J. Am. Chem. Soc. 1988, 110, 6585–6586

Novel Rates and Mechanisms of CO Substitution of Similar 17- and 18-Electron Metal Carbonyls

Noel C. Hallinan, Giancarlo Morelli, and Fred Basolo*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received May 31, 1988

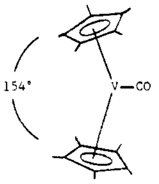
It has been established by the seminal work of Brown,[1] followed by extensive studies in several other laboratories,[2] that 17-electron metal carbonyl radicals such as $MnCO_5$ and $Re(CO)_5$ are CO substitution labile. Furthermore, in every case studied[1b,2a] where substitution is fast, it proceeds by an associative pathway involving a 19-electron transition state or active intermediate. We recently reported[3] the first kinetic study of a 17-electron metal carbonyl that is substitution inert but which reacts by a dissociative process. Numerous examples have shown that in the absence of any unfavorable steric or electronic effects,[4] 17e complexes undergo rapid associative ligand substitution. Dissociative substitution for such systems is usually slow. It is also generally believed that 17-electron systems react much faster than corresponding 18-electron compounds. We wish to report preliminary results that provide an example of (a) 17e and 18e systems that undergo substitution at similar rates and (b) a slow associative substitution pathway for a 17e vanadium complex. The reactions investigated involve CO exchange in various analogous L_2MCO compounds (eq 1).

$$L_2M^{13}CO + CO \rightleftharpoons L_2MCO + {}^{13}CO \qquad (1)$$

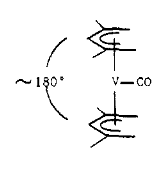
(L = Cp, pd, dmCh;[5] M = V, Cr)

Our earlier studies[6] showed that the rate of associative CO substitution of $V(CO)_6$ (17e) is 10^{10} times faster than the corresponding reactions of $Cr(CO)_6$ (18e). In contrast to this huge difference in rates of reaction between 17- and 18-electron compounds, we now find that (Cp)(pd)CrCO (18e)[7] reacts at about the same rate ($k_1 = 2.11 \times 10^{-4}\ s^{-1}$ at 60 °C) as (Cp)(pd)VCO (17e) ($k_1 = 2.73 \times 10^{-4}\ s^{-1}$ at 60 °C). Qualitatively, the earlier and the present observations are readily understood on the basis of an energy/reaction coordinate diagram. For the rapid associative substitution of a 17e versus 18e system, it is clear that the less stable 17e substrate involves a 19e transition state which is more stable than the 20e transition state required by the more stable 18e substrate. The lower activation energy involved in the associative substitution reaction of the 17e system leads to a faster reaction rate compared to the 18e system (Figure 1). Contrast this with the well-known fact[8] that 16e compounds are generally more stable than their 15e counterparts, and it follows that the activation energies for dissociative substitution of 17e and 18e systems may be of similar magnitude (Figure 2). Thus one expects differences in rates of dissociative ligand substitution of 17e and 18e systems to be smaller than for corresponding associative reactions.

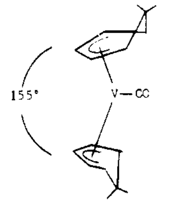
Although in general ligand substitution reactions of 17e organometallic complexes that take place by an associative reaction mechanism are rapid, we report here an example of a complex that undergoes substitution only by an associative pathway but reacts slowly. The compound is $(dmCh)_2VCO$(17e),[9] and its rate of CO exchange is compared with related compounds in Table I. The metal carbonyls in this table are represented by structures I,[10a] II,[10b,c] and III.[9] The more rigid structure and shorter M–C bond lengths of the pentadienyl complex II cause steric retardation of nucleophilic attack. Further, a dihedral angle of about 150° for I and III compared to 180° for II implies that I and III have a more sterically accessible binding site for nucleophilic attack (represented in Table I as + for steric, relative to − for II).



