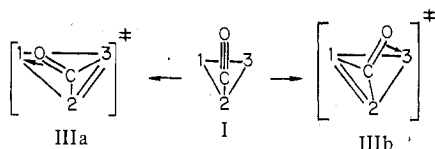
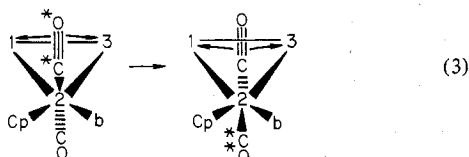


the process I \rightarrow II involves conversion of the $\mu_3:\eta^2$ -CO to a two-electron-donor μ_3 bridge, it may be accompanied by the formation of two Nb=Nb double bonds (delocalized over the metal triangle). Structures IIIa and IIIb represent alternative



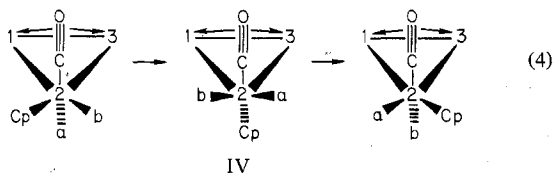
structures which accomplish the observed kinetic symmetrization while requiring the formation of only one Nb=Nb bond. It is notable that the four-electron-donor binding geometry in III has not been observed for CO, although it is known for isoelectronic C=CH₂.¹⁴

At a temperature of 26 °C, the $\mu_3:\eta^2$ -carbonyl rearrangement shown in eq 2 has been slowed, yet some dynamic process still occurs to yield three rather than the six resonances for the 2 and 5 ring protons expected for structure I. A process such as eq 3, which effects transfer of the $\mu_3:\eta^2$ -CO func-



tionality to the opposite face of the triangle, yields a time-average mirror plane *coincident* with the Nb₃ plane. In spite of the successful prediction of three 2,5 proton chemical shifts, this process is inconsistent with the observed spectra since it requires *three* distinct methyl resonances.

On the other hand, the local deformation process in eq 4



generates a time-averaged mirror plane *perpendicular* to the Nb₃ triangle. While this generates the observed three chemical shifts for the 2 and 5 protons, it does so in a curious fashion. The ring protons on Nb(2) yield an AA'BB' spin system as a result of the mirror symmetry of IV. The rings on Nb(1) and Nb(3) are equivalent, but each is a CDEF spin system, containing more lines than the AA'BB' set. It follows that the 2,5 proton resonance associated with Nb(2) should be notably better resolved (i.e., "taller" or "sharper") than that (those) on the remaining rings. This conforms to the spectra observed at -56 °C (see also the expanded spectrum in Figure 2). We assign multiplets a and b to the 3,4 and 2,5 protons, respectively, on Nb(2). Multiplets c-f comprise the CDEF

(14) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415. A close approximation to this binding mode exists in HFe₄(CO)₁₃⁻: Manassero, M.; Sansoni, M.; Longoni, G. *J. Chem. Soc., Chem. Commun.* **1976**, 919.

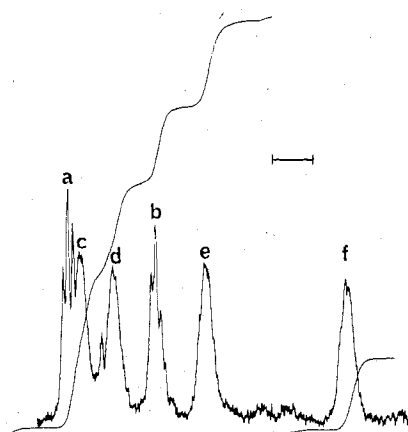


Figure 2. Expanded spectrum of the ring protons of (C₅H₄CH₃)₃-Nb₃(CO)₇ in C₆D₆ at 220 MHz and 16 °C. Horizontal bar indicates 20 Hz.

spin systems of the remaining rings.¹⁵ The rapid occurrence of the process in eq 4 also explains the observation of two, not three, methyl resonances at -56 °C; this process begins to slow perceptibly at -78 °C.

