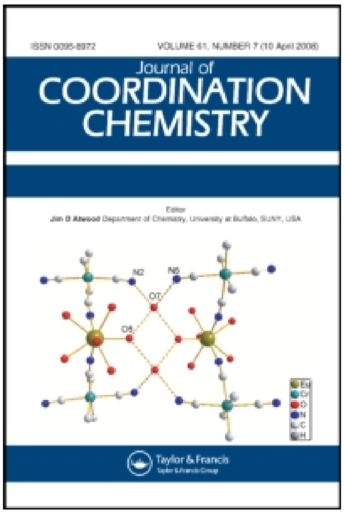

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KINETICS OF SUBSTITUTION OF NICOTINAMIDE AT PENTACYANO(NICOTINAMIDE)IRON(II) BY DIMETHYL SULFOXIDE IN AQUEOUS AND NON-AQUEOUS SOLVENTS

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The effect of organic cosolvent on the rate constant and activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ of substitution of nicotinamide at pentacyano(nicotinamide)iron(II) by dimethyl sulfoxide was investigated in mixtures containing up to 50% methanol, *t*-butanol, acetone, acetonitrile, glycerine and glycol. From correlations between the logarithm of the rate constant and Grunwald-Winstein Y values, and between $\delta_m\Delta G^{\ddagger}$ and excess Gibbs free energy of mixing G^E, the effect of the change in the solvation on the reaction rate was elucidated. The effects of pH on the reaction rate and activation parameters, and the effect of organic cosolvent on the shift of the charge-transfer band of the complex mentioned above are also reported.

INTRODUCTION

The medium effects on the kinetics of the substitution reactions of pentacyanoferrates(II), $[Fe(CN)_5L]^{3-}$ (L = *N,N*-dimethylenediamine, 3-cyanopyridine, 4-cyanopyridine, 3,5-dimethylpyridine and piperidine) have been the subject of several studies.[1–5] In these papers the discussion is concerned with the influence of the nonaqueous component of the mixed solvents on the solvation of both the initial and transition state. Pseudo-first-order conditions were ensured, maintaining the concentration of the leaving ligand in excess. It was found that the reaction rate is influenced mainly by the solvation of the transition state.[6] The dependence of $\delta_m\Delta G^{\ddagger}$ on the excess free enthalpy indicates that the rate of dissociation of ligand L from $[Fe(CN)_5L]^{3-}$ correlates with the hydrophobicity of that ligand.[2,5,7] The protonation equilibria play also an important role.[8,9] Deprotonation causes a decrease of reaction rate that can again be interpreted in terms of the solvation of transition state. Hence it follows that the character of the ligand will influence the dependence of the reaction rate on the mole fraction of nonaqueous component. Therefore in the present work we investigated the influence of cosolvent on reaction rate and activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ of the reaction (*1*) as well as on the equilibrium (*2*).

$$[Fe(CN)_5 na]^{3-} + DMSO \rightarrow [Fe(CN)_5 DMSO]^{3-} + na \qquad (1)$$

$$[Fe(CN)_5 py]^{3-} + na \rightleftharpoons [Fe(CN)_5 na]^{3-} + py \qquad (2)$$

The study of the equilibrium gives some new information on the investigated reaction. With regard to the possible protonation of the CN ligand in an acid medium,

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and deprotonation of -CO-NH_2 group in an alkaline solution, the influence of pH on reaction rate and activation parameters was studied. The solvation of the complex ion in mixed solvents and its changes with solvent composition causes solvatochromism which was also measured.

