Coordination Chemistry Reviews, 114 (1992) 269–295
Elsevier Science Publishers B.V., Amsterdam

High-pressure mechanistic studies on thermal and photochemical reactions of pentacyanoferrate complexes

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(Received 20 August 1991)

CONTENTS

ABBREVIATIONS

A^{2-}	ascorbate dianion
$B_{12}H_2O^+$	aquocobalamin
$B_{12}py^+$	pyridinecobalamin
bipy	2,2′-bipyridine
CMP	cytidine-5′-monophosphate
3CNpy	3-cyanopyridine
4CNpy	4-cyanopyridine
cyt	cytochrome c
DMF	dimethylformamide
DMSO	dimethylsulphoxide
ein	ethylenediimine
en	ethylenediamine

0010-8545/92/$15.00

EtOH	ethanol
$glut^-$	glutathione anion
GSH	glutathione
GSSG	diglutathione
H_2A	L-ascorbic acid
HA^-	ascorbate anion
HRP	horseradish peroxidase
HRP comp.II	horseradish peroxidase compound II
Me_2bsb	Schiff base of 2-benzoylpyridine and 3,4-dimethylaniline
Me_2py	dimethylpyridine
$3,5Me_2py$	3,5-dimethylpyridine
2Mepz	2-methylpyrazine
MeOH	methanol
pz	pyrazine
pzc	pyrazinecarboxylate
py	pyridine

A. INTRODUCTION

The most extensively studied transition metal cyano compounds, in terms of the variety of complexes and the range of metal oxidation states, are those of iron. Among them, the pentacyanoferrates(II) and (III) are probably the most suitable for systematic theoretical and applied studies [1–10].

The numerous kinetic investigations involving these complexes have contributed considerably to the understanding of the mechanisms of ligand substitution and electron transfer processes. In the majority of these studies, conventional kinetic techniques were employed, and kinetic data were reported as a function of concentration, pH, ionic strength and solvent composition. Much emphasis was placed on the meaning of the thermal activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ obtained from the temperature dependence of the process. However, all of these data were, in many cases, insufficient to resolve some mechanistic discrepancies and an additional kinetic variable was needed to strengthen the assignment or to distinguish between alternatives.

Over recent years, high-pressure kinetic techniques have been applied with success to the elucidation of the inorganic reaction mechanisms [11–24]. In the same way as temperature-dependence studies describe the energetics of the process, pressure-dependence studies reveal information on the volume profile of the process. The interpretation of activation and reaction volumes of inorganic systems in solution has become a powerful mechanistic tool. It not only assists in the elucidation of the reaction mechanism, but also adds a further dimension to the kinetic parameters such that the suggested mechanism must also account for these effects.

The present manuscript is an attempt to summarize the high-pressure kinetic studies on thermal and photochemical reactions of pentacyanoferrate complexes. It is hoped that a compilation of high-pressure kinetic data for this group of complexes will improve the understanding of the intimate nature of the underlying reactions, illustrate the usefulness of pentacyanoferrate complexes in model kinetic studies and convincingly prove the utility of activation volumes as a mechanistic indicator.

B. ACTIVATION AND REACTION VOLUME

Pressure is a fundamental physical property that influences the value of different thermodynamic and kinetic parameters. The relationships between these parameters and pressure find their origin in the fundamental thermodynamic equation that describes the pressure dependence of a chemical potential, μ_i, of a solute species i in an ideal dilute solution

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i \tag{1}$$

where $\bar{V}_i$ denotes partial molar volume of the species i.

If we consider a chemical reaction of the type

$$\mathrm{A + B \xrightarrow{k} AB} \tag{2}$$

the simplest conceivable mechanism can be formulated according to the transition state theory as follows.

$$\mathrm{A + B \rightleftharpoons (A - - - B)^{\neq} \rightarrow AB} \tag{3}$$

The reaction volume $\Delta\bar{V}$ is then defined by

$$\Delta\bar{V} = \bar{V}_{\mathrm{AB}} - \bar{V}_{\mathrm{A}} - \bar{V}_{\mathrm{B}} \tag{4}$$

and the activation volume $\Delta V^{\neq}$ by

$$\Delta V^{\neq} = \bar{V}_{\neq} - \bar{V}_{\mathrm{A}} - \bar{V}_{\mathrm{B}} \tag{5}$$

The reaction volume may be measured directly by dilatometry or calculated from the partial molar volumes of the reactant and product species determined from density measurements. $\Delta\bar{V}$ can also be obtained from the pressure dependence of the overall equilibrium constant, K, for the reaction studied.

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta\bar{V}}{RT} \tag{6}$$

The volume of activation, $\Delta V^{\neq}$, the difference between the partial molar volumes of the transition state and the reactants, can be determined only from the pressure dependence of the rate constant k

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\neq}}{RT} \tag{7}$$

$\Delta V^{\neq}$ may be positive or negative, depending on whether the reaction is slowed down or accelerated with pressure.

The measured volume of activation $\Delta V^{\neq}$ is usually considered as the sum of two components: an intrinsic part ($\Delta V^{\neq}_{\text{intr}}$), which represents the change in volume due to changes in bond lengths and angles, and a solvation part ($\Delta V^{\neq}_{\text{solv}}$), which represents the volume changes due to electrostriction and other effects acting on the surrounding solvent molecules during the activation process. It is principally the intrinsic contribution that is the mechanistic indicator.

Partial molar, reaction and activation volume data can be combined to construct a reaction volume profile that describes the volume changes that occur along the reaction coordinate. The volume profile and corresponding energy profile based on the transition state theory for reaction (3) can be presented schematically as in Fig. 1(a), (b).

The advantage of the volume profile is the absolute partial molar volume scale employed, i.e. it is known where the initial, transition and final states are, in terms of volume. In contrast, only energy differences ($\Delta H^{\neq}$ and ΔH^0) are available for the energy profile and it is difficult to visualize at what energy level these changes occur.

C. REACTIONS OF PENTACYANOFERRATE COMPLEXES

(i) Ligand substitution reactions

Substitution reactions of the type

$$\mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightarrow \mathrm{ML}_n\mathrm{Y} + \mathrm{X} \tag{8}$$

are generally discussed in terms of a dissociative (D), interchange (I) or associative (A) mechanism, depending on the degree of bonding between M and X, and M and Y in the transition state of the process [25]. If bond making is predominant (A), a significant decrease in molar volume of the reactants is expected in the transition state, compared with a significant increase in volume when bond cleavage is predominant (D). In the case of an interchange process, both bond formation and bond cleavage occur to a varying degree and relatively small volume effects are expected, i.e. slightly negative for an $\mathrm{I_a}$ and slightly positive for an $\mathrm{I_d}$ mechanism. This interpretation is based on considering an intrinsic volume contribution originating from changes in bond lengths and bond angles only, and applies excellently to symmetrical chemical reactions such as solvent exchange processes. Many unsymmetrical substitution reactions are accompanied by major changes in charge distribution, dipole

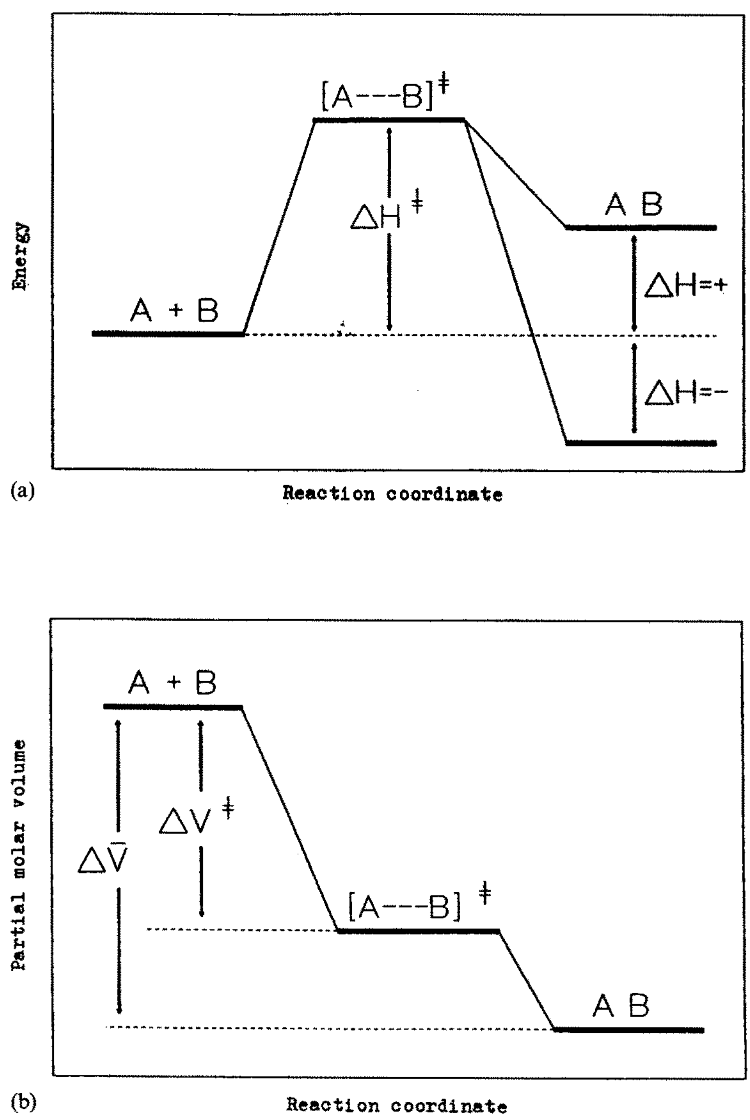


Fig. 1. The energy (a) and volume (b) profile for reaction
$A + B \rightleftharpoons (A - - - B)^{\neq} \rightarrow AB$

moment and dipole–dipole interaction, so that volume changes due to electrostriction effects, i.e. $\Delta V^{\neq}_{\mathrm{solv}}$, must be taken into consideration.

