

# Trends in Reactivity for Ligand-Exchange Reactions of Octahedral Metal Carbonyls

Gerard R. Dobson

Department of Chemistry, North Texas State University, Denton, Texas 76203

Received June 2, 1975

Octahedral metal carbonyls and derivatives offer an opportunity for fundamental mechanistic studies of complexes of a characteristic inorganic stereochemistry under very favorable experimental conditions. Moreover, these species are related to organometallic complexes exhibiting catalytic activity in important commercial processes such as polymerizations and hydroformylation. A clear understanding of factors influencing ligand-substitution processes in metal carbonyls thus can ultimately contribute to a knowledge of catalytic mechanisms.

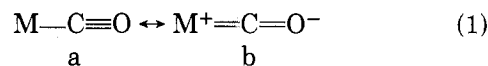
The most studied complexes, in which the metal is Cr, Mo, W, or Mn, are typically "inert", and therefore their substitution reactions commonly proceed at easily measurable rates at ambient and readily accessible higher reaction temperatures. The molecular nature of most such substrates facilitates study in nonpolar organic solvents, minimizing the effects of solvation on reactivity, and avoiding problems which arise in the study of ionic species. Color changes which often accompany such reactions and the presence of intense, infrared carbonyl stretching absorptions permit the convenient spectrophotometric determination of reaction rates. Detailed discussions of experimental procedures have been presented in several papers.<sup>1-3</sup>

Diverse derivatives of the parent carbonyls have been synthesized. Thus the steric and electronic properties of reaction substrates can be varied widely. Moreover, carbonyl stretching frequencies, and force constants derived from them, furnish useful probes of bonding in metal carbonyls and derivatives. Conditions thus are propitious to investigations of reactions of closely related series of octahedral complexes with the objective of correlating mechanism and reactivity with the steric and electronic nature of reactants and products.

This Account deals with trends in reactivity observed in thermal substitution reactions of the group 6B metal hexacarbonyls (metal = Cr, Mo, W), the pentacarbonyls of Mn(I) containing halide, pseudohalide, and related substituents, and their Lewis base (L) substitution products.

**Bonding in Octahedral Metal Carbonyls and Derivatives.** A discussion of substrate reactivity requires a brief consideration of bonding in these species. Bonding in the hexacarbonyls,  $M(\text{CO})_6$  ( $M = \text{Cr, Mo, W}$ ), involves dative  $\sigma$ -bond formation through overlap of a (slightly antibonding) orbital, essentially a lone pair on carbon,<sup>4</sup> with a vacant  $d^2sp^3$  hybrid orbital on the

metal, and  $\pi$  "backbonding" between filled metallic orbitals of  $t_{2g}$  symmetry and vacant  $\pi^*$  orbitals on CO (Figure 1). Thus it is expected that increased  $\sigma$  bonding of CO to the metal should lead to an increased C–O bond order, while increased  $\pi$  bonding of the metal to CO should result in a decreased C–O bond order. The changes in occupancy of the  $\pi^*$  orbitals on CO have been held to exert a dominant influence on carbonyl stretching frequencies and Cotton–Kraihanzel force constants derived from them.<sup>5</sup> This influence is exemplified by data in Table I. As the C–O bond order decreases with increased  $\pi^*$  orbital occupancy, carbonyl stretching frequencies ( $\nu(\text{CO})$ ) and force constants ( $F(\text{CO})$ ) will be expected to decrease. Lower  $\nu(\text{CO})$  and  $F(\text{CO})$  imply a greater contribution of (1b) to a resonance description of M–C–O bonding, and thus a higher M–C bond order is implied by lower  $\nu(\text{CO})$  and  $F(\text{CO})$ .<sup>6</sup>



In simple substitution products of the parent carbonyls, bonding is more complex. Lewis base substituents whose donor atoms are members of the second or later main groups, e.g., phosphines or sulfides, unlike those containing first-row donor atoms, such as amines, possess energetically accessible, vacant  $d_\pi$  orbitals which can also enter into  $\pi$  bonding with the transition metal. However, with few exceptions, ligands which replace CO in substitution products are relatively poor  $\pi$  acceptors, and thus the successive replacement of CO by L leads to progressively lower  $\nu(\text{CO})$  and  $F(\text{CO})$  as the carbonyls accept a greater and greater share of metallic  $d_\pi$  electron density in competition with those substituents (Table I).

Jones<sup>7</sup> and, later, Cotton<sup>5</sup> have discussed the anisotropy of  $\pi$  bonding in octahedral complexes. In simplest terms, the influence of a substituent on the extent of  $\pi$  bonding is expected to be about twice as great at a position trans to the substituent than at a cis position since L and the trans (axial) CO share two metallic  $d_\pi$  orbitals, while L and cis (equatorial) CO (Figure 2, for

(1) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586 (1965).

(2) M. N. Memering, A. Moradi-Araghi, and G. R. Dobson, *J. Coord. Chem.*, **2**, 271 (1973).

(3) G. R. Dobson and J. R. Paxson, *J. Chem. Educ.*, **49**, 67 (1972).

(4) L. H. Jones, *J. Mol. Spectrosc.*, **9**, 130 (1962).

(5) Calculations of Cotton–Kraihanzel force constants employ an energy-factored force field. The force constants are generally held to be a more direct indicator of bonding properties within a series of related complexes than the carbonyl stretching frequencies themselves: F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(6) It should be noted that there need be no necessary relationship between stretching frequencies or force constants and bond strengths or reactivities, although such relationships are often observed. See, e.g., F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, p 539.

(7) L. H. Jones in "Advances in the Chemistry of the Coordination Compounds", S. Kirschner, Ed., Macmillan, New York, N.Y., 1961, pp 398–411.

Gerard R. Dobson was born in Lynbrook, N.Y., and received a B.S. degree from Florida Southern College, and a Ph.D. in Inorganic Chemistry from Florida State University in 1964. He has served on the faculties of the University of Georgia, the University of South Dakota, and North Texas State University, where he is presently Professor of Chemistry. His research interests involve mechanistic and spectroscopic studies of metalloorganic complexes.