EXPERIMENTAL

The sodium salt of pentacyano-nicotinamideferrate was prepared by the method described in[10] for pentacyano-isonicotinohydrazideferrate, sodium ammine-pentacyanoferrate being the initial compound. [$Na_3[Fe(CN)_5na].5H_2O$: calc.: C, 28.3; H, 3.4; N, 21.0%; found: C, 28.1; H, 3.3; N, 20.0%]. The absorption spectra were measured using a SPECORD UV-VIS spectrophotometer; kinetic measurements were made on SPECOL 10 and SPECOL 210 spectrophotometers linked to a K 200 recorder and a TEC-1 A/D converter (all Carl Zeiss, Jena). The reaction was followed by measuring the absorbance change of a reaction mixture placed in a 1 cm thermostatted (±0.2 K) cell. The measurements were performed at 400 nm during at least three half-lives of the reaction. In order to prevent equation of the initial complex, nicotinamide was supplied to the reaction mixture. The concentration of dimethyl sulfoxide in the reaction solution was 0.1 mol dm^{-3}. Under these conditions the dissociation of the nicotinamide ligand is the rate determining step, and the reaction is of the first-order. The reaction product $[Fe(CN)_5DMSO]^{3-}$ exhibits an absorption maximum at 352 nm.[11] The rate constants were evaluated from the measured absorbance as a function of time by the Guggenheim's method. Each constant given in the tables is an average of 4-6 independent values. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined from the temperature dependence of the rate constants, and the accuracy of these quantities was evaluated accordingly.[12] In connection with the study of the dependence of the reaction rate on pH, the following buffer solutions were used: phtalate (pH 2.2-5.9), phosphate (6.0-8.0), borate (8.0-10.2), and carbonate (10.0-11.0). The relative stability constant was evaluated by the literature procedure.[13] The absorbance of equilibrated solutions was measured after 90 min. at 670 nm.

RESULTS AND DISCUSSION

Pentacyano(nicotinamide)iron(II) shows and absorption maximum at $\lambda = 398$ nm ($\varepsilon = 2.7 \times 10^2$ dm^2 mol^{-1}) in neutral solution (pH=7). The shift of this absorption band

TABLE I

The effect of various electrolytes on substitution of nicotinamide at pentacyano(nicotinamide)iron(II) by dimethyl sulfoxide. ($C_{[Fe(CN)_5na]^{3-}} = 3.5 \times 10^{-4}$ mol dm^{-3}, $c_{DMSO} = 0.1$ mol dm^{-3} $c_{na} = 4 \times 10^{-3}$, $T = 293.2$ K).

electrolyte	c (mol dm^{-3})	$k \times 10^3$ (s^{-1})
none	added	1.23 ± 0.02
$NaClO_4$	1.0	1.22 ± 0.03
$LiClO_4$	1.0	1.13 ± 0.02
$Mg(ClO_4)_2$	0.4	1.08 ± 0.02
$Mg(ClO_3)_2$	1.0	0.86 ± 0.05
Na_2SO_4	1.0	1.12 ± 0.02

TABLE II
Dependence of the rate constant and activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the substitution of nicotinamide at pentacyano(nicotinamide)iron(II) by dimethyl sulfoxide on pH.

pH	$k \times 10^3$ (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
2.2	2.77 ± 0.15	95 ± 4.5	101 ± 15
3.0	3.65 ± 0.11	107 ± 3.3	154 ± 11
4.0	3.25 ± 0.07	108 ± 2.7	145 ± 9
5.0	3.22 ± 0.12	110 ± 3.9	151 ± 13
5.9	3.30 ± 0.07	108 ± 3.0	138 ± 10
7.0	3.38 ± 0.07	107 ± 3.5	131 ± 12
8.0	3.36 ± 0.10	105 ± 2.9	135 ± 10
9.0	3.18 ± 0.12	108 ± 4.0	151 ± 13
10.0	3.25 ± 0.10	108 ± 3.6	144 ± 12
11.0	3.13 ± 0.11	110 ± 3.4	171 ± 11
^{c}NaOH(mol dm^{-3})			
0.01	3.57 ± 0.04	105 ± 2.7	151 ± 9
0.1	3.31 ± 0.11	108 ± 3.0	164 ± 10
0.5	2.32 ± 0.12	108 ± 3.6	131 ± 12
0.8	2.03 ± 0.15	92 ± 2.6	83 ± 9
1.0	1.53 ± 0.13	95 ± 3.4	109 ± 11

by about 30 nm to higher energies was observed at pH = 2.2–3.0. Because $c_{DMSO} >> c_{na}$ the experimental rate constant is identical with the rate constant of release of nicotinamide from the investigated complex ($k_{exp} = k_{diss}$). The reaction rate was not influenced by further addition of dimethyl sulfoxide.