High-pressure kinetic studies of the substitution reactions of pentacyanoferrate complexes include examples of anation, aquation, solvolysis and ligand substitution [26–35].

(a) Anation

During anation reactions, an aquo ligand is replaced by an entering nucleophile. Many such reactions occur according to an interchange mechanism (I) in which the rate-determining step is preceded by ion-pair formation between the reactant species. The experimentally determined volume of activation must then be correlated for the volume change arising from the precursor ion-pair formation step in order to obtain the $\Delta V^{\neq}$ value for the actual interchange step. In a number of anation reactions, the process follows a purely dissociative (D) mechanism and no contribution from $\Delta V^{\neq}_{\mathrm{solv}}$ is then expected since the leaving group (water) is uncharged.

The kinetics of the substitution of coordinated water in $[\mathrm{Fe(CN)_5H_2O}]^{3-}$ at ambient pressure has been studied using a large variety of entering ligands [9]. The rate dependence on the charge of the entering ligand and the lack of a variation in the enthalpies of activation was interpreted as evidence for a dissociative interchange mechanism.

A volume of activation for substitution on $[\mathrm{Fe(CN)_5H_2O}]^{3-}$ has, for the first time, been measured [26] via the thermal recombination of $[\mathrm{Fe(CN)_5H_2O}]^{3-}$ with CN^- following the photoaquation of $[\mathrm{Fe(CN)_6}]^{4-}$. The estimated value of $\Delta V^{\neq} = +13.5 \pm 1.5\ \mathrm{cm\ mol^{-1}}$ is 75% of the molecular volume of water ($18.0\ \mathrm{cm^3\ mol^{-1}}$), and is a strong indication of a D mechanism. For dissociation of a water molecule from the complex, no charge effects are obtained and the five-coordinated activated complex should occupy a similar volume as the stable six-coordinated complex [13]. Kelm and Palmer have pointed out that, due to electrostatic compression around the charged complex ion, the molecular volume of the solvent in the second and third coordination spheres is significantly less than that of the bulk solvent [11,14].

The activation volumes recently found [27] for the anation of $[\mathrm{Fe(CN)_5H_2O}]^{3-}$ by glutathione, imidazole and some amino acids are all significantly positive (Table 1), and once more support the operation of a limiting D mechanism for anation reactions of $[\mathrm{Fe(CN)_5H_2O}]^{3-}$.

Smaller activation volumes, although also positive, have been reported [28,29] for the formation reaction of low spin d^5 pentacyanoferrate(III) complexes with cytosine, cytidine and CMP

$$[\mathrm{Fe^{III}(CN)_5H_2O}]^{2-} + \mathrm{L} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [\mathrm{Fe^{III}(CN)_5L}]^{2-} + \mathrm{H_2O} \tag{9}$$

This difference and the fact that $\Delta V\,(k_f)$ depends significantly on the nature of L (see Table 1) suggests that formation reactions of the studied $[\mathrm{Fe(CN)_5L}]^{2-}$ complexes must probably follow an $\mathrm{I_d}$ (dissociative interchange) mechanism, as outlined in the scheme

$$\begin{tikzcd} {[\mathrm{Fe^{III}(CN)_5H_2O}]^{2-} + \mathrm{L}} \arrow[r, shift left, "K_1"] & \{[\mathrm{Fe^{III}(CN)_5H_2O}]^{2-},\mathrm{L}\} \arrow[l, shift left] \arrow[d, shift right, "k_2"'] \\ & {[\mathrm{Fe^{III}(CN)_5L}]^{2-} + \mathrm{H_2O}} \arrow[u, shift right, "k_{-2}"'] \end{tikzcd} \qquad (10)$$

TABLE 1

Activation parameters for the anation of $Fe(CN)_5H_2O^{n-}$

$Fe(CN)_5H_2O^{n-} + L \rightarrow Fe(CN)_5L^{n-} + H_2O$

n	L	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V^{\neq}$ (25°C) (cm^3 mol^{-1})	Remarks	Ref.
3	CN^-	76.9	+41.8	$+13.5 \pm 1.5$	$\mu = 1.0$ M	26,36
3	glut$^-$	76.1	+54.3	$+14.1 \pm 0.4$	pH = 6.0 $\mu = 0.5$ M	27,37
3	imidazole	63.5	+12.5	$+15.5 \pm 0.7$	$\mu = 0.1$ M	27,38
3	his	64.4^a	+20.9^a	$+17.0 \pm 0.4$	pH = 7.5 $\mu = 0.1$ M	27,38
3	met	69.8^a	+41.8^a	$+17.9 \pm 0.4$	pH = 6.5 $\mu = 0.1$ M	27,38
3	gly$^-$	61.4	+12.5	$+16.4 \pm 0.6$	pH = 11.7 $\mu = 0.1$ M	27,38
3	β-ala$^-$	59.8	+10.0	$+16.8 \pm 0.2$	pH = 11.7 $\mu = 0.1$ M	
2	cytosine	134 ± 6	$+120 \pm 20$	$+3.1 \pm 0.6^b$	pH = 6 $\mu = 0.1$ M	29
2	cytidine	116 ± 10	$+63 \pm 34$	$+4.5 \pm 0.2^b$	pH = 6 $\mu = 0.1$ M	29
2	CMP	97.0 ± 10	$+5 \pm 32$	$+6.3 \pm 1.0^b$	pH = 6 $\mu = 0.1$ M	29

[a] pH = 8–9.

[b] $T = 40$°C.

According to this mechanism, $\Delta V^{\neq}(k_f)$ is a composite quantity, e.g. $\Delta V^{\neq}(k_f) = \Delta \bar{V}(K_1) + \Delta V^{\neq}(k_2)$. It may be reasonable to expect that $\Delta \bar{V}(K_1)$ will be very similar for the different L, such that the variation in $\Delta V^{\neq}(k_f)$ is strongly related to the nature of L. The overall $\Delta \bar{V}(= \Delta V^{\neq}(k_f) - \Delta V^{\neq}(k_d))$ for reaction (9) decreases from approximately zero to -5 and -6 cm^3 mol^{-1} for the binding of cytosine, cytidine and CMP, respectively. These $\Delta \bar{V}$ values once again roughly correlate with the partial molar volume of the entering ligand.

(b) Aquation and solvolysis

The spontaneous aquation reactions are usually very slow. In contrast, they are orders of magnitude faster in acidic or basic medium.

The nitropentacyanoferrate(III) complex was found [39] to be relatively stable in aqueous solutions in the pH range $5 \leqslant pH \leqslant 10$. In a more acidic medium, acid-catalysed aquation occurs and the reaction product is $[Fe(CN)_5H_2O]^{2-}$; in basic medium (pH > 10) hydrolysis to $[Fe(CN)_5OH]^{3-}$ occurs [30,39]. For the acid-catalysed aquation, a dependence of the observed rate constant on the square of the acid concentration was found. A mechanism consisting of acid-catalysed aquation of a protonated nitro complex according to scheme (11) was proposed [30] to account for these observations as well as the activation parameters (Table 2).

$$[\mathrm{Fe(CN)_5NO_2}]^{3-} + \mathrm{H}^+ \overset{K}{\rightleftharpoons} [\mathrm{Fe(CN)_5NO_2H}]^{2-}$$

$$[\mathrm{Fe(CN)_5NO_2H}]^{2-} + \mathrm{H}^+ \xrightarrow{k} [\mathrm{Fe(CN)_5NO}]^{-} + \mathrm{H_2O}$$

$$[\mathrm{Fe(CN)_5NO}]^{-} + \mathrm{H_2O} \xrightarrow{\text{fast}} [\mathrm{Fe(CN)_5H_2O}]^{2-} + \mathrm{NO}^+ \qquad (11)$$

The process is characterized by a relatively low activation enthalpy ($\Delta H^{\neq} = +43 \pm 3$ kJ mol^{-1}) characteristic for the breakage of a secondary N–O bond and very similar to that found for the cleavage of O–C bonds in the acid-catalysed decarboxylation of carbonate complexes. The significantly negative value for the activation entropy ($\Delta S^{\neq} = -80 \pm 10$ J K^{-1} mol^{-1}) presumably results from the formation of a highly ordered transition state involving bond formation with the proton prior to loss of H_2O. The pressure dependence of this reaction was studied at two acid concentrations, and in both cases the observed rate constant decreases only slightly with increasing pressure, resulting in slightly positive activation volumes ($[H^+] = 0.2$ M : $\Delta V^{\neq} = +2.2$ cm^3 mol^{-1}; $[H^+] = 0.5$ M : $\Delta V^{\neq} = 1.9$ cm^3 mol^{-1}). Since the observed rate constant is a composite function, it follows that $\Delta V^{\neq} = \Delta \bar{V}(K) + \Delta V^{\neq}(k)$. However, since $\Delta V^{\neq}$ shows no remarkable acid dependence, it can be concluded that $\Delta \bar{V}(K)$ is either very small or independent of pH. It is also difficult to predict the magnitude of $\Delta V^{\neq}(k)$ since this step involves bond formation, charge neutralization and cleavage of the O–N bond. The overall almost zero value for $\Delta V^{\neq}$ indicates that this component is most probably also close to zero and that intrinsic and solvational volume contributions cancel each other.

