

## Kinetics and Mechanism of the Solvolysis Reaction of Nitropentacyanoferrate(III)

G. STOCHEL\* and R. VAN ELDIK\*\*

Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, F.R.G.

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### Abstract

The solvolysis reactions of  $\text{Fe}(\text{CN})_5\text{NO}_2^{3-}$  were studied kinetically in  $\text{CH}_3\text{OH}$ , DMSO and DMF as a function of  $[\text{H}^+]$ ,  $[\text{OH}^-]$ , temperature and pressure. The first-order rate constant in neutral medium increases along the series of solvents  $\text{H}_2\text{O} \ll \text{CH}_3\text{OH} < \text{DMSO} < \text{DMF}$ , which corresponds approximately with the electron-donation ability of the solvent. The activation enthalpy varies between 116 and 137  $\text{kJ mol}^{-1}$  whereas the activation entropy varies between 50 and 140  $\text{J K}^{-1} \text{mol}^{-1}$  for the investigated solvents. The latter values and the large positive volumes of activation (between +20 and +27  $\text{cm}^3 \text{mol}^{-1}$ ) underline the dissociative nature of the solvolysis process.

### Introduction

The kinetics and mechanism of ligand (L) substitution in pentacyano(ligand L)ferrate(III) ions have been extensively studied [1–17]. The substitution reactions are all dissociative in nature, although both D (dissociative) and  $I_d$  (interchange dissociative) mechanisms can equally well explain all the kinetic observations in aqueous solution. A series of studies [10–17] was undertaken in mixed solvents in order to distinguish between these mechanisms. For most of the studied systems, remarkably small effects of solvent composition on kinetic parameters (rate constant, activation enthalpy) were found. Blandamer *et al.* [16] pointed out, that these small effects could result from large but almost equal effects on the initial and transition states. On the other hand, it is noteworthy that the rate of dissociation of L from  $\text{Fe}(\text{CN})_5\text{L}^{n-}$  in some organic solvents is several orders of magnitude larger than in aqueous solutions [17, 18]. Recently we reported on the extreme stability of the nitropentacyano complex of iron(III) in aqueous solution in the pH range 5–10 [19, 20]. It is therefore of interest to

study the solvolysis reactions of this iron(III) complex in some organic solvents to see whether an enhanced lability shows up as reported for the iron(II) complexes. Furthermore, preliminary results indicated indeed a lower stability of  $\text{Fe}(\text{CN})_5\text{NO}_2^{3-}$  in DMSO [19].

### Experimental

#### Materials

$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}_2]$  was prepared and analysed by the published method [19]. All organic solvents were of analytical grade. In some experiments dry DMSO ( $\pm 0.03\%$   $\text{H}_2\text{O}$ ) and dry DMF ( $\pm 0.05\%$   $\text{H}_2\text{O}$ ) were used. For some kinetic runs solvents were purified from eventual traces of acids on an  $\text{Al}_2\text{O}_3$  column. Composition of all solvent mixtures are expressed in volume %. The ionic strength was adjusted with  $\text{KClO}_4$  or  $\text{NaClO}_4$ .  $\text{HClO}_4$  and  $\text{NaOH}$  were used to adjust the pH in acidic and basic media, respectively. Chemicals of analytical reagent grade and doubly distilled water were used throughout this study.

#### Kinetics

Solutions of  $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}_2]$  ( $5 \times 10^{-4}$ – $1 \times 10^{-3}$  M) in DMSO were freshly prepared by dissolving appropriate amounts of  $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}_2]$ . Due to the low solubility of  $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}_2]$  in other solvents, solutions for kinetic runs were prepared by dissolving the complex in a very small amount of water, such that after mixing with the appropriate solvent the water content was less than 0.5% (v/v). The reaction progress was studied by following the increase in absorption at 400 ( $\text{CH}_3\text{OH}$ ), 426 (DMS), 414 (DMF) and the decrease at 555 nm.

Kinetic measurements at ambient pressure were performed for the slow reactions in the thermostated ( $\pm 0.1$  °C) cell compartment of a Shimadzu UV-250 spectrophotometer and for the fast reactions on a Durrum D110 stopped-flow spectrophotometer ( $\pm 0.1$  °C). Similar measurements at elevated pressure were performed with the aid of a thermostated ( $\pm 0.1$  °C) high pressure cell [21] built into a Zeiss DMR 10 spectrophotometer. First-order kinetic runs (up to three half-lives) were observed for the studied systems.

\*On leave from the Department of Chemistry, Jagiellonian University, 30600 Kraków, Poland.

