Activation Volumes and Solvent Effects on Bimolecular Reactions of Low-spin d^6 Complexes

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Summary Activation volumes for reactions of [Fe(4-Me-phen)$_3$]$^{2+}$ with cyanide and with peroxodisulphate, and of Mo(bipy)(CO)$_4$ with cyanide in various solvents suggest that cyanide or peroxodisulphate desolvation is a dominant feature in transition state formation.

THERE can be little doubt that the second-order term in the rate laws [equation (1)] for reactions of low-spin iron(II)-di-imine complexes with such nucleophiles as hydroxide, methoxide, or cyanide arises from a bimolecular reaction

$$-\mathrm{d[complex]/d}t = \{k_1 + k_2\,[\mathrm{nucleophile}]\}[\mathrm{complex}] \quad (1)$$

between complex and nucleophile, although there is still controversy over the point of attack of the nucleophile.[1] However it has recently been reported that activation volumes for reactions of the [Fe(bipy)$_3$]$^{2+}$ and [Fe(phen)$_3$]$^{2+}$ cations with hydroxide or cyanide ion lie within the range +19·7 to +21·5 cm^3 mol^{-1} in aqueous solution.[2] These observations are difficult to reconcile with the expected decrease in volume on going from the initial state to the transition state for an associative mechanism. The authors interpret their results in terms of a two-step mechanism, analogous to the Eigen–Wilkins mechanism of complex formation, in which dissociative activation dominates in determining the observed activation volume.[2,3] We here suggest, with appropriate experimental evidence, that solvation effects, specifically desolvation of the anionic nucleophile, may play a large part in determining both the magnitude and the sign of the activation volume in reactions of this type.

We have measured rates of reaction of 2,2′-bipyridyltetracarbonylmolybdenum, Mo(bipy)(CO)$_4$, with cyanide ion in methanol and in dimethyl sulphoxide, and of the iron(II) complex of 4-methyl-1,10-phenanthroline, [Fe(4-Me-phen)$_3$]$^{2+}$, with cyanide ion in water and in aqueous methanol and with peroxodisulphate ion in water, at atmospheric pressure and at pressures up to 1·4 kbar (at 298·2 K). The apparatus for measuring rates at elevated pressures, described in more detail elsewhere,[4] consists essentially of a simple thermostatted bomb from which samples can be taken at appropriate time intervals for spectrophotometric monitoring of concentrations. Our results are indicated graphically in the Figure, whose caption indicates the concentrations of reactants used. Derived activation volumes are listed in the Table; we have assumed linear dependence of logarithms of rate constants on applied pressure.

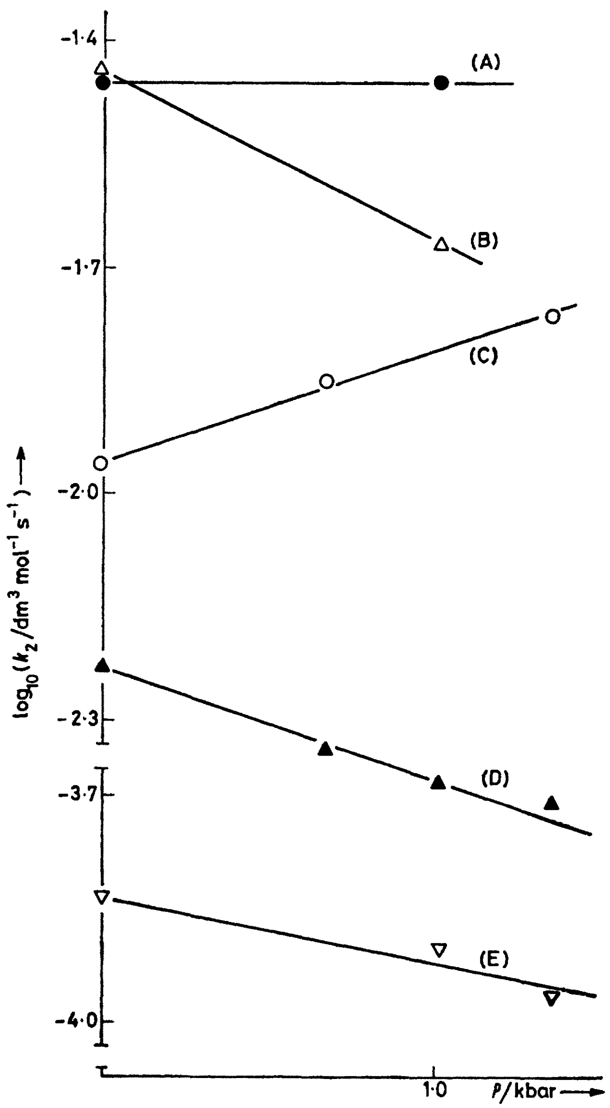

FIGURE. The dependence of second-order rate constants, k_2 (298·2 K), on pressure. Reactions, with initial concentrations given (dm^3 mol^{-1}) in parentheses: (A) [Fe(4-Me-phen)$_3$]$^{2+}$ (5×10^{-5}) + $K_2S_2O_8$ (5×10^{-3}) in water; (B) [Fe(4-Me-phen)$_3$]$^{2+}$ (5×10^{-5}) + KCN ($3·3 \times 10^{-2}$) in aqueous methanol (33·3% by volume methanol); (C) Mo(bipy)(CO)$_4$ (10^{-4}) + Et_4NCN ($6·4 \times 10^{-2}$) in dimethyl sulphoxide; (D) Fe(4-Me-phen)$_3^{2+}$ (5×10^{-5}) + KCN ($3·3 \times 10^{-2}$) in water; (E) Mo(bipy)(CO)$_4$ (10^{-4}) + Et_4NCN ($6·4 \times 10^{-2}$) in methanol.