**Table I**  
**Carbonyl Stretching Frequencies and C-K Force Constants for Metal Carbonyls and Derivatives**

A. CO and M(CO) <sub>6</sub>		$\nu(\text{CO}), \text{cm}^{-1}$ <sup>a</sup>	
CO		2155	
Mn(CO) <sub>6</sub> <sup>+</sup>		2096 (T <sub>1u</sub> )	
Cr(CO) <sub>6</sub>		2000 (T <sub>1u</sub> )	
V(CO) <sub>6</sub> <sup>-</sup>		1859 (T <sub>1u</sub> )	
B. LM <sub>o</sub> (CO) <sub>5</sub> , L =		$F(\text{CO}, \text{ax})$ mdyn/Å <sup>b</sup>	$F(\text{CO}, \text{equat})$ mdyn/Å <sup>b</sup>
CO			16.52
P(OPh) <sub>3</sub>		15.97	16.14
Ph <sub>3</sub>		15.57	15.99
C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>		14.65	15.83
C. Extent of substitution			
Mo(CO) <sub>6</sub>			16.52
(PPh <sub>3</sub> )Mo(CO) <sub>5</sub>		15.57	15.99
<i>cis</i> -(diphos)Mo(CO) <sub>4</sub> <sup>c</sup>		14.87 <sup>d</sup>	15.47
<i>cis</i> -(PPh <sub>3</sub> ) <sub>3</sub> Mo(CO) <sub>3</sub>			14.03 <sup>e</sup>

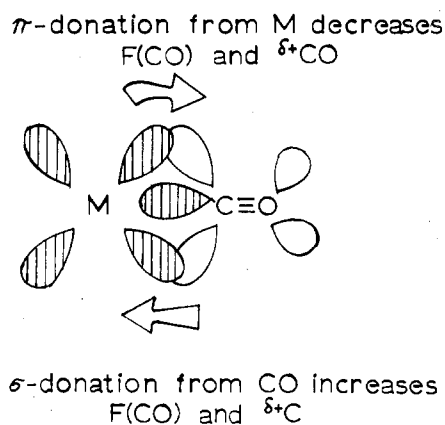
<sup>a</sup> E. W. Abel and F. G. A. Stone, *Q. Rev., Chem. Soc.*, **23**, 26 (1969). <sup>b</sup> R. A. Brown, Ph.D. Thesis, North Texas State University, 1971. <sup>c</sup> diphos = 1,2-bis(diphenylphosphino)ethane. <sup>d</sup> Reference 16. <sup>e</sup> Calculated from frequencies given in R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

LM(CO)<sub>5</sub> complex) share but one. Thus, on the basis of  $\pi$  bonding, it is expected that  $F(\text{CO}, \text{axial}) < F(\text{CO}, \text{equatorial})$ .<sup>5</sup>

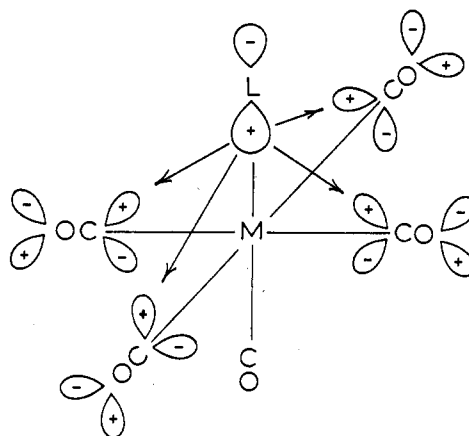
The recent theoretical work of Fenske et al.<sup>8,9</sup> has indicated a third bonding mechanism, "direct donation"<sup>8</sup> (Figure 2), to be operative in some derivatives of octahedral metal carbonyls. This mechanism involves a "through-space" interaction between the p<sub>z</sub> "lone pair" orbital on the substituent and the proper linear combination of  $\pi^*$  orbitals of the equatorial carbonyls.

MacDiarmid, Corey, et al. had independently proposed an axial substituent-equatorial carbonyl interaction for trigonal-bipyramidal cobalt carbonyl complexes and for substituted octahedral complexes of Mn, XMn(CO)<sub>5</sub> (X = formally one-electron-donating substituent).<sup>10</sup> It was noted in support of such an interaction that the equatorial carbonyls were displaced toward X when on the basis of the relative steric properties of CO(axial) and X the opposite effect was to be expected. Structural evidence for a wide variety of XMn(CO)<sub>5</sub> and related complexes, which indicates that the average X-Mn-C(equatorial) bond angle is significantly less than 90° and is the result of an intramolecular electronic interaction, has been summarized by Clegg and Wheatley.<sup>11</sup> A molecular orbital calculation for Mn<sub>2</sub>(CO)<sub>10</sub> has also supported the existence of such an interaction, which was viewed as a very important stabilizing factor for what had been termed "unsupported" metal-metal bonds.<sup>12</sup>

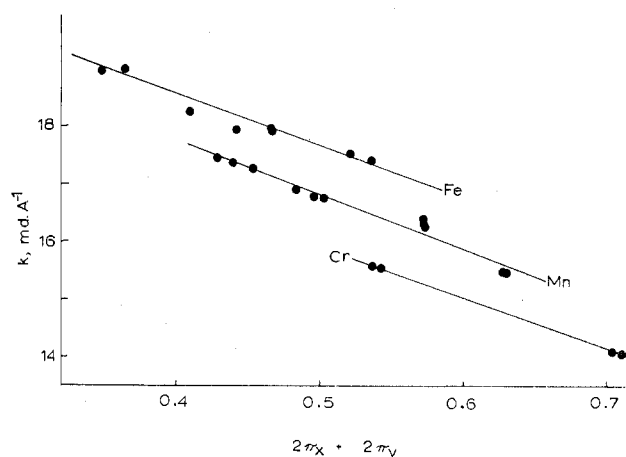
The relative contributions of the three bonding mechanisms to carbonyl stretching force constants have been illustrated by Hall and Fenske,<sup>9</sup> who have obtained an excellent linear plot of weighted Mulliken "orbital occupancies" of the lone-pair orbitals on C (5 $\sigma$ ) and the



**Figure 1.**  $\sigma$ - and  $\pi$ -bonding mechanisms between CO and a transition metal.<sup>37</sup>



**Figure 2.** The Fenske "direct donation" bonding mechanism.



**Figure 3.** C-K  $F(\text{CO})$  vs. Fenske  $\pi$ -orbital occupancies.

$\pi^*$  orbitals on CO ( $2\pi_x$  and  $2\pi_y$ ), as determined through approximate, parameter-free molecular orbital calculations for series of halide carbonyl derivatives of Cr, Mn, and Fe of varying degrees of substitution. The elimination of the  $5\sigma$  orbital occupancies from that plot, so that only the occupancies of the  $\pi^*$  orbitals are considered, affords the series of plots shown in Figure 3 in which  $F(\text{CO})$  for complexes of each metal are grouped together. These linear, parallel plots suggest that while influences of changes in CO-to-metal  $\sigma$  bonding on  $F(\text{CO})$  vary from metal to metal, the occupancies of the  $\pi^*$  orbitals as determined through consideration of  $\pi$  bonding and direct donation alone satisfactorily account for  $F(\text{CO})$  for the complexes of a given metal.<sup>13</sup> Carbonyl stretching data also suggest  $\sigma$ -bonding influences

(8) R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, **9**, 1053 (1970).