In the Table I are set out the rate constants obtained at different ionic strengths adjusted with various electrolytes. The most remarkable decrease in the rate constant was observed in the presence of Mg^{2+} ions.

Table II shows the dependence of rate constant and activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ on pH within the pH range 4–11 and in 0.01–1.0 mol dm^{-3} NaOH. Decrease of the reaction rate was observed at concentrations higher than 0.5 mol dm^{-3} NaOH. No change in the spectrum of $[Fe(CN)_5na]^{3-}$ was observed with and without the presence of dimethyl sulfoxide in 0.5 mol dm^{-3} NaOH during several half-lives. Table III shows the dependence of rate constant and activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ on the concentration of organic cosolvent. Table IV shows the dependence of relative stabilities K on the mole fraction of cosolvent.

Figure 1 shows the correlation dependence $\log k_{T_2} = f(\log k_{T_1})$, which was obtained from the reported rate constants for several pentacyanoferrate(II) complexes.[10] Point 6 on this dependence corresponds to $[Fe(CN)_5na]^{3-}$. On Figure 2 is shown the dependence of transfer function $\delta_m \Delta G^{\ddagger}$ values on excess Gibbs free energy of mixing G^E. The values G^E for organic cosolvent were obtained from Ref. 14 and $\delta_m \Delta G^{\ddagger}$ values were calculated by equation (*3*)

$$\delta_m \Delta G^{\ddagger} = RT \log (k_{H_2O}/k_{x_2}) \qquad (3)$$

where k_{H_2O} and k_{x_2} are the rate constants for water and water-cosolvent, respectively. In Figure 3 Grunwald-Winstein dependences $\log k = \log k_0 + mY$ are illustrated.[15] The slopes of these dependences changed from m = 0.43 in mixtures of water-glycol to m = −0.14 in water-acetone. Figure 4 shows correlation dependences between standard free energy ΔG° and excess free energy of mixing G^E. Figure 5 shows the dependence of the wavelength of the charge transfer band of $[Fe(CN)_5na]^{3-}$ on the mole fraction of water.

TABLE III

Dependence of rate constant and activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the substitution of nicotinamide at pentacyano(nicotinamide)iron(II) by dimethyl dulfoxide on the mole fraction of organic cosolvent. ($C_{[Fe(CN)_5na]^{3-}} = 3.5 \times 10^{-4}$ mol dm^{-3}. $c_{DMSO} = 0.1$ mol dm^{-3} $c_{na} = 4 \times 10^{-3}$ mol dm^{-3}; T = 298.2 K).

