Volumes of Activation for Dissociative (*D*) Mechanisms: The Substitution of Pentacyanoferrate(II) Complexes by Various Nucleophiles

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The dissociative step of a dissociative, or *D*, substitution mechanism exhibits a volume of activation, $\Delta V_1^‡$, which is independent of the nature of the incoming nucleophile. For the reaction of $[Fe(CN)_5(3,5Me_2\text{-py})]^{3-}$ ($3,5Me_2$-py = 3,5-dimethylpyridine) with $[CN]^-$, $\Delta V_1^‡ = 20.5 \pm 0.8$ cm^3 mol^{-1}; with pyrazine, $\Delta V_1^‡ = 21.2 \pm 1.0$ cm^3 mol^{-1}; and with imidazole, $\Delta V_1^‡ = 20.3 \pm 1.0$ cm^3 mol^{-1}. For the reaction of $[Fe(CN)_5(3CN\text{-py})]^{3-}$ (3CN-py = 3-cyanopyridine) with $[CN]^-$, $\Delta V_1^‡ = 20.6 \pm 0.5$ cm^3 mol^{-1}. These volumes of activation are shown to correspond to stretching of the Fe–N bond in the activated complex from 65 to 88% of the distance corresponding to complete dissociation of the leaving group from the $[Fe(CN)_5]^{3-}$ moiety.

THE dissociative, or *D*, mechanism for substitution of a six-co-ordinate complex $[ML_5X]$ by a nucleophile Y may be written in the generalised scheme (1) and (2) in which

$$[ML_5X] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [ML_5] + X \qquad (1)$$

$$[ML_5] + Y \xrightarrow{k_3} [ML_5Y] \qquad (2)$$

the reverse of reaction (2) is assumed to be negligible. The intermediate $[ML_5]$ is considered to persist as a species of reduced co-ordination number which exhibits distinctive reactivities towards different nucleophiles. Alternatively, $[ML_5]$ may rapidly equilibrate with a strongly interacting solvent, such as water, to form a complex $[ML_5(\text{solvent})]$ whose reactivity may be measured independently in favourable cases.

When the substitution reaction is conducted with an excess of Y then a steady-state treatment of reactions (1) and (2) shows that the observed first-order rate coefficient $k_{\text{obs.}}$ is described by the function (3). Equation (3) provides a set of kinetic criteria which may be applied to assess a possible *D* mechanism, as follows.

$$k_{\text{obs.}} = k_1k_3[Y]/(k_2[X] + k_3[Y]) \qquad (3)$$

(1) At low [Y], $k_{\text{obs.}}$ is linearly dependent on [Y] but, with increasing [Y], ultimately attains a limiting value of the rate-determining step k_1. However, an ion-pair interchange mechanism also exhibits the same func-

tional dependence on [Y]. It is also important, especially for charged nucleophiles, to establish that the limiting value of $k_{\text{obs.}}$ is not influenced by changes in the nature of the reaction medium at high [Y].

(2) The observed limiting rate coefficient, k_1, should have a value which is independent of the nature of the nucleophile Y; this may be tested directly with a variety of nucleophiles. Nevertheless, it is possible that equality of k_1 values for different nucleophiles could arise because the reaction temperature is an isokinetic temperature. Compensatory changes in $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ are rarely investigated for *D* mechanisms.

(3) At a constant concentration of X, $1/k_{\text{obs.}}$ should be linearly dependent on $1/[\text{Y}]$ and, assuming a *D* mechanism, this enables the reactivity ratio (discrimination) of $[\text{ML}_5]$ for X and Y, $k_2 : k_3$, to be evaluated. This ratio should vary with the chemical nature of different nucleophiles.

(4) For the special case where X = solvent, then the limiting rate coefficient k_1 should equal the rate coefficient for solvent exchange, k_{ex}.

These criteria establish the independent kinetic character of the intermediate $[\text{ML}_5]$ but provide little information on the detailed mechanism of the dissociative step, k_1. In principle, this information could be provided by the additional criterion (5).

(5) The limiting dissociation rate coefficient k_1 should exhibit values of $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ which are independent of the nature of the nucleophile Y. The nature and charge of the leaving group X will influence the sign and magnitude of $\Delta S_1^{\ddagger}$ and $\Delta H_1^{\ddagger}$.

