Table II. Activation Enthalpy of Solvent Exchange at Some Bivalent Metal Ions (kJ mol^{-1}) and Crystal Radius of These Metal Ions (nm)

Solvent	Co^{2+}	Fe^{2+}	Mn^{2+}	Ni^{2+}	VO^{2+}
Acetonitrile (MeCN)	47.7^a	40.6^g	30.3^j	68.4^m	29.5^p
Ammonia (NH$_3$)	46.8^b		33.4^k	46.0^n	
N,N-Dimethyl-formamide (DMF)	56.8^c			62.7^c	54.8^q
Dimethyl sulfoxide (DMSO)	51.0^d			54.3^d	
Methanol (MeOH)	57.7^e	50.2^h	28.4^h	66.0^e	50.2^r
Water (H$_2$O)	47.2^f	32.2^i	36.8^l	58.0^o	57.3^s
Crystal radius/nm	0.082	0.083	0.091	0.078	0.092^t

^{a} R. J. West and S. F. Lincoln, *Inorg. Chem.*, **11**, 1688 (1972). ^{b} H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *ibid.*, **4**, 1061 (1965). ^{c} N. A. Matwiyoff, *ibid.*, **5**, 788 (1966). ^{d} L. S. Frankel, *ibid.*, **10**, 814 (1971). ^{e} Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964). ^{f} A. H. Zeltman, N. A. Matwiyoff, and L. O. Morgan, *J. Phys. Chem.*, **73**, 2689 (1969). ^{g} R. J. West and S. F. Lincoln, *Aust. J. Chem.*, **24**, 1169 (1971). ^{h} F. W. Breivogel, *J. Chem. Phys.*, **51**, 445 (1969). ^{i} T. J. Swift and R. E. Connick, *ibid.*, **37**, 307 (1962). ^{j} W. L. Purcell and R. S. Marianelli, *Inorg. Chem.*, **9**, 1724 (1970). ^{k} M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Am. Chem. Soc.*, **91**, 6318 (1969). ^{l} M. Grant, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **10**, 71 (1971). ^{m} S. F. Lincoln and R. J. West, *Aust. J. Chem.*, **24**, 255 (1973). ^{n} H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 206 (1965). ^{o} J. W. Neely and R. E. Connick, *J. Am. Chem. Soc.*, **94**, 3419, 8646 (1972). ^{p} N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **8**, 65 (1969). ^{q} G. A. Miller and R. E. D. McClung, *J. Chem. Phys.*, **58**, 4358 (1973). ^{r} N. S. Angerman and R. B. Jordan, unpublished results cited in p. ^{s} K. Wüthrich and R. E. Connick, *Inorg. Chem.*, **6**, 583 (1967). ^{t} M. B. Palma-Vittorelli, M. U. Palma, D. Palumbo, and F. Sgarlata, *Nuovo Cimento*, **3**, 718 (1956).

Table III. ΔH_d Values (kJ mol^{-1})

	Co^{2+}	Fe^{2+}	Mn^{2+}	Ni^{2+}	VO^{2+}
MeCN	23.6	23.4	22.4	24.2	22.3
NH$_3$	41.7	41.4	39.3	42.9	39.0
DMF	18.7	18.6	17.6	19.2	17.5
DMSO	9.6	9.5	9.0	9.9	9.0
MeOH	32.4	32.2	30.6	33.3	30.4
H$_2$O	8.5	8.5	8.1	8.8	8.0

Table IV. Coefficients a and b in Equation 3

	Co^{2+}	Fe^{2+}	Mn^{2+}	Ni^{2+}	VO^{2+}
a	0.7705	0.7752^a (0.9292)^b	0.1629	0.9530	−0.4157
b	0.8730	0.6738^a (0.5535)^b	0.8747	0.9833	1.365

^{a} Calculated with data for MeCN and MeOH. ^{b} Calculated with data for MeCN, MeOH, and H$_2$O.

as merely apparent. For manganese(II) a is much lower than for cobalt(II), nickel(II), and iron(II). We should await more solvent exchange data for this metal ion before we know definitively whether some solvent exchange data are not correct or the present model fails and some other mechanism should be considered to be involved in the solvent exchange of manganese(II) ion.

The value of b is not far from unity; process (2) is in effect similar to evaporation–condensation.

With the values of a and b given in Table IV $\Delta H^\ddagger_{ex}$ values can be reproduced according to eq 3. As seen from Table V, eq 3 reproduces $\Delta H^\ddagger_{ex}$ values for cobalt(II) ion to within ±3 kJ mol^{-1} which is within the claimed experimental error for most NMR studies (±2–4 kJ mol^{-1}). However, for the other metal ions the correlation is not as good as for cobalt(II) ion as evident from Figure 2.