x_2	$k \times 10^3$ (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
0	1.75 ± 0.07	107.0 ± 3.0	104 ± 8
		methanol	
0.047	1.72 ± 0.08	100.0 ± 2.1	104 ± 7
0.100	1.69 ± 0.06	100.1 ± 2.0	88 ± 7
0.160	1.72 ± 0.03	102.2 ± 2.1	111 ± 7
0.229	1.78 ± 0.05	103.8 ± 2.1	118 ± 8
0.309	2.02 ± 0.09	101.3 ± 2.8	112 ± 9
		t-butanol	
0.021	1.52 ± 0.07	108.0 ± 2.5	109 ± 8
0.046	1.45 ± 0.04	105.2 ± 2.4	129 ± 8
0.076	1.59 ± 0.04	104.1 ± 2.0	140 ± 7
0.113	1.56 ± 0.03	106.7 ± 1.7	197 ± 6
0.155	1.56 ± 0.05	110.0 ± 2.7	136 ± 9
		glycol	
0.035	1.08 ± 0.05	102.3 ± 2.7	187 ± 9
0.075	1.01 ± 0.05	104.2 ± 3.1	163 ± 10
0.121	0.846 ± 0.010	103.8 ± 2.0	161 ± 7
0.175	0.826 ± 0.025	106.9 ± 3.1	131 ± 10
0.240	0.709 ± 0.021	110.2 ± 2.5	130 ± 8
		glycerol	
0.031	1.42 ± 0.05	99.3 ± 2.0	120 ± 7
0.067	1.10 ± 0.03	101.2 ± 2.0	127 ± 7
0.110	0.890 ± 0.014	101.9 ± 2.1	132 ± 7
0.161	0.675 ± 0.010	105.0 ± 1.9	133 ± 7
0.217	0.473 ± 0.010	106.8 ± 2.2	137 ± 8
		acetonitrile	
0.036	2.16 ± 0.08	107.2 ± 2.1	83 ± 7
0.077	2.67 ± 0.02	104.9 ± 2.0	75 ± 7
0.126	3.05 ± 0.02	104.0 ± 2.0	72 ± 7
0.182	3.71 ± 0.18	93.2 ± 2.5	37 ± 8
0.249	4.33 ± 0.16	88.7 ± 2.1	25 ± 7
		acetone	
0.026	1.68 ± 0.03	104.8 ± 1.5	117 ± 5
0.058	1.65 ± 0.06	103.6 ± 2.0	140 ± 7
0.096	2.11 ± 0.08	110.4 ± 3.0	149 ± 10
0.141	2.24 ± 0.05	111.2 ± 1.5	149 ± 5
0.198	2.88 ± 0.07	109.8 ± 3.0	149 ± 10

Table IV

Dependence of relative stabilities, K, for the equilibrium between the pyridine and nicotinamide complexes $[Fe(CN)_5L]^{3-}$ (Equation (*2*) in text) on solvent composition at 298.2 K.

methanol		*t*-butanol		glycol	
x_2	K	x_2	K	x_2	K
0	1.04	0	1.04	0	1.04
0.047	1.17	0.021	1.14	0.031	1.03
0.100	1.23	0.046	1.14	0.067	1.08
0.160	1.32	0.076	1.27	0.110	1.09
0.229	1.40	0.113	1.57	0.161	1.07

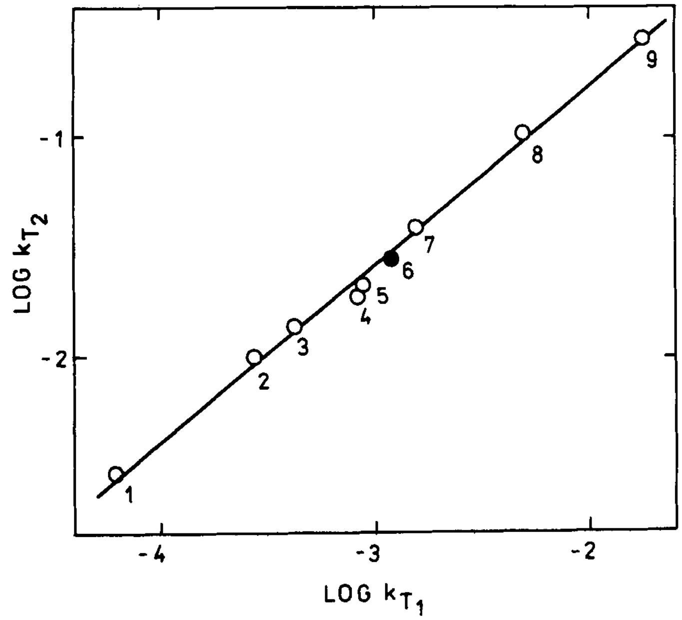


FIGURE 1 Relation between log k_{T_2} and log k_{T_1} for ligand substitution at $[Fe(CN)_5L]^{3-}$ ions; $T_1 = 25°$, $T_2 = 50°$, L = 1 — SO_3^{2-}; 2 — *N*-methylpyrazinium; 3 — pyrazine; 4 — isonicotinamide; 6 — nicotinamide; 7 — pyridine; 8 — ethylenediamine; 9 — NH_3.