Criteria (1)—(4) were first applied [1-3] in aqueous systems to the substitution of $[\text{Co(CN)}_5(\text{OH}_2)]^{2-}$ by a variety of anionic and nitrogen nucleophiles. A range of reactivity ratios was established and the approximate equality of k_1 and k_{ex} was demonstrated. Subsequently *D* mechanisms have been proposed for substitutions of both sulphito-complexes of cobalt(III) [4-6] and of $[\text{RhCl}_5(\text{OH}_2)]^{2-}$,[7] and the evidence has been reviewed.[8]

Criterion (5) has been applied [9] to the reactions of aromatic nitrogen heterocycles, L, with $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ [equation (4)] but limiting dissociation conditions were not achieved.

$$[\text{Fe(CN)}_5(\text{OH}_2)]^{3-} + \text{L} \longrightarrow [\text{Fe(CN)}_5\text{L}]^{3-} + \text{H}_2\text{O} \quad (4)$$

The second-order rate coefficients varied from 296 to 550 dm^3 mol^{-1} s^{-1} whilst $\Delta H^{\ddagger}$ values varied from 63.2 to 70.3 kJ mol^{-1} and $\Delta S^{\ddagger}$ varied from 17 to 42 J K^{-1} mol^{-1}. Limiting rates have been established for the related substitution by the 4-methylpyrazinium cation ($[\text{mpz}^+]$) of a variety of pentacyanoferrate(II) complexes of six different nitrogen heterocycles [equation (5)] for which $\Delta S_1^{\ddagger}$ varied from 36 to 72 J K^{-1} mol^{-1} depending on the nature of the leaving group L. The attainment of a limiting rate, and the positive values of $\Delta S^{\ddagger}$ for neutral leaving groups, constitute good evidence for a *D* mechanism.

$$[\text{Fe(CN)}_5\text{L}]^{3-} + [\text{mpz}]^{+} \longrightarrow [\text{Fe(CN)}_5(\text{mpz})]^{2-} + \text{L} \quad (5)$$

We now propose an additional criterion for the assessment of a *D* mechanism.

(6) For an uncharged leaving group, the volume of activation $\Delta V_1^{\ddagger}$ for the limiting dissociative step should have a positive value which is independent of the nature of the incoming nucleophiles.

We further propose that a knowledge of $\Delta V_1^{\ddagger}$ should enable the deduction of structural details of the activated complex for the limiting dissociative step. For this step the configuration of the activated complex should be one in which the M–X bond is stretched and the leaving group X protrudes further into the solvent, sweeping out an additional volume $V_{\delta\text{X}}^{\ddagger}$. The partial molar volume of the complex $[\text{ML}_5\text{X}]$ can be visualized as made up of partial molar volume contributions from the $[\text{ML}_5]$ moiety (V_{ML_5}) and the ligand X(V_{X}). The dissociative reaction may then be represented in volume terms in the following manner:

$$\begin{array}{ccc} [\text{ML}_5\text{X}] & \rightleftharpoons & [\text{ML}_5 \cdots \text{X}]^{\ddagger} \\ (V_{\text{ML}_5} + V_{\text{X}}) & & (V_{\text{ML}_5}^{\ddagger} + V_{\text{X}}^{\ddagger} + V_{\delta\text{X}}^{\ddagger}) \end{array}$$

Thus we can write equation (6).

$$\Delta V_1^{\ddagger} = (V_{\text{ML}_5}^{\ddagger} + V_{\text{X}}^{\ddagger} + V_{\delta\text{X}}^{\ddagger}) - (V_{\text{ML}_5} + V_{\text{X}}) \quad (6)$$

In the interpretation of $\Delta V_1^{\ddagger}$, it is fruitful to compare the volume terms V_{ML_5} with $V_{\text{ML}_5}^{\ddagger}$, and V_{X} with $V_{\text{X}}^{\ddagger}$. We have already shown [10] that, for metal complexes having central charges of 2+ and 3+ and metal–ligand bond distances ranging from 200 to 240 pm, the compressibilities of such complexes should fall in the range 0.90×10^{-6}—2.8×10^{-6} bar^{-1}.* In the dissociative limit, the moiety $[\text{ML}_5]$ in the activated complex could be entirely independent of X and it could then assume a five-co-ordinate configuration. Our calculated compressibilities establish that the intrinsic volume of a five-co-ordinate species with an unoccupied sixth site should be only 0.1 cm^3 mol^{-1} less than the intrinsic volume of the species $[\text{ML}_5]$ constrained in a six-co-ordinate configuration. We can thus set $V_{\text{ML}_5} = V_{\text{ML}_5}^{\ddagger}$ to a maximum uncertainty which is less than the likely experimental error in $\Delta V_1^{\ddagger}$ ($\geqslant +0.5$ cm^3 mol^{-1}). Similarly, our force-constant calculations [11] show that the compressibility of an isolated ligand, such as X, is negligible, so that $V_{\text{X}} = V_{\text{X}}^{\ddagger}$. We may therefore

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* Throughout this paper: 1 bar = 10^5 Pa; 1 atm = 101 325 Pa.

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simplify equation (6) to the form (7). If X is assigned an effective cross-sectional area A_X and the M–X bond is extended in the transition state a distance Δl, then the excluded volume [11,12] will simply be (8). This analysis

$$\Delta V_1^{\ddagger} = V_{\delta X}^{\ddagger} \qquad (7)$$

$$\Delta V_1^{\ddagger} = V_{\delta X}^{\ddagger} = A_X \Delta l \qquad (8)$$

does not allow for secondary solvation effects and for our present purpose we exclude charged leaving groups for which additional considerations of electrostriction will apply.

