electron-transfer steps is reversible. Whereas the analysis does not require the reversible process to be strictly Nernstian, it remains that significant slowing from Nernstian charge-transfer kinetics could give two quasi-reversible steps and lead to errors in our interpretation of the significance of the activation parameters. We have simulated voltammograms for the EE mechanism in which specific values of $E°$, k_s, and α were assumed for each separate step and compared the results with those of Figure 3, in which the simulations employed an $n(app) = 2$, $k_s(app) = 5.5$ ($\pm$ 1.5) $\times 10^{-4}$ cm/s, and $\alpha(app) = 0.38 \pm 0.02$. There was complete agreement between the two approaches when the appropriate k_s and α values were used for the first step (ca. 5×10^{-4} cm/s and 0.36, respectively), provided that the second step had an $E°$ at least 200 mV positive of $E°$, and that the second electron-transfer step was rapid [k_s (2) > 1 cm/s]. Significant deviations in the peak separation were apparent if $k_s(2)$ dropped below about 0.5 cm/s, so we take this value as a crude lower limit for $k_s(2)$, associated with the reaction of eq 7. This is certainly a reasonable lower limit for the second reduction of the $Os_6(CO)_{18}$ cluster. For comparison purposes, the reduction of cyclooctatetraene to its monoanion is uncommonly slow for a cyclic polyolefin, but subsequent reduction of the planar monoanion to the dianion is more rapid by about two orders of magnitude.[36,59]

Finally, we note that the time range of the quantitative CV analysis is fairly limited, essentially to scan rates below 1000 mV/s, since there are higher values to give increasing errors due to solution resistance. In a mechanistic study, we would like to have data over about three orders of magnitude, but only about 1.5-orders is available in our experiments. Other approaches are being pursued to extend this kinetic window in other chemical systems involving multiple electron transfer.

VI. The Two-Electron Reduction of $Os_6(CO)_{18}^{2-}$. As mentioned above, there is a second polarographic reduction for $Os_6(CO)_{18}$ at -2.15 V. This was also a two-electron wave, since the I value on the second plateau was 9.2, almost exactly four times that of the one-electron $Co_3(CO)_9C(CH_3)$ standard. Thus, the reduction of the dianion formally results in a tetraanion. However, the second reduction did not yield a stable product. CV measurements at less than $v = 100$ mV/s showed no anodic wave coupled to the reduction. However, at faster scans, an anodic wave grew in at about -1.7 V (Figure 7), making the second reduction process look remarkably like the first (two-electron wave, large ΔE_p). It is possible that this reduction involves the two-electron transfer of eq 2 and the wave at -1.7 V is due to reoxidation of the

(50) Reference 21 pp 153–158.
(51) Hale, J. M. In "Reactions of Molecules at Electrodes"; Hush, N. S., Ed.; Wiley-Interscience: New York, 1971; p 229.
(52) Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639.
(53) Vidal, J. L.; Walker, W. E.; Pruett, R. L.; Schoening, R. C. *Inorg. Chem.* **1979**, *18*, 129.
(54) Vollenbroek, F. A.; van den Berg, J. P.; van der Velden, J. W. A.; Bour, J. J. *Inorg. Chem.* **1980**, *19*, 2685.
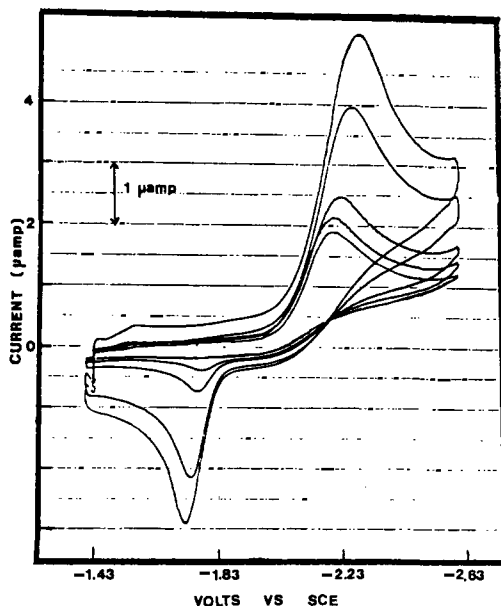(55) Briant, C. E.; Hall, K. P.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1984**, 290.
(56) Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225.
(57) Corey, E. R.; Dahl, L. F. *Inorg. Chem.* **1962**, *1*, 521.

