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Kinetics of the Reaction of Pentacyanonitrosylferrate(II) with Aliphatic Amines

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The reactions of pentacyanonitrosylferrate(II) with ethyl-, n-propyl-, n-butyl-, cyclohexyl- and benzylamines were studied in dilute aqueous solution at 8.6–9.6 pH and 15–35 °C. Nitrosation, diazotation and deamination processes take place in the reactions resulting in alcohols and N_2 gas as final products. On the basis of spectrophotometric and gas-volumetric experiments the rate law was determined as follows.

$$v = k[RNH_2][Fe(CN)_5NO^{2-}]$$

The dependence on pH was interpreted by the protonation equilibria of the amines. From the function of the logarithm of rate constants vs. *reciprocal temperature, relatively small activation enthalpies (15–70 kJ mol^{-1}) and extremely high negative activation entropies [(–80) – (–240) J K^{-1} mol^{-1}] were found. The mechanism was interpreted by the analogy with nitrous acid diazotation.*

A parallel trend was observed between the rate constants at 25 °C and the basicity constants of the amines.

Introduction

The study of the reactions of pentacyanonitrosylferrate (PNF) with inorganic amines [1] (ammonia, hydroxylamine and hydrazine) initiated investigations involving the nitrosation-diazotisation of organic amino compounds by nitrosyl complexes. The basic reactions were found at the beginning of this century [2], but were applied only for the preparation of some amine-containing complexes [3, 4]. The organic products of several reactions were determined by Maltz and co-workers [5] and the special nitrosating behaviour of PNF was observed. According to our earlier study with amino acids [6] and nucleobases [7] these nitrosation reactions may have synthetic organic importance. Therefore we began a systematic study of the reaction of PNF with different amine-containing organic compounds to investigate the factors determining the reactivity of amine groups towards PNF. In this paper the results of the kinetic studies with aliphatic amines, ethyl-, n-propyl-, n-butyl-, cyclohexyl- and benzylamines are summarized.

Experimental

Materials

$Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (REACHIM) and the amines (Fluka) were reagent grade commercial products. The amines were freshly distilled before use. The ionic strength was adjusted with $NaClO_4$ which was prepared from $HClO_4$ and $NaHCO_3$ and recrystallized. Boric acid (as buffer) and the other reagents were analytical pure commercial products. $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was prepared by Hoffman's method [2].

Methods

The reactions were followed gas-volumetrically and spectrophotometrically. The products were identified by the UV–visible spectra of the solutions and by the mass spectra of the gas evolved. The amount of the organic end-products were determined by permanganate titration [8].

Instruments

Beckman Acta III, Hitachi-Perkin-Elmer 139 and 402 spectrophotometers, QGA-2 (ATOMKI) quadrupole mass spectrometer were used. The gas volumetric measurements were carried out using a Warburg instrument and a home-made gas burette system.

Results

Stoichiometry of the Reactions

The reactions are indicated by gas evolution and a color change. The only gaseous product is N_2 according to the mass spectrometric measurements. The change in color is due to the formation of $Fe(CN)_5H_2O^{3-}$ and $Fe(CN)_5amine^{3-}$, in excess of the reagent amines, respectively. One mole of N_2 forms from one mole of complex, which is the same ratio as in the reactions of nitrous acid with aliphatic amines. Only primary aliphatic alcohols can be detected as organic products by mass spectrometric and gas chromatographic experiments, while in the reactions of nitrous acid with the corresponding amino acids secondary alcohols and olefines are obtained in about the same quantity as the primary alcohols [9]. Maltz *et al.* also observed this trend in

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TABLE I. The Amount of N_2 and ROH Formed in the Reaction of 1 Mole of $Na_2[Fe(CN)_5NO]$.

	Ethyl-amine	n-Propyl-amine	n-Butyl-amine	Cyclohexyl-amine	Benzyl-amine
N_2	0.98	1.00	1.00	0.99	0.98
ROH	0.92	0.89	0.82	0.86	0.90

$[Na_2Fe(CN)_5NO]$ = 0.5 mol dm^{-3}; [Amine] = 1.0 mol dm^{-3}; pH = 9.0 (borate buffer); T = 25 °C.

TABLE II. Condition of Reactions at the Kinetic Measurements.

Method	[Amine] mol dm^{-3}	$[Fe(CN)_5NO^{2-}]$ mol dm^{-3}	pH	Temperature °C
Spectrophotometry	0.05–0.2 0.025–0.1[a]	0.005–0.02	8.6–9.6	15–35
Gas-volumetry	0.1–0.4 0.05–0.2[b] 0.02–0.08[a]	0.005–0.02	9.6	25

Ionic strength = 1.0. [a] At benzylamine. [b] At cyclohexylamine.

the products ratio: mostly 20% of other products were found besides the primary alcohols. The quantitative determination was carried out as follows. After the reaction was complete, the mixture was acidified and then distilled. The cyanide in the condensate was precipitated by silver nitrate. After filtration the amount of alcohol was determined permanganometrically.

The results of the stoichiometric measurements are summarized in Table I. According to this the stoichiometry of the reactions is:

$$Fe(CN)_5NO^{2-} + RNH_2 + OH^- = Fe(CN)_5H_2O^{3-} + N_2 + ROH \quad (1)$$

where: R = C_2H_5, n-C_3H_7, n-C_4H_9, benzyl, cyclohexyl.

Kinetic Measurements

The reactions were followed by spectrophotometric measurement of the product $Fe(CN)_5H_2O^{3-}$ and gas-volumetrically. After 20–30% conversion the spectrophotometric measurements were modified by the presence of N_2 bubbles, while for gas volumetry the determination of the starting point is less exact. Consequently the two methods are complementary.

For the spectrophotometric evaluation, the equation

$$v_0 = \frac{1}{\epsilon_A - \epsilon_N}\frac{dA}{dt} \quad (2)$$

was used, where ϵ_A is the extinction coefficient of the aqua complex, ϵ_N is that of PNF at 395 nm, dA/dt is the limiting slope of a plot of A *vs.* t at zero time, v_0 is the initial rate.

However, the absorbance is influenced by different side-reactions:

1. Light causes a small amount of decomposition of PNF to the aqua complex; this does not influence its analytical concentration, but does affect the absorbance because of the high extinction coefficient of the aqua complex.
2. When the amines are in excess they can enter into the coordination sphere:

$$Fe(CN)_5H_2O^{3-} + RNH_2 \longrightarrow Fe(CN)_5NH_2R^{3-} + H_2O \quad (3)$$

Therefore the value of ϵ_N was determined by extrapolation of the absorbance to t = 0. The value of ϵ_A was determined by measuring the absorbance of aquapentacyanoferrate in the presence of amines. In this way the values of ϵ_A were found as follows: 415 with ethyl-, 420 with n-propyl-, n-butyl- and cyclohexyl-, and 425 with benzylamines.

In the experiments the amine concentrations were varied between 0.05–0.8 *M*, the complex concentrations were between 0.005–0