(9) M. E. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 1619 (1972).

(10) A. D. Berry, E. R. Corey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. H. Wayland, *J. Am. Chem. Soc.*, **92**, 1940 (1970).

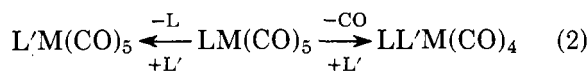
(11) W. Clegg and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 424 (1974).

(12) D. A. Brown, W. J. Chambers, N. J. Fitzpatrick, and R. M. Rawlinson, *J. Chem. Soc. A*, 720 (1971).

on  $\nu(\text{CO})$  and  $F(\text{CO})$  to be minimal within a series of derivatives of the same transition metal.<sup>14</sup> The plots exhibited in Figure 3 are also reasonable in view of the slightly antibonding nature of the lone-pair orbitals on carbon in that the  $F(\text{CO})$  increase in the order  $\text{Cr} < \text{Mn} < \text{Fe}$ , as the greater effective nuclear charge on  $\text{M}$  increases the extent of  $\text{OC} \rightarrow \text{M}$   $\sigma$  bonding.

The extent of the direct donation effect is expected to increase with increasing covalent radius and decreasing effective nuclear charge of the donor atom in the substituent, and with decreasing atomic radii of the metal atoms ( $\text{Mn} < \text{Cr} < \text{Mo} \approx \text{W}$ ).<sup>9</sup> Substantial corroborative evidence (carbonyl stretching band intensities,<sup>15</sup> carbonyl stretching,<sup>16,17</sup> metal-carbon stretching,<sup>14,17</sup> and mass spectral<sup>18</sup> data) has been cited in support of an  $\text{X}-\text{CO}$  (equatorial) interaction, and equations have been developed which have provided parameters which reflect the relative contributions of  $\pi$  bonding and direct donation to  $F(\text{CO})$  in complexes other than the metal carbonyl halides.<sup>14,16,17</sup>

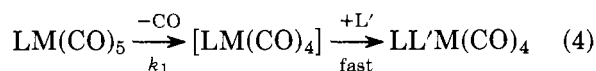
**Ligand Substitution Processes.** "Simple" substitution reactions of octahedral metal carbonyls and derivatives involve replacement of a carbonyl or another ligand by a nucleophile, for example



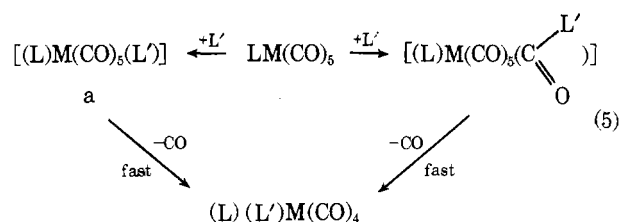
These reactions may usually be encompassed within a two-term rate law:

$$-\text{d}[\text{LM}(\text{CO})_5]/\text{d}t = k_1[\text{LM}(\text{CO})_5]_a + k_2[\text{LM}(\text{CO})_5][\text{L}']_b \quad (3)$$

The ligand-independent path governed by  $k_1$  (3a) is consistent with rate-determining fission of a metal-carbon bond to form a five-coordinate intermediate, which then undergoes attack by the nucleophile to yield the product(s), e.g.



For reactions of specific complexes in nonpolar solvents in which it is highly probable that this mechanism is applicable, arguments have been presented which indicate that the process approaches  $\text{SN1}$  (limiting),<sup>19</sup>  $\text{D}$ ,<sup>20</sup> behavior.<sup>21</sup> In such cases, enthalpies of activation should be closely related to  $\text{M}-\text{C}$  bond dissociation energies. The ligand-dependent path governed by  $k_2$  (3b) could involve interaction by  $\text{L}'$  either at the metal atom or at a carbonyl carbon:



For derivatives containing a bidentate chelating ligand, a ring-opening mechanism can also lead to a ligand-dependent term in the observed rate law.

**The Ligand-Independent Path.** In general, the rates of substitution reactions of the group 6B hexacarbonyls via a dissociative path vary as  $\text{Mo} \sim \text{Cr} \ll \text{W}$ . A possible explanation for the relative inertness of  $\text{W}(\text{CO})_6$  and its substitution products to reaction via rate-determining dissociation of  $\text{CO}$  lies in the results of Jones and co-workers, who have reported normal coordinate analyses for all three hexacarbonyls, in which a general quadratic force field was employed.<sup>22</sup> The carbonyl and metal-carbon stretching force constants obtained indicate that the  $\text{C}-\text{W}$   $\sigma$  bonds are appreciably stronger than  $\text{C}-\text{Mo}$  and  $\text{C}-\text{Cr}$   $\sigma$  bonds.

Early qualitative and quantitative rate observations led Angelici and Graham<sup>1</sup> to propose a rule of reactivity which has been found to be well obeyed within series of derivatives of the same degree of substitution and stereochemistry: Pearson "hard"<sup>23</sup> bases labilize carbonyls relative to "soft" bases. As Angelici has pointed out, however,  $\pi$ -bonding arguments alone have proven to be exceedingly unreliable in the prediction of reaction rates via dissociation of  $\text{CO}$  within such series.<sup>24</sup> The basis of Angelici's rule has been discussed in terms of both transition-state and ground-state bonding arguments. It has been noted by Atwood and Brown<sup>25</sup> that dissociative reactions of the hexacarbonyls proceed at rates slower than do those of substitution products,  $\text{LM}(\text{CO})_5$ , which presumably<sup>26</sup> react via dissociation of a *cis* (equatorial) carbonyl. This observation has been rationalized in terms of a thermodynamic "site preference" for a substituent which is a poorer  $\pi$  acceptor than  $\text{CO}$  to occupy a position in the basal plane of a 16-valence-electron, five-coordinate square-pyramidal intermediate formed upon  $\text{CO}$  loss.<sup>27,28</sup> Since the transi-

(22) L. H. Jones, R. G. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).