(58) Lewis, J.; Johnson, B. F. G. *Pure. Appl. Chem.* **1982**, *54*, 97.
(59) Smith, W. H.; Bard, A. J. *J. Electroanal. Chem.* **1977**, *76*. 19.

Figure 7. Cyclic voltammograms of the second reduction wave of Os₆-(CO)₁₈ in THF/Bu₄NPF₆ at a platinum bead electrode. The increasing currents arise from scans at 70, 100, 160, 460, and 680 mV/s, respectively.

Scheme V. Predicted Idealized Structural Relationships of $Os_6(CO)_{18}{}^{2-}$ and $Os_6(CO)_{18}{}^{4-}$ from Reaction of Eq 2
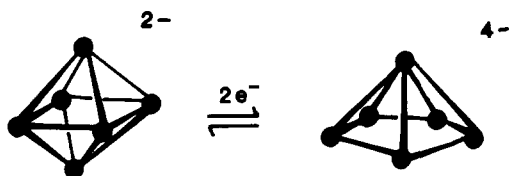
tetraanion. PSEP theory[12] predicts that addition of 2 electrons to the octahedral $Os_6(CO)_{18}{}^{2-}$ should result in formation of the nido-cluster $Os_6(CO)_{18}{}^{4-}$ having a pentagonal pyramid structure. (Scheme V). The latter structure is derived from a pentagonal bipyramid with one open vertex. Unfortunately, because of the transient nature of the electrolysis product, the structure responsible for the wave at −1.7 V could not be investigated.

VII. The Oxidation of $Ru_6(CO)_{18}{}^{2-}$. The ruthenium analogue of the osmium dianion cluster has been prepared and structurally

characterized[60,61] as a distorted octahedron, but the neutral compound $Ru_6(CO)_{18}$ has yet to be reported. Our attempts at generating the neutral compound electrochemically from the dianion failed, for although an oxidation wave was observed (E_{pa} = +0.17 V at Pt electrode at v = 100 mV/s), this wave was chemically irreversible in either THF or CH_2Cl_2 even at scan rates up to 10 V/s. The neutral ruthenium cluster can be concluded to be highly unstable.

Conclusions

The title compound has been demontrated to reduce via an overall two-electron process to a dianion, without formation of a thermodynamically stable monoanion. The voltammetric waves are treated as arising from a quasi-reversible two-electron process, which is not that unusual for "simple" metal ion couples (e.g., Zn^{2+}, Zn),[62] but which is rare for metal complexes. The voltammetric behavior is consistent with the rate-determining electron transfer involving formation of a monoanion, which is rapidly reduced by another electron to give a stable dianion. The activation enthalpy of 8 kcal/mol for the first step is ascribed in part to the energy needed to transform the cluster from a bicapped tetrahedral structure in the neutral compound to an octahedral structure in the transient monoanion.

(60) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; Machin, P.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1976**, 945.

(61) Jackson, P. F.; Johnson, B. F. G.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1979**, 735.

(62) Written in this fashion, the couple is deceptively simple. In fact, there is considerable disagreement of the mechanism and kinetics of the reduction of Zn^{2+}. See for leading references: (a) Bond, A. M.; Grabaric, B. S.; Jones, R. D.; Rumble, N. W. *J. Electroanal. Chem.* **1979**, *100*, 625. (b) Payne, D. A.; Bard, A. J. *J. Electrochem. Soc.* **1972**, *119*, 1665.