TABLE 2

Activation parameters for the reaction

$\mathrm{Fe^{III}(CN)_5NO_2^{3-}} + \mathrm{S} \rightarrow \mathrm{Fe^{III}(CN)_5S^{2-}} + \mathrm{NO_2^-}$

S (solvent)	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V^{\neq}$ (25°C) (cm^3 mol^{-1})	Remarks	Ref.
H_2O	43 ± 3	-80 ± 10		$\mu = 0.5$ M	30
H_2O			$+2.2 \pm 0.1$	pH = 0.7	30
H_2O			$+1.9 \pm 0.1$	pH = 0.3	30
H_2O	97 ± 9	$+42 \pm 30$	$+20.1 \pm 1.0$	pH = 13	30
CH_3OH	116 ± 2.4	$+50.7 \pm 7.7$	$+19.6 \pm 1.8$[a]		31
DMSO	137 ± 0.7	$+141 \pm 1.3$	$+25.9 \pm 1.1$		31
DMF	122 ± 1.4	$+180 \pm 2.0$	$+26.9 \pm 1.5$		31

[a] $T = 45$°C.

The base hydrolysis reaction

$$[\mathrm{Fe^{III}(CN)_5NO_2}]^{3-} + \mathrm{OH^-} \longrightarrow [\mathrm{Fe^{III}(CN)_5OH}]^{3-} + \mathrm{NO_2^-} \tag{12}$$

was found to be catalysed by iron(II) species and exhibits pseudo-zero-order kinetics. In the presence of $[\mathrm{Fe^{II}(CN)_5NO_2}]^{4-}$ as catalyst, aquation of this complex is the rate-determining step of the process, which is followed by a rapid electron transfer and deprotonation according to the scheme

$$[\mathrm{Fe^{II}(CN)_5NO_2}]^{4-} + \mathrm{H_2O} \xrightarrow{k} [\mathrm{Fe^{II}(CN)_5H_2O}]^{3-} + \mathrm{NO_2^-} \tag{13a}$$

$$[\mathrm{Fe^{II}(CN)_5H_2O}]^{3-} + [\mathrm{Fe^{III}(CN)_5NO_2}]^{3-} \longrightarrow [\mathrm{Fe^{III}(CN)_5H_2O}]^{2-} + [\mathrm{Fe^{II}(CN)_5NO_2}]^{4-} \tag{13b}$$

$$[\mathrm{Fe^{III}(CN)_5H_2O}]^{2-} + \mathrm{OH^-} \rightleftharpoons [\mathrm{Fe^{III}(CN)_5OH}]^{3-} + \mathrm{H_2O} \tag{13c}$$

In this way, the concentration of $[\mathrm{Fe^{II}(CN)_5NO_2}]^{4-}$ remains constant throughout the base hydrolysis process and reaction (13a) attains pseudo-zero-order behaviour as observed for the disappearance of $[\mathrm{Fe^{III}(CN)_5NO_2}]^{3-}$. A significantly positive volume of activation ($\Delta V^{\neq} = +20.1 \pm 1.0\ \mathrm{cm^3\ mol^{-1}}$) and activation entropy ($\Delta S^{\neq} = +42 \pm 30\ \mathrm{J\ K^{-1}\ mol^{-1}}$) for the process (13a) suggests that a dissociative mechanism is operating. The volume of activation for this reaction, i.e. for the process

$$[\mathrm{Fe^{II}(CN)_5NO_2}]^{4-} \rightarrow [\mathrm{Fe(CN)_5^{3-}} - - -\mathrm{NO_2^-}]^{\neq} \tag{14}$$

is in good agreement with values of around $20\ \mathrm{cm^3\ mol^{-1}}$ reported for the other substitution reactions of a series of Fe(II) complexes of the type $[\mathrm{Fe^{II}(CN)_5L}]^{n-}$ (see Table 3). Charge dilution on going to the transition state will result in a decrease in electrostriction and may contribute to the positive value of $\Delta V^{\neq}$, but by not more than a few $\mathrm{cm^3\ mol^{-1}}$.

The solvolysis reactions of $[\mathrm{Fe^{III}(CN)_5NO_2}]^{3-}$ were studied by high-pressure kinetic techniques in methanol, dimethylsulphoxide and dimethylformamide [31]. For all the solvents studied, the substitution process follows the overall reaction

$$[\mathrm{Fe^{III}(CN)_5NO_2}]^{3-} + \mathrm{S} \rightarrow [\mathrm{Fe(CN)_5S}]^{2-} + \mathrm{NO_2^-} \tag{15}$$

where S = DMF, DMSO, $\mathrm{CH_3OH}$. The observed rate constants decrease significantly with increasing pressure, resulting in large positive volumes of activation (see Table 2). These values strongly support the dissociative nature of reaction (15), for which the proposed mechanism is given in the scheme

$$\begin{tikzcd}[\mathrm{Fe^{III}(CN)_5NO_2}]^{3-} \arrow[r, shift left, "k_1"] & {[\mathrm{Fe^{III}(CN)_5}]^{2-} + \mathrm{NO_2^-}} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2", "\mathrm{S}"'] \\ & {[\mathrm{Fe^{III}(CN)_5S}]^{2-}}\end{tikzcd} \tag{16}$$

TABLE 3

Activation parameters for the ligand-for-ligand substitution reactions involving pentacyanoferrates

Reaction	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V^{\neq}$ (25°C) (cm^3 mol^{-1})	Remarks	Ref.
$Fe^{II}(CN)_5L^{3-} + CN^- \rightarrow Fe^{II}(CN)_6^{4-} + L$					
$L = 3,5\text{-}Me_2py$	108 ± 3	$+58.5 \pm 8.4$	$+20.5 \pm 0.8$	$\mu = 0.5$ M	32
3-CNpy	93 ± 1	$+16.3 \pm 4.3$	$+20.6 \pm 0.5$		32
4-CNpy	105	+50	+20.6		33
pz	110	+59	+13		33,35
2-Mepz	114	+44	+19.4		33
4-phenylpyridine			+10		35
4-(1-butylpentyl)pyridine			+16	20% CH_3OH	35
N-(*n*-pentyl)pyrazinium			+10		35
$Fe^{II}(CN)_5L + X \rightarrow Fe^{II}(CN)_5X + L$					
$L = 3,5\text{-}Me_2py$ $X = pz$			$+21.2 \pm 1.0$	$\mu = 0.5$ M	32
$3,5\text{-}Me_2py$ imH			$+20.3 \pm 1.0$	$\mu = 0.5$ M	32
NH_3 py	102 ± 1	$+63 \pm 5$	$+16.4 \pm 0.6$	$\mu = 1.0$ M	34
NH_2CH_3 py	103 ± 3	$+54 \pm 10$	$+24.0 \pm 1.0$	$\mu = 1.0$ M	34
$NH_2C_2H_5$ py	104 ± 2	$+63 \pm 8$	$+16.3 \pm 1.5$	$\mu = 1.0$ M	34
$NH_2(i-C_3H_7)$ py	84 ± 3	$+9 \pm 10$	$+18.5 \pm 0.6$	$\mu = 1.0$ M	34
NH_2CH_2Ph py	96 ± 3	$+4 \pm 11$	$+17.4 \pm 1.4$	$\mu = 1.0$ M	34

where S = solvent.

Differences in the solvation of $[Fe^{III}(CN)_5NO_2]^{3-}$ were suggested to control the kinetics of reaction (15) in the various solvents. The interaction of the solvent with the cyanide ligands results in an increased electron density on the metal centre, which will then favour a dissociative reaction mode for the replacement of nitrite. Not only does the rate constant parallel the trend in donor number (DN) of the solvent, but even $\Delta V^{\neq}$ becomes more positive on increasing DN. Thus the electron-donating ability of the solvent mobilizes the electron density towards the metal centre and induces a dissociative mechanism.