In order to test our criterion (6) based on $\Delta V_1^{\ddagger}$ values we selected for study the substitution reactions (9) [3,5Me$_2$-py = 3,5-dimethylpyridine, Y = CN$^-$, pyrazine (pz), or imidazole (imH)] and (10) (3CN-py = 3-cyanopyridine). The detailed substitution kinetics of reac-

$$[\mathrm{Fe(CN)_5(3,5Me_2\text{-}py)}]^{3-} + \mathrm{Y}^{n-} \longrightarrow [\mathrm{Fe(CN)_5Y}]^{(3+n)-} + \mathrm{3,5Me_2\text{-}py} \qquad (9)$$

$$[\mathrm{Fe(CN)_5(3CN\text{-}py)}]^{3-} + [\mathrm{CN}]^- \longrightarrow [\mathrm{Fe(CN)_6}]^{4-} + \mathrm{3CN\text{-}py} \qquad (10)$$

tions (9) and (10) have already been established [13] and both substrates attain a single, characteristic, limiting dissociation rate at nucleophile concentrations exceeding 0.003 mol dm^{-3}. All the substitution reactions proceed to completion with excess of nucleophile and exhibit excellent first-order rate characteristics. In addition, studies with a comprehensive range of mixed solvents show [13] that the dissociation rate k_1 is relatively insensitive to solvent composition, and specific interactions of solvent molecules with the heterocyclic leaving group are likely to be small. The nucleophiles in reactions (9) and (10) were selected to exemplify different charge types, size, and stereochemistry whilst the two leaving groups are of different geometric and electronic characteristics.

EXPERIMENTAL

Reagents.—The salts Na$_3$[Fe(CN)$_5$(3,5Me$_2$-py)] and Na$_3$[Fe(CN)$_5$(3CN-py)] were prepared by published methods;[14] they analysed satisfactorily {Found: C, 33.5; H, 3.65; N, 19.8; O, 13.0. Na$_3$[Fe(CN)$_5$(3,5Me$_2$-py)]·3.5H$_2$O requires C, 33.9; H, 3.80; N, 19.8; O, 13.2. Found: C, 30.2; H, 2.80; Fe, 13.1; N, 23.0. Na$_3$[Fe(CN)$_5$(3CN-py)]·4H$_2$O requires C, 30.6; H, 2.80; Fe, 13.0; N, 22.7%}. Provided the preparations were used within 6 weeks of their initial synthesis, reproducible kinetic behaviour was exhibited. Sodium cyanide, pyridine, pyrazine, imidazole, and sodium perchlorate were AnalaR grade materials and were used without further purification.

Kinetic Procedures.—Kinetic runs at atmospheric pressure were conducted in 1-cm silica cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. The kinetic runs were monitored at 360 {[Fe(CN)$_5$(3,5Me$_2$-py]$^{3-}$} and 410 nm {[Fe(CN)$_5$(3CN-py)]$^{3-}$}. Rate constants were computed (PDP 11) from the observed variation of optical absorbance using a standard least-mean-squares program.

Kinetic runs at high pressure were conducted in a 1-cm cell inside a specially designed [15] high-pressure optical cell fitting in the cell compartment of a Varian 635 D recording spectrophotometer. The two reactant solutions were placed in the two separate compartments of a simple diaphragm mixer within the optical cell. After temperature equilibration had been established the two solutions were rapidly mixed (1 s), and the high-pressure cell was sealed and then pumped to the desired pressure. The temperature increase due to pressurization, monitored by a platinum resistance element inside the pressure cell, was dissipated within 2—3 min. Usually, 10 min were allowed for complete temperature equilibration and stability in kinetic behaviour. The reaction was then monitored at 370 nm for 2—3 reaction half-times ($t_{\frac{1}{2}}$ varied from 10 to 30 min) and first-order rate constants were computed (Cyber 6400) using a standard least-mean-squares program.

RESULTS

Earlier studies [13] demonstrated that, for the substitution of both [Fe(CN)$_5$(3,5Me$_2$-py)]$^{3-}$ and [Fe(CN)$_5$(3CN-py)]$^{3-}$ by [CN]$^-$, limiting first-order dissociation rates were attained at cyanide concentrations >0.003 mol dm^{-3}. For the former complex, $k_{obs.} = (1.31 \pm 0.04) \times 10^{-3}$ s^{-1} over the range [CN$^-$] = 0.003—0.024 mol dm^{-3}. The value determined in the pressure vessel at atmospheric pressure and at [CN$^-$] = 0.05 mol dm^{-3} was $k_{obs.} = (1.33 \pm 0.04) \times 10^{-3}$ s^{-1}. For the [Fe(CN)$_5$(3CN-py)]$^{3-}$ anion, $k_{obs.} = (2.15 \pm 0.08) \times 10^{-3}$ s^{-1} over the range [CN$^-$] = 0.003—0.021 mol dm^{-3} compared to the value determined in the pressure vessel at atmospheric pressure, $k_{obs.} = (2.06 \pm 0.06) \times 10^{-3}$ s^{-1} at [CN$^-$] = 0.05 mol dm^{-3}. The agreement between values determined in quite distinct experimental facilities (the atmospheric pressure runs at Leicester and the runs in the pressure vessel at Melbourne) is thus very satisfactory. For all the pressure measurements, constant nucleophile concentrations of 0.05 mol dm^{-3} were used throughout the series.