(23) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(24) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

(25) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, submitted for publication; T. L. Brown, personal communication.

(26) A recent isotopic exchange study for  $\text{Mn}(\text{CO})_5\text{Br}$  has revealed that initial  $\text{Mn}-\text{C}$  bond breaking occurs almost exclusively at the equatorial positions: J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 3380 (1975).

(27) Substantial evidence has been presented that 16-valence-electron, pentacoordinate metal carbonyls and related complexes exhibit square-pyramidal, rather than trigonal-bipyramidal geometry, both in solution and in inert matrices. See, e.g., J. D. Black and P. S. Braterman, *J. Organometal. Chem.*, **63**, C19 (1973); J. D. Black and P. S. Braterman, *J. Am. Chem. Soc.*, **97**, 2908 (1975); J. K. Burdett, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 157 (1975); D. J. Darensbourg and H. H. Nelson, III, *J. Am. Chem. Soc.*, **96**, 6511 (1974); P. R. Hoffman and K. G. Caulton, *ibid.*, **97**, 4221 (1975); J. K. Burdett, *Inorg. Chem.*, **14**, 375 (1975); R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, **97**, 4791 (1975); J. K. Burdett, M. A. Graham, R. N. Perutz, M. Poliakoff, A. J. Rest, J. J. Turner, and R. F. Turner, *ibid.*, **97**, 4805 (1975); R. N. Perutz and J. J. Turner, *Inorg. Chem.*, **14**, 263 (1975).

(28) Evidence has also recently been presented which suggests that the intermediate  $[\text{Ph}_3\text{PW}(\text{CO})_4]$ , formed through dissociation of an amine ligand from *cis*-(amine) $(\text{PPH}_3)\text{W}(\text{CO})_4$  species, is fluxional, and that the species in which  $\text{PPH}_3$  is in the equatorial plane rather than in the axial position of the square pyramid is thermodynamically the more stable, in agreement with the Atwood-Brown proposal: D. J. Darensbourg, A. Moradi-Araghi, and G. R. Dobson, *J. Organometal. Chem.*, in press.

(13) However, the apparent lack of a significant influence on  $F(\text{CO})$  of changes in  $\text{CO}$ -to-metal  $\sigma$  bonding in octahedral derivatives of a given metal in no way implies that  $\sigma$  bonding effects do not influence reactivity in such complexes.

(14) R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta*, **6**, 65 (1972).

(15) G. Keeling, S. F. A. Kettle, and I. Paul, *J. Chem. Soc. A*, 3143 (1971).

(16) R. T. Jernigan, R. A. Brown, and G. R. Dobson, *J. Coord. Chem.*, **2**, 47 (1972).

(17) G. R. Dobson, *Ann. N.Y. Acad. Sci.*, **239**, 237 (1974).

(18) F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **92**, 2324 (1970).

(19) Basolo and Pearson, ref 6, p 128.

(20) C. H. Langford and H. B. Gray, "Ligand Substitution Processes", W. A. Benjamin, New York, N.Y., 1965, Chapter 1. The Ingold terminology for the classification of reactions as to type will be employed in this discussion. The Ingold classifications of  $\text{SN1}$  (limiting),  $\text{SN1}$ ,  $\text{SN2}$ , and  $\text{SN2}$  (limiting) correspond roughly to the Langford-Gray classifications  $\text{D}$ ,  $\text{I}_d$ ,  $\text{I}_a$ , and  $\text{A}$ , respectively.

(21) W. D. Covey and T. L. Brown, *Inorg. Chem.*, **12**, 2820 (1973).

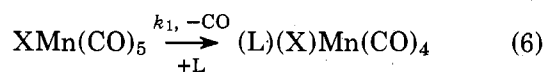
Table II  
Infrared and Activation Data for  $\text{XMn}(\text{CO})_5$  Substrates Which React with L via a Dissociative Path

$\text{XMn}(\text{CO})_5$	$F(\text{CO})$ , mdyn/Å		$\nu(\text{MC}, E)$ , $\text{cm}^{-1}$	$\Delta H^*$ , kcal/mol	Stereochem. of product (L = $\text{PPh}_3$ )
	Axial	Equatorial			
Cl	16.22	17.50	418 <sup>b</sup>	26.9 ± 0.4 <sup>d</sup>	Cis
Br	16.26	17.41	422 <sup>b</sup>	29.2 ± 0.4 <sup>d</sup>	Cis
I	16.30	17.28	427 <sup>b</sup>	31.6 ± 0.4 <sup>d</sup>	Cis
$\text{Ph}_3\text{Ge}$	16.33	16.70	478 <sup>c</sup>	39.4 ± 1.4 <sup>e</sup>	Trans
$\text{Ph}_3\text{Sn}$	16.34	16.64	477 <sup>c</sup>	41.4 ± 1.3 <sup>e</sup>	Trans

<sup>a</sup> W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968). <sup>b</sup> Frequencies: I. S. Butler and H. K. Spendjian, *Can. J. Chem.*, **47**, 4117 (1969); assignments: D. K. Ottesen, H. B. Gray, L. H. Jones, and M. Goldblatt, *Inorg. Chem.*, **12**, 1051 (1973). <sup>c</sup> R. Ugo, S. Cenini, and F. Bonati, *Inorg. Chim. Acta*, **1**, 451 (1967). <sup>d</sup> R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962). <sup>e</sup> E. P. Ross and G. R. Dobson, *Inorg. Chim. Acta*, **5**, 199 (1971).

tion state arising through carbonyl dissociation probably closely resembles this intermediate,<sup>21</sup> the path leading to dissociation of an equatorial carbonyl will be lowered in energy by poorly  $\pi$ -accepting ligands, i.e., "hard" bases. The site preference model thus is consistent with Angelici's rule of reactivity.

