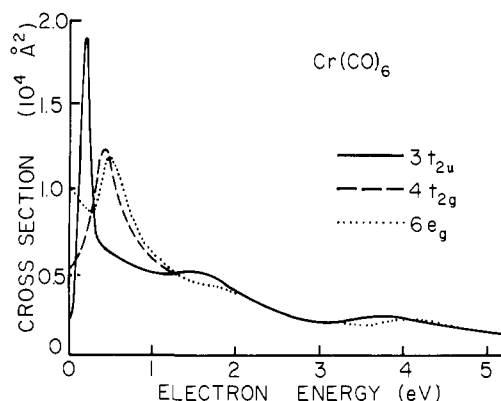**Figure 1.** Ion current vs. electron impact energy on $Cr(CO)_6$. The ions are essentially all $Cr(CO)_5^-$.

Figure 2. Calculated continuum MS-Xα elastic electron scattering cross section vs. electron energy for $Cr(CO)_6$ for three different potentials obtained by adding 0.5 electrons to the $3t_{2u}$, $4t_{2g}$, and $6e_g$ orbitals, respectively.

for use in the continuum calculation by adding 0.5 electrons to various empty orbitals, iterating to self-consistency, and subtracting out the effect of a stabilizing Watson sphere as described previously.[2] The cross sections shown in Figure 2 were determined from potentials corresponding to $3t_{2u}$, $4t_{2g}$, and $6e_g$ orbital occupations, which have calculated attachment energies of 1.7, 0.9, and 0.2 eV, respectively, within the bound-state stabilization approach.[2] A number of lower energy empty orbitals ($9t_{1u}$, $9a_{1g}$, $2t_{2u}$, $3t_{2g}$, and $2t_{1g}$) are predicted to generate stable anions. The calculated cross sections are similar to the experimental result, each showing maxima well below 1 eV and a shoulder between 1.2 and 2 eV. A decomposition of the cross section by the symmetry of the continuum electron for the $3t_{2u}$ potential shown in Figure 3 establishes that the low-energy maximum arises from the t_{2g} channel and the shoulder at 1.6 eV from the t_{2u} channel. The continuum MS-Xα results should be considered preliminary since we have used a small basis set more appropriate for bound-state calculations and have not explored the effect of adding higher partial waves.[6] Although the attachment energies from the bound-state calculation are in reasonable agreement with the calculated positions of the cross-section maxima, it is apparent that our previous analysis was somewhat oversimplified as evidenced by the substantial contributions in nonresonant channels and the unexpectedly low cross section in the e_g channel (also

(6) Dehmer, J. L.; Dill, D. In "Electron–Molecule and Photon–Molecule Collisions"; Rescigno, T., McKoy, V., Schneider, B., Eds.; Plenum Press: New York, 1978.
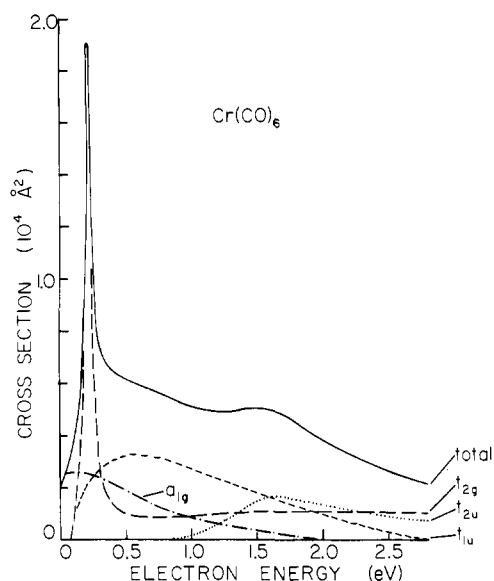
Figure 3. Decompoisition of calculated cross section by symmetry of continuum electron for the scattering potential given by occupation of the $3t_{2u}$ orbital (e_g and t_{1g} channels give $\sigma < 30$ Å^2 and are not shown).

predicted by the RHF calculation[4]). It also appears that the RHF and MS-Xα calculations give the same order of anion states but that all the states lie higher by about 2 eV in the RHF calculation. A further comparison of RHF and MS-Xα results will be the subject of a later report.

(7) **Note Added in Proof:** We have recently learned of similar ion current results for $Cr(CO)_6$ obtained by Pignataro et al.: Pignataro, S.; Foffari, A.; Grasso, F.; Cantone, B. *Z. Phys. Chem. (Wiesbaden)* **1965**, *47*, 106.