TABLE 1

First-order rate coefficients, $10^3 k_{obs.}$/s^{-1},* for reactions of [Fe(CN)$_5$(3,5Me$_2$-py)]$^{3-}$ with various nucleophiles (Y) in aqueous solution at 298 K and at various pressures; initial [complex] = 0.004 mol dm^{-3}, [Y] = 0.05 mol dm^{-3}, and I=0.5 mol dm^{-3} (maintained with sodium perchlorate)

L	Pressure/bar				
	1	345	690	1 034	1 379
[CN]$^-$	1.33 ±0.04 (6)	0.96 ±0.02 (3)	0.71 ±0.02 (4)	0.515 ±0.015 (3)	0.41 ±0.02 (5)
pz	1.27 ±0.03 (6)	0.90 ±0.03 (3)	0.70 ±0.02 (4)	0.515 ±0.02 (3)	0.39 ±0.01 (5)
imH	1.25 ±0.03 (4)	0.94 ±0.03 (3)	0.71 ±0.02 (4)	0.520 ±0.025 (3)	0.40 ±0.02 (3)

* Figures in parentheses are the number of separate determinations of $k_{obs.}$; errors quoted are standard deviations of the mean.

In Table 1, values of $k_{obs.}$ are recorded at five different pressures for the substitution of [Fe(CN)$_5$(3,5Me$_2$-py)]$^{3-}$ by three different nucleophiles, [CN]$^-$, pyrazine, and imidazole. At any given pressure, the value of $k_{obs.}$ is constant, within

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experimental error, irrespective of the nature of the nucleophile. This confirms the earlier kinetic evidence[13] for a *D* mechanism.

The volume of activation, $\Delta V^\ddagger$, for these substitutions was evaluated from relation (11) which assumes that $\Delta V^\ddagger$ is

$$(\partial \ln k_{\text{obs.}}/\partial P)_T = -\Delta V^\ddagger/RT \qquad (11)$$

itself pressure independent. Figure 1 illustrates the pressure variation of $-\log_{10}(k_P/k_{0.001})$ for the three nucleophiles and each of the plots shows a high degree of linearity.

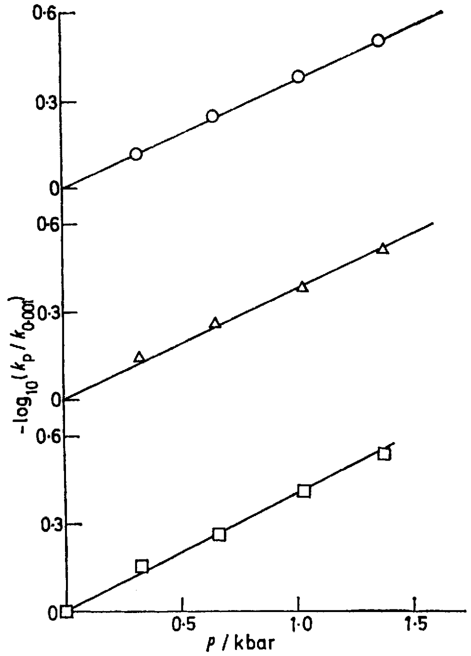

FIGURE 1 Variation of first-order rate coefficients with pressure for reactions of $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$ with imH (○), pz (△), and $[CN]^-$ (□) in aqueous solutions at 298 K; initial [complex] = 0.004 mol dm^{-3}, [nucleophile] = 0.05 mol dm^{-3}, I = 0.5 mol dm^{-3} ($Na[ClO_4]$)

We conclude that the compressibility coefficient of activation, $\Delta\beta^\ddagger = -(\partial\Delta V^\ddagger/\partial P)_T$, is zero within experimental error. This is to be expected for a neutral leaving group since finite values of $\Delta\beta^\ddagger$ usually arise in reactions involving solvent electrostriction by newly generated ions.[10] The gradients of the three plots in Figure 1 are virtually identical and the corresponding $\Delta V^\ddagger$ values (Table 3) all fall close to a mean value of 20.7 ± 0.9 cm^3 mol^{-1}.

