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Registry No. $Na^+Fe(CO)_4CN^-$, 70982-66-0; Na^+(15-c-5)$Fe(CO)_4CN^-$, 70982-67-1; $Na^+Mo(CO)_5CN^-$, 15040-37-6; Na^+(15-c-5)$Mo(CO)_5CN^-$, 70982-65-9; $Na^+Mn(CO)_5$, 13859-41-1; Na^+(15-c-5)$Mn(CO)_5^-$, 59890-72-1; $Na^+Mn(CO)_4PPh_3^-$, 19457-74-0; $Na^+HFe(CO)_4^-$, 53558-55-7; $PPN^+HFe(CO)_4^-$, 56791-54-9.

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Department of Chemistry **Marcetta Y. Darensbourg***
Tulane University **H. L. C. Barros**
New Orleans, Louisiana 70118

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The Transition State for Octahedral Substitution and the Interpretation of Volumes of Activation: The Role of Nonlabile Ligands

Sir:

In recent years, the most important innovations in understanding of the mechanism of octahedral substitution have followed from analysis of pressure dependence and volumes of activation ($\Delta V^\ddagger$). Notably, the negative value of $\Delta V^\ddagger$ (which is, in addition, pressure independent) associated with a process like water exchange at a Cr(III) center is crucial to the recognition of the associative contribution to this activation process.[1] After the realization of the significance of the $\Delta V^\ddagger$ results, information documenting the more traditional test of associative character—rate sensitivity to the nature of the entering group[2]—was reported.[1] Interestingly, this last test has not received universal assent.[3] The sensitivity of reactions at Cr(III) centers to nucleophilicity seems to be qualitatively different from that observed in highly associative reactions like those at Pt(II) centers. This is despite the fact that the observed activation volumes are quite negative and that the slopes of linear free energy relationships are those predicted by a theory of strongly associative substitution derived from a one-dimensional potential function by German and Dogonadze (see ref 1 and papers cited therein).

Table I. Rates of Dissociative Water Loss from Representative Complexes at 25 °C

complex[a]	log [k (s^{-1})]	complex[a]	log [k (s^{-1})]
$Ni(OH_2)_6^{2+}$	4.5	$Co(OH_2)_6^{2+}$	6.4
$Ni(OH_2)_5Cl^+$	5.1	$Co(OH_2)_5NH_3^{2+}$	7.2
$Ni(NH_3)_3(OH_2)_3^{2+}$	6.4	$Mn(OH_2)_6^{2+}$	6.8
$Ni(en)_2(OH_2)_2^{2+}$	6.5	$Mn(phen)(OH_2)_4^{2+}$	7.1
$Ni(bpy)_2(OH_2)_2^{2+}$	4.8	$Fe(OH_2)_6^{3+}$	4.3
$Ni(EDTA)OH_2^-$	5.8	$Fe(OH_2)_3Cl_3$	5.3

[a] Ligand abbreviations: en, ethylenediamine; bpy, bipyridine; EDTA, ethylenediaminetetraacetic acid; phen, 1,10-phenanthroline.

It seems likely that there is an additional variable which has not yet been fully evaluated. A clue to the problem can be found in the focus of the discussion which has surrounded octahedral substitution. The discussion concentrates on the *leaving* and *entering* ligands.[2] (The bonds to these ligands are the ones considered in defining the terms associative and dissociative and in the one-dimensional theory of Dogonadze and German.) However, it was clear to Pearson[4] that well-documented examples of *dissociative* reaction occur with activation energies well *below* (much less than half) *the bond dissociation energies*! The other factor is the stabilization of the transition state afforded by the remaining five ligands which are not either the leaving or the entering ones. In Table I, we collect evidence which shows that the remaining five ligands do have a very significant effect on the rate of dissociative substitution reactions. The observed effect is one in which ligands of greater σ-donor power stabilize the center of reduced coordination number as one would expect.

In order to interpret the important data coming from $\Delta V^\ddagger$ measurements, it is desirable to evaluate the contribution of the nonlabile ligands to volume change. We begin with the dissociative reaction. As one ligand is lost, the remaining five must strengthen bonds. This will lead to two contributions to the volume of activation which are negative. These are (i) compression of the bonds which reduce the volume of the primary coordination sphere and (ii) collapse of the solvent onto this contracted primary coordination sphere. In a dissociative substitution process, these two negative contributions will be balanced by a major positive contribution from the transfer of the leaving group from the first to the second coordination sphere. The most clearly documented case of dissociative substitution occurs in complexes of Co(III) where correlations based on all of $\Delta G^\ddagger$, $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger$ point clearly to the completeness of the dissociation of the leaving group in the transition state and the lack of bonding to the entering group.[1] In a representative reaction, the water-exchange process of $Co(NH_3)_5OH_2^{3+}$, the value of $\Delta V^\ddagger$ is 1.2 mL mol^{-1} for a reaction with, of course, a ΔV° of zero.[1] This modest positive value suggests that the negative terms ap-

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Table II. Measures of Susceptibility to Contraction at a Metal Center as a Function of Position in the First Transition Series

	Cr	Mn	Fe	Co	Ni
diff of empirical radius,[7] M(II)–M(III), nm	15	14	12	11	10
fundamental freq of ν_3 vib,[8] cm^{-1}					
$M(NH_3)_6^{2+}$		307	321	327	334
$M(pyO)_6^{2+}$ [a]		311	320	331	342

[a] pyO = pyridine *N*-oxide.

proximately cancel the positive terms for reactions at this center.