(I)[10a]



(II)[10b,c]



(III)[9]

The IR carbonyl stretching frequencies and EPR isotropic coupling constants are also informative (Table I). The greater electron-withdrawing ability of the dimethyl cyclohexadienyl ligand compared to cyclopentadienyl is reflected in the CO frequencies of 1912 and 1881 cm^{-1}, respectively. One might expect that the more positively charged vanadium in III would be more susceptible to nucleophilic attack than in I. However, the opposite is observed. The rate of substitution of III is 10^{-4} times that of I. This is believed to reflect the position of the unpaired electron. If this electron occupies a largely metal based singly occupied orbital, then a more positively charged vanadium will lead to reduced delocalization of this unpaired spin from the metal center. EPR data in Table I is consistent with this argument. It would appear that nucleophilic attack on a metal orbital containing an electron may be retarded relative to the same system with that electron largely delocalized onto the ligands. Thus, I is expected to have a more favorable electronic distribution of the unpaired electron for nucleophilic attack (represented in Table I as + for electronic, relative to − for II and III).

Compound II reacts almost exclusively by a dissociative pathway, in accord with associative retardation by both steric and electronic factors. Complex III reacts entirely by an associative pathway, although its electronic retardation is expected to be similar to II. This would suggest that the greater steric accessibility of III relative to II permits III to react by an associative pathway. However, electronic factors are important, and in the case of $(dmCh)_2VCO$ it gives us a rare example of a slow associative substitution reaction for a 17e metal carbonyl. The fastest to react is $(Cp)_2VCO$ which experiences less steric and less electronic retardation than do compounds II and III to associative substitution. Though a ring slippage mechanism[11] cannot be discounted, there is good evidence[12] that $(Cp)_2VCO$ undergoes

---

[1] (a) Brown, T. L. *Ann. N. Y. Acad. Sci.* **1980**, *333*, 80. (b) Herrinton, T. R.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 5700.

[2] (a) Fox, A.; Malito, J.; Poë, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1052. (b) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71. (c) Richmond, M. G.; Kochi, J. K. *Organometallics* **1987**, *6*, 254. (d) Arewgoda, M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 5633. (e) Bagchi, R. N.; Bond, A. M.; Colton, R.; Luscombe, D. L.; Moir, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 3352. (f) Miholva, D.; Vlcek, A. A. *J. Organomet. Chem.* **1985**, *279*, 317. (g) Donovan, B. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1988**, *110*, 2335. (h) Summers, D. P.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5238.

[3] Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Gedridge, R. W.; Newbound, T. D.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 4860.

[4] (a) Therien, M. J.; Ni, C. L.; Anson, F. C.; Osteryoung, J. G.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 4037. (b) Ellis, J. E.; Faltynak, R. A.; Rochfart, G. L.; Stevens, R. E.; Zank, G. A. *Inorg. Chem.* **1980**, *19*, 1082. (c) McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 1007.

[5] Cp = η^5-cyclopentadienyl, pd = η^5-pentadienyl, and dmCh = η^5-6,6-dimethylcyclohexadienyl.

[6] Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032.

[7] Freeman, J. W.; Wilson, D. R.; Ernst, R. D.; Smith, P. B.; Klendworth, D. D.; McDaniel, M. P. *J. Polym. Sci.* **1987**, *25*, 2063.

[8] Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

[9] Wolczanski, P. T.; DiMauro, P. T. *Organometallics* **1987**, *6*, 1947. X-ray structure of III is for the Ti compound, believed to be similar for the V system.

[10] (a) Gambarotta, S.; Floriani, C.; Chiaesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739. (b) Ernst, R. D. *Struct. Bonding (Berlin)* **1984**, *57*. (c) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56.

[11] (a) Shuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. (b) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

0002-7863/88/1510-6585$01.50/0

Figure 1. Energy/reaction coordinate diagram for an associative 18e and 17e ligand substitution reaction.