The mechanism of cyanide attack at the di-imine complexes Mo(bipy)(CO)$_4$, [Fe(4-Me-phen)$_3$]$^{2+}$, [Fe(phen)$_3$]$^{2+}$, and [Fe(bipy)$_3$]$^{2+}$ in the various solvents is expected to be the same, yet the activation volumes ($\Delta V^{\ddagger}$) range from +22 to −9 cm^3 mol^{-1}. However, the extent of cyanide, hydroxide, or peroxodisulphate desolvation required when these species are incorporated into the respective transition states will depend on their extent of solvation in the initial state. Data on single ion hydration enthalpies (*e.g.* between −288 and −326 kJ mol^{-1} for cyanide)[5] and on Gibbs' free energies of transfer ($\delta_m\mu^{\ominus}$) from water into mixed and non-aqueous media[6] (*cf.* Table) suggest markedly lower solvation in methanol than in water, and less solvation still in dimethyl sulphoxide. The qualitative correlation between

TABLE. Activation volumes ($\Delta V^{\ddagger}$; 298·2 K) for bimolecular reactions of low-spin d^6 complexes in various solvents, and Gibbs' free energies of transfer of cyanide ion [$\delta_m\mu^{\ominus}(CN^-)$][a] from water into the respective solvent media.

Reaction	Solvent	$\Delta V^{\ddagger}$/cm^3 mol^{-1}	$\delta_m\mu^{\ominus}(CN^-)$/kJ mol^{-1}
$Mo(bipy)(CO)_4 + CN^-$	Me_2SO	−9	+35[d]
$Mo(bipy)(CO)_4 + CN^-$	MeOH	+4	+9[d] or +14[e]
$Fe(4\text{-}Me\text{-}phen)_3^{2+} + CN^-$	$MeOH–H_2O$[b]	+13	+2[e] or 0[f]
$Fe(4\text{-}Me\text{-}phen)_3^{2+} + CN^-$	H_2O	+10	0
$Fe(phen)_3^{2+} + CN^-$	"	+19·8[c]	0
$Fe(bipy)_3^{2+} + CN^-$	"	+20·9[c]	0
$Fe(phen)_3^{2+} + OH^-$	"	+19·7[c]	—
$Fe(bipy)_3^{2+} + OH^-$	"	+21·5[c]	—
$Fe(4\text{-}Me\text{-}phen)_3^{2+} + S_2O_8^{2-}$	"	0	—

[a] On the molar scale, from ref. 6. [b] 33⅓% methanol, by volume before mixing. [c] From ref. 2. [d] Using the assumption $\delta_m\mu^{\ominus}(AsPh_4^+) = \delta_m\mu^{\ominus}(BPh_4^-)$. [e] Using de Ligny *et al*.s' assumptions (*cf*. ref. 6). [f] Using Wells's assumptions (*cf*. ref. 6).

$\Delta V^{\ddagger}$ and $\delta_m\mu^{\ominus}(CN^-)$ values (*cf*. Table) suggests that cyanide desolvation is indeed an important factor. The $\Delta V^{\ddagger}$ determined thus represents a balance between contributions of opposite sign from the associative nature of transition state formation and from anion desolvation, with $\Delta V^{\ddagger} = 0$ for peroxodisulphate oxidation of the $[Fe(4\text{-}Me\text{-}phen)_3]^{2+}$ cation suggesting an equal balance here.

We therefore conclude that desolvation of the anion makes an important contribution to the observed values for $\Delta V^{\ddagger}$ for second-order reactions of these d^6 complexes, and that positive $\Delta V^{\ddagger}$ values may still arise from associative attack. We do not wish to imply that these are the only two factors involved, as the marked difference between $\Delta V^{\ddagger}$ values for attack at the $[Fe(phen)_3]^{2+}$ and at the $[Fe(4\text{-}Me\text{-}phen)_3]^{2+}$ cations, which parallels the trend reported earlier for aquation of $[Fe(X\text{-}phen)_3]^{2+}$ cations with X = H, 4,7-Me_2, and 5-NO_2, indicates that specific ligand effects also operate. Solubility and time-scale limitations preclude, at the moment, a full investigation of the three variables of nature of complex, nature of anion, and nature of solvent.

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[1] R. D. Gillard, *Coord. Chem. Rev.*, 1975, **16**, 67; J. Burgess, in 'Inorganic Reaction Mechanisms, volume 7,' ed. A. G. Sykes, Chem. Soc. Specialist Periodical Reports, in the press.

[2] G. A. Lawrance, D. R. Stranks, and S. Suvachittanont, *Inorg. Chem.*, 1979, **18**, 82.

[3] D. R. Stranks, personal communication.

[4] F. M. Mekhail, P. Askalani, J. Burgess, and R. Sherry, *Transition Met. Chem.*, submitted for publication.

[5] H. D. B. Jenkins and K. F. Pratt, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1775.

[6] M. J. Blandamer, J. Burgess, and A. J. Duffield, *J. Chem. Soc., Dalton Trans.*, 1980, 1.