Calculated values of the first and second terms of the right-hand side of eq 3 are also included in Table V. The

Table V. Calculated $\Delta H^\ddagger_{ex}$ for Cobalt(II) Ion

			$\Delta H^\ddagger_{ex}$, kJ mol^{-1}		
	$a\,\Delta H_d$	$b\,\Delta H_v$	Calcd	Obsd	Difference
MeCN	18.18	29.01	47.2	47.7	−0.5
NH$_3$	32.13	17.35	49.5	46.8	+2.7
DMF	14.41	41.48	55.9	56.8	−0.9
DMSO	7.40	46.17	53.6	51.0	+2.6
MeOH	24.96	32.68	57.6	57.7	−0.1
H$_2$O	6.55	38.40	45.0	47.2	−2.2

contribution of the ΔH_d term is about twice as large as that of the ΔH_v term for the ammonia exchange, while for the exchange of the other solvents the ΔH_v term is more important than the ΔH_d term. Especially for the exchange of N,N-dimethylformamide, dimethyl sulfoxide, and water, the large ΔH_v term is leveled down by the small ΔH_d term. In consequence the activation enthalpy of the exchange of these solvents does not differ much despite the large differences in ΔH_d and ΔH_v.

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Comments on the Reduction of Nitrate by Diammonium Oxopentachloromolybdate(V) in Dimethylformamide[1]

AIC60114T

Sir:

The reduction of nitrate by molybdenum(V) in DMF has recently been reported.[1] The source of the molybdenum(V) was (NH$_4$)$_2$[MoOCl$_5$], and the interpretation of the observed

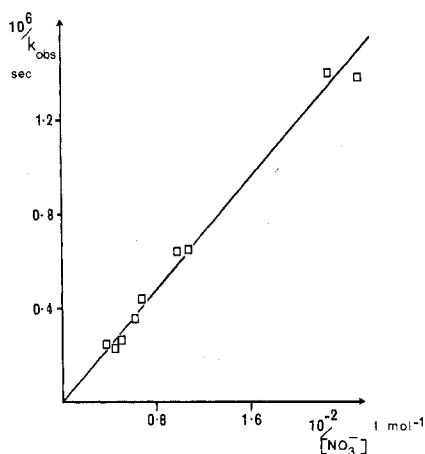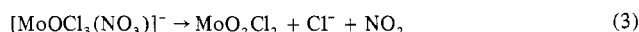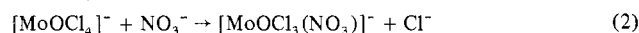**Figure 1.** Variation of k_{obsd} with $[NO_3^-]$ in the absence of added chloride. The data were taken from ref 1.

kinetic behavior was based upon a rapid preequilibrium (eq 1), followed by the substitution (eq 2) of the resultant five-coordinate species prior to the redox reaction (eq 3).

$$[MoOCl_5]^{2-} \rightarrow [MoOCl_4]^- + Cl^- \tag{1}$$

$$[MoOCl_4]^- + NO_3^- \rightarrow [MoOCl_3(NO_3)]^- + Cl^- \tag{2}$$

$$[MoOCl_3(NO_3)]^- \rightarrow MoO_2Cl_2 + Cl^- + NO_2 \tag{3}$$

As an extension of our earlier studies,[2] we have used electron spin resonance spectroscopy to investigate the nature of the molybdenum(V) species formed when $[MoOCl_5]^{2-}$ is dissolved in dried DMF. The results obtained show clearly that, at the high dilutions[3] of molybdenum(V) employed for the kinetic study,[1] the complex formed almost exclusively ($\geq 95\%$) is $[MoOCl_4(DMF)]^-$ (with $\bar{g} = 1.947$), presumably formed via reaction 4. The $\bar{g}$ value for $[MoOCl_4(DMF)]^-$ was char-
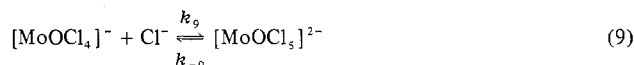
$$[MoOCl_5]^{2-} + DMF \rightarrow [MoOCl_4(DMF)]^- + Cl^- \tag{4}$$
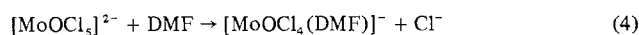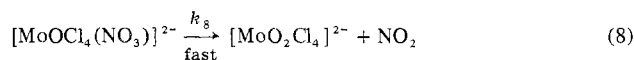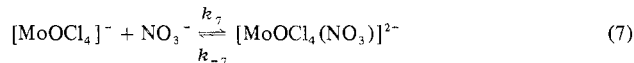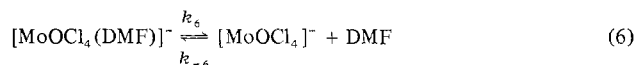
acterized by reacting $[Et_4N][MoOCl_4]$ with DMF in the molar ratio 2:1 in CH_2Cl_2 solution. The ESR spectrum of this solution contained two signals of equal intensity at $\bar{g} = 1.955$ (attributed to $[MoOCl_4]^-$) and $\bar{g} = 1.947$ (attributed to $[MoOCl_4(DMF)]^-$). In DMF trace quantities of a species assigned as $[MoOCl_3(DMF)_2]$ ($\bar{g} = 1.941$) were also observed suggesting further substitution according to equilibrium 5