Our ability to rule out facile face-to-face transfer of the $\mu_3:\eta^2$ -CO functionality (eq 3) below 26 °C speaks for the stability of this unit and more particularly for the enhanced activation energy of the required 6 e⁻ \rightarrow 2 e⁻ donor interconversion (transition state in eq 3). This result from the low-temperature process suggests that structure III may be preferable to II for the $\mu_3:\eta^2$ -CO rearrangement in eq 2.

Several recent efforts to achieve homogeneous variants of Fischer-Tropsch hydrogenations have pointed to the importance of metal-oxygen bonding to the activation of CO.¹⁶ Heterogeneous Fischer-Tropsch reactions, including methanation, have been proposed to proceed through surface carbide intermediates resulting from dissociative CO chemisorption. Since these features are either present or nascent in I ($\nu(\text{CO}) = 1330 \text{ cm}^{-1}$),⁷ the reactivity of this cluster toward H₂ is of interest. Preliminary observations show the production of methane, ethane, and ethylene from (C₅H₄R)₃Nb₃(CO)₇ (R = H or Me) under mild conditions (80 °C, 0.9 atm of H₂ in benzene or toluene). We will describe these results in detail when mechanistic studies are complete.

Acknowledgment. We thank Professor Herrmann for a preprint describing the crystal structure of (C₅H₅)₃Nb₃(CO)₇ and the National Science Foundation (Grant CHE 77-10059) for financial support. Douglas Plautz is acknowledged for his contributions to the synthetic work.

Registry No. (C₅H₅)Nb(CO)₄, 12108-03-1; (C₅H₄Me)Nb(CO)₄, 32984-99-9; (C₅H₅)₃Nb₃(CO)₇, 72228-91-2; (C₅H₄Me)₃Nb₃(CO)₇, 74381-16-1.

(15) These assignments are consistent with the high-temperature chemical shifts: e.g., the broad ring proton resonance in Figure 1A is the average of peaks b, e, and f. Also, the more rapid coalescence of peaks a, c, and d is a consequence of their more similar chemical shifts.

(16) Manriquez, J.; McAlister, D.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. Demitras, G. C.; Muettterties, E. L. *Ibid.* **1977**, *99*, 2796. Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *Ibid.* **1977**, *99*, 5829.

Correspondence

Volumes of Activation and Mechanistic Assignments in Octahedral Substitution

Sir:

Langford¹ has raised the question of the contribution of nonreacting ligands to volumes of activation (ΔV^*) in octahedral substitution—a topic I had previously remarked upon

(1) Langford, C. H. *Inorg. Chem.* **1979**, *18*, 3288.

briefly² but which clearly requires further commentary in the broad context of mechanistic assignment.

First, as a matter of historical accuracy, measurement of ΔV^* for the Cr(H₂O)₆³⁺ water-exchange reaction³ was made for the specific purpose of seeking *independent evidence* for the possibility, already apparent to us from consideration of

(2) Lo, S. T. D.; Sisley, M. J.; Swaddle, T. W. *Can. J. Chem.* **1978**, *56*, 2609.

(3) Stranks, D. R.; Swaddle, T. W. *J. Am. Chem. Soc.* **1971**, *93*, 2783.

the systematics of rate and thermodynamic data on $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$ aquations⁴ but first stated explicitly by Espenson,⁵ that the mechanism of substitution in $\text{Cr}(\text{III})$ aquo ions is appropriately described by the associative interchange (I_a) model and not, as the then prevailing opinion insisted, by the I_d or D alternative. An earlier quest⁶ for such confirmation subsequently proved to be indecisive because of its emphasis on the behavior of the aquo(nitrato)chromium(III) ion, which is now recognized as anomalous.⁷ Thus, our early work on pressure effects on octahedral-substitution kinetics was carried out in support of more conventional studies, rather than vice versa as Langford¹ implies.