TABLE 2

First-order rate coefficients,* $10^3k_{\text{obs.}}/\text{s}^{-1}$, for reaction of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ with $[CN]^-$ in aqueous solution at 298 K and at various pressures; initial [complex] = 0.004 mol dm^{-3}, $[CN^-]$ = 0.05 mol dm^{-3}, and I = 0.5 mol dm^{-3} ($Na[ClO_4]$)

P/bar	1	345	690	1 034	1 379
$10^3k_{\text{obs.}}$/ s^{-1}	2.06 ±0.06 (5)	1.53 ±0.05 (4)	1.13 ±0.04 (4)	0.87 ±0.03 (4)	0.65 ±0.03 (4)

* The number of separate determinations of $k_{\text{obs.}}$ is given in parentheses; errors quoted are standard deviations of the mean.

Values of $k_{\text{obs.}}$ for substitution of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ by $[CN]^-$ are listed in Table 2 for five different pressures. The value of $k_{\text{obs.}}$ at any given pressure for this substrate anion is different from that observed for the $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$ substrate anion, as is to be expected for different leaving groups in a general *D* mechanism. The value of $\Delta V^\ddagger$ for the $[CN]^-$ substitution of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ was deduced using equation (11) and Figure 2 shows the excellent linearity of the plot of log $(k_P/k_{0.001})$ against pressure, and thus the pressure independence of $\Delta V^\ddagger$ itself. The value, $\Delta V^\ddagger$ = 20.6 ± 0.5 cm^3 mol^{-1}, found for this reaction is identical with the mean value recorded for substitution of $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$ by three different nucleophiles (Table 3).

TABLE 3

Volumes of activation, $\Delta V^\ddagger$/cm^3 mol^{-1},* for reactions of $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$ and $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ with various nucleophiles at 298 K and at I = 0.5 mol dm^{-3} ($Na[ClO_4]$)

Reactants		$\Delta V^\ddagger$/cm^3 mol^{-1}
$[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$	+ $[CN]^-$	20.5 ± 0.8
	+ pz	21.2 ± 1.0
	+ imH	20.3 ± 1.0
$[Fe(CN)_5(3CN\text{-}py)]^{3-}$	+ $[CN]^-$	20.6 ± 0.5

* Errors quoted are standard deviations.

The temperature variation of $k_{\text{obs.}}$ at 1 atm pressure was established for the reactions of the $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$ and $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ anions with cyanide in aqueous solution. For each reaction two independent series of runs were conducted at potassium cyanide concentrations of 0.2, 0.4, and 0.6 mol dm^{-3}, in all cases at an ionic strength of 0.6 mol dm^{-3} at each temperature. Under all conditions, the values of $k_{\text{obs.}}$ at the three cyanide concentrations were equal within experimental error. Mean values of $k_{\text{obs.}}$ for the two substrates are listed in Table 4. For $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ the calculated activation parameters are $\Delta H^\ddagger$ = 93.0 ± 1.3 kJ mol^{-1} and $\Delta S(298)^\ddagger$ = 16.3 ± 4.3 J K^{-1} mol^{-1}, whilst for $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$, $\Delta H^\ddagger$ = 108.0 ± 2.5 kJ mol^{-1} and $\Delta S(298)^\ddagger$ = 58.5 ± 8.4 J K^{-1} mol^{-1}.

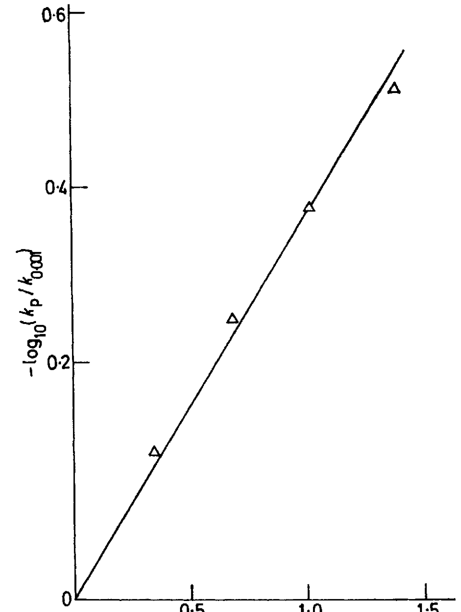

FIGURE 2 Variation of first-order rate coefficient with pressure for reaction of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ with $[CN]^-$ in aqueous solution at 298 K; initial [complex] = 0.004 mol dm^{-3}, $[CN^-]$ = 0.05 mol dm^{-3}, I = 0.5 mol dm^{-3} ($Na[ClO_4]$)

DISCUSSION

A *D* mechanism for the substitution of $[Fe(CN)_5(3,5\text{-}Me_2\text{-}py)]^{3-}$ by various nucleophiles may be written in the form of equations (12) and (13) as already suggested [13] by the attainment of a limiting substitution rate, k_1, at high concentrations of nucleophiles.