The Co(III) center has a d^6 configuration which implies six electrons in the t_{2g} π-antibonding levels. This configuration will resist contraction on passage to the transition state. The only nonlabile configuration more resistant to such contraction is the d^8 configuration with σ-antibonding levels filled as well. At Ni(II) centers, exchange of water from hexaaquo ions has an activation volume of 7 mL mol^{-1} according to recent inference by extension from appropriate complex formation reactions.[5] This value may reflect the positive contribution of transfer of water to the second coordination sphere with minimum contribution of the negative terms. A value near 10 mL mol^{-1} would seem reasonable for the *positive* term associated with that transfer since a large part of the 18 mL molar volume of water is associated with the open H-bond structure, which would be collapsed in the second coordination sphere. The smallest volume that could reasonably be established for the second sphere would be a close-packed value near 9 mL mol^{-1}. A reasonable maximum for close-packed water is near 14 mL mol^{-1}.

It is difficult to estimate the minimum value of negative terms for bond contraction because there are serious differences between the environments in which five-coordination is stabilized for X-ray crystallographic examination and the environments of common octahedral systems. We shall attempt to see if the above estimate of 10 mL is reasonable for the positive term. A Ni(II)–water bond in one five-coordinate complex has been estimated at 2.10 Å[6] compared to the normal radius sum of 2.16 Å.[7] This would suggest a contraction of 0.06 Å in a radius of about 3 Å. The contribution to $\Delta V^{\ddagger}$ corresponds to about −4 mL mol^{-1}. This suggests that the volume change for transfer of a water molecule to the second coordination sphere is approximated by about 10 mL mol^{-1}. This agrees with the argument above.

We can now consider trends across the first transition series. Earlier transition metals with few t_{2g} electrons should be more susceptible to contraction. This is indicated by two trends tabulated in Table II. Here both the radius difference between the M(II) and M(III) oxidation states of the ions[7] and the values of metal ligand stretching frequencies[8] imply the expected trend in "contractibility". From this, we would expect an *increase* in the *negative* contributions to the volume of activation as we move to the left from the Ni(II) case. Two other trends can be identified, but with less assurance. The comparison given above between Ni(II) and Co(III) data suggests that the negative contribution to volumes of activation may be larger for 3+ than for 2+ ions. This is reasonable. When the bond energy increases, there is more to be compensated by the remaining five ligands after a dissociation, and the attraction from the center is correspondingly more powerful. Second, the negative contribution to volumes of activation should become more important as the central ion becomes larger down a triad in the periodic table.

The argument to this point implies (predicts?) that the volumes of activation should become mildly negative for reactions at centers like Fe(II) and Mn(II) where other evidence indicates dissociative substitution. The data are not yet available. Some data are available for M(III) ions, but the evidence as to the dissociative or associative character of reactions is less clear-cut for Fe(III) and Rh(III) centers. It is quite possible, however, that these reactions are sufficiently dissociative that the factors identified above account for the volumes of activation observed[1] or expected. It remains to ask what expectations are for activation volume for associative reactions such as those at Cr(III) centers.

The associative nature of the transition state for substitution at Cr(III) is demonstrated by the clear evidence that there is a discrimination among entering ligands although that discrimination is not as large as is observed in reactions of square-planar d^8 complexes.[1,2,4] It would be tempting to suggest that the reaction was only weakly associative. This contention might adequately account for the observed volume of activation since a large negative term for contraction of the five nonlabile ligands might still be expected and some reduction to the positive term would follow from an associative contribution to activation. Indeed, we could almost imagine a nearly constant volume of activation from the dissociative to associative limits of octahedral substitution at an easily compressed center. This would be because the negative term in the dissociative mechanism would decline as the reaction became more associative but the positive term from ligand dissociation would decrease and then become negative as the reaction became more associative. In addition, a strongly associative reaction would no doubt finally go over to a positive contribution by the nonlabile ligands as the transition state resembles a fully seven-coordinate structure expanded by interligand repulsion. $\Delta V^{\ddagger}$ may be a weak criterion of mechanism at an easily compressed center.

There has been some tendency in the literature to regard $\Delta V^{\ddagger}$ as a very direct probe of the relation of the leaving and entering ligands in octahedral substitutions. This follows from the proposition that $\Delta V^{\ddagger}$ is a most direct measure of transition-state "structure" as opposed to "energetics". The premise is acceptable but the conclusions need to be tempered until a full study of the large role played by the five nonlabile ligands in octahedral substitution is complete.

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Metal Ions Group, Chemistry
Carleton University
Ottawa, Canada K1S 5B6

Cooper H. Langford

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