(c) Ligand-for-ligand substitution

Ligand-for-ligand substitution usually occurs in non-coordinating solvents or in the presence of strong nucleophiles for which the competition with the solvent molecule is negligible.

The available volumes of activation for the substitution of ligand L in $[Fe^{II}(CN)_5L]^{4-}$ complexes (see Table 3) are all positive and independent of the entering group. For the reaction of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ with cyanide, $\Delta V^{\neq} = +20.5$ cm^3 mol^{-1}; with pyrazine, $\Delta V^{\neq} = +21$ cm^3 mol^{-1}; and with imidazole, $\Delta V^{\neq} = 20.2$ cm^3 mol^{-1} have been reported [32]. Similar volumes of activation have been found for the reactions of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$, $[Fe(CN)_5(4CN\text{-}py)]^{3-}$ and $[Fe(CN)_5(2\text{-}Mepz)]^{3-}$ with CN^- [32,33].

The large positive volume of activation that is independent of the nature of entering ligand provides very strong evidence in favour of a dissociative mechanism for the ligand substitution process. The volume of activation arises primarily from the stretching of the Fe–N bond on attaining the transition state with the leaving group sweeping out a consequential volume change in the surrounding solvent. Sullivan et al. [32] have shown that the values found correspond to the elongation 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.

Recently, an attempt has been made to find a correlation between the activation volume for the limiting dissociative substitution reactions of $[Fe(CN)_5L]^{n-}$ complexes and the volume of the leaving group [34,35]. Such correlation has earlier been found in the case of a limiting associative mechanism for square-planar substitution, where $\Delta V^{\neq}$ becomes more negative with increasing size of the entering nucleophile due to the more effective overlap of the molecular spheres, as defined by van der Walls radii [20]. For a limiting dissociative mechanism, one might expect $\Delta V^{\neq}$ to increase with increasing size of the leaving group. Although the sizes of the leaving group in $[Fe(CN)_5L]^n$ complexes were changed over a large range, no specific effect on the associated volumes of activation could be observed (see Table 3). As was hinted earlier, 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. Both of these factors may vary with the nature of the leaving group in such a way that an almost constant volume increase is observed. Furthermore, the position of the transition state may vary with the nature of the leaving group and may result in an 'early' or 'late' transition state as controlled by the leaving group. The other factor which may well distort any attempted correlation of $\Delta V^{\neq}$ with intrinsic or swept out volume is solvation [34,35].

(ii) Electron transfer reactions

Electron transfer reactions between two metal centres can be classified as inner-sphere or outer-sphere according to whether electron transfer occurs through a shared first-coordination-sphere ligand or whether it takes place between metal complexes with their first coordination spheres intact. It is reasonable on the basis of these two mechanisms to expect significantly different pressure dependencies [40] not only when the electron transfer step is rate-determining, but also when precursor species formation or successor dissociation is rate-determining. A preliminary theoretical prediction [13] based mainly on the Marcus–Hush theory revealed an apparently close correlation with experimentally observed volumes of activation (invariably positive for an inner-sphere mechanism and significantly negative for an outer-sphere mechanism), but later work [41] showed this to be wrong, and the correlation must be more complicated than originally predicted. In an effort to improve the understanding and to resolve the apparent discrepancy, different possible parameters were taken into account (e.g. the overall volume of reaction, some special interactions between ligands and solvent molecule, solvent rearrangement and collisional contributions in controlling the dynamic effects of the reaction medium, solvation of initial state and activated complex, the adiabacity or non-adiabacity of the process etc.) [40–45].

High-pressure kinetic studies involving pentacyanoferrate complexes make a meaningful contribution to the better understanding of the intimate molecular nature of the outer- and inner-sphere electron transfer processes [46–58].

(a) Outer-sphere electron transfer (OSET)

The pressure dependence of the self-exchange electron transfer reaction for the ferricyanide–ferrocyanide ion couple in aqueous alkali halide solution was investigated electrochemically [46], and strongly positive $\Delta V^{\neq}_{\mathrm{obs}}$ values were reported (see Table 4). This reaction between two highly charged substitutionally inert anions is necessarily outer-sphere and one might expect a negative $\Delta V^{\neq}$ value. The observed strongly positive volume of activation probably reflects the involvement of the alkali

TABLE 4

Activation parameters for outer-sphere electron transfer reactions involving pentacyanoferrates

Reaction		$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V^{\neq}$ (25°C) (cm^3 mol^{-1})	Remarks	Ref.
$Fe^{II}(CN)_6^{4-} + Fe^{III}(CN)_6^{3-} \rightarrow Fe^{III}(CN)_6^{3-} + Fe^{II}(CN)_6^{4-}$						
		17.6	−133.8	+13	1 M KCl	46
				+30	1 M NaCl	46
				+41	1 M LiCl	46
$Co(edta)^- + Fe^{II}(CN)_6^{4-} \rightarrow Co^{2+} + Fe^{III}(CN)_6^{3-}$				$+13.4 \pm 0.5$	$\mu = 1.0$ M	48
$Co(NH_3)_4(NH_2R)X^{(3-n)+} + Fe^{II}(CN)_6^{4-}$ $\rightarrow Co^{2+} + 4NH_3 + NH_2R + X^{n-} + Fe^{III}(CN)_6^{3-}$						
$R = H$	$X = H_2O$	102 ± 5	$+79 \pm 15$	$+26.5 \pm 2.4$	pH = 4.7 M $\mu = 0.5$ M	50
H	H_2O			$+37.6 \pm 1.2$	$\mu = 0.5$ M	49
H	pyridine	118 ± 8	$+113 \pm 29$	$+29.8 \pm 1.4$	$\mu = 1.0$ M	50
H	pyridine			$+30.7 \pm 1.3$	$\mu = 1.0$ M	51
H	pyridine			$+23.9 \pm 1.0$	$\mu = 1.0$ M	48
H	DMSO	84 ± 2	$+25 \pm 8$	$+34.4 \pm 1.1$	$\mu = 1.0$ M	50
H	N_3^-	104 ± 6	$+44 \pm 20$	$+18.8 \pm 1.1$	$\mu = 1.0$ M	54
H	Cl^-	85 ± 3	$+11 \pm 8$	$+25.9 \pm 3.1$	$\mu = 1.0$ M	54
CH_3	Cl^-	114 ± 4	$+112 \pm 14$	$+25.1 \pm 1.5$	$\mu = 1.0$ M	54
i-C_4H_9	Cl^-	103 ± 2	$+87 \pm 8$	$+31.3 \pm 0.9$	$\mu = 1.0$ M	54

metal cations in the transition state. The rate of electron transfer in solution between ions of like charge is frequently increased by involvement of the counter ions which are inevitably present. This phenomenon is especially marked in the case of anion–anion OSET [40].

Quite an extensive series of data is presently available for non-symmetrical OSET reactions [47–56]. Outer-sphere redox reactions are multistep processes in which an encounter complex (usually ion pair) is formed within a rapid pre-equilibrium followed by rate-determining electron transfer. For the reactions between hexacyanoferrate(II) and different amminecobalt(III) complexes (eqn. (17)), it was possible to separate the ion pair formation constant (K_{IP}) and the electron transfer rate constant (k_{ET}) in a kinetic way [47–54].

$$\mathrm{Co(NH_3)_4(NH_2R)X^{(3-n)+}} + \mathrm{Fe(CN)_6^{4-}} \overset{K_{IP}}{\rightleftharpoons} \{\mathrm{Co(NH_3)_4(NH_2R)X^{(3-n)+}, Fe(CN)_6^{4-}}\}$$

$$\{\mathrm{Co(NH_3)_4(NH_2R)X^{(3-n)+}, Fe(CN)_6^{4-}}\} \xrightarrow{k_{ET}} \mathrm{Co^{2+}} + 4\mathrm{NH_3} + \mathrm{NH_2R} + \mathrm{X^{n-}} + \mathrm{Fe(CN)_6^{3-}} \qquad (17)$$

For closely related systems, $\Delta\bar{V}(K_{IP})$ exhibits tremendous fluctuation (see Table 5). Because of the large error limits due to the indirect way in which the pressure dependence of K is obtained and the unknown nature of the ion pair produced as precursor species, it is difficult to predict volume changes based on partial molecular overlap and partial charge neutralization. On the other hand, the $\Delta V^{\neq}(k_{ET})$ values are all substantially positive and do not exhibit a clear trend with the nature of the substituents on the Co(III) centre (Table 4).

Two explanations were offered to account for the observed $\Delta V^{\neq}(k_{ET})$ values.