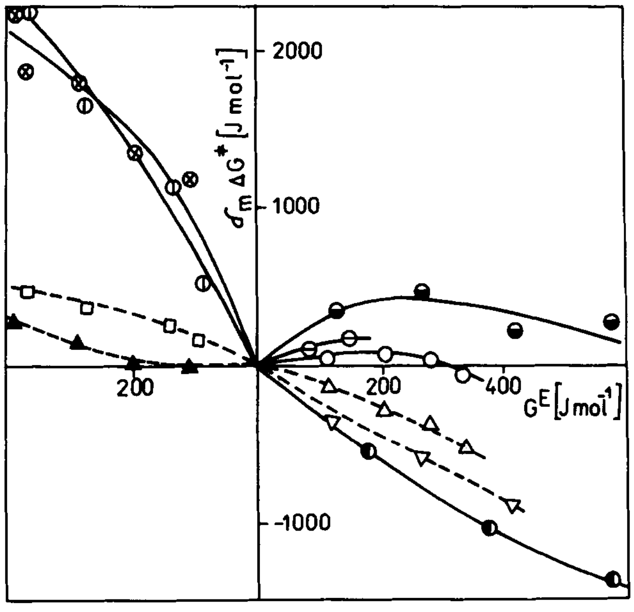


FIGURE 2 Relation between $\delta_m \Delta G^{\neq}$ and G^1 for limiting rates of substitution at $[Fe(CN)_{5na}]^{3-}$ in binary aqueous mixtures. Co-solvents (○) methanol, (⊖) acetone, (◒) *t*-butanol, (◐) acetonitrile, (⦶) glycerol, (⊗) glycol and for limiting rates of subtitution at $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ from the literature.[4] Co-solvents (Δ) methanol; (▼) *t*-butanol; (▲) glycol; (□) glycerol.

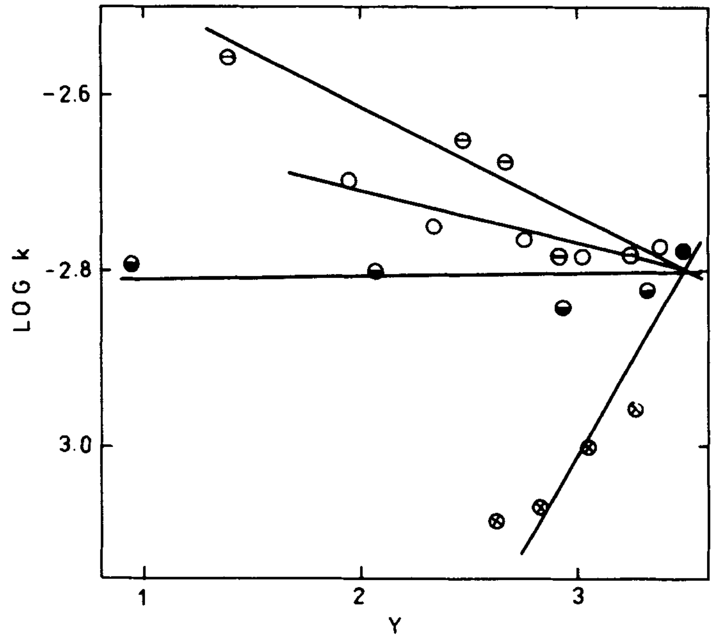


FIGURE 3 Grunwald-Winstein plot for reaction of $[Fe(CN)_5na]^{3-}$ with DMSO under limiting conditions. Co-solvents (●) H_2O; (○) methanol; (◓) *t*-butanol; (⊖) acetone; (⊗) glycol.