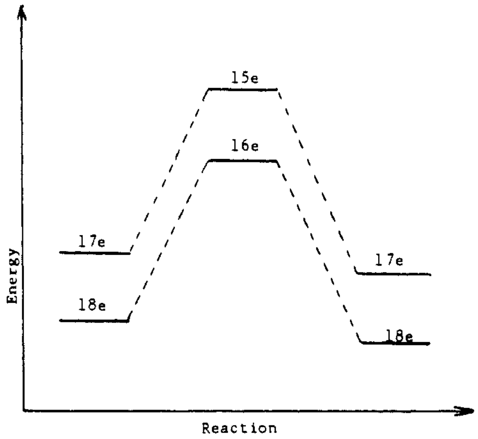


Figure 2. Energy/reaction coordinate diagram for a dissociative 18e and 17e ligand substitution reaction.

Table I. Associative Rates of CO Exchange and EPR Data for $(\eta^5\text{-L})_2VCO$ Complexes

complex	k_2,[a] $M^{-1}\ s^{-1}$	ν_{CO}, cm^{-1}	A_{iso}, G	ref	steric[b]	electronic[b]
I $(Cp)_2VCO$	ca. 800	1881	28.8	3	+	+
II $(pd)_2VCO$	0.0038[c]	1959	79.1	3	–	–
III $(dmCh)_2VCO$	0.0734	1912	71	9, this work	+	–

[a] At 60 °C. In decalin $[L_2MCO] = 5 \times 10^{-3}$ M for I and II, $[L_2MCO] = 1 \times 10^{-2}$ M for III. [b] Favorable for associative reaction represented +, unfavorable represented –. [c] Reacts mostly by dissociative pathway with $k_1 = 8.1 \times 10^{-6}\ s^{-1}$.

associative CO substitution without involving ring slippage. Detailed papers on each of these observations, along with other examples, will be reported later.

Acknowledgment. We thank Professors Richard D. Ernst and Peter T. Wolczanski and their students Jeffrey W. Freeman and Peter T. DiMauro, respectively, for samples of the compounds used in this study and for helpful discussions. We thank Professor William C. Trogler for a preprint of ref 12 prior to publication. Support from the National Science Foundation (CHE-8514366) is gratefully acknowledged.

Supplementary Material Available: A plot of the rate of reaction (k_{obsd}) versus concentration of CO which shows the reaction is exclusively associative (1 page). Ordering information is given on any current masthead page.

---

(12) Miller, G. A.; Therien, M. J.; Trogler, W. C., submitted for publication.

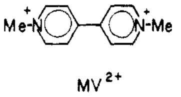
Direct Observation of Superoxide Electron Transfer with Viologens by Immobilization in Zeolite

K. B. Yoon and J. K. Kochi*

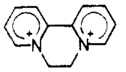
Department of Chemistry, University of Houston
University Park, Houston, Texas 77204

Received May 23, 1988
Revised Manuscript Received July 29, 1988

The presence of supercages and channels of various sizes in zeolites has provided the opportunity for shape-selective catalysis.[1] Furthermore such molecular pockets are potentially useful for the immobilization of reactive intermediates that are otherwise subject to rapid diffusive annihilation in solution.[2] It is important however to establish the viability of spectroscopic characterization for such trapped species in a solid matrix. As a test case, we chose the biologically relevant reduction of dioxygen by bipyridinium cation radicals (MV^+ and DQ^+) as produced by photosystem I in chloroplasts during herbicidal action.[3] Although it has been widely accepted that electron transfer to superoxide pertains,[4] i.e.,



MV^{2+}



DQ^{2+}

(1)

the experimental evidence is indirect,[4,5] owing to the transient character of superoxide in protic media.[6] As a result, little is known about even the reversibility of electron transfer in eq 1.