\*\*Author to whom correspondence should be addressed.

## Results and Discussion

The stability of  $\text{Fe}(\text{CN})_5\text{NO}_2^{3-}$  is much greater in aqueous solution than in  $\text{CH}_3\text{OH}$ , DMSO or DMF. In aqueous solution, acid-catalysed aquation occurs at  $\text{pH} < 5$  and base hydrolysis at  $\text{pH} > 10$  [19, 20]. Figure 1a shows the changes with time of the ab-

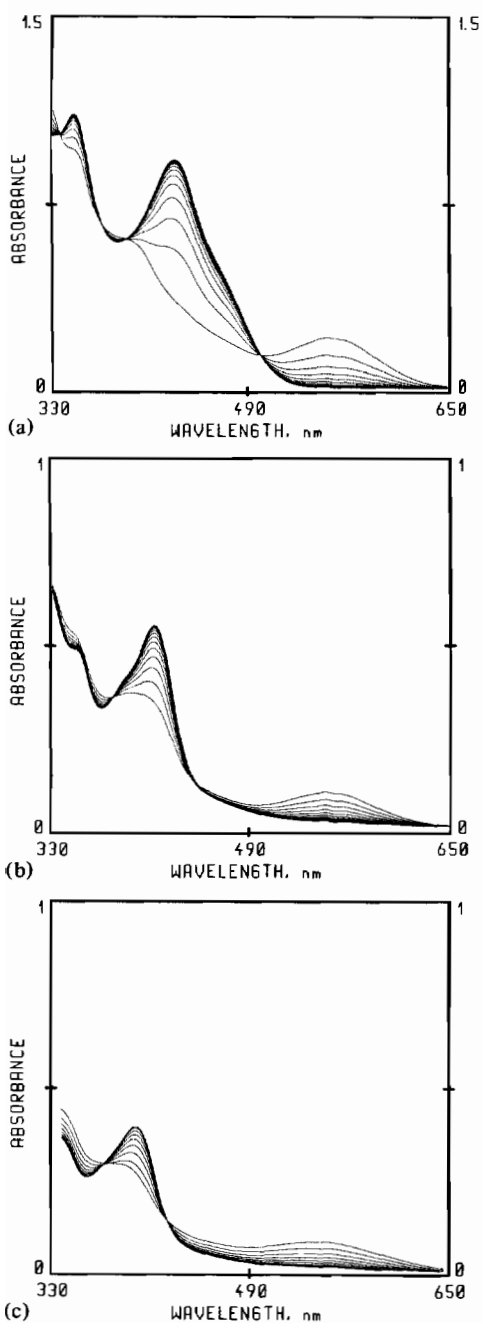
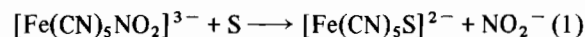


Fig. 1. Repetitive scan spectra for solvolysis of  $\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2^{3-}$  in DMSO (a), DMF (b),  $\text{CH}_3\text{OH}$  (c).  $[\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2^{3-}] = 5 \times 10^{-4}$  M;  $\Delta t = 60$  min (a); 3 min (b); 10 min (c); temperature = 25 °C (a), 25 °C (b), 50 °C (c); 1 cm optical path.

sorption spectra of  $5 \times 10^{-4}$  M  $\text{Fe}(\text{CN})_5\text{NO}_2^{3-}$  in DMSO. Four isosbestic points at 337, 361, 370 and 477 nm are observed during the reaction. The final spectrum as well as the constant isosbestic points clearly indicate that the only product formed is  $\text{Fe}(\text{CN})_5\text{DMSO}^{2-}$  [22, 23].

Similar spectral changes are also observed for  $5 \times 10^{-4}$  M solutions of  $\text{Fe}(\text{CN})_5\text{NO}_2^{3-}$  in  $\text{CH}_3\text{OH}$  (Fig. 1b) and in DMF (Fig. 1c). The final spectra are consistent with those reported for  $\text{Fe}(\text{CN})_5\text{CH}_3\text{OH}^{2-}$  and  $\text{Fe}(\text{CN})_5\text{DMF}^{2-}$ , respectively [22, 23]. For all studied solvents the substitution process follows the overall reaction



where  $\text{S} = \text{CH}_3\text{OH}$ , DMSO, DMF

The reactions in DMF and  $\text{CH}_3\text{OH}$  were carried out in the presence of 0.5% water (see 'Experimental'). Such a small amount of water should not drastically change the character of the solvents. This aspect was investigated by studying the solvolysis reaction in dry DMSO and in the presence of small added quantities of water (see Table 1). The observed rate constant is affected by the presence of water as well as by the ionic strength of the medium. Both these parameters slow down the solvolysis process. Nevertheless, the effects are negligible for a water content of 0.03–0.5% (v/v) and for ionic strengths between 0.003 and 0.01 M.

