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LETTER

Activation volumes for dissociation of pentacyanoferrates(II): the role of ligand size*

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Many years ago it was found that the volumes of activation for dissociative loss of 3-cyanopyridine and of 3,5-dimethylpyridine from their respective pentacyanoferrate(II) complexes $[Fe(CN)_5(Xpy)]^{3-}$ in aqueous solution were large and positive (Table 1) [1]. This was seen as confirmatory evidence in favour of a limiting dissociative, D or S_N1(lim), mechanism, as earlier proposed for substitution at pentacyanometallates [2]. Since then two more large positive activation volumes have been found for reactions of this type, involving loss of the 4-cyanopyridine or 2-methylpyrazine groups (Table 1) [3]. Also since then doubts have been cast as to the limiting dissociative nature of substitution at pentacyanometallates, particular of cobalt(III) [4, 5]. We remain convinced [6] of the essentially D nature of the ligand loss process from pentacyanoferrates(II) $[Fe(CN)_5L]^{3-}$, especially in the light of the magnitude of the positive $\Delta V^{\neq}$ values. One might expect $\Delta V^{\neq}$ to increase with increasing size of the leaving group, especially in view of the recent report of an exceptionally large $\Delta V^{\neq}$ for base hydrolysis of a particularly bulky cobalt(III) complex [7]. By chance the volumes of the leaving ligands involved in the published $\Delta V^{\neq}$ studies (Table 1) are all rather similar. We were therefore keen to determine $\Delta V^{\neq}$ for some larger leaving groups, to see if there is any correlation of $\Delta V^{\neq}$ with leaving group volume.

Complexes $Na_3[Fe(CN)_5L]\cdot nH_2O$ were prepared for L = pyrazine, 4-phenylpyridine, 4-(1-butylpentyl)-pyridine and *N*-(n-pentyl)pyrazinium (Na_2 salt), from sodium nitroprusside via the ammine and aqua intermediates in the usual manner [1, 3, 6]. Rate constants for reaction of these complexes with cyanide (0.10 mol dm^{-3} KCN(AnalaR)) were measured at atmospheric pressure and at pressures up to 1 kbar using the apparatus and techniques described earlier [8]. As before, the ratio of the rate constant under pressure to that at atmospheric pressure determined concurrently on samples taken from the same reaction mixture was determined each time. The experimental results are reported in Table 1, which also gives activation volumes derived from our experimental results (log k_p/k_o versus P plots are linear within experimental uncertainty, as illustrated in Fig. 1).

The relation between activation volume and leaving ligand size is indicated in Fig. 2. We do not have values for the intrinsic volumes of all the ligands involved, so we have used relative molecular mass, RMM, as the x ordinate in this Figure. This in no way affects the conclusion that there is no correlation of $\Delta V^{\neq}$ with leaving ligand volume. As hinted earlier [1], it is the volume swept out by the leaving ligand on attaining the transition state which is probably a key factor. Both the shape of the leaving group and the percentage extension of the iron–nitrogen bond are thus contributory factors. The latter is likely to be similar for the range of ligands included in Fig. 2, for these pentacyanoferrate(II) complexes are all rather similar in nature, stability and reactivity. However the shape factor needs investigation through, for example, comparisons of activation volumes for quinoline, 4-phenyl and 4-t-butylpyridine as leaving groups. These ligands have very similar volumes, but quinoline subtends a much larger angle at the iron (Fig. 3(a) versus (b)). Complementarily, pyridine and 4-phenylpyridine would sweep out very similar volumes on leaving (Fig. 3(b) and (c)), despite their volume difference. The other factor which may well distort any attempted correlation of $\Delta V^{\neq}$ with intrinsic or swept-out volume is solvation. This is more difficult to prove, since partial molar volumes for substituted pyridine (or amine) ligands will be dominated by hydration of the donor nitrogen atoms – which are, of course, not free for hydration when complexed to an $Fe(CN)_5{}^{3-}$ moiety. Solvation effects, believed to be relatively small in methanol–water mixtures [3] but significant in aqueous mixtures containing other cosolvents such as acetone [9], can be probed through comparisons such as pyridine versus pyrazine, 4-cyano- versus 4-methylpyridine, or 4-phenylpyridine versus 4,4′-bipyridyl as leaving groups, or through the effect of change of medium on observed activation volume [10].

The main conclusion, of a dramatic lack of correlation between activation volume and leaving ligand

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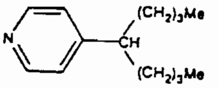
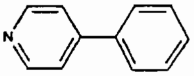
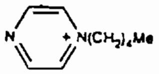
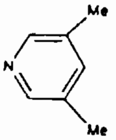
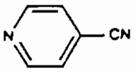
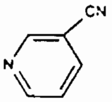
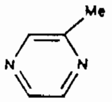
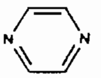
TABLE 1. Ratios of rate constants under high pressure and at one atmosphere (k_p/k_o), and derived activation volumes, for substitution at pentacyanoferrates(II), $[Fe(CN)_5L]^{3-}$, in aqueous solution at 298.2 K

L	RMM of L	k_p/k_o at P (kbar) =					ΔV^{*} (cm^3 mol^{-1})
		0.35	0.50	0.70	0.75	1.00	
	205		0.70		0.60	0.52	+16[a]
	155	0.87		0.74		0.66	+10
	151		0.85			0.68	+10
	107						+21[b]
	104						+21[c]
	104						+21[b]
	94						+19[c]
	80	0.83		0.71		0.60	+13

[a]In 20% MeOH (solubility difficulties in water). [b]From ref. 3. [c]From ref. 1.