However, there is also evidence that substrate ground-state bonding properties are consistent with the observed rates of reaction within a series of substitution products.<sup>17</sup> Table II presents data for derivatives which exhibit rate behavior consistent with Angelici's rule and for which activation parameters for the dissociative path, for the reaction



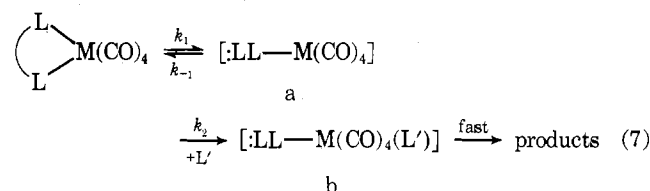
have been determined. From the values of  $F(\text{CO}, \text{axial})$  it can be inferred that the  $\pi$ -bonding abilities of the substituents differ rather little despite the observed substantial differences in reactivity. However, force constants for the equatorial carbonyls ( $F(\text{CO}, \text{equatorial})$ ) differ appreciably, and in a manner consistent with the expected changes in direct donation by X. Their variations, and those of  $\nu(\text{MC})$  of  $E$  symmetry, predominantly the antisymmetric stretch of the equatorial carbonyls, are consistent with those expected on the basis of eq 1 and with the observed enthalpies of activation ( $\Delta H_1^*$ ) for Mn-C bond breaking. This observation also suggests that it is an equatorial metal-carbon bond which ruptures in the rate-determining step. The ultimate stereochemistry of the reaction product (Table II) thus does not necessarily reveal the site of metal-carbon bond breaking.<sup>26,28</sup> While axially substituted products are observed for reactions of  $\text{Ph}_3\text{E}-\text{Mn}(\text{CO})_5$  with triphenylphosphine, the ultimate product stereochemistry has been attributed to isomerization of the five-coordinate intermediate after initial equatorial M-C bond fission.<sup>29</sup>

The data summarized in Table II offer a tentative explanation of Angelici's "rule of reactivity"<sup>1</sup> in terms of substrate ground-state bonding properties in that  $\pi$ -bonding effects greatly strengthen the axial metal-carbon bond, dictating equatorial CO dissociation. At the equatorial positions, substantial direct donation effects are expected for substituents bonding through "soft" donor atoms. These effects should strengthen the equatorial M-C bonds, decreasing the probability of CO dissociation relative to that for derivatives of "hard" bases; in the latter, "direct donation" effects are expected to be weaker.

(29) E. P. Ross, R. T. Jernigan, and G. R. Dobson, *J. Inorg. Nucl. Chem.*, **33**, 3375 (1971).

The Mn data (Table II) were selected as a favorable, illustrative example. In these complexes the short Mn-C bond length enhances the direct donation interaction,<sup>10</sup> and their relatively high carbonyl stretching frequencies indicate more limited  $\pi$  bonding of the metal to CO. For other metals, the relative influences of  $\sigma$ ,  $\pi$ , and direct donation, as well as transition-state effects, are expected to differ. Thus, it has been suggested that, in  $\text{LW}(\text{CO})_5$  complexes,  $\sigma$ -bonding effects, while not appreciably influencing  $\nu(\text{CO})$ , may also exert significant influences on reactivity via carbonyl dissociation.<sup>14</sup> The general trends in reactivity observed for other systems are, however, also consistent with an important direct donation influence as well. It is probable that both ground-state and transition-state influences are important in reactivity via the dissociative path.

**The Ring-Opening Mechanism.** A ligand-dependent path (3b) is observed in many reactions of octahedral metal carbonyls and derivatives. While this path may be associative, involving rate-determining interaction of substrate and ligand, such rate behavior is often best attributed to a ring-opening mechanism in substrates which contain bidentate chelate rings. The applicable mechanism is



Assuming a steady-state concentration of intermediate (eq 7a), this mechanism yields the rate law

$$-d[(\text{L}_2)\text{M}(\text{CO})_4]/dt = k_1 k_2 [(\text{L}_2)\text{M}(\text{CO})_4] \times [\text{L}'] / (k_{-1} + k_2 [\text{L}']) \quad (8)$$

Often, the high "local concentration"<sup>24</sup> of the free end of the bidentate ligand in (7a) has dictated that  $k_{-1} \gg k_2 [\text{L}']$ . In this limiting case, eq 8 becomes

$$-d[(\text{L}_2)\text{M}(\text{CO})_4]/dt = k_1 k_2 / k_{-1} [(\text{L}_2)\text{M}(\text{CO})_4] [\text{L}'] \quad (9)$$

a rate law indistinguishable from (3b). However, the two mechanisms, ring-opening and rate-determining attack by  $\text{L}'$ , have been distinguished on the basis of entropies of activation (more positive for the ring-opening mechanism).<sup>30</sup> In a number of instances, nonlimiting rate behavior ( $k_{-1} \sim k_2 [\text{L}']$ , eq 8) has been observed.<sup>31</sup>

(30) G. C. Faber and G. R. Dobson, *Inorg. Chem.*, **7**, 584 (1968).

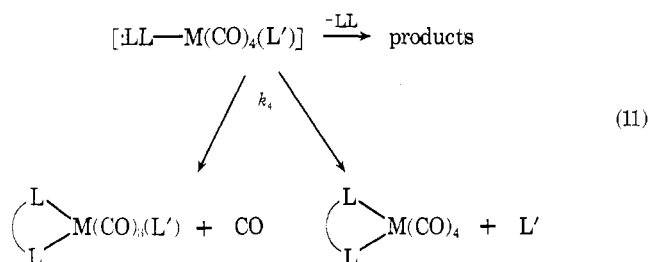
(31) See, e.g., G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, **4**, 87 (1970), and references cited therein.

In these cases, the expression

$$1/k_{\text{obsd}} = 1/k_1 + k_{-1}/(k_1 k_2 [L']) \quad (10)$$

can be obtained employing the pseudo-first-order rate constant,  $k_{\text{obsd}}$  (large excess of  $L'$ ). Thus, "reciprocal plots" of  $1/k_{\text{obsd}}$  vs.  $1/[L']$  are expected to be linear. Such linear plots have been observed for many systems, and support for the ring-opening mechanism has also come from studies in which reaction intermediates such as (7a) have been "trapped"<sup>32</sup> and in which intermediates such as (7b) have been isolated and characterized.<sup>33</sup>

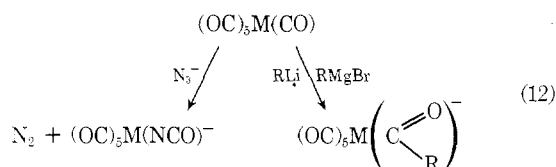
The extensive study of systems containing bidentate chelating ligands has revealed the ring-opening mechanism to be common, particularly for bidentate ligands bonding through nitrogen and sulfur donor atoms and which contain flexible chelate ring backbones. In certain instances, rate data and the identity of the observed reaction products support ring reclosure in intermediates such as in eq 7b, (governed by  $k_4$ ), followed by loss of  $L'$  or CO, to afford the substrate or a product containing the chelating species.<sup>30,34</sup>



Thus, failure to observe loss of the bidentate chelating ligand during the course of the reaction need not rule out the operation of the ring-opening mechanism.