TABLE 5

Thermodynamic parameters for ion-pair formation according to

$$\mathrm{Co(NH_3)_4(NH_2R)X^{(3-n)+}} + \mathrm{Fe(CN)_6^{4-}} \overset{K}{\rightleftharpoons} \{\mathrm{Co(NH_3)_4(NH_2R)X^{(3-n)+}, Fe(CN)_6^{4-}}\}$$

R	X^{n-}	ΔH^0 (kJ mol^{-1})	ΔS^0 (J K mol^{-1})	$\Delta\bar{V}$ (cm^3 mol^{-1})	Remarks	Ref.
H	H_2O			-15.0 ± 8.0	pH = 4.7, $\mu = 0.5$ M	50
H	H_2O			$+3.5 \pm 0.6$	$\mu = 0.5$ M	49
H	pyridine			$+23.4 \pm 3.3$	$\mu = 1.0$ M	48
H	DMSO	-8 ± 21	-240 ± 67	-11.0 ± 3.0	$\mu = 1.0$ M	50
H	N_3^-	$+2 \pm 14$	-204 ± 46	-16.0 ± 2.0	$\mu = 1.0$ M	54
H	Cl^-	$+28 \pm 8$	-120 ± 27	-3.0 ± 8.0	$\mu = 1.0$ M	54
CH_3	Cl^-	-20 ± 9	-280 ± 29	$+3.0 \pm 2.0$	$\mu = 1.0$ M	54
iC_4H_9	Cl^-	-4 ± 3	-240 ± 9	-6.0 ± 1.0	$\mu = 1.0$ M	54

The Sendai group [48,49] argued that the expansion of the cobalt complex on going from low-spin Co(III) to high-spin Co(II) can contribute substantially (20–30 cm^3 mol^{-1}) to $\Delta V^{\neq}(k_{\mathrm{ET}})$; the Frankfurt group [50–54] suggested that the increase in molar volume of ca. 43 cm^3 mol^{-1} on going from $[\mathrm{Fe(CN)_6}]^{4-}$ ($\bar{V}=$ 89.7 cm^3 mol^{-1}) to $[\mathrm{Fe(CN)_6}]^{3-}$ ($\bar{V}=$ 132.6 cm^3 mol^{-1}) largely accounts for the observed data. Recent theoretical calculations [53,54] underline the important contribution arising from the overall increase in volume of ca. 65 cm^3 mol^{-1} during the ET step.

The values of $\Delta V^{\neq}$ in Table 4 are approximately 50% of the overall $\Delta\bar{V}$, i.e. the transition state for the electron transfer process is about halfway between the reactant and product states on a volume basis. For some quantitative interpretation of the data, $\Delta V^{\neq}$ was calculated theoretically [54] according to the equation

$$\Delta V^{\neq} = \Delta V^{\neq}_{\mathrm{IR}} + \Delta V^{\neq}_{\mathrm{SR}} + \Delta V^{\neq}_{\mathrm{COUL}} + \Delta V^{\neq}_{\mathrm{DH}} + \Delta V^{\neq}_{\mathrm{NA}} + \Delta V^{\neq}_{\mathrm{LS/HS}} + \lambda^{\neq}\Delta V \tag{18}$$

where volume changes resulting from the internal rearrangement of the two reacting molecules ($\Delta V^{\neq}_{\mathrm{IR}}$), the rearrangement of the surrounding solvent molecules ($\Delta V^{\neq}_{\mathrm{SR}}$), the Coulombic work required to bring the reactants together ($\Delta V^{\neq}_{\mathrm{COUL}}$). Debye–Hückel or other electrolyte effects ($\Delta V^{\neq}_{\mathrm{DH}}$), a term for the non-adiabacity of the process ($\Delta V^{\neq}_{\mathrm{NA}}$), the effect of low-spin to high-spin change on the Co centre ($\Delta V^{\neq}_{\mathrm{LS/HS}}$) and a term for non-symmetrical reactions ($\lambda^{\neq}\Delta V$) are included. The reaction parameter $\lambda^{\neq}$ can change between 0 and 1 depending on the location of the transition state along the reaction coordinate. The sum of the first six terms in eqn. (18) was found to be close to zero and to vary between -0.4 and 2.0 cm^3 mol^{-1} [54]. The authors therefore calculated a value of $\lambda^{\neq}$ that would lead to the experimentally observed $\Delta V^{\neq}$ reported in Table 4. Equation (18) satisfactorily describes the experimental $\Delta V^{\neq}$ value when $\lambda^{\neq}$ has values between 0.37 and 0.59 with an average of 0.48 ± 0.07 [54].

Saito and co-workers [55] have examined the pressure dependence of the quenching of the photo-excited tris(2,2′-bipyridine) ruthenium(II) cation $[\mathrm{Ru(bipy)_3}]^{2+}$ in water by OSET with hexacyanoferrates and other oxidative or reductive quenchers (Q). Strongly positive and negative volumes of activation, $\Delta V^{\neq}_{\mathrm{obs}}$, were found for $\mathrm{Q} = [\mathrm{Mo(CN)_8}]^{4-}$ and Eu^{2+}, respectively, which is in line with the general trends according to the charge type noted above, but for cases in which the quenching rate constant k_{q} approached the diffusion-controlled limit, as in the case of hexacyanoferrates, $\Delta V^{\neq}_{\mathrm{obs}}$ was close to zero, i.e. the pressure effect became negligible.

(b) Inner-sphere electron transfer (ISET)

Pentacyanoferrate complexes are capable of participating in inner-sphere electron transfer reactions in two ways. A bridged precursor may be formed by substitution of the coordinated ligand on $[\mathrm{Fe(CN)_5L}]^{n-}$, especially if the ligand is a labile species such as $\mathrm{H_2O}$. The pentacyanoferrate complex may also supply the bridging ligand, either one of the cyanides or an appropriate sixth ligand, such as pyrazine.

Activation volumes were measured [56–58] for intramolecular electron transfer within $[(NH_3)_5Co^{III}(\mu\text{-pz})Fe^{II}(CN)_5]$, $[(NH_3)_4Co^{III}(pzc)Fe^{II}(CN)_5]^-$ and $[(en)_2Co^{III}(pzc)Fe^{II}(CN)_5]^-$ complexes obtained in the former way. The extreme value of 38 $cm^3\ mol^{-1}$ found for the $[(NH_3)_5Co^{III}(\mu\text{-pz})Fe^{II}(CN)_5]$ complex is among the largest positive activation volumes ever observed for electron transfer reactions of metal complexes [56,58]. This large positive activation volume cannot be accounted for by the sum of the intrinsic volume change (theoretical estimation $< 20\ cm^3\ mol^{-1}$) and the solvation volume change due to the change in electrostriction (theoretical estimation $< 6.5\ cm^3\ mol^{-1}$). It has been suggested that hydrogen bonding interaction of the solvent molecules with coordinated cyanide ligands leads to a greater expansion from Fe(II) to Fe(III) than is predicted from electrostatic considerations [56].

For intramolecular electron transfer within the pyrazine carboxylate-bridged dinuclear complex $[(en)_2Co^{III}(pzc)\ Fe^{II}(CN)_5]^-$, rate constants ($k_{ET}$) were reported for water and aqueous methanol (up to 80% of methanol) [57,58]. Activation volumes for this process in water and in 60% methanol are 24 $cm^3\ mol^{-1}$ and 7 $cm^3\ mol^{-1}$, respectively. The large positive activation volume for k_{ET} in water suggests considerable solvation of the binuclear complex in the approach to the transition state for electron transfer. This deduction is supported by an analogous interpretation of large positive activation entropies for electron transfer within other similar $Co^{III}\text{–LL–}Fe^{II}(CN)_5$ complexes. There is probably a significant positive contribution to $\Delta V^{\neq}$ arising from cobalt–ligand bond stretching during transition state formation, but this must be small as $\Delta V^{\neq}$ in 60% methanol is only $+7\ cm^3\ mol^{-1}$. This is unlikely to be a contribution from iron–cyanide bond stretching or shortening, since iron–cyanide bond lengths are essentially equal in $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. Thus it was suggested that $\Delta V^{\neq}$, especially in water, is dominated by the solvation on forming the transition state.

(iii) Photochemical and photophysical processes

The overall photochemical process is the result of a sequence of events, any of which can be influenced by pressure. In order to evaluate activation volumes of photochemical reactions, it is important to understand the effect of pressure on all primary processes which deactivate or communicate with the excited state responsible for the photochemistry observed [59–65]. In addition to processes which involve net product formation, non-radiative and radiative deactivation, intersystem crossing, internal conversion from upper states to reactive states and equilibrium between excited states of comparable energy must all be considered. Although the treatment and interpretation of such data are usually much more complicated than for thermally induced reactions, the obtained information may be unique since high-pressure studies are one of only a few methods available to obtain mechanistic information on excited-state processes.