Efforts to substantiate mechanistic assignments based on traditional criteria with information from high-pressure studies continue to meet with encouraging success (see ref 2, 8, and 9 for recent examples), while new observations by Merbach et al.¹⁰⁻¹³ and ourselves¹⁴ of ΔV^* values of some +6 to +10 cm^3/mol for several solvent-exchange reactions of $\text{Ni}(\text{II})$ and $\text{Co}(\text{II})$ ions are in full accordance with the well-documented assignments of the I_d mechanism in these cases. Most recently, Merbach and co-workers¹³ have reported that solvent-exchange reactions at $\text{Fe}(\text{II})$ and $\text{Mn}(\text{II})$ centers proceed with *near-zero* and markedly *negative* ΔV^* values, respectively, a phenomenon which they attribute (correctly, as I shall argue) to a mechanistic crossover from dissociative to associative activation as one goes from $\text{Ni}(\text{II})$ to $\text{Mn}(\text{II})$. Langford's arguments¹ appear to predict this behavior on the basis of the influence of nonreacting ligands rather than of mechanistic change. I contend, first, that these arguments are incorrectly applied and, second, that the assertion¹ that "other evidence indicates dissociative substitution" in simple high-spin $\text{Mn}(\text{II})$ and $\text{Fe}(\text{II})$ complexes is not well-founded—indeed, the results of Merbach et al. should serve to alert fast-reaction specialists to the lack of definitive mechanistic studies on relevant $\text{Fe}(\text{II})$ and $\text{Mn}(\text{II})$ systems.

The basic principle underlying the assignment of mechanism on the basis of the sign of ΔV^* values in symmetrical reactions not involving solvational change (specifically, solvent-exchange reactions) is what has been termed the *pressure-coordination rule*^{15,16} which states in effect that an increase in pressure will favor processes which involve an increase in coordination number (CN) and, conversely, suppress those in which the coordination number decreases. This is obviously not directly testable for the transient *activational* changes in CN involved in interchange mechanisms, but the comparative mechanistic studies of the kind outlined above indicate the rule to be valid in the kinetic context. One can, however, readily test the rule as it applies to pressure-induced coordination changes in solids, and Gutmann and Mayer show that the rule is followed in every known case (with one possible, but unconvincing, exception¹⁷).¹⁶

A related phenomenon described by Gutmann and Mayer¹⁶ is what they call the *pressure-distance paradox*, whereby the *shortest* interatomic distances may increase on the application of pressure, rather than decrease as one might naively expect, if an increase in coordination number occurs. Langford's thesis is clearly related to this (or, more precisely, to the inverse case in which the shortest distances decrease on reduction of CN) and has validity inasmuch as the bond-making or -breaking contributions to ΔV^* may be compensated *in part* by the expansion or contraction, respectively, of the other metal-ligand distances. This same point has been made independently by Vanni and Merbach¹⁸ and ourselves.² It must be recognized, however, that even if the shortest interatomic distances increase as the pressure is increased, the *total* volume of the system must still decrease: thus, such changes as may occur in these shortest distances (in substitution mechanisms, those between the central metal and the ligands of the first coordination sphere) cannot outweigh the contribution made to the overall volume change made by the *longer range* interactions (here, metal to nonbonded species). This is not surprising, since changes in the volume of a fluid system occur very largely through changes in the amount of empty space available between the molecules, as these are in themselves only very slightly compressible (cf. the "infinite molecule" diamond). So it turns out that the pressure-coordination rule is valid independently of the pressure-distance paradox, as solid-state studies show,¹⁶ and its application to mechanistic questions, as currently practiced, is fully supported by the experimental facts of solid-state and solution studies.