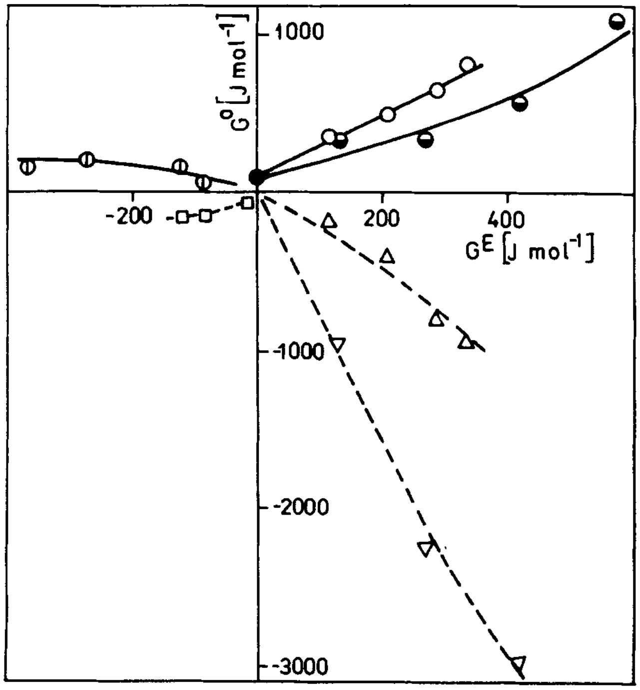


FIGURE 4 Relation between ΔG° and G^E in binary aqueous mixtures for the equilibrium between pyridine and the $[Fe(CN)_5na]^{3-}$ ion and for the equilibrium between pyridine and the $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ ion.[4] Symbols as in Figure 2.

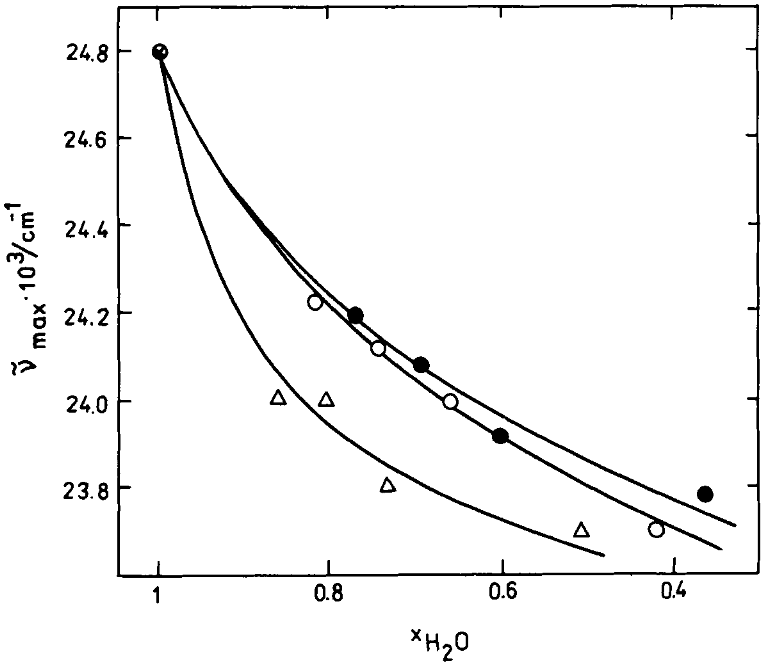


FIGURE 5 Dependence of the energy of the change-transfer band of $[Fe(CN)_{5na}]^{3-}$ on mole fraction of water. (●) methanol; (○) acetonitrile; (△) acetone, (⊗) water.

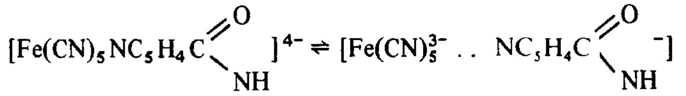
Pyridine and its derivatives are bonded to iron through their nitrogen atoms[10,16] in pentacyanoiron(II) complexes. All these complexes exhibit an absorption band in the visible region. The shift of the absorption band of $[Fe(CN)_5na]^{3-}$ observed in acid solutions is connected with CN group protonation. A similar shift was observed for other complexes of the $[Fe(CN)_5L]^{3-}$ type.[16]

The dependence $\log k_{T_2} = f(\log k_{T_1})$, (Figure 1), whose substance and consequences were described in Ref. 17, was linear. It has been noted that all the pentacyanoferrates in Figure 1 undergo identical dissociative reactions under given conditions.