TABLE 4

Variation of first-order rate constants, $10^3k_{obs.}/s^{-1}$, with temperature for reaction of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ and of $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$ with cyanide in aqueous solution at atmospheric pressure and at $I = 0.6$ mol dm^{-3} ($K[NO_3]$)

(*a*) $[Fe(CN)_5(3CN\text{-}py)]^{3-}$					
T/K	297.7	302.7	306.4	309.2	314.2
$10^3k_{obs.}/s^{-1}$	2.03	3.92	6.0	8.8	15.3
(*b*) $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$					
T/K	298.6	302.2	305.0	309.2	311.1
$10^3k_{obs.}/s^{-1}$	1.33	2.11	3.4	5.7	7.9

The first major finding in this investigation is that, under conditions where k_1 is rate determining, the step described by k_1 exhibits a large positive volume of activation, $\Delta V^{\ddagger} = 20.7 \pm 0.9$ cm^3 mol^{-1}, irrespective of whether the nucleophiles $[CN]^-$, pyrazine, or imidazole are employed. This finding justifies our proposed criterion (6) for characterizing the dissociative step of a *D* mechanism. The sign and magnitude of $\Delta V^{\ddagger}$ constitutes very strong evidence for the limiting dissociative character of reaction (12) and we show below how this $\Delta V^{\ddagger}$ value may be used to infer structural information on the nature of the activated complex for this step.

The rate coefficient for the dissociative step, k_1, is

$$[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + 3,5Me_2\text{-}py \quad (12)$$

$$[Fe(CN)_5]^{3-} + Y^{n-} \xrightarrow{k_3} [Fe(CN)_5Y]^{(3+n)-} \quad (13)$$

relatively insensitive to the composition of a range of mixed aqueous solvents; [13] the Grunwald–Winstein *m* value is found to be negative (−0.1). This suggests that changes in solvation of the leaving $3,5Me_2$-py group are relatively unimportant in the dissociative step. There remains unresolved, however, whether or not the species $[Fe(CN)_5]^{3-}$ remains five-co-ordinate for a time period in which it can exhibit distinctive kinetic reactivity towards different nucleophiles, as measured by the ratio $k_2' : k_3$. It is possible that the intermediate forms the aqua-species $[Fe(CN)_5(OH_2)]^{3-}$ which is known to undergo substitution [9] at rates which are considerably faster than k_1. Thus James and Murray [16] invoked the intermediate $[Fe(CN)_5(OH_2)]^{3-}$ in the $[CN]^-$ and HCN substitution of $[Fe(CN)_5(py)]^{3-}$. Whilst kinetic criteria alone cannot discriminate between these two possible forms of the intermediate, we incline to the view that $[Fe(CN)_5]^{3-}$ is the reactive form since the reaction is rather insensitive to the nature of the solvent. What can be deduced from the large positive value of $\Delta V^{\ddagger}$ is that water, as a nucleophile, is not involved in the step k_1.

The volume of activation for the k_1 step may be visualized as arising primarily from the stretching of the Fe–N bond to form the transition state with the $3,5Me_2$-py leaving group sweeping out a consequential volume in the surrounding solvent. The $[Fe(CN)_5]^{3-}$ moiety may simultaneously rearrange to a distorted square pyramid but it will be assumed that this would involve only changes in bond angles, and not bond lengths, with no consequential volume change.

Figure 3 presents a scale representation of the proposed activated complex for reaction of $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$ in which the component atoms have been assigned their usual covalent and van der Waals radii. In the ground state, substituents in the 3, 4, and 5 positions of the heterocycle should be in contact with solvent and the two methyl groups will be surrounded by solvent molecules. When the $3,5Me_2$-py group moves out to form the transition state the solvent should be able to adapt to the motion of the two methyl groups; the volume vacated as the methyl groups move out should be occupied by solvent molecules and no net volume change should occur from the methyl motion. The volume swept out by the $3,5Me_2$-py leaving group should therefore arise from motion of the 1, 2, and 6 substituents out into the solvent. The $3,5Me_2$-py ring may be assigned [17] a thickness of 370 pm and the width is defined effectively by the extremities of the 2,6 hydrogen atoms, namely 670 pm (distance *b* in Figure 3). If the Fe–N bond extension in the transition state is Δl(pm), then $\Delta V^{\ddagger} = 10^{-30} N_A \times 370 \times 670 \times \Delta l = 20.7$, hence $\Delta l = 139$ pm and the Fe–N bond is stretched from 197 pm in the ground state to 336 pm in the transition state. Complete separation of the Fe and N atoms may be

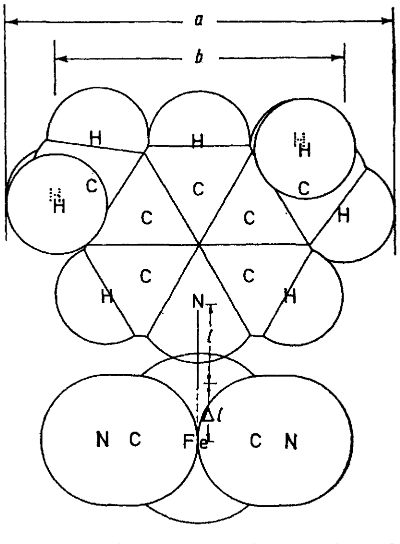

FIGURE 3 Representation to scale of the activated complex for the dissociative reaction of $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$. l = Ground-state Fe–N distance = 195 pm; Δl = Fe–N bond extension (139 pm) to generate the activated complex assuming dimension *b*. Extremities of complex are a = 910 pm and b = 670 pm (see text)

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[16] A. D. James and R. S. Murray, *J.C.S. Dalton*, 1975, 1530.