Kinetic data for reaction (1) as a function of temperature and solvent are summarized in Table 2. The dependence of  $k_{\text{obs}}$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  on the nature of the solvent is clearly demonstrated. The observed

TABLE 1. Dependence of the Rate Constant for the Solvolysis of  $[\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2]^{3-}$  in DMSO on the % Volume of Water and Ionic Strength

$\text{H}_2\text{O}$ (%) (v/v)	$\mu^a$ (M)	$T$ (°C)	$k_{\text{obs}}$ ( $\text{s}^{-1}$ )
0	0.003	25	$(1.17 \pm 0.01) \times 10^{-4}$
1			$(8.50 \pm 0.03) \times 10^{-5}$
5			$(5.50 \pm 0.05) \times 10^{-5}$
0	0.01	25	$(1.10 \pm 0.01) \times 10^{-4}$
0.5			$(1.05 \pm 0.01) \times 10^{-4}$
1	0.1	25	$(8.10 \pm 0.03) \times 10^{-5}$
5			$(4.80 \pm 0.01) \times 10^{-5}$
0	0.1	35	$(5.60 \pm 0.04) \times 10^{-4}$
0.5			$(5.50 \pm 0.04) \times 10^{-4}$
1	0.5	25	$(6.50 \pm 0.02) \times 10^{-5}$
5			$(3.80 \pm 0.01) \times 10^{-5}$
0	0.5	35	$(3.50 \pm 0.01) \times 10^{-4}$
1			$(3.40 \pm 0.02) \times 10^{-4}$
2.5			$(2.50 \pm 0.01) \times 10^{-4}$
5			$(1.80 \pm 0.01) \times 10^{-4}$

<sup>a</sup>KClO<sub>4</sub>.

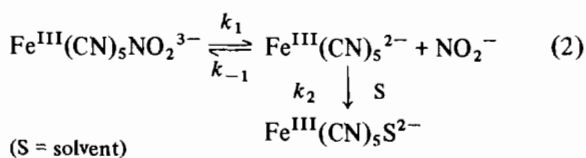
TABLE 2. Rate and Activation Parameters for the Solvolysis of  $\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2^{3-}$ 

Solvent	Solvent parameters			Temperature (°C)	$k_{\text{obs}}$ (s <sup>-1</sup> )	$\Delta G^\ddagger$ (25 °C) (kJ mol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )
	$DN^a$	$AN^b$	$pK_a^c$					
DMF	26.6	16		17	$(3.19 \pm 0.03) \times 10^{-4}$	89.56	$121.8 \pm 0.6$	$180.3 \pm 2.0$
				20	$(5.39 \pm 0.03) \times 10^{-4}$			
				25	$(1.25 \pm 0.01) \times 10^{-3}$			
				30	$(2.93 \pm 0.05) \times 10^{-3}$			
				32	$(3.99 \pm 0.05) \times 10^{-3}$			
DMSO	29.8	19.3	0.91	20	$(4.47 \pm 0.08) \times 10^{-5}$	95.47	$137.4 \pm 0.3$	$140.5 \pm 0.8$
				25	$(1.18 \pm 0.03) \times 10^{-4}$			
				30	$(2.96 \pm 0.01) \times 10^{-4}$			
				35	$(7.32 \pm 0.05) \times 10^{-4}$			
CH <sub>3</sub> OH	23.5	41.3	-2.08	35	$(5.25 \pm 0.05) \times 10^{-5}$	101.4	$116.5 \pm 2.4$	$50.7 \pm 7.7$
				40	$(1.07 \pm 0.01) \times 10^{-4}$			
				45	$(2.15 \pm 0.01) \times 10^{-4}$			
				50	$(4.58 \pm 0.03) \times 10^{-4}$			
H <sub>2</sub> O	18	54.8		25	after 48 h no changes <sup>d</sup>			

<sup>a</sup>Refs. 24, 25. <sup>b</sup>Refs. 24, 25, 27. <sup>c</sup>Refs. 26, 28. <sup>d</sup>Ref. 19.

pseudo-first-order rate constant increases along the series  $\text{H}_2\text{O} \ll \text{CH}_3\text{OH} < \text{DMSO} < \text{DMF}$ , which seems to correlate with the electron donation ability (DN) of the solvent.