The reaction rate has been changed with ionic strength only very little; at higher ionic strengths, little decrease of rate constant was found, a specific effect of cations being observed to some extent (Table I). The effect of Mg^{2+} ions is probably connected with the formation of the ion-pair $\{Mg^{2+}, [Fe(CN)_5na]^{3-}\}$. No substantial change of rate constant and activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ in the pH interval 4–11 was observed. Small changes of reaction rate in the pH interval mentioned above (Table II) could be due to different types of buffer solutions and different ratios of electrolyte concentrations in these solutions. A smaller decrease of reaction rate at pH = 2 is connected with CN-group protonation. In strongly alkaline media the deprotonation of the $-CO-NH_2$ group can be expected in the same way as the deprotonation of the $-CO-NH-NH_2$ group at pentacyano(isonicotinohydrazide)iron(II) ion.[8]

The ligand deprotonation is reflected in the reaction rate decrease. In comparison with the isonicotinohydrazide ligand, where the decreases in reaction rate was observed at pH = 10, for the nicotinamide ligand the reaction rate decrease occurred only in very strong base (0.5 mol dm^{-3} NaOH). It can be assumed that no hydrolysis of the amide group occurred. If the contrary were true, the spectrum in the visible region would be changed in a manner akin to pentacyanoferrate(II) complexes with isonicotinic acid and isonicotinamide.[16]

According to previous workers,[6] for the given type of reaction, the change in the solvation shell of the transition state is decisive. The decrease in reaction rate caused by deprotonation can be then explained by a destabilisation of the transition state of the investigated complex, in which the negative charge will be delocalised at the ligand (*4*)



$$[\mathrm{Fe(CN)_5NC_5H_4C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{NH}}]^{4-} \rightleftharpoons [\mathrm{Fe(CN)}_5^{3-}\,..\,\mathrm{NC_5H_4C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{NH}}{}^{-}] \qquad (4)$$

The decrease in reaction rate of the deprotonated form of the complex may be also explained by easier formation of ion-pairs with the complex ion. In strongly alkaline media a decrease in activation enthalpy and entropy was observed, this effect being contrary to that reported earlier.[8]

As with similar reactions of pentacyano(3,5-dimethylpyridine)iron(II) ion[4] and pentacyano(piperidine)iron(II) ion[1,2] effects of added non-aqueous solvent on the reaction rate and activation parameters were observed. In typically aqueous solvents, ($G^E > 0, |TS^E| > |H^E|$, G^E, S^E and H^E are excess parameters of mixing) as methanol, *t*-butanol and acetone the rate constants and $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ have been changed with concentration of cosolvent only by small amounts (Table III).