[17] L. Pauling, ' Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, ch. 7.

taken [18] to be reached when the two atoms are separated by a distance equal to the sum of their respective van der Waals radii, *i.e.* 205(Fe) + 150(N) = 335 pm. Consequently this simplified structural model suggests that in the transition state the Fe–N bond is elongated to 139/158 or *ca.* 88% of the distance required to effect complete dissociation of the N-heterocycle from the Fe atom. On the other hand, if the effective width of the 3,5Me$_2$-py group were taken to be the distance apart of the 3- and 5-methyl groups (910 pm, distance *a* in Figure 3) then Δl = 102 pm and the percentage Fe–N bond extension would still be 65% of that required for complete Fe–N bond rupture. From either estimate, the bond extension to form the activated complex is very substantial.

Stretching of the Fe–N bond to 339 pm in the transition state still does not create a gap large enough for a solvent water molecule, diameter 276 pm, to approach the Fe atom close enough to effect bonding. Any slightly increased solvation of the transition state, as suggested by mixed-solvent studies, should occur in the neighbourhood of the five negative cyano-groups of the $[Fe(CN)_5]^{3-}$ moiety. This solvation may accompany rearrangement of the $[Fe(CN)_5]^{3-}$ to a distorted square pyramid and could make a small negative volume contribution to $\Delta V^\ddagger$. In this sense, the estimate of the Fe–N bond elongation in the transition state may be an underestimate but the nature of the approximations involved does not justify further consideration. Nevertheless, it does seem significant that for this step in the *D* mechanism, which generates a kinetically recognizable intermediate, the leaving group is almost completely free in the activated complex. In our earlier study [18] of aquation of $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline), which is dissociative in character but is probably best described as reacting through an I_d mechanism, since no intermediate is kinetically recognizable, the Fe–N bond extension was estimated as 39% of the distance required for complete Fe–N dissociation.

It is interesting to compare the estimated bond elongation in transition-state formation for the iron(II) complex with that in model dissociative reactions of organometallic and organic substrates. In the demercuration reactions [19] of $[HgR]^+$ ions, in which the neutral mercury atom is visualized as the leaving group, bond elongations of 160 and 230 pm have been estimated for R = Et and Pr^i respectively. Since van der Waals radii are usually *ca.* 80 pm greater than covalent radii for most atoms, these bond elongations are close to 100% of the van der Waals sum of the Hg and C atoms. Similarly, in the unimolecular elimination of trialkylsulphonium halides,[20] in which desolvation by dispersal of charge is believed to be unimportant, the C–S bond is calculated to undergo a bond elongation of 100 pm or *ca.* 63% of the distance for complete carbon–sulphur bond rupture. The dissociative trialkyl phosphite substitution of carbonyls of Ni, Mo, and Cr is estimated [21] to involve bond elongations of 140, 170, and 270 pm representing 60, 72, and 100% of the distance necessary for metal–carbon bond rupture. A corresponding estimation [22,23] for solvolysis of t-butyl chloride is complicated by the charge separation in the activated complex and the consequent electrostriction changes. However, such estimates and guesses of bond elongation that have been made for other reactions are usually much less than the 65–88% bond stretch estimated for our *D* [or S_N1(lim.)] reaction.

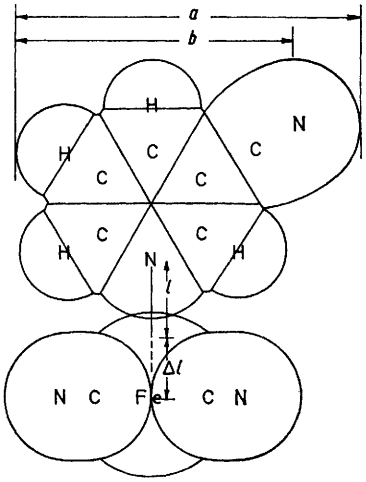

FIGURE 4 Representation to scale of the activated complex for the dissociative reaction of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$. l = Ground-state Fe–N distance (195 pm); Δl = Fe–N bond extension (137 pm) to generate activated complex assuming dimension *b*. Extremities of complex are *a* = 840 pm and *b* = 670 pm (see text)