The photochemical reactivity of low-spin d^6 iron(II) cyano complexes has been known for some time [2–5, 8–10, 66–72]. The first photochemical reaction of these complexes studied under pressure was photoaquation of $[Fe(CN)_6]^{4-}$

$$[Fe(CN)_6]^{4-} + H_2O \xrightarrow{h\nu} [Fe(CN)_5H_2O]^{2-} + CN^- \qquad (19)$$

Finston and Drickamer [26] have investigated the effect of pressure on reaction (19) by following the photo-induced changes in conductivity. The first-order photocurrent risetime was correlated to the relative quantum efficiency of the photoaquation process. The dark decay of the photocurrent yielded a relative value of the bimolecular rate constant for the reverse reaction (20) (see the above discussion).

$$[Fe(CN)_5H_2O]^{3-} + CN^- \xrightarrow{k_{th}} [Fe(CN)_6]^{4-} + H_2O \qquad (20)$$

The $\Delta V_{\Phi}^{\neq}$ values of 6.2 ± 0.4 and 5.1 ± 0.4 cm^3 mol^{-1} were measured in water and 20% EtOH/H_2O, respectively. By assuming a pressure-independent excited-state lifetime and non-radiative rates, the activation volume for the excited-state process was calculated from the relationship

$$\Delta V_{P}^{\neq} = (1 - \Phi_P)^{-1} \Delta V_{\Phi}^{\neq} \qquad (21)$$

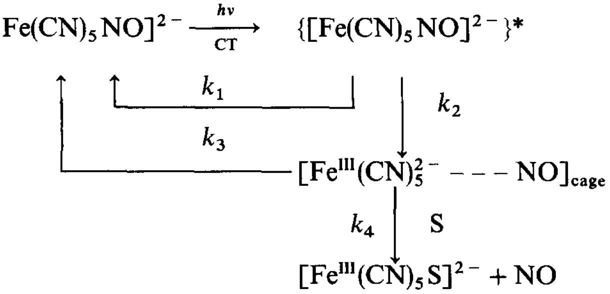
The $\Delta V_{P}^{\neq}$ values estimated in this way were +7.7 and 8.7 cm^3 mol^{-1} for water and 20% EtOH, respectively. The authors [26] concluded that the smaller positive value of $\Delta V_{P}^{\neq}$ compared with that reported for the thermal back reaction indicates an interchange dissociative (I_d) mechanism for the excited-state reaction. However, as pointed out by DiBenedetto and Ford [60], taking into account the fact that the excited-state reaction is likely to occur in a much earlier transition state and that the reactive excited state of $[Fe(CN)_6]^{4-}$ (probably the $^3T_{1g}$ LF state in this case) would be significantly larger than the corresponding ground state, the observed $\Delta V_{P}^{\neq}$ may be a reasonable value for a limiting D pathway for the photoreaction as well.

The photo-oxidation of $[Fe(CN)_5NO]^{2-}$ is one of a few charge transfer photochemical reactions of transition metal complexes investigated under pressure. The photochemistry of $[Fe(CN)_5NO]^{2-}$ at ambient pressure has been studied by numerous investigators [66–72], and photo-oxidation of the metal centre (i.e. MLCT) accompanied by solvation of the NO ligand was reported to be the major reaction mode in aqueous and non-aqueous liquid media

$$[Fe(CN)_5NO]^{2-} \xrightarrow{h\nu} [Fe(CN)_5S]^{2-} + NO \qquad (22)$$

In these studies, arguments were presented in favour of associative and dissociative reaction modes. The process is significantly affected by the properties of the solvent and the viscosity of the medium. Quantum yields for the production of $[Fe(CN)_5S]^{2-}$

were found [73] to decrease with increasing donor number and viscosity of the solvent. High-pressure studies revealed that the rate-determining step in the photo-oxidation mechanism is of the D type. For all the investigated systems an increase in pressure was accompanied by a significant decrease in the photo-oxidation quantum yield. A summary of the values of $\Delta V^{\neq}_{\Phi}$ calculated from plots of ln Φ versus pressure is given in Table 6. These values seem to be fairly wavelength-independent and only the quantum yield is significantly affected by solvent. The latter trend correlates with the fluidity of the medium as mentioned above, and points to the participation of a cage-recombination mechanism as outlined in the scheme.



(23)

where S = solvent. In this scheme, k_2 represents the rate constant for the radical pair-formation step. The observed photo-oxidation yield for the mechanism outlined in (23) is given by the expression in

$$\Phi = \left\{\frac{k_2}{k_1 + k_2}\right\}\left\{\frac{k_4}{k_3 + k_4}\right\} = \Phi_0\left\{\frac{k_4}{k_3 + k_4}\right\} \tag{24}$$

TABLE 6

Values of $\Delta V^{\neq}_{\Phi}$ and $\Delta V^{\neq}_{P}$ for the reaction

$[Fe(CN)_5NO]^{2-} + S \rightarrow [Fe(CN)_5S]^{2-} + NO$

as a function of solvent and excitation energy[a]

Solvent	λ_{irr} (nm)	Φ[b] (mol einstein^{-1})	$\Delta V^{\neq}_{\Phi}$ (cm^3 mol^{-1})	$\Delta V^{\neq}_{P}$ (cm^3 mol^{-1})
H_2O	436	0.17	+7.7 ± 0.4	+8.8 ± 0.4
	313	0.37	+5.5 ± 0.7	+7.8 ± 1.0
CH_3OH	436	0.39	+7.2 ± 0.5	+10.3 ± 0.6
	313	0.63	+6.5 ± 0.8	+13.0 ± 1.9
DMSO	436	0.33	+7.9 ± 0.3	+11.1 ± 0.4
	405	0.39	+7.5 ± 1.1	+11.4 ± 1.6
	313	0.42	+8.4 ± 1.3	+14.1 ± 1.0

[a] Ref. 73.

[b] Values at ambient pressure, i.e. 0.1 MPa.

where Φ_0 represents the primary quantum yield for radical pair formation/bond cleavage. Φ_0 and k_3 are expected to be independent of viscosity whereas k_4 is expected to decrease with increasing viscosity. It is therefore not surprising that Φ^{-1} depends linearly on the viscosity of the medium as reported above, with an intercept Φ_0^{-1}. The value of Φ_0 is such that $\Phi_{H_2O}/\Phi_0 = 0.82$, indicating that no significant cage effects are present in pure water. However, this ratio deviates significantly from unity for the other solvents and cage effects do play a significant role in those cases. The observed pressure effects and apparent volumes of activation, $\Delta V^{\neq}_{\Phi}$, mainly present the contribution from k_2, i.e. the formation of the caged radical pair, and support the dissociative nature of this reaction. If we assume that k_1 for non-radiative deactivation exhibits a minor pressure dependence [61,62,73–75], then $\Delta V^{\neq}_{P}$ for the k_2 step can be estimated from a plot of $\ln(\Phi/(1-\Phi))$ versus pressure in the usual way. The corresponding values in Table 6 show a very similar trend to $\Delta V^{\neq}_{\Phi}$, and the larger values found in MeOH and DMSO are partly ascribed to the pressure dependence of the viscosity of the solvent. The expected increase in viscosity with increasing pressure, especially for DMSO, will result in a decrease in Φ and a more positive $\Delta V^{\neq}$ value. The results definitely rule out the possibility of an associative reaction mode and reveal the intimate nature of the dynamics of the excited-state species.

A remarkable difference in the pressure sensitivity of the photo-chemical and thermal electron transfer processes for two systems $[(NH_3)_4Co^{III}(\mu\text{-pzc})Fe^{II}(CN)_5]^-$ and $[(NH_3)_5Co^{III}(\mu\text{-pz})Fe^{II}(CN)_5]$ was reported recently [58]. The activation volumes for the thermal electron-transfer reactions are large and positive (Table 7), whereas for the photo-induced MLCT processes close to zero. The pressure independence of the photo-induced electron transfer process was discussed according to the

TABLE 7

Activation parameters for the reaction

$(X)_zCo^{III}(\mu\text{-L})Fe^{II}(CN)_5 \rightarrow Co^{2+} + zX + Fe^{III}(CN)_5L$

$(X)_z$	L	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V^{\neq}$ (25°C) (cm^3 mol^{-1})	Slit width (mm)	Ref.
$(NH_3)_5$	pz	103 ± 6	+75 ± 21		2.0	76
		130 ± 5	+165 ± 5	+37 ± 1	1.4	56
				+10.6 ± 0.7	2.0	58
				+34.6 ± 1.4	0.1	58
$(NH_3)_4$	pzc	83 ± 2	+2 ± 7		1.0	58
				+27.3 ± 0.9	0.1	58
				+3.0 ± 2.1	2.0	58
		95 ± 4	+40 ± 13		2.0	76
$(en)_2$	pzc			+28.4 ± 2.0	1.0	58
				+24	1.0	57

two-steps electron transfer mechanism. First, during MLCT excitation electron density is transferred from Fe(II) to the pyrazine or pyrazinecarboxylate ligand as shown by the equation

$$[(NC)_5Fe^{II}(\mu\text{-}L)Co^{III}(NH_3)_5 \xrightarrow{h\nu} [(NC)_5Fe^{III}(\mu\text{-}L^-)Co^{III}(NH_3)_5] \qquad (25)$$

The subsequent first-order process observed during irradiation must involve the transfer of the electron from the bridging ligand to the cobalt centre. Since the quantum yield for these photo-induced reactions are almost unity [76] any effect of pressure on the photochemical rate constant will not effect the quantum yield. This means that $Fe^{III}(\mu\text{-}L^{-})Co^{III}$ is produced rapidly during continuous irradiation and undergoes L–to–Co(III) electron transfer during the first-order decay. According to the pressure independence of the photo-induced electron transfer process, no significant volume change is associated with the reduction of Co(III) following MLCT excitation. The major volume increase observed in thermal electron transfer must occur during the oxidation of Fe(II).