Electrochemical Reduction of Molybdenum(II) and Tungsten(II) Halide Cluster Ions. Electrogenerated Chemiluminescence of $Mo_6Cl_{14}{}^{2-}$

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Recent work in our laboratory has revealed that the excited-state chemistry of hexanuclear molybdenum(II) and tungsten(II) halide cluster ions is unusually rich.[1-3] A new class of powerful inorganic oxidants ($M_6X_{14}^-$) has been identified in our electrochemical and photochemical studies, but hitherto it has not been possible to obtain reduced cluster species. Here we report experiments in which the reduced cluster $Mo_6Cl_{14}{}^{3-}$ has been produced cleanly, thereby making it possible to observe the electrogenerated chemiluminescence (ECL) of $Mo_6Cl_{14}{}^{2-}$.

Five $M_6X_{14}{}^{2-}$ (M = Mo, X = Cl, Br; M = W, X = Cl, Br, I) cluster ions were examined by cyclic voltammetry at potentials as low as −2.2 V and as high as 2.2 V vs. SCE in CH_3CN solution. All the cluster ions show irreversible oxidation waves in their cyclic voltammograms at potentials more positive than their respective

(1) Maverick, A. W.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 1298–1300.
(2) Maverick, A. W.; Najdzionek, J. S.; MacKenzie, D.; Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1878–1882.
(3) Nocera, D. G.; Gray, H. B., manuscript in preparation.
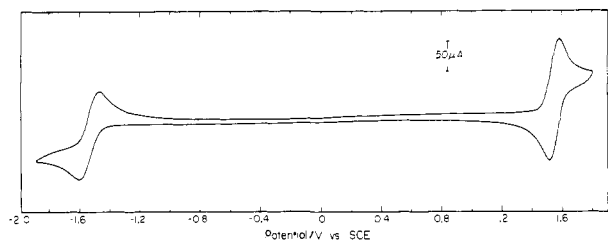
Figure 1. Cyclic voltammogram of 2 mM $(Bu_4N)_2Mo_6Cl_{14}$ in $CH_3CN/0.1$ M Bu_4NClO_4 at 25 °C (scan rate 200 mV s^{-1}; Pt-button working, Ag-wire reference, and Pt-wire auxiliary electrodes). The potential was referenced to a ferrocene internal standard and related to the SCE reference using a value of 0.31 V vs. SCE for the $Fc^{+/0}$ couple (Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; p 701).
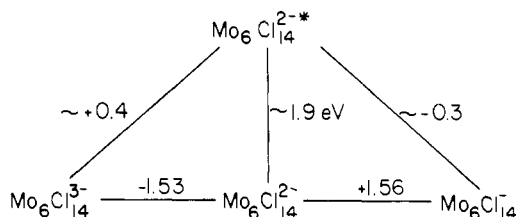
Figure 2. Modified Latimer diagram for $(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN (electrode potentials/V vs. SCE).

one-electron oxidation couples.[1-3] The five clusters also exhibit reduction waves at potentials more negative than -1.5 V vs. SCE; for $Mo_6Cl_{14}^{2-}$, a quasi-reversible one-electron wave with a half-wave potential of -1.53 V vs. SCE is attributed to the $Mo_6Cl_{14}^{2-/3-}$ couple (Figure 1).[4] Both oxygen and water must be rigorously excluded in order to obtain a well-defined reduction wave.[5]

A modified Latimer diagram shows that the energy that would be released upon combination of $Mo_6Cl_{14}^{3-}$ and $Mo_6Cl_{14}^-$ (3.1 eV) is sufficient to produce one excited cluster ion $(Mo_6Cl_{14}^{2-*}$: ϕ_{em} = 0.19, τ = 0.32 ms in CH_3CN at 25 °C)[2] (Figure 2). And, indeed, red ECL is observed upon pulsing the potential applied to a Pt working electrode with a square-wave potential program of 1.80 and -1.80 V vs. SCE.[6] The uncorrected ECL spectrum of a stirred acetonitrile solution of $Mo_6Cl_{14}^{2-}$ is identical with the uncorrected emission spectrum produced by steady-state irradiation of $Mo_6Cl_{14}^{2-}$ in CH_3CN (Figure 3). ECL is observed only when the potential applied to the Pt working electrode is stepped into the one-electron oxidation–reduction waves of $Mo_6Cl_{14}^{2-}$, thereby indicating that the effect is attributable to an annihilation reaction between electrogenerated $Mo_6Cl_{14}^{3-}$ and $Mo_6Cl_{14}^-$ in which one ground-state ion $(Mo_6Cl_{14}^{2-})$ and one excited ion $(Mo_6Cl_{14}^{2-*})$ are produced.

