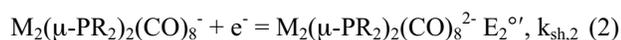
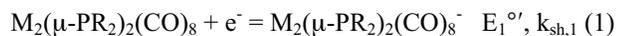


Concerted Two-Electron Transfer and Metal-Metal Bond Breaking in Ligand-Bridged Binuclear Complexes. Relevance to Nitrogen Fixation

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The iron-molybdenum cofactor (FeMoco) active site of the enzyme nitrogenase consists of a polynuclear Mo-Fe-S cluster in which the Fe-Mo and Fe-Fe distances in the semi-reduced state suggest the presence of metal-metal bonding (1). These intermetal distances appear to be too short to allow binding of substrate N₂. Thus, it has been suggested that reduction and metal-metal bond cleavage may be required to open the Fe-Mo-S framework and create an N₂ binding site (2). Structural changes of this nature are observed upon chemical reduction of polynuclear Fe-Mo-S model compounds (3) and electrochemical reduction of ligand-bridged binuclear carbonyls such as M₂(μ-SR)₂(CO)₈ (M = Mo, W) (4,5). The concerted two-electron character of the latter reactions is congruent with the proposal that nitrogenase operates via a series of two-electron/two-proton steps (6).

This work examines the kinetics and thermodynamics of coupled two-electron transfer and metal-metal bond cleaving/forming reactions in binuclear M₂(μ-SR)₂(CO)₈^{0/2-} (7) and M₂(μ-PR)₂(CO)₈^{0/2-} (8) (M = Mo, W) complexes. These reactions occur by sequential one-electron steps, e.g.:



in which the second charge transfer is thermodynamically more favorable than the first, i.e., $E_1^{o'} < E_2^{o'}$. Inverted potential behavior (9) results from the structural changes that accompany reduction of the metal-metal bonded M(I)₂ centers to non-bonded M(0)₂. In the course of this process M-M distances increase by ~1.0 Å, but each M₂(μ-E)₂ (E = RS⁻, R₂P⁻) unit remains intact, a feature that may be important in maintaining structural integrity in a biological redox component.

We have studied the influence of metal atom and bridging ligand on the kinetics and thermodynamics of reactions 1 and 2. Reduction of the sulfido-bridged complexes is facile in comparison with their phosphido-bridged analogs. Thus, we have compared the behavior of Mo₂(μ-PPh)₂(CO)₈^{0/2-} and W₂(μ-PPh)₂(CO)₈^{0/2-}. Electrode kinetic studies show that the standard potentials of both couples are inverted by ca. 180 mV and that the rate constant of reaction 2 is about one order of magnitude smaller than $k_{sh,1}$. Moreover, $k_{sh,2}$ is about 3 times smaller for M = W than for M = Mo. These findings suggest that

References

- (1) Peters, J.W.; Stowell, M.H.B.; Soltis, S.M.; Finnegan, M.G.; Johnson, M.K.; Rees, D.C. *Biochemistry*, **1997**, *36*, 1181.
- (2) Kisker, C.; Schindelin, H.; Rees, D.C. *Annu. Rev. Biochem.* **1997**, *66*, 233.
- (3) Han, J.; Beck, K.; Ockwig, N.; Coucouvanis, D. *J. Am. Chem. Soc.* **1999**, *121*, 10448.
- (4) Smith, D.A.; Zhuang, B.; Newton, W.E.; McDonald, J.W.; Schultz, F.A. *Inorg. Chem.* **1987**, *26*, 2524.
- (5) Fernandes, J.B.; Zhang, L.Q.; Schultz, F.A. *J. Electroanal. Chem.* **1991**, *297*, 145.
- (6) Thorneley, N.F.; Lowe, D.J. In *Molybdenum Enzymes*; Spiro, T.G., Ed.; Wiley and Sons: New York, NY, 1985, pp 221-284.
- (7) Darensbourg, D.J.; Sanchez, K.M.; Reibenspies, J. *Inorg. Chem.* **1988**, *27*, 3636.
- (8) Shyu, S.G.; Calligaris, M.; Nardin, G.; Wojcicki, A. *J. Am. Chem. Soc.* **1987**, *109*, 3617.
- (9) Evans, D.H.; Hu, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 194.
- (10) DiMaio, A.J.; Rheingold, A.L.; Chin, T.T.; Pierce, D.T.; Geiger, W.E. *Organometallics*, **1998**, *17*, 1169.