In water-*t*-butanol and water-acetone mixtures the minimum of $\log k = f(x_2)$ was observed at a mole fraction $x_2 \sim x_2^{*}$, at which ratio the cosolvent exerts its maximum water structure-forming effect. In typically non-aqueous solvents ($G^E < 0, |H^E| > |TS^E|$) as glycerine and glycol, the reaction rate decreased with increasing concentration of non-aqueous cosolvent, while the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ changed only slightly. Reaction rates increased with the concentration of acetonitrile, which solvent belongs to typically non-aqueous positive solvents ($G^E > 0, |H^E| > |TS^E|$) while the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ decreased. Figure 2 clearly illustrates the different effects of cosolvent on the investigated reaction. The results for water-*t*-butanol fall in the positive $\delta_m\Delta G^{\ddagger}$ - positive G^E quadrant while for mixtures of water with methanol and acetone respectively, no change has been observed over the given concentration range. For reaction of pentacyano(piperidine)iron(II),[1] pentacyano(3,5-dimethylpyridine) iron(II)[4] and tris(5-nitro-1,10-phenanthroline)iron(II)[14] all the results for typically aqueous solvents fall into the negative $\delta^{m}\Delta G^{\ddagger}$ - positive G^E quadrant. This fact has been ascribed to efficient solvation of hydrophobic groups of the ligands in the transition state. The stabilisation of the activated complex caused by this solvation enhances the reaction rate. Hence in water-methanol and water-acetone (up to $x_2 = 0.15$) no marked change of the solvation shell of the nicotinamide complex apparently took place in the transition state. In water-*t*-butanol mixtures the activated complex is destabilised. A similar trend of dependence $\delta_m\Delta G^{\ddagger} = f(G^E)$ for the piperidine complex[2] in water-acetonitrile was observed for the $[\mathrm{Fe(CN)_5na}]^{3-}$ ion. Figures 2 and 4 clearly illustrate the difference in hydrophobic properties of the ligands 3,5-dimethylpyridine and nicotinamide. For typically non-aqueous negative solvents (glycerine, glycol) the results for 3,5-dimethylpyridine and nicotinamide complexes, respectively, fall into the positive $\delta_m\Delta G^{\ddagger}$ - negative G^E quadrant with the values of $\delta_m\Delta G^{\ddagger}$ for the second complex about 4 times higher than for the former at the same x_2. In the mixture of water with glycerine and glycol prevailing intercomponent interactions associated with hydrogen bonding can explain the greater decrease in reaction rate observed for $[\mathrm{Fe(CN)_5na}]^{3-}$ than for $[\mathrm{Fe(CN)_5(3,5\text{-}Me_2py)}]^{3-}$. The hydrophilic nicotinamide ligand, due to the presence of the amido group, is solvated to a greater extent than the 3,5-$\mathrm{Me_2py}$ ligand. Thus, addition of a cosolvent which can bond water molecules causes a marked change in the solvation shell of nicotinamide.

Specific solvent effects can be also observed on the Grunwald-Winstein plot (Figure 3). For reactions with a dissociative mechanism, positive m values[19] are characteristic. Negative m values have been reported for substitutions at pentacyano(3,5-dimethylpyridine)iron(II) ion in water-*t*-butanol, in water-methanol and in water-ethanol mixtures (m = -0.1[4]) at (*N,N*-dimethylenediamine)iron(II) ion in water-methanol (m = -0.3[3]) and for the aquation of hexabromorhenate (m = -0.55[20]). Negative m values can be explained by different solvation of the parts of the complex containing the hydrophilic CN groups and the hydrophobic ligand.[4] From similar changes of rate constants for reactions of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$, $[Fe(CN)_5(3\text{-}CNpy)]^{3-}$ and $[Fe(CN)_5(3\text{-}Clpy)]^{3-}$ on going from water to 40% *t*-butanol it has been concluded[4] that the solvation of the leaving group does not play an important role. The effect of the nature of the solvent on m values for the $[Fe(CN)_5na]^{3-}$ ion shows that in this case the change of reaction rate can be connected with the solvation of the leaving group, nicotinamide.

The dependence of relative stabilities K (*2*) on cosolvent concentration reflects the differences between nicotinamide and 3,5-Me_2py ligands (Table IV). Different trends of plots $G^\circ = f(G^E)$ for nicotinamide and 3,5-Me_2py (Figure 4) also refer to different solvation of nicotinamide with its hydrophilic group and ligands with hydrophobic groups.

The charge transfer spectrum of $[Fe(CN)_5na]^{3-}$ varies markedly with solvent composition as is the case with other $[Fe(CN)_5L]^{3-}$ complexes.[4,21] In all investigated solvents the bathochromic shift occurs with increasing mole fraction of organic cosolvent especially in water-acetone, water-acetonitrile and water-methanol mixtures. From the fact that the dependence of CT band energy on the mole fraction of water (or non-aqueous cosolvent) is not linear (Figure 5), as well as from the character of this dependence, it can be concluded[21,22] that is the investigated solvents preferential solvation of the complex ion by the nonaqueous cosolvent occurs.

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