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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) centers[9] may be a manifestation of these effects in an A process.

These considerations clearly support Merbach's contention[13] that the change in sign of ΔV^* for solvent exchange on going from Ni^{2+} and Co^{2+} through Fe^{2+} to Mn^{2+} 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 suggestion[19] that Co(III) ammines 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_2^{2-},[23] possibly because the Mn^{2+} ion is fairly large and electronically of spherical symmetry (high-spin $3d^5$, or $t_{2g}{}^3e_g{}^2$). 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 Mn^{2+} ion, as one proceeds to Fe^{2+}, Co^{2+}, and Ni^{2+}, 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) ($4d$–$t_{2g}{}^6$).[2,9] 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 $M(NH_3)_5OH_2^{3+}$ 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 critique[1] 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 $Co(NH_3)_5OH_2^{3+}$, singled out by Langford,[1] may be atypical, ΔV^* being only +1.2 $cm^3\ mol^{-1}$ as against +6 for *trans*-$Co(en)_2(OH_2)_2^{3+}$;[28] be this as it may, we have previously shown[29] 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 labilize 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 epexegesis, 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.

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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

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Table I. Activation Enthalpy for the Dissociation ($\Delta H_d^{\ddagger}$) of Nickel Complexes of Thiocyanate and Isoquinoline in Different Solvents and Some Solvent Parameters

	$\Delta H_d^{\ddagger}$/kJ mol^{-1}				
solvent[a]	NiSCN[b]	Ni-*i*-quin[d]	DN[e]	ΔH_d/ kJ mol^{-1} [f]	δ[g]
MeCN	75.2	71.9	14.1	24.2	12.11
DMF	63.5	58.1	26.6	19.2	11.77
Me_2SO	58.1[c]	56.4	29.8	9.9	12.93[h]
MeOH	83.2[c]	80.7	19.0	33.3	14.50
PC		74.0	15.1	2.8	13.30[h]
H_2O	73.2	67.3	18.0	8.8	16.35[i]

[a] MeCN = acetonitrile; DMF = dimethylformamide; Me_2SO = DMSO = dimethyl sulfoxide; MeOH = methanol; PC = propylene carbonate. [b] Reference 2. [c] Reference 3. [d] Reference 4. [e] Donor number: Gutmann, V. "Coordination Chemistry in Nonaqueous Solutions"; Springer-Verlag: New York, 1968. [f] Enthalpy for solvent dissociation taken from ref 1. [g] Solubility parameter: Hoy, K. L. "Tables of Solubility Parameters"; Union Carbide Corp.: South Charleston, W. Va., 1969. [h] Hansen, C. M.; Skaarup, K. *J. Paint Technol.* 1967, *39*, 511. [i] Estimated value for 0.1 M perchlorate solution: Wakahayashi, T.; Omori, S.; Suzuki, N. *J. Inorg. Nucl. Chem.* 1964, *26*, 2255.

thought that the dielectric properties of the solvent also should be an important factor in the consideration of dissociation kinetics as in the case of solvent exchange at metal ions.[1]

The dissociation of a ligand L from a complex $NiLS_5$ can be considered to involve three processes: (1) the ligand L dissociates from the complex $NiLS_5$; (2) the dissociated ligand L is incorporated in the bulk solvent; (3) a solvent molecule leaves the bulk solvent, approaches to and is accommodated in the vacated coordinated site of NiS_5, yielding NiS_6.

This postulation does not imply that these processes occur separately by a purely dissociative (D) mechanism. In the dissociative-interchange (I_d) mechanism, in which the dissociation of the ligand L and the coordination of a solvent molecule occur concurrently, the activation enthalpy appears to differ little from the present consideration.

Process 1 is postulated to require energy directly proportional to the solvent dissociation energy and inversely proportional to the electron-donating ability of the coordinated solvent. Process 2 is thought to be similar to the process of dissolution of the ligand L in the solvent. Thus the energy needed in process 2 should be related to the solubility parameter (δ) of the solvent in some way. Then if the activation enthalpy of dissociation ($\Delta H_d^{\ddagger}$) of the ligand L from the complex $NiLS_5$ is assumed to be proportional to the solubility parameter for simplicity, the following expression is obtained:

$$\Delta H_d^{\ddagger} = a(\Delta H_d)(\mathrm{DN})^{-1} + b\delta \qquad (1)$$

where a and b are constants characteristic of the metal ion. The donor number DN is used as a measure of electron-donating ability of solvent. The enthalpy of solvent dissociation from a metal ion (ΔH_d) may be derived from the modified Born equation and is given by

$$\Delta H_d = -0.5N(ze)^2(r + r')^{-1}\epsilon^{-1}(1 + T\partial \ln \epsilon/\partial T)_P \quad (2)$$

where the symbols have their usual meanings. Values of ΔH_d for various metal ions and solvents have been compiled in ref 1. The values of ΔH_d for nickel ion are given in Table I together with the activation enthalpy of dissociation of the nickel complexes with thiocyanate and isoquinoline.