It may, of course, be possible to devise or discover cases in which exceptional circumstances such as severe steric constraints might invalidate the above analysis, but, in the vast majority of real cases, the sign of ΔV^* for solvent exchange may be taken as a reliable criterion of mechanism. It is probably still too soon² for us to attempt to account quantitatively for the *magnitude* of $|\Delta V^*|$ in a given system, but for water we can establish an approximate upper limit by noting that the octahedral interstices in a cubic close-packed array of spheres of radii 138 pm (the "radius" of tetrahedrally coordinated water in ice-I) have radii of 57 pm, which is close to the crystal radii of the smaller trivalent metal ions of the first transition series. Thus the molar volume of coordinated water in, e.g., $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ should be close to that of the close-packed array, viz., 9.0 $\text{cm}^3 \text{mol}^{-1}$, and consequently the transfer of water from the first coordination sphere of these ions to bulk water at 298 K (as in a D mechanism) would cause a volume change of about $18.0 - 9.0 = 9.0 \text{ cm}^3 \text{mol}^{-1}$. For water-exchange reactions occurring by an I mechanism (involving first and second coordination spheres in isolation from bulk solvent), $|\Delta V^*|$ could range up to $19.6 - 9.0 = 10.6 \text{ cm}^3 \text{mol}^{-1}$ if the water of the second sphere is highly H bonded and so ice-I-like, as when the bound ligands have very acidic protons; otherwise, rather smaller $|\Delta V^*|$ values should result.^{19,20} Indeed, for substitution in aqueous $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$, the classic D process, $\Delta V^* = +8$ to $+9 \text{ cm}^3 \text{mol}^{-1}$,²¹ while for water exchange $\Delta V^* = -9 \text{ cm}^3 \text{mol}^{-1}$ for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ (I_a),³ +7 for $\text{Ni}(\text{H}_2\text{O})_6^{3+}$ (I_d),¹² and -3 to -6 for $\text{M}(\text{NH}_3)_5\text{OH}_2^{3+}$ ($\text{M} = \text{Ir}, \text{Rh}, \text{Cr}; \text{I}_a$).^{19,20}

It is unlikely that "collapse of solvent onto [a] contracted primary coordination sphere" (or expansion with an enlarged one), identified by Langford¹ as a possible contribution to ΔV^* , would be important in an *interchange* mechanism, where changes in CN are transient; there is evidence²² to suggest, however, that solvent-shell collapse or expansion may occur when intermediates of augmented or reduced CN are long-

(4) Swaddle, T. W.; Guastalla, G. *Inorg. Chem.* **1968**, *7*, 1915.

(5) Espenson, J. H. *Inorg. Chem.* **1969**, *8*, 1554.

(6) Carey, L. R.; Jones, W. E.; Swaddle, T. W. *Inorg. Chem.* **1971**, *10*, 1566.

(7) Mitchell, M. L.; Montag, T.; Espenson, J. H.; King, E. L. *Inorg. Chem.* **1975**, *14*, 2862.

(8) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 572.

(9) Fairhurst, M. T.; Swaddle, T. W. *Inorg. Chem.* **1979**, *18*, 3241.

(10) Newman, K. E.; Meyer, F. K.; Merbach, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 1470.

(11) Meyer, F. K.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1979**, *18*, 2142.

(12) Documun, Y.; Earl, W. L.; Merbach, A. E. *Inorg. Chem.* **1979**, *18*, 2754.

(13) Meyer, F. K.; Newman, K. E.; Merbach, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 5588.

(14) Fairhurst, M. T.; Yano, Y.; Swaddle, T. W. *Inorg. Chem.*, in press.

(15) Neuhaus, A. *Chimia* **1964**, *18*, 93.

(16) Gutmann, V.; Mayer, H. *Struct. Bonding (Berlin)* **1976**, *31*, 49.

(17) The behavior of metallic Yb under pressure is complicated but includes a phase change involving a change in CN from 12 to (8 + 6) on increasing the pressure beyond 4 GPa; whether this constitutes a *reduction* in CN is a moot point: Hall, H. T.; Merrill, L. *Inorg. Chem.* **1963**, *2*, 618.

(18) Vanni, H.; Merbach, A. E. *Inorg. Chem.* **1979**, *18*, 2758.