ECL from inorganic species previously has been limited to mononuclear metal complexes containing chelating aromatic ligands.[7-9] In these complexes, the organic ligands strongly interact with the metal atom, and the excited states possess substantial ligand character. Observation of $Mo_6Cl_{14}^{2-}$ ECL is

Figure 3. ECL spectrum of $(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN at 25 °C using a cyclic square wave at 100 Hz between 1.80 and -1.80 V vs. SCE. Black circles illustrate the luminescence spectrum of $(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN with 436-nm excitation. Spectra are not corrected for photomultiplier or monochromator response.

important in the sense that it opens the way for detailed exploration of the kinetic and mechanistic features of highly exergonic electron-transfer reactions involving symmetric (O_h) all-inorganic species. Further investigations of the ECL properties of these cluster ions should allow key aspects of electron-transfer theories to be evaluated more rigorously than has been possible previously.

Effect of a CO Ligand on the Reactivity of Co_2^+ toward Alkanes

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The group 8 atomic transition-metal positive ions activate both C–H and C–C bonds in alkanes in the gas phase.[1-8] Co_2^+, however, is unreactive toward alkanes.[2] We wish to report that addition of a CO ligand to Co_2^+ causes it to efficiently attack C–H bonds in alkanes. Co_2CO^+ reacts with butane according to reaction 1. Reaction 1a accounts for 90% of the total reaction.

$$Co_2CO^+ + n\text{-}C_4H_{10} \rightarrow Co_2COC_4H_6^+ + 2H_2 \quad (1a)$$

$$Co_2CO^+ + n\text{-}C_4H_{10} \rightarrow Co_2COC_4H_8^+ + H_2 \quad (1b)$$

The overall rate constant for the reaction, approximately 2×10^{-9} cm^3 s^{-1}, is at least 2 orders of magnitude greater than the greatest possible value for the rate constant for any reaction between Co_2^+ and n-butanes.

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(4) Both the oxidation and reduction waves in Figure 1 are observed independently upon scanning anodically and cathodically from the rest potential. This result rules out the possibility that either wave arises from a product derived from oxidation or reduction of $Mo_6Cl_{14}^{2-}$.
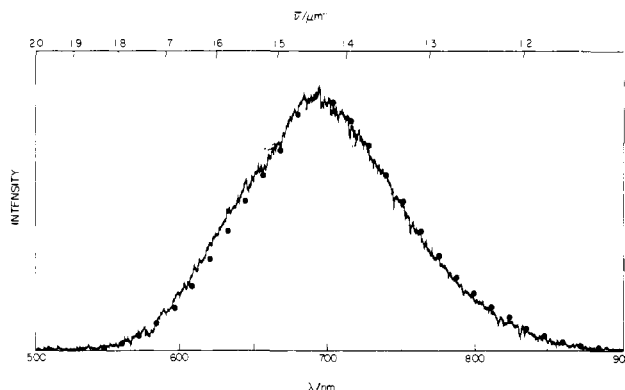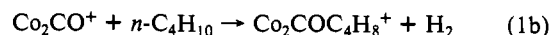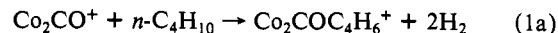
(5) All manipulations (including solvent transfers and sample additions) were conducted in a specially designed high-vacuum electrochemical cell with Pt-wire working, Pt-mesh auxiliary, and Ag-wire reference electrodes.

(6) Pulse trains (1–100 Hz) were obtained with a PAR 175 universal programmer. A high-vacuum electrochemical cell was used for all ECL experiments.

(7) Ru(II) π-acid chelates: (a) Gonzales-Velasco, J.; Rubinstein, I.; Crutchley, R. J.; Lever, A. B. P.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 822-825. (b) Abruña, H. D.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 2641-2642. (c) Rubinstein, I.; Bard, A. J. *Ibid.* **1981**, *103*, 512-516. (d) Luttmer, J. D.; Bard, A. J. *J. Phys. Chem.* **1981**, *85*, 1155-1159. (e) Glass, R. S.; Faulkner, L. R. *Ibid.* **1981**, *85*, 1160-1165. (f) Wallace, W. L.; Bard, A. J. *Ibid.* **1979**, *83*, 1350-1357 and references therein.

(8) Pd(II) and Pt(II) metalloporphyrins: Tokel-Takvoryan, N. E.; Bard, A. J. *Chem. Phys. Lett.* **1974**, *25*, 235-238.

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(2) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129-7131.

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(4) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 787-791.

(5) Armentrout, P. B; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501-6502.

(6) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963-968.

(7) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565-3569.

(8) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736-742.