When we utilize $\exp[-c(\mathrm{DN})]$, a monotonic decreasing function with increasing DN, instead of $(\mathrm{DN})^{-1}$ for taking into account the electron-donating effect of coordinated solvent molecule, $\Delta H_d^{\ddagger}$ can be correlated by

$$\Delta H_d^{\ddagger} = a'(\Delta H_d)\exp[-c(\mathrm{DN})] + b'\delta \qquad (3)$$

From eq 1 and 3, respectively, we have immediately

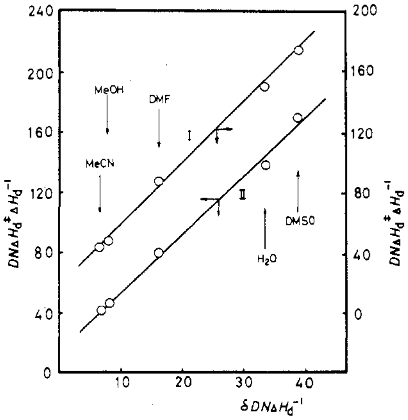

Figure 1. Activation enthalpy of dissociation of nickel complexes according to eq 4: I, NiSCN; II, Ni-*i*-quin. See Table I for solvent abbreviations.

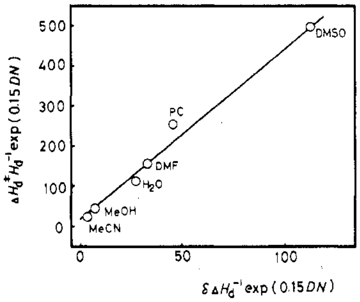

Figure 2. Activation enthalpy of dissociation of nickel isoquinoline according to eq 5. See Table I for solvent abbreviations.

$$\Delta H_d^{\ddagger}(\Delta H_d)^{-1}(\mathrm{DN}) = a + b\delta(\Delta H_d)^{-1}(\mathrm{DN}) \qquad (4)$$

$$\Delta H_d^{\ddagger}(\Delta H_d)^{-1}\exp[c(\mathrm{DN})] = a' + b'\delta(\Delta H_d)^{-1}\exp[c(\mathrm{DN})] \qquad (5)$$

The $\Delta H_d^{\ddagger}$ data found in Table I are plotted according to eq 4 (Figure 1). The correlation is excellent. The value for propylene carbonate is too high to be accommodated in the correlation derived from eq 4: the line in Figure 1 predicts a $\Delta H_d^{\ddagger}$ value of about 54 kJ mol^{-1} instead of the actual value 74 kJ mol^{-1} for propylene carbonate. At present it is not clear why the $\Delta H_d^{\ddagger}$ value for propylene carbonate deviates from the correlation derived from eq 1.

Then the $\Delta H_d^{\ddagger}$ data for the nickel isoquinoline complex are plotted according to eq 5 (Figure 2). Though the value for propylene carbonate is still a little too high, the correlation seems satisfactory with the value of $c = 0.15$. Thus it may be said that the correlation of (3) can cover a wider range of solvent than the correlation of (1).

Equations 1 and 3 could be useful in predicting the activation enthalpy for the dissociation of a ligand from a metal complex in different solvents. It would be an interesting future problem to test the applicability of the present approach to the other metal complexes in different solvents.

Registry No. $NiSCN(MeCN)_5$, 74331-37-6; $NiSCN(DMF)_5$, 74331-38-7; $NiSCN(Me_2SO)_5$, 74331-39-8; $NiSCN(MeOH)_5$, 18549-31-0; $NiSCN(H_2O)_5$, 74331-40-1; Ni(*i*-quin)$(MeCN)_5$, 60489-03-4; Ni(*i*-quin)$(DMF)_5$, 60489-05-6; Ni(*i*-quin)$(Me_2SO)_5$, 60489-02-3; Ni(*i*-quin)$(MeOH)_5$, 60489-01-2; Ni(*i*-quin)$(PC)_5$, 60489-04-5; Ni(*i*-quin)$(H_2O)_5$, 60489-00-1; MeCN, 75-05-8; DMF, 68-12-2; Me_2SO, 67-68-5; MeOH, 67-56-1; PC, 108-32-7.

Laboratory of Analytical Chemistry
Faculty of Science
Nagoya University
Nagoya, 464 Japan

Motoharu Tanaka

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