**The "Associative" Path.** Since rate behavior exhibiting a dependence on the concentration of the incoming ligand may be attributable to a ring-opening mechanism for (chelate) $\text{M(CO)}_4$  complexes, reactions of the hexacarbonyls ( $M = \text{Cr, Mo, W}$ ) and their monosubstituted derivatives ( $\text{LM(CO)}_5$ ) will be examined to illustrate "associative" rate behavior.

Available evidence supports two discrete sites of bimolecular interaction in octahedral metal carbonyls and derivatives, at a carbonyl carbon and at the metal atom. Strong nucleophiles such as carbanions derived from organolithium<sup>35</sup> or Grignard<sup>36</sup> reagents and the azide ion<sup>37</sup> interact at a carbonyl carbon; the carbonyl is transformed in process 12:



In contrast, phosphines, phosphites, and related nucleophiles have been found to enter into "simple" ligand-substitution processes (eq 2). The absence of carbonylation or rearrangement products (eq 12) does

(32) W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, **13**, 627 (1974).

(33) L. D. Schultz and G. R. Dobson, *J. Coord. Chem.*, in press; A. Moradi-Araghi and G. R. Dobson, unpublished results.

(34) B. J. McKerley, G. C. Faber, and G. R. Dobson, *Inorg. Chem.*, **14**, 2275 (1975).

(35) G. R. Dobson and J. R. Paxson, *J. Am. Chem. Soc.*, **95**, 5925 (1973).

(36) M. Y. Darensbourg, H. L. Conder, D. J. Darensbourg, and C. Hasday, *J. Am. Chem. Soc.*, **95**, 5919 (1973).

Table III

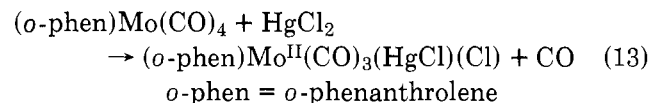
Enthalpies of Activation (Associative Path) for Reactions of  $\text{M(CO)}_6$  ( $M = \text{Cr, Mo, W}$ ) with Tri(*n*-butyl)phosphine and Tetraethylammonium Azide

M	$\Delta H^*$ , kcal/mol		Difference
	$\text{P}(n\text{-C}_4\text{H}_9)_3^a$	$(\text{C}_2\text{H}_5)_4\text{NN}_3^b$	
Cr	$25.5 \pm 2.9$	$18.2 \pm 0.6$	$7.3 \pm 3.5$
Mo	$21.7 \pm 1.3$	$15.3 \pm 0.8$	$6.4 \pm 2.1$
W	$29.2 \pm 1.6$	$12.8 \pm 1.0$	$16.4 \pm 2.6$

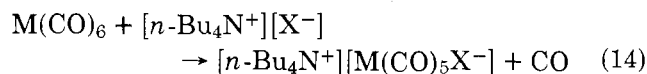
<sup>a</sup> Reference 38. <sup>b</sup> Reference 37.

not rule out attack at carbon in these ligand-dependent reactions, as is indicated in eq 5. However, different patterns of reactivity as a function of the identity of the metal atom suggest attack at the metal atom in these reactions since reactions proceeding via a single mechanism should exhibit very similar rate behavior as a function of  $M$ . This point is illustrated in Table III which presents activation data for reactions of  $\text{M(CO)}_6$  ( $M = \text{Cr, Mo, W}$ ) with tri(*n*-butyl)phosphine<sup>38</sup> and the azide ion.<sup>37</sup> Enthalpies of activation parallel one another for Cr and Mo but differ greatly for W. The divergent enthalpies of activation observed for reactions of  $\text{W(CO)}_6$  are very suggestive of attack at the metal by tri(*n*-butyl)phosphine since the stronger coordination of CO to  $\text{W}^{22}$  is expected to remove electron density from the carbonyl carbon and to transfer it to the metal, inhibiting nucleophilic attack at the metal and facilitating attack at the carbonyl carbon.

The distinguishing difference in the electronic nature of nucleophiles such as  $\text{R}^-$  and  $\text{N}_3^-$  and phosphines and phosphites is the ability of the latter to enter into appreciable  $d_\pi$ - $d_\pi$  bonding with the metal as the consequence of the availability of energetically accessible, vacant  $d_\pi$  orbitals. Indeed, it is well-established that strongly electrophilic reagents, halogens and pseudo-halogens, such as  $\text{HgCl}_2$ ,<sup>39</sup> "oxidize" metal carbonyls and derivatives, e.g.,



The initial interaction almost certainly involves  $\pi$  bonding. It may be speculated that the presence of vacant orbitals of  $\pi$  symmetry in phosphines, phosphites, and ligands with similar bonding properties may assist in "directing" attack to the metal atom rather than to a carbonyl carbon. Such an interaction would envision appreciable stabilization of the transition state through  $\pi$  bonding. Interestingly, the reactions of  $\text{M(CO)}_6$  with tetra(*n*-butyl)ammonium halides (eq 14) have been suggested to proceed via attack at either reaction site, at the metal atom for Mo and W and at a carbonyl carbon for the smaller chromium.<sup>40</sup>



$M = \text{Cr, Mo, W}; X = \text{Cl, Br, I}$

(37) H. Werner, W. Beck, and H. Engelmann, *Inorg. Chim. Acta*, **3**, 331 (1969).

(38) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 2082 (1967).

(39) R. T. Jernigan and G. R. Dobson, *Inorg. Chem.*, **11**, 81 (1972).

(40) J. E. Pardue, M. N. Memering, and G. R. Dobson, *J. Organometal. Chem.*, **71**, 407 (1974).