(iv) Bioinorganic processes

The structure and dynamic properties of biochemical systems can be significantly modified by pressure [77–86]. The chemical processes involving heme proteins are probably the most related to organic and inorganic chemistry at high pressure since covalent bonds are formed and broken during the process of ligand binding. Changes in the electronic configuration of the iron atom play an important part in the reactions of spin equilibria and redox processes. Some of these processes can be studied on inorganic model systems.

Pentacyanoferrate(II) complexes have been employed at ambient pressure in several kinetic studies involving amino acids and metalloproteins [9,38]. The low-spin d^6 electronic configuration and labile sixth coordination site makes it a useful model for iron centres in proteins such as haemoglobin and the cytochromes.

High-pressure kinetic studies of the binding of imidazole, glutathione and some amino acids to $[Fe(CN)_5]^{3-}$ moiety were discussed in Sect. C.(i). For all the ligands studied, significantly positive volumes of activation have been found (see Table 1), suggesting that the formation reactions of the $[Fe(CN)_5L]^{3-}$ complexes proceed according to a limiting D mechanism instead of an I_d mechanism as was proposed on the basis of the data obtained by conventional kinetic techniques [9].

For the reaction of aquopentacyanoferrate(III) with cytosine, cytidine and CMP an interchange dissociative (I_d) mechanism was proposed on the basis of high-pressure kinetic studies (see the discussion in Sect. C.(i)).

Pentacyanoferrate complexes are capable of forming homo- and heterobinuclear metal complexes. The bridging ligands in these complexes are either a cyanide ion or a bidentate heterocycle such as 4,4′-bipyridine or pyrazine [9].

It has recently been reported [87,88], that nitroprusside and other pentacyanoferrate(II/III) compounds form heterobinuclear complexes with aquocobalamin in which the cyanide ligand is the bridge. Although substitution reactions of cobalamins have attracted significant attention from kineticists for many years, conventional kinetic techniques were employed in the majority of these studies. The mechanistic interpretation of the data was restricted by the shortage of the activation parameters for the rate-determining step, with the result that differentiation between the operation of an I_d or a D mechanism for the substitution reaction of aquocobalamin was not possible. Application of high-pressure kinetic techniques in the study of the anation of aquocobalamin by cyanoferrates [88] gave the additional activation parameter $\Delta V^{\neq}$. Significantly positive volumes of activation for the reaction

$$B_{12}\text{-}H_2O^+ + L \xrightarrow{k} B_{12}\text{-}L^+ + H_2O \tag{26}$$

(see Table 8) favour the operation of a D instead of an I_d mechanism, although the interpretation of the data was complicated to some extent due to solvational contributions arising from charge neutralization during bond formation with anionic ligands. The addition of a complete set of kinetic and thermodynamic volume parameters for the reaction

$$B_{12}\text{-}H_2O^+ + py \rightleftharpoons B_{12}\text{-}py^+ + H_2O \tag{27}$$

involving a neutral entering or leaving group has assisted the assignment of the intimate nature of the process (26) [89]. The pressure dependence of the rate and equilibrium constants enables the construction of an overall reaction volume profile (Fig. 2), which clearly demonstrates the significant increase in volume during the dissociation of $B_{12}H_2O^+$ (k_1) and $B_{12}py^+$ (k_{-2}). The value of 7.4 $cm^3\ mol^{-1}$ for $\Delta V^{\neq}(k_1)$ (Fig. 2) is very reasonable for a dissociative mechanism, especially since we are dealing with intrinsic volume changes in the absence of significant changes in electrostriction. Furthermore, this value should be significantly smaller than $\Delta V^{\neq}(k_{-2})$ on the basis of the large difference in partial molar volume of H_2O and py. The volume profile (Fig. 2) reported for the reaction with py presents an overall picture of the structural changes that occur during processes (28) on a volume basis.

$$B_{12}H_2O^+ + L \rightleftharpoons B_{12} + H_2O + L \rightleftharpoons B_{12}L^+ + H_2O \tag{28}$$

Only a very small part of the iron in the human body is involved in electron transfer reactions. From all the known metalloproteins, cytochrome c is probably the best characterised haem protein which takes part in redox reactions. The kinetics of the outer-sphere reaction of pentacyanoferrate complexes with ferricytochrome c has been investigated at ambient pressure to probe the intrinsic rates and sites for electron transfer in the metalloproteins [9].

Heremans et al. [42] have studied the pressure dependence of the reaction

$$\text{cytFe(III)} + [Fe(CN)_6]^{4-} \rightleftharpoons \text{cytFe(II)} + [Fe(CN)_6]^{3-} \tag{29}$$

with the temperature-jump relaxation technique. The reaction volume is

TABLE 8

Activation and reaction volumes of bioinorganic processes involving penteacyanoferrate complexes

Reaction	$\Delta V^{\neq}_{obs}$ (cm^3 mol^{-1})	$\Delta V^{\neq}_{calc}$ (cm^3 mol^{-1})	$\Delta \bar{V}$ (cm^3 mol^{-1})	Remarks	Ref.
$B_{12}H_2O^+ + Fe^{II}(CN)_5X$					
$\rightarrow B_{12}NCFe^{II}(CN)_4X + H_2O$					
$X = CN^-$	$+16.2 \pm 1.2$			pH = 6.0, $\mu = 0.13$ M	88
NO	$+8.9 \pm 0.5$			pH = 6.0, $\mu = 0.1$ M	88
$B_{12}H_2O^+ + Fe^{III}(CN)_5H_2O^{2-}$					
$\rightarrow B_{12}NCFe^{III}(CN)_4H_2O^+ + H_2O$	$+8.2 \pm 0.8$			pH = 6.0, $\mu = 0.1$ M	88
$B_{12}H_2O^+ + N_3^- \rightarrow B_{12}N_3 + H_2O$	$+6.9 \pm 0.2$			pH = 6.4, $\mu = 0.5$ M	88
$B_{12}H_2O^+ + py \rightarrow B_{12}py^+ + H_2O$	$+8.7 \pm 1.2$			pH = 6.7, $\mu = 0.5$ M	89
$B_{12}py^+ + H_2O \rightarrow B_{12}H_2O^+ + py$	$+16.9 \pm 0.8$			pH = 6.7, $\mu = 0.5$ M	89
$B_{12}H_2O^+ + py \rightleftharpoons B_{12}py^+ + H_2O$			-8.2 ± 2.0	pH = 6.7, $\mu = 0.5$ M	89
			-12.0 ± 2.0	pH = 6.7, $\mu = 0.5$ M	89
cytFe(III) + $Fe(CN)_6^{4-} \rightarrow$ cytFe(II) + $Fe(CN)_6^{3-}$	$+13.0$	$+16.7$	$+37.0$		42
HRPcomp.II(FeIV) + $Fe(CN)_6^{4-}$					
$\rightarrow$ HRP(FeIII) + $Fe(CN)_6^{3-}$	$+6.7$				93
$H_2A + 2Fe(CN)_6^{3-} \rightarrow A + 2H^+ + 2Fe(CN)_6^{4-}$	-16.6 ± 0.5	-15.5		pH = 0.3, $\mu = 1$ M	94
	-15.0 ± 1.0			pH = 5.0, $\mu = 1$ M	94
	-16.3 ± 0.4	-14.3		pH = 5.3, $\mu = 1$ M	94
2GSH + $Fe(CN)_6^{3-}$	-22.0 ± 1.5			pH = 6.0, $\mu = 0.5$ M	95
$\rightarrow$ GSSG + $Fe(CN)_6^{4-} + 2H^+$	-20.9 ± 1.1			pH = 7.0, $\mu = 0.5$ M	95