(19) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.

(20) Swaddle, T. W.; Stranks, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 8357.

(21) Palmer, D. A.; Kelm, H. *Z. Anorg. Allg. Chem.* **1979**, *450*, 50.

(22) Kotowski, M.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 2555.

lived relative to solvational relaxation, i.e., in A or D processes. The strongly negative ΔV^* values associated with substitution involving net chemical change at Ru(III) centers⁹ may be a manifestation of these effects in an A process.

These considerations clearly support Merbach's contention¹³ that the change in sign of ΔV^* for solvent exchange on going from Ni²⁺ and Co²⁺ through Fe²⁺ to Mn²⁺ is due to a change in mechanism from I_d to I_a. To understand why this occurs, it is perhaps helpful to take the heterodox view (cf. our suggestion¹⁹ that Co(III) amines are anomalous among M(III) complexes) that it is to be expected that the mechanism of substitution at Mn(II) centers will be I_a or A, since it is known that Mn(II), though usually 6-coordinate, can achieve stable 7-coordination even in such a simple complex as Mn(EDTA)(OH)₂²⁻,²³ possibly because the Mn²⁺ ion is fairly large and electronically of spherical symmetry (high-spin 3d⁵; or t_{2g}³e_g²). Now, in associative attack on an octahedral ion, the incoming nucleophile must approach from an interaxial direction, and, by microscopic reversibility, the outgoing ligand must also move into interaxial space. In both cases, the increase in the interaxial electron density, i.e., in the population of the t_{2g} orbitals above the t_{2g}³ of the spherically symmetrical Mn²⁺ ion, as one proceeds to Fe²⁺, Co²⁺, and Ni²⁺, will result in a progressively increased resistance to associative activation, resulting in a marked reduction in lability through increases in the enthalpy of activation and the emergence of an alternative I_d or D mechanism (as these are not so directly affected by t_{2g} populations).

This simple qualitative argument (cf. ref 13), which emphasizes the importance of t_{2g} electron densities in determining the effectiveness of nucleophilic attack in octahedral substitution, would also explain a higher degree of associative character in Cr(III) complexes (3d-t_{2g}³) relative to spin-paired Co(III) (3d-t_{2g}⁶),¹⁹ and Ru(III) (4d-t_{2g}⁵) vis-à-vis Rh(III) (4d-t_{2g}⁶).²⁹ Furthermore, since the 4d orbitals are more diffuse than the 3d but not much different from the 5d spatially,²⁴ we can understand the reported increases in associative character between Cr(III) (3d-t_{2g}³) and Mo(III) (4d-t_{2g}³)²⁵ and between Co(III) and Rh(III),²⁶ while Rh(III) and Ir(III) should be similar, as indeed the ΔV^* data on aquo exchange in M(NH₃)₅OH₂³⁺ indicate.¹⁹ Our earlier commentaries^{19,26} on the Co(III)-Rh(III)-Ir(III) phenomena emphasized central-ion size as an arbitrator of mechanism, largely because steric effects were discernible, but the crystal radii of transition-metal ions are themselves influenced in larger measure by d-orbital populations,²⁷ so that the previous rationale represents a special case of the present one. Langford's argument,¹ that the t_{2g} population affects ΔV^* through the "susceptibility [of complexes] to contraction" rather than through influencing the reaction mechanism, is unconvincing, since it is the e_g electrons, and not the t_{2g}, that are concentrated along the metal-ligand axes and so provide the resistance to compression in an octahedral complex.