The pressure dependence of reaction (1) was studied in the range 1–1000 atm. In every case the observed rate constant decreases significantly with increasing pressure (Table 3) resulting in large positive volumes of activation,  $\Delta V^\ddagger$ . These values strongly support the dissociative nature of reaction (1), for which the suggested mechanism is given in (2).



Neglecting the reverse replacement of S by  $\text{NO}_2^-$ , because of the large excess of S over  $\text{NO}_2^-$  and the relative stability of the final reaction product  $\text{Fe}^{\text{III}}(\text{CN})_5\text{S}^{2-}$ , application of the steady-state approximation to the hypothetical intermediate  $\text{Fe}^{\text{III}}(\text{CN})_5^{2-}$  results in the rate law (3).

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{S}]}{k_{-1} [\text{NO}_2^-] + k_2 [\text{S}]} \quad (3)$$

Under the reaction conditions employed,  $[\text{S}] \gg [\text{NO}_2^-]$  such that eqn. (3) reduces to  $k_{\text{obs}} = k_1$ , the rate constant for the dissociation of  $\text{NO}_2^-$  from  $\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2^{3-}$ .

The studied reactions are quite specific in that the attacking ligand S is simultaneously the solvent

TABLE 3. Effect of Pressure on the Solvolysis of  $\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2^{3-}$ 

Solvent	$T$ (°C)	Pressure (MPa)	$k_{\text{obs}}$ (s <sup>-1</sup> )	$\Delta V^\ddagger$ (cm <sup>3</sup> mol <sup>-1</sup> )
DMF	25	5	$(9.50 \pm 0.08) \times 10^{-4}$	$26.9 \pm 1.5$
		25	$(7.85 \pm 0.05) \times 10^{-4}$	
		50	$(5.49 \pm 0.04) \times 10^{-4}$	
		73	$(4.74 \pm 0.03) \times 10^{-4}$	
		100	$(3.36 \pm 0.04) \times 10^{-4}$	
DMSO	25	5	$(1.03 \pm 0.02) \times 10^{-4}$	$25.9 \pm 1.1$
		27.5	$(7.76 \pm 0.70) \times 10^{-5}$	
		50	$(6.20 \pm 0.35) \times 10^{-5}$	
		75	$(4.90 \pm 0.18) \times 10^{-5}$	
CH <sub>3</sub> OH	45	0.1	$(2.15 \pm 0.01) \times 10^{-4}$	$19.6 \pm 1.8$
		25	$(1.84 \pm 0.03) \times 10^{-4}$	
		50	$(1.43 \pm 0.01) \times 10^{-4}$	
		75	$(1.34 \pm 0.02) \times 10^{-4}$	
		100	$(9.97 \pm 0.20) \times 10^{-5}$	

in which reaction (1) proceeds. Therefore, in the kinetic analysis of reaction (1) properties of S should be considered as characteristic for the attacking ligand and for the solvent. It was reported [29, 30] that the  $\sigma$ -donor capacity, reflected by the  $pK_a$  of the protonated form, is the dominant factor in affinities of ligands for the  $\text{Fe}^{\text{III}}(\text{CN})_5^{2-}$  moiety. But considering the reaction conditions employed and the suggested limiting dissociative mechanism, S seems to play a more important role as a solvent than as a ligand. The solvation of the leaving ligand  $\text{NO}_2^-$  in the transition state appears to be of secondary importance. One would expect  $\text{NO}_2^-$  to be better solvated in water than in the studied organic

solvents, with the result that the rate constant should follow an increasing AN and not an increasing DN of the solvent. Therefore difference in the solvation of  $\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2^{3-}$  seems to control the kinetics of reaction (1).

In this respect it is important to note that the redox system  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  has been studied in detail for many different solvents [27]. The nitrogen atoms in both complexes could in principle act as electron pair donors, although the donor properties are significantly stronger for the Fe(II) than for the Fe(III) complex. Fe(III) is a much stronger electron acceptor than Fe(II) and is a much weaker  $\pi$ -electron pair donor. Acceptor-donor interactions between  $\text{Fe}(\text{CN})_6^{4-}$  and the solvent molecules were postulated to be responsible for the drastic shift in  $E_{1/2}$  for the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  system to more negative values in organic solvents, viz. 0.95 (H<sub>2</sub>O), 0.46 (CH<sub>3</sub>OH), -0.27 (DMSO) and -0.30 V (DMF).