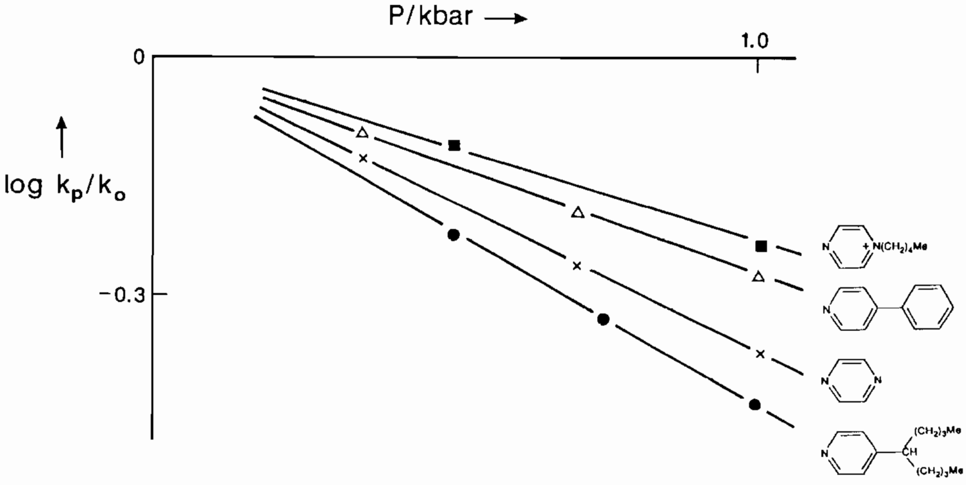


Fig. 1. Dependence of log(k_p/k_o) on pressure for substitution at $[Fe(CN)_5L]^{3-}$ anions, with L as specified (●, in 20% MeOH; others in water; all at 298.2 K).

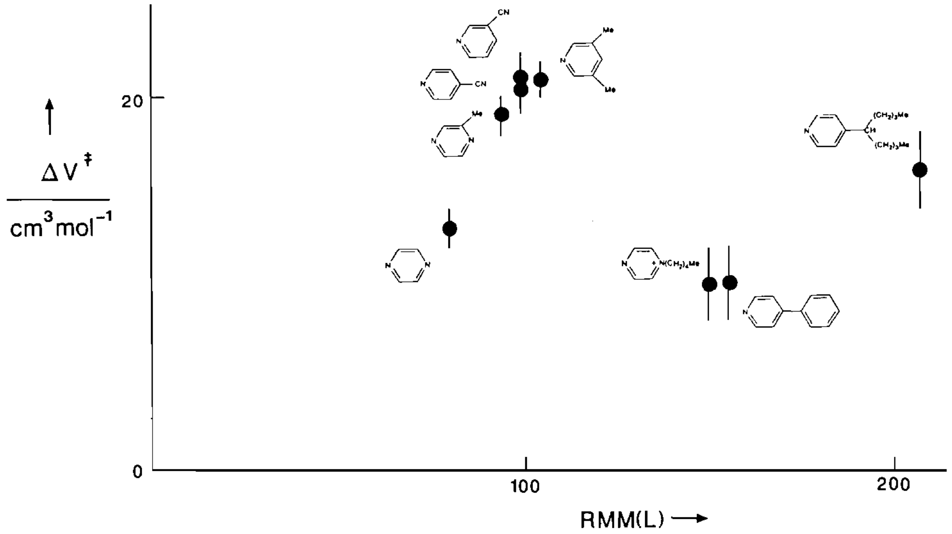


Fig. 2. Relation between activation volumes for dissociative substitution at substituted pyridine and pyrazine complexes $[Fe(CN)_5L]^{3-}$ and RMM of the respective ligands.

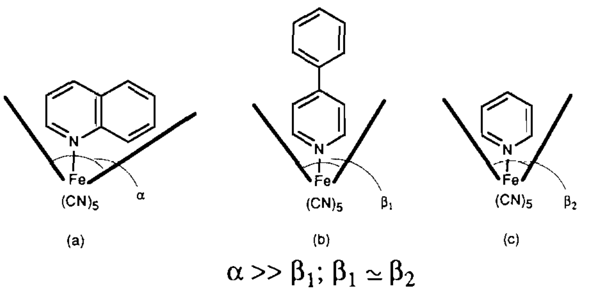


Fig. 3. Significance of ligand shape.

volume for simple dissociation of a series of pentacyanoferrates(II), is clear. Understanding the reasons for the observed pattern will require many more experimental results, as is apparent from the likely contributing factors enumerated in the preceding paragraph.

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