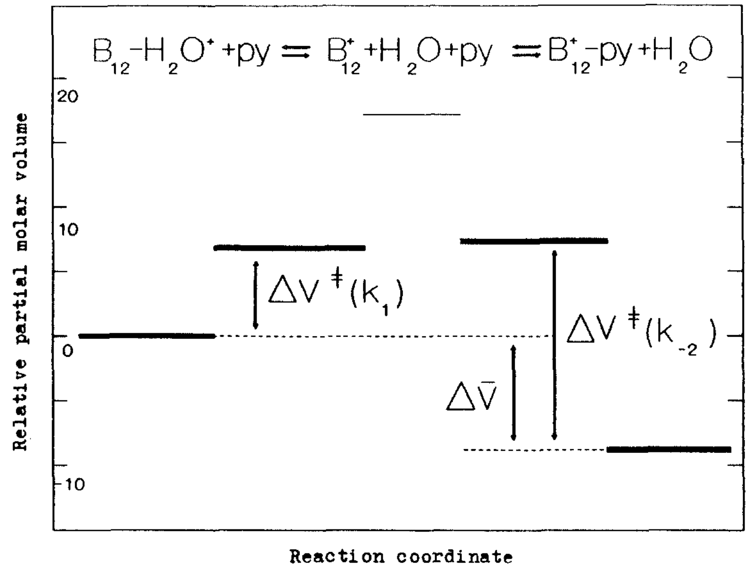


Fig. 2. Volume profile for the system
$B_{12}H_2O^+ + py \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B_{12}^+ + H_2O + py \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B_{12}py^+ + H_2O$

+37 $cm^3\ mol^{-1}$, and the experimental activation volume is +13 $cm^3\ mol^{-1}$. The large positive activation volume for the process, which is doubtless outer-sphere, was explained by the influence of the reaction volume. Heremans et al. have found for a series of OSET reactions of bioinorganic systems, that the trend in $\Delta V^{\neq}$ parallels that in $\Delta\bar{V}$ from which the important conclusion was reached that $\Delta V^{\neq}$ for electron transfer processes can only be interpreted more meaningfully when the reaction volume is known [42,90,91].

From the reaction volumes obtained for hexacyanoferrates, it is possible to calculate the change in partial molar volume of the protein as a function of the oxidation state. The value depends on the assumed molar volumes for the inorganic ions. With the recent values of Spitzer et al. [92], Heremans et al. found that the reduced state is 5 $cm^3\ mol^{-1}$ larger than the oxidized state [78].

The activation volumes for the OSET reactions of the HRP (horseradish peroxidase) compound II (Fe(IV)) with several reductants have been measured by Ralston et al. [93]. The positive value for ferrocyanide (+6.7 $cm^3\ mol^{-1}$) can reasonably be explained [42] by assumption that the activation volume is determined by the reaction volume.

Very recently, the oxidation of L-ascorbic acid and glutathione in the reactions with hexacyanoferrate(III) has also been studied by high-pressure kinetic techniques [94,95]. For the first reaction, rate and activation parameters were reported [94] for the two main reactants at pH < 7, i.e. the oxidation of L-ascorbic acid (H_2A) and the ascorbate anion (HA^-). The results are in agreement with the overall reaction scheme

$$H_2A \xrightleftharpoons{K_1} HA^- + H^+$$

$$HA^- \xrightleftharpoons{K_2} A^{2-} + H^+$$

$$H_2A + Fe(CN)_6^{3-} \xrightarrow{k_a} Fe(CN)_6^{4-} + H_2A^{\cdot +} \tag{30a}$$

$$HA^- + Fe(CN)_6^{3-} \xrightarrow{k_b} Fe(CN)_6^{4-} + HA^{\cdot} \tag{30b}$$

$$A^{2-} + Fe(CN)_6^{3-} \xrightarrow{k_c} Fe(CN)_6^{4-} + A^{\cdot -} \tag{30c}$$

$$H_2A^{\cdot +}/HA^{\cdot}/A^{\cdot -} + Fe(CN)_6^{3-} \xrightarrow{\text{fast}} Fe(CN)_6^{4-} + A + 2H^+$$

The activation parameters (Table 8) support the operation of outer-sphere electron transfer mechanism and the $\Delta V^{\neq}_{\text{exp}}$ are in good agreement with those calculated theoretically using the improved Stranks–Marcus–Hush relationships. The similarity in $\Delta V^{\neq}$ for k_a and k_b paths of the reaction indicates that its value is not effected by the charge on the species being oxidized, viz. H_2A and HA^-.

Reaction of hexacyanoferrate(III) with glutathione (GSH) was studied [95] in the pH range $6 < pH < 7.6$, where the mononegative ion is the predominant species. Oxidation of this ion leads to diglutathione (GSSG) and hexacyanoferrate(II) according to the overall reaction

$$2GSH + 2Fe(CN)_6^{3-} \rightarrow GSSG + 2Fe(CN)_6^{4-} + 2H^+ \tag{31}$$

The large negative activation volume (Table 8) as well as other activation parameters suggest that in this case also an outer-sphere electron transfer mechanism is operating. The significantly negative values of $\Delta V^{\neq}$ found for the oxidation of both L-ascorbic acid and glutathione indicate that charge creation, which is accompanied by an increase in electrostriction, must play a dominant role during the electron transfer process. In this respect it is informative to compare the above results in which the reduction of $Fe(CN)_6^{3-}$ occurs with those reported for the reverse process, i.e. the oxidation of $Fe(CN)_6^{4-}$ [54]. In that work, it was argued that the oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ can be expected to be accompanied by a total volume increase of ca. 43 $cm^3\ mol^{-1}$, based on the partial molar volumes of the reactants (see p. 282). If these arguments are now superimposed on the present systems, an overall volume decrease of ca. 40 $cm^3\ mol^{-1}$ would be expected for the reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$, such that a $\Delta V^{\neq}$ of ca. $-20\ cm^3\ mol^{-1}$ would be quite realistic for such processes (see Table 8).

D. REACTIONS OF OTHER CYANOFERRATE COMPLEXES

For the peroxodisulphate oxidation of $[Fe(CN)_4(bipy)]^{2-}$, the $\Delta V^{\neq}$ was found to be close to zero [96]. The value of approximately zero for $\Delta V^{\neq}$ implies that the

TABLE 9

Activation volumes for peroxodisulphite oxidation of iron(II)–diimine–cyanide complexes[a]

Complex	Solvent	$\Delta V^{\neq}$ ($cm^3\ mol^{-1}$)
$Fe(CN)_4(ein)^{2-}$	H_2O	+4.6
$Fe(CN)_4(phen)^{2-}$	H_2O	−2.1
$Fe(CN)_2(bipy)_2$	H_2O	−7.2
$Fe(CN)_4(Me_2bsb)^{2-}$	H_2O	−10.2
$Fe(CN)_4(phen)^{2-}$	60% DMSO	−3.6
$Fe(CN)_4(bipy)^{2-}$	60% DMSO	−8.3

[a] $T = 25°C$, ref. 97.

change of state of solvation in going to the transition state balances the intrinsic $\Delta V^{\neq}$ for the formation of a bimolecular transition state, generally believed to be about $-10\ cm^3\ mol^{-1}$ [96,97]. The important role played by complex solvation is more apparent if one compares $\Delta V^{\neq}$ values for the $[Fe(CN)_4(diimine)]^{2-}$ anions (Table 9). These range from a value of $-10\ cm^3\ mol^{-1}$ for the complex with the large and hydrophobic Me_2bsb ligand to $+5\ cm^3\ mol^{-1}$ for ein, the smallest and least hydrophobic ligand [97]. The former value is approximately that expected for bimolecular process in which the solvation contribution to $\Delta V^{\neq}$ is negligible.

For iron(II) and iron(III) cyanide–diimine complexes, the effect of pressure on charge transfer bands has recently been described [98]. The results showed that the pressure effect (similar to the temperature and solvent effects) on the LMCT spectra of the iron(III) complexes are opposite to those on the MLCT spectra of analogous iron(II) complexes [98].

E. CONCLUDING REMARKS

Pressure effects on thermal and photochemical reactions of pentacyanoferrate complexes provide a valuable new insight into the mechanistic interpretation of these reactions. Because pentacyanoferrate compounds are often used as model systems in the study of catalytic, biological, environmental and energy-related processes, the most detailed description of the molecular nature of their reactions is of great interest. The interpretation of the activation and reaction volumes sometimes allowed differentiation of probable mechanisms, which was not possible by employing conventional kinetic techniques. In other cases, the pressure studies revealed additional parameters to strengthen the mechanistic assignments. However, as for other activation parameters, the usefulness of $\Delta V^{\neq}$ for mechanistic discrimination is limited by the complexity of the reaction studied. The fact that pentacyanoferrate complexes are usually charged species often introduces a complicating factor into the interpretation of $\Delta V^{\neq}$. However, this problem also arises in the neutralization of the more widely used activation parameters, viz. $\Delta H^{\neq}$ and $\Delta S^{\neq}$. The concept of a volume change can be at least more readily visualized than the more intangible entropy of activation. More importantly, the generally superior accuracy of $\Delta V^{\neq}$ coupled with the possibility of measuring both the overall volume change $\Delta \bar{V}$ and the absolute volume of the proposed transition state makes activation volume a very useful supplementary tool in mechanistic assignments.

ACKNOWLEDGEMENTS

The author wishes to thank Professor R. van Eldik (University of Witten/Herdecke) for helpful discussions. Financial support of the author's work in this area by the Alexander von Humboldt Foundation and the Polish Academy of Science is gratefully acknowledged.

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