We find that MV^+ and DQ^+ can be efficiently incorporated into zeolite-Y. Thus when the solid was slurried with 10^{-5} M $MV^+PF_6^-$ under an inert argon atmosphere, the blue solution was bleached, and the color was transferred to the colorless zeolite-Y. Small amounts of $MV^+PF_6^-$ were successively added until the acetonitrile solvent remained slightly blue, even after prolonged stirring.[7] The total amount of $MV^+PF_6^-$ incorporated in the brilliant blue zeolite corresponded to roughly 20% occupancy of the supercages.[8] A bright green zeolite was obtained by similarly

---

(1) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974. Csicsery, S. M. *Zeolite Chemistry and Catalysis*; Rabo, J. A., Ed.; ACS Monograph 171, Washington, DC, 1976; p 680ff.

(2) Compare (a) Herron, N. *Inorg. Chem.* **1986**, *25*, 4714. (b) Howe, R. F.; Lunsford, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 5156. (c) Howe, R. F.; Lunsford, J. H. *J. Phys. Chem.* **1975**, *79*, 1836. (d) Schoonheydt, R. A.; Pelgrims, J. J. *J. Chem. Soc., Dalton Trans.* **1981**, 914. (e) Winscom, C. J.; Lubitz, W.; Diegruber, H.; Moseler, R. *Stud. Surf. Sci. Catal.* **1982**, *12*, 14.

(3) (a) Summers, L. A. *The Bipyridinium Herbicides*; Academic: New York, 1980. (b) Fedtke, C. *Biochemistry and Physiology of Herbicide Action*; Springer-Verlag: Berlin, 1982. (c) Rabinowitch, H. D.; Fridovich, I. *Photochem. Photobiol.* **1983**, *37*, 679. (d) See, also: Krall, J.; Bagley, A. C.; Mullenbach, G. T.; Hallewell, R. A.; Lynch, E. R. *J. Biol. Chem.* **1988**, *263*, 1910.

(4) (a) Harbour, J. R.; Bolton, J. R. *Biochem. Biophys. Res. Commun.* **1975**, *64*, 803. (b) Chia, L. S.; McRae, D. G.; Thompson, J. E. *Physiol. Plant.* **1982**, *56*, 492. (c) Bowyer, J. R.; Camilleri, P. *Biochim. Biophys. Acta* **1985**, *808*, 235. (d) Sinha, B. K.; Singh, Y.; Krishna, G. *Biochem. Biophys. Res. Commun.* **1986**, *135*, 583.

(5) (a) Epel, B. L.; Neumann, J. *Biochim. Biophys. Acta* **1973**, *325*, 520. (b) Youngman, R. J.; Dodge, A. D. *Z. Naturforsch.* **1979**, *34C*, 1032. (c) Elstner, E. F.; Henpel, A. *Z. Naturforsch.* **1974**, *29C*, 559.

(6) (a) Farrington, J. A.; Ebert, M.; Land, E. J.; Fletcher, K. *Biochim. Biophys. Acta* **1973**, *314*, 372. (b) Moreover the ESR spectrum of O_2^- is not observable in solution owing to its degenerate ground state. See: Kasai, P. H.; Bishop, R. J., Chapter 6 in ref 8b.

(7) To ensure completely anhydrous conditions, sodium zeolite-Y was initially dehydrated fully at 200 °C for 5 h at 10^{-5} Torr. After $PQ^{\cdot+}$ and $DQ^{\cdot+}$ were introduced via rigorously purified and anhydrous acetonitrile, the blue and green zeolites were further activated at 150 °C for 2 h at 10^{-5} Torr.

(8) See, however: (a) Rabo, J. A.; Kasai, P. H. *Prog. Solid State Chem.* **1975**, *9*, 1. (b) Rabo, J. A. *Zeolite Chemistry and Catalysis*; Rabo, J. A., Ed.; ACS Monograph 171; American Chemical Society, Washington, DC, 1976; Chapter 5.

0002-7863/88/1510-6586$01.50/0