$$[MoOCl_4(DMF)]^- + DMF \rightarrow MoOCl_3(DMF)_2 + Cl^- \tag{5}$$

which is proposed on the basis that the relative intensity of the signal at $\bar{g} = 1.941$, as compared with that at 1.947, decreases as $[Cl^-]$ increases. Thus the value of $\bar{g} = 1.941$ which is close to that[2] of $[MoOCl_5]^{2-}$ does *not* indicate the presence of this latter species. Furthermore, no signal characteristic[2] of either $[MoOCl_5]^{2-}$ or $[MoOCl_4]^-$ could be observed even in DMF solutions containing $[MoOCl_5]^{2-}$ and Et_4NCl in respective concentrations $\geq 1:60$. The absence of the coordinatively unsaturated ion $[MoOCl_4]^-$ is not surprising in view of the capacity of DMF to act[4] as a moderately strong donor solvent.

Consequently, we believe that the starting point for Taylor and Spence's interpretation of their kinetic data is incorrect. We wish to suggest an alternative scheme which is in accord with both the ESR and kinetic data and is also consistent with earlier interpretations proposed for the oxidation of $MoOCl_3(OPPh_3)_2$ by nitrate[5] and nitrite.[6] This involves

reactions 6–8 subsequent to equilibrium 4.

$$[MoOCl_4(DMF)]^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} [MoOCl_4]^- + DMF \tag{6}$$

$$[MoOCl_4]^- + NO_3^- \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} [MoOCl_4(NO_3)]^{2-} \tag{7}$$

$$[MoOCl_4(NO_3)]^{2-} \overset{k_8}{\underset{fast}{\longrightarrow}} [MoO_2Cl_4]^{2-} + NO_2 \tag{8}$$

$$[MoOCl_4]^- + Cl^- \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} [MoOCl_5]^{2-} \tag{9}$$

Application[7] of the steady-state condition to the $[MoOCl_4]^-$ concentration leads to rate expression 10, where P is the

$$\frac{d[P]}{dt} = \frac{k_6 k_7 [MoOCl_4(DMF)^-][NO_3^-]}{k_{-6}[DMF] + k_7[NO_3^-] + k_9[Cl^-]} \tag{10}$$

oxidized product. The form of the integrated rate expressions based upon (10) is consistent with the kinetic data of Taylor and Spence.[1] In the presence of added chloride we obtain expression 11 which is supported by a plot of $[NO_3^-]/k_{obsd}$

$$\frac{1}{k_{obsd}} = \frac{1}{k_6} + \frac{k_{-6}[DMF]}{k_6 k_7 [NO_3^-]} + \frac{k_9[Cl^-]}{k_6 k_7 [NO_3^-]} \tag{11}$$

vs. $[Cl^-]$ at essentially constant $[NO_3^-]$. In the absence of added chloride, a first-order dependence of k_{obsd} on $[NO_3^-]$ is obtained (Figure 1), indicating $k_6 \gg k_{obsd}$ under the experimental conditions of ref 1.

In addition to the above comments, we again wish to point out that, providing the redox potentials are favorable, the general criteria established[8] for redox reactions lead to the prediction[9] that a facile electron-transfer process between an oxomolybdenum(V) center and NO_3^- requires that the latter be coordinated to the former with one (and only one) oxygen atom cis to the oxo group. The relative inertness of the oxomolybdenum(V) center toward oxidation by nitrate in Taylor and Spence's system[1] would appear to be due to the presence of a large excess of a moderately strong donor solvent which competes very effectively with the nitrate ion in substitution process(es) at the oxomolybdenum(V) center.

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