Langford's critique¹ of the interpretation of ΔV^* data seems to reflect three underlying concerns—that the well-known influence of nonreacting ligands on rate parameters should also manifest itself in ΔV^* , that the range of nucleophilicities in octahedral substitution for which associative activation is claimed is less than in the classically associative Pt(II) systems, and that the pattern of nonreactive ligand effects on I_d substitutions is not much different from that for reactions said to be I_a. The first concern has been dealt with generally above,

but we should note that the case of Co(NH₃)₅OH₂³⁺, singled out by Langford,¹ may be atypical, ΔV^* being only +1.2 cm³ mol⁻¹ as against +6 for *trans*-Co(en)₂(OH)₂³⁺,²⁸ be this as it may, we have previously shown²⁹ that the former value can be accounted for fully without invoking compensatory contributions from the nonreacting ligands. The second problem is more apparent than real; in octahedral substitution, associative activation seems usually to occur as I_a rather than A mechanisms and therefore shows less pronounced characteristics than in square-planar complexes. In any case, "hard" bases will be more effective at "hard" centers like Cr(III), and "soft" nucleophiles more effective at "soft" centers such as Pt(II),^{19,30} and, since the polarizability which goes along with "softness" is a major factor influencing nucleophilic power,³¹ it follows that a Pt(II) system will display a much greater selectivity toward nucleophiles than a Cr(III) system. As for the third concern, the influence of electron-releasing nonreacting ligands through the σ system of an octahedral complex will be to weaken the σ bond to the departing group and hence stabilize it, regardless of the mode of activation. As emphasized above, electronic influences on the t_{2g} orbitals (π system) of the complex would be needed to affect associative activation, but such effects could also stabilize or destabilize intermediates of reduced CN in a D process; detailed consideration of this is inappropriate here.

Finally, by way of belated epexegetis, the reader is cautioned that the "one-dimensional" models of ref 19, which Langford criticizes, refer specifically to interchange processes and were intentionally naively formulated in order to make some simple qualitative points concerning the distinction between I_d and I_a processes in the context of the roles of the incoming and outgoing ligands alone.

- (28) Tong, S. B.; Krouse, H. R.; Swaddle, T. W. *Inorg. Chem.* **1976**, *15*, 2643.
 (29) Jones, W. E.; Carey, L. R.; Swaddle, T. W. *Can. J. Chem.* **1972**, *50*, 2739.
 (30) Pearson, R. G. *Science (Washington, D.C.)* **1966**, *151*, 172.
 (31) Edwards, J. O. "Inorganic Reaction Mechanisms"; W. A. Benjamin: New York, 1964; Chapter 4.

Department of Chemistry
 The University of Calgary
 Calgary, Alberta, Canada T2N 1N4

T. W. Swaddle

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Activation Enthalpy for the Dissociation of Nickel Complexes in Nonaqueous Solvents

Sir:

The activation enthalpy of solvent exchange at some bivalent metal ions has been correlated with the solvent dissociation enthalpy and the heat of evaporation of the solvent.¹ Solvent exchange kinetics is an important technique in understanding mechanisms of complex formation. The dissociation of a metal complex constitutes a back-reaction to complex formation and is also important in studies of metal complexes in solution.

The rate constant of dissociation of the nickel thiocyanate complex has been correlated with the Gutmann donor number (DN).² Later it was claimed that the activation enthalpy, instead of the rate constant itself, for the dissociation of nickel complexes was a linear function of donor number.^{3,4} It is

- (23) Richards, S.; Pedersen, B.; Silverton, J. V.; Hoard, J. L. *Inorg. Chem.* **1964**, *3*, 27.
 (24) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley-Interscience: New York, 1972; pp 923-924.
 (25) Sasaki, Y.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1048.
 (26) Swaddle, T. W. *Can. J. Chem.* **1977**, *55*, 3166.
 (27) van Santen, J. H.; van Weiringen, J. S. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 420.

- (1) Tanaka, M. *Inorg. Chem.* **1976**, *15*, 2325.
 (2) Dickert, F.; Hoffmann, H.; Janjic, T. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 712.
 (3) Chattopadhyay, P. K.; Kratochvil, B. *Can. J. Chem.* **1977**, *55*, 1609.
 (4) Chattopadhyay, P. P.; Kratochvil, B. *Inorg. Chem.* **1976**, *15*, 3104.