The second major finding in this investigation is that the volume of activation for the dissociative reaction of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ with $[CN]^-$ is identical (20.6 ± 0.5 cm^3 mol^{-1}) to that observed (20.5 ± 0.8 cm^3 mol^{-1}) for $[CN]^-$ reaction with $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$. The former complex anion reacts 55% faster at 298 K than the latter anion under identical conditions and the overall structural dimensions of 3CN-py differ significantly from 3,5-Me$_2$-py (Figure 4). However, in the structural model discussed above it was concluded that substituents in the 3, 4, and 5 positions do not contribute effectively to any volume increase as the heterocycle moves out into the solvent to generate the transition state. The volume change was attributed to motion of the 2 and 6 substituents as the Fe–N bond is stretched. In this respect, 3CN-py is equivalent in its dimensions to 3,5Me$_2$-py (*b* = 670 pm, Figure 4). The equal $\Delta V^\ddagger$ values can therefore be attributed to an equal stretching of the Fe-N bond from 197 pm in the ground state to 336 pm in the transition state. On the other hand, if the dimension *a* = 910 pm (Figure 4) is assigned to the effective width of the 3CN-py group, then Δl = 110 pm which is 70% of the distance required for complete iron-nitrogen bond rup-

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[18] J.-M. Lucie, D. R. Stranks, and J. Burgess, *J.C.S. Dalton*, 1975, 245.

[19] K. R. Brower, B. Gray, and T. K. Konkol, *J. Amer. Chem. Soc.*, 1966, **88**, 1681.

[20] K. R. Brower and J. S. Chan, *J. Amer. Chem. Soc.*, 1965, **87**, 3396.

[21] K. R. Brower and T. Chan, *Inorg. Chem.*, 1973, **12**, 2198.

[22] K. R. Brower, *J. Amer. Chem. Soc.*, 1963, **85**, 1401.

[23] E. Whalley, *Ann. Rev. Phys. Chem.*, 1967, **18**, 205.

ture. Thus both $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$ and $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ substitute through a *D* mechanism involving stretching of the Fe–N bond by *ca.* 65—88% of that required for complete dissociation.

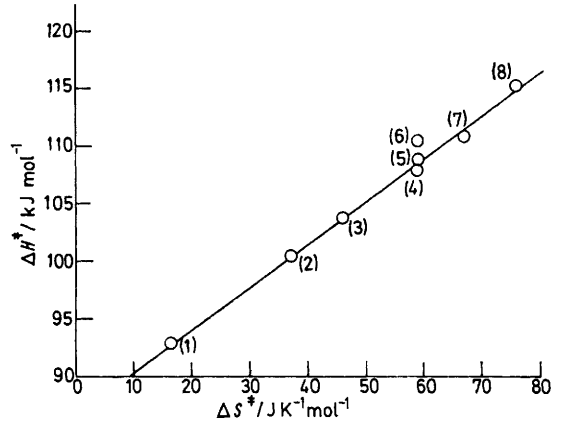

FIGURE 5 Isokinetic plot for the general reaction $[Fe(CN)_5L]^{3-} + Y \longrightarrow [Fe(CN)_5Y]^{3-} + L$. Leaving group, L: 3CN-py (1) (this work); 4Me-py (2); py (3); $3,5Me_2$-py (4) (this work); $C_5H_4NCONH_2$-4 (5); pz (6); 4,4′-bipyridyl (7); and $[mpz]^+$ (8). Unless otherwise stated, the data are from ref. 14

Although the structural model used here to interpret $\Delta V^{\ddagger}$ values is necessarily a very simplified one, it does enable a more incisive picture of the activated complex to be drawn than that possible with corresponding $\Delta S^{\ddagger}$ values. Whereas $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$ and $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ exhibit virtually identical $\Delta V^{\ddagger}$ values, the $\Delta S^{\ddagger}$ values (58.5 ± 8.4 and 16.3 ± 4.3 J K^{-1} mol^{-1} respectively) differ significantly. It seems likely that these $\Delta S^{\ddagger}$ values reflect important contributions from the solvent since Figure 5 shows that these two substrates, together with the pentacyanoiron(II) substrates studied by Toma and Malin, exhibit an isokinetic relation with a gradient of 378 ± 18 K. Changes in $\Delta H^{\ddagger}$ are largely compensated by changes in $\Delta S^{\ddagger}$ and this phenomenon is often attributed to solvent-interaction effects.[24] For example, the onset of extra rotational modes of solvent molecules in close proximity to the $[Fe(CN)_5]^{3-}$ and heterocycle moieties would make positive contributions to $\Delta S^{\ddagger}$; no corresponding contribution would be made to $\Delta V^{\ddagger}$. It is significant that the two substrates in the present study involve a wide separation in the plot of $\delta(\Delta H^{\ddagger})$ against $\delta(\Delta S^{\ddagger})$ yet exhibit virtually identical $\Delta V^{\ddagger}$ values.

We conclude therefore that a knowledge of $\Delta V^{\ddagger}$ for a dissociative mechanism provides not only a useful test for the generation of a dissociated intermediate but it also enables some conclusions to be drawn as to the structure of the activated complex for the dissociative process. The interpretation of $\Delta S^{\ddagger}$ in terms of mechanism is likely to be complicated by solvent-interaction effects.

[6/2096 *Received*, 15*th November*, 1976]

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[24] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2198.