The results of the present study also confirm that the interaction of  $\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2^{3-}$  with the solvent molecules can not be neglected, although the effect will be weaker than for the Fe(II) complexes. From the data in Table 2 it can be concluded that the rate of solvolysis increases with increasing DN of the solvent. The interaction of the solvent with the cyanide ligands results in an increased electron density on the metal center, which will then favour a dissociative reaction mode for the replacement of nitrite. Not only does the rate constant parallel the trend in *DN* of the solvent, but even  $\Delta V^\ddagger$  becomes more positive on increasing *DN*. Thus the electron donating ability of the solvent mobilizes the electron density toward the metal center and induces the dissociative mechanism. The magnitude of  $\Delta V^\ddagger$  is in good agreement with that reported for the solvolysis reactions of Fe(II) complexes in general (refs. 20, 31 and literature cited therein), which supports the operation of a D mechanism.

#### Catalytic Effects of Acid and Base

For aqueous solutions of  $\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2^{3-}$  we recently reported acid-catalysed aquation and base hydrolysis in acidic (pH < 5) and basic (pH > 10) media, respectively [19, 20]. Base hydrolysis was found to be catalysed by iron(II) species [20]. It is of interest to see whether such catalytic effects also occur in non-aqueous media.

Spectral changes recorded for all studied solvents in the presence of HClO<sub>4</sub> were the same as in the absence of acid and clearly suggested solvolysis of the NO<sub>2</sub><sup>-</sup> ligand. The rate of dissociation of NO<sub>2</sub><sup>-</sup> was found to be strongly affected by the concentration of acid. In the presence of acid the rates were up to several orders of magnitude larger than in pure solvents. For example, in the presence of  $6 \times 10^{-2}$  M acid in DMSO the rate increases into the stopped-

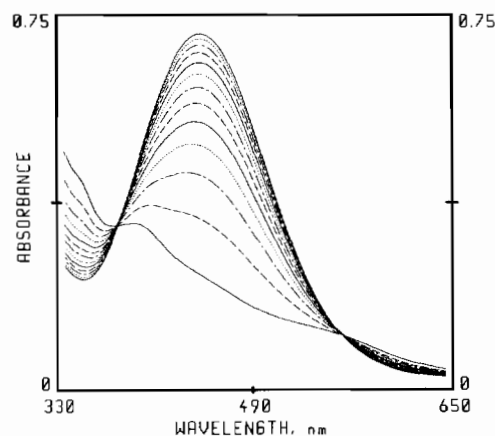


Fig. 2. Repetitive scan spectra for solvolysis of  $\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2^{3-}$  in CH<sub>3</sub>OH in the presence of NaOH. [ $\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}_2^{3-}$ ] =  $5 \times 10^{-4}$  M; [NaOH] =  $10^{-2}$  M;  $\Delta t$  = 10 min; temperature = 50 °C; 1 cm optical path.

flow range (ca.  $10^4$  times the rate in pure DMSO). In the presence of acid the nitrite ligand is presumably protonated, as suggested for the reaction in water [19, 20], which results in the weakening of the Fe-N bond and an increase in rate constant.

The influence of base (NaOH) on the solvolysis reaction of  $\text{Fe}(\text{CN})_5\text{NO}_2^{3-}$  was different in protic (CH<sub>3</sub>OH) and aprotic (DMSO, DMF) organic solvents. For methanolic solution, formation of the  $\text{Fe}(\text{CN})_5\text{OCH}_3^{3-}$  complex was observed (Fig. 2). The rate constant for this process increases slightly with increasing [OH<sup>-</sup>] and no evidence for the catalytic effect of iron(II) species was observed. The reaction follows a first-order rate law. For aprotic solvents (DMSO, DMF), the reaction paths in the presence of base are more complicated. Addition of aqueous NaOH results in the formation of  $\text{Fe}(\text{CN})_5\text{OH}^{3-}$ , which is in agreement with the production of this species in mixed aqueous solvents during the reaction of  $\text{Fe}(\text{CN})_5\text{S}^{2-}$  with OH<sup>-</sup> [22]. On the contrary, when solid NaOH is used (ca.  $10^{-2}$  M)  $\text{Fe}(\text{CN})_5\text{S}^{2-}$  complexes are produced in all the studied solvents with almost no increase in rate constant. It follows that the Fe(II) catalysed path observed during the aquation of  $\text{Fe}(\text{CN})_5\text{NO}_2^{3-}$  in basic medium [20], does not show up in the investigated solvents.

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