Table IV  
Rates of Reaction of Group 6B Metal Carbonyl Substrates (S) with Lewis Bases (L) via Associative and Dissociative Paths

S	L	T, °C	10 <sup>4</sup> k <sub>1</sub> , sec <sup>-1</sup>	10 <sup>4</sup> k <sub>2</sub> , M <sup>-1</sup> sec <sup>-1</sup>	F(CO), mdyn/Å	
					Axial	Equatorial
Cr(CO) <sub>6</sub> <sup>a</sup>	PPh <sub>3</sub>	130.7	1.38	0.450		16.49 <sup>f</sup>
W(CO) <sub>6</sub> <sup>a</sup>	PPh <sub>3</sub>	165.7	1.15	0.888		16.41 <sup>f</sup>
Mo(CO) <sub>6</sub> <sup>a</sup>	PPh <sub>3</sub>	112.0	2.13	1.77		16.52 <sup>f</sup>
Mo(CO) <sub>6</sub> <sup>a</sup>	P- <i>n</i> -Bu <sub>3</sub>	112.0	2.13	20.5		16.52 <sup>f</sup>
Mo(CO) <sub>6</sub> <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub>	112.0	2.44	4.4		16.52 <sup>f</sup>
Mo(CO) <sub>6</sub> <sup>c</sup>	[ <i>n</i> -Bu <sub>4</sub> N <sup>+</sup> ][Br <sup>-</sup> ]	55.0		32.4		16.52 <sup>f</sup>
Mo(CO) <sub>5</sub> (py) <sup>d</sup>	P(OCH <sub>2</sub> ) <sub>3</sub> CCH <sub>3</sub>	47.9	9.3	~4.8	14.56 <sup>g</sup>	15.94
[Mo(CO) <sub>5</sub> Br] <sup>-e</sup>	PPh <sub>3</sub>	19.6	1.34	4.1	14.39 <sup>g</sup>	15.53
[Mo(CO) <sub>5</sub> I] <sup>-e</sup>	PPh <sub>3</sub>	29.8	1.13	1.8	14.12 <sup>g</sup>	15.64
[Mo(CO) <sub>5</sub> I] <sup>-e</sup>	P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> F) <sub>3</sub>	29.8	1.13	2.8	14.12 <sup>g</sup>	15.64
[Mo(CO) <sub>5</sub> I] <sup>-e</sup>	P( <i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl) <sub>3</sub>	29.8	1.13	3.6	14.12 <sup>g</sup>	15.64

<sup>a</sup> Reference 38; decalin solvent. <sup>b</sup> J. E. Pardue and G. R. Dobson, *Inorg. Chim. Acta*, submitted for publication; decalin solvent. <sup>c</sup> Reference 40; chlorobenzene solvent. <sup>d</sup> J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, **87**, 5590 (1965); 1,2-dichloroethane solvent. <sup>e</sup> Reference 43; diglyme solvent. <sup>f</sup> Taken from G. R. Dobson, I. W. Stolz, and R. K. Shelime, *Adv. Inorg. Chem. Radiochem.*, **8**, 1 (1966). <sup>g</sup> Calculated from  $\nu(\text{CO})$  given in E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963); KBr pellet.

**"Attack" at the Metal Atom.** The possibility that a bona fide bimolecular path involving attack at the metal could be accessible for reactions of octahedral metal carbonyls requires some comment. A dissociative path in which there is a predominance of bond breaking in the transition state is expected to be more favored than would a path involving the formation of a sterically crowded seven-coordinate activated complex such as in eq 5a. With few exceptions, "typical" octahedral transition-metal complexes have been found to react by paths which involve predominant metal-ligand bond breaking.<sup>41</sup> Moreover, the metal atoms in octahedral metal carbonyls and derivatives might be considered to be even less likely candidates for nucleophilic attack since they bear only slightly positive charges,<sup>42</sup> and their filled metallic t<sub>2g</sub> orbitals are directed along the probable paths of ligand attack.

Conversely, these considerations should render the metal atoms susceptible to attack by  $\pi$  electrophiles (ligands which possess vacant orbitals which can accept metallic d <sub>$\pi$</sub>  electron density). Moreover, seven-coordinate metal carbonyl species such as in eq 13a are known, particularly for the larger Mo and W atoms.

Data for the associative path (Table IV) are not strictly comparable in the absence of activation parameters and in view of the different solvents and nucleophiles employed. However, they do clearly indicate a trend toward greater reactivity via the associative path for substrates with lower carbonyl stretching force constants, i.e., for those in which the metal atoms bear a greater d <sub>$\pi$</sub>  electron density.

Moreover, the influence of  $\pi$  bonding on reactivity is further suggested for reactions of Mo(CO)<sub>5</sub>I<sup>-</sup> for which  $\nu(\text{CO})$  indicate appreciable  $\pi$ -electron density at the metal, with the ligands P(*p*-C<sub>6</sub>H<sub>4</sub>X)<sub>3</sub> (X = H, F, Cl), in that rates for the bimolecular path increase H < F < Cl, the order of increasing Hammett  $\sigma_{\text{para}}$  for those substituents.<sup>43</sup> Thus, the rates of reaction increase with increasing electron withdrawal by X in the "nucleophile". It should be noted further that in one case where

the volume of activation ( $\Delta v^*$ ) for a reaction proceeding predominantly via a second-order rate law, that of tri(*n*-butyl)phosphine with W(CO)<sub>6</sub> in cyclohexane, has been reported, its value suggests more bond making than bond breaking in the transition state.<sup>44</sup>

However, a striking feature of the reactivity of metal carbonyl substrates with Lewis bases is that their reactions proceed through concurrent ligand-dependent and ligand-independent reaction paths over a wide range of substrate reactivities (Table IV). This observation suggests the same factors influencing reactivity via the dissociative mechanism also to be of importance in associative reactivity as well. On this basis, it is reasonable to presume that appreciable bond breaking occurs in the transition state, as has been suggested by Covey and Brown<sup>21</sup> based upon comparisons of enthalpies of activation for the dissociative and associative paths.

The present evidence thus is equivocal with respect to the precise nature of the interaction in the transition state but does hint that the process may be a concerted one which involves both bond making and bond breaking in the transition state and for which both transition-state  $\pi$ -stabilization and "site preference" effects<sup>25</sup> and ground-state bonding energies may exert important influences upon reactivity.

**Conclusions and Future Prospects.** Data thus far accumulated have provided tentative explanations for observed trends in reactivity for ligand-exchange reactions of octahedral metal carbonyls. While rate data presently available for such reactions are not as extensive as might be desired, the understanding of reactivity thus far developed should spur the orderly acquisition of additional data, particularly activation data, for substrates in which the substituents exhibit widely varying bonding properties, and for a wide range of nucleophiles. Detailed studies in which volumes of activation are determined for "associative" processes could shed further light on the relative extent of bond making and bond breaking in the transition state.

It will be important to establish sites of reactivity in substrates and the electronic and stereochemical nature of reaction intermediates more firmly. The recently

(41) Basolo and Pearson in ref 6, pp 234-238.

(42) See, e.g., (a) R. L. Barinskii and C. G. Nadzhakov, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **24**, 407 (1960), and (b) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968).

(43) A. D. Allen and P. F. Barrett, *Can. J. Chem.*, **46**, 1655 (1968).

(44) K. R. Brower and T. S. Chen, *Inorg. Chem.*, **12**, 2198 (1973).

synthesized, stereospecifically labeled metal carbonyl substitution products of the types *cis*-(L)<sup>13</sup>CO-M(CO)<sub>4</sub><sup>45,46</sup> and *cis*-(L<sub>2</sub>)(<sup>13</sup>CO)M(CO)<sub>3</sub><sup>46</sup> can afford unequivocal information about the sites of reactivity through studies of the degree of label retention during the course of their ligand-exchange reactions. The development and perfection of matrix-isolation techniques which involve cocondensation of a metal carbonyl and an inert gas matrix material such as Ar have facilitated the study of species formed upon uv irradiation. Many such species may resemble highly reactive intermediates formed through thermal reactions.<sup>27</sup> It is anticipated that theoretical calculations for such intermediates<sup>47</sup> will augment experimental observations of their relative stabilities, their geometries, and the orientations of their substituents. Such studies should provide useful insight into the nature of reaction intermediates and paths of reaction.

(45) C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, **12**, 1286 (1973).

(46) M. A. Cohen and T. L. Brown, *Inorg. Chem.*, **15**, 1417 (1976); D. J. Darensbourg and G. R. Dobson, unpublished results.

(47) A recent paper has described molecular orbital calculations for penta-coordinate metal carbonyls of square-pyramidal and trigonal-bipyramidal geometries: A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975).

Other developments of a theoretical nature, particularly, molecular orbital calculations of increasing sophistication for series of derivatives, are expected to be tested employing reactivity data and physical data such as ir and uv-visible spectra. The increasing availability of <sup>13</sup>C NMR instrumentation is affording a growing body of data which may eventually prove to be of use in this regard.<sup>48</sup>

Future studies of these and other kinds should ultimately lead to detailed understanding of ligand-exchange processes in octahedral metal carbonyls.

*It is a pleasure to acknowledge the contributions to this research area of my past and present students and postdoctoral fellows, whose names are to be found among the references. The financial support of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the Robert A. Welch Foundation, and the North Texas State University Faculty Research Fund is gratefully acknowledged. Professors D. J. Darensbourg, M. Y. Darensbourg, and T. L. Brown have made helpful comments regarding this presentation.*

(48) For a recent review, see L. J. Todd and J. R. Wilkinson, *J. Organometal. Chem.*, **77**, 1 (1974).

## Importance of Nonseparability in Quantum Mechanical Transition-State Theory

William H. Miller

*Department of Chemistry, and Materials and Molecular Research Division of the Lawrence Berkeley Laboratory, University of California, Berkeley California 94720, and University Chemical Laboratory, Cambridge, England*

*Received January 22, 1976*

The transition-state theory<sup>1</sup> of chemical kinetics has without doubt provided the most useful phenomenological framework for parameterizing rate constants for a wide variety of chemical reactions. Recently,<sup>2-7</sup> however, there has been interest in investigating the dynamical basis of transition-state theory and trying to learn the extent to which it provides a *quantitative* description of rate constants for elementary bimolecular reactions.

One of the practical motivations for this recent direction of research is the recognition that, for chemical reactions with significant activation energy, transition-state theory describes the *threshold* region of the reactive cross section quite well, and this<sup>8</sup> is the energy regime most important for determining the thermal rate constant. Since the threshold region is often described rather poorly by classical trajectory methods<sup>9</sup>—which

are useful for describing many other aspects of the dynamics of simple chemical reactions—transition-state theory is an important complement to trajectory methods. (It is interesting that an analogous complementarity also exists experimentally: the “modern” methods of chemical kinetics—e.g., crossed molecular beams, infrared chemiluminescence, various laser techniques, etc.—provide dynamical information about reactions which have little or no activation energy (or at energies significantly above any threshold), but it is difficult to extract information about the threshold

(1) The development of transition-state theory is associated with the names of Wigner, Pelzer, Polanyi, Evans, and particularly Eyring; see, for example, the brief historical discussion and bibliography in K. J. Laidler, “Theories of Chemical Kinetics”, McGraw-Hill, New York, N.Y., 1969, pp 41–43. The classic textbook reference to traditional transition-state theory is S. Gladstone, K. J. Laidler, and H. Eyring, “Theory of Rate Processes”, McGraw-Hill, New York, N.Y., 1941.

(2) R. A. Marcus, *J. Chem. Phys.*, **45**, 2138, 2630 (1966); **46**, 959 (1967).

(3) J. C. Keck, *Adv. Chem. Phys.*, **13**, 85 (1967); *Adv. At. Mol. Phys.*, **8**, 39 (1972).

(4) K. Morokuma and M. Karplus, *J. Chem. Phys.*, **55**, 63 (1971).

(5) G. W. Koeppel and M. Karplus, *J. Chem. Phys.*, **55**, 4667 (1971).

(6) (a) P. Pechukas and F. J. McLafferty, *J. Chem. Phys.*, **58**, 1622 (1973); (b) *Chem. Phys. Lett.*, **27**, 511 (1974).

(7) W. H. Miller, *J. Chem. Phys.*, **61**, 1823 (1974).

(8) See, for example, R. Wolfgang, *Acc. Chem. Res.*, **2**, 248 (1969).

(9) For recent reviews, see D. L. Bunker, *Methods Comput. Phys.*, **10**, 287 (1971), and R. N. Porter, *Annu. Rev. Phys. Chem.*, **25**, 317 (1974).

William H. Miller is Professor of Chemistry at University of California, Berkeley, and is currently a J. S. Guggenheim Memorial Fellow on sabbatical leave from the Department of Chemistry. He was born in Kosciusko, Miss., and received his B.S. degree from Georgia Institute of Technology. Following receipt of the Ph.D. from Harvard in 1967, he spent 2 years at Harvard as Junior Fellow before joining the Berkeley faculty. He is a Camille and Henry Dreyfus Teacher-Scholar. Professor Miller's research interests have primarily involved the theory of atomic and molecular collision phenomena (chemical reactions, most importantly), and in particular the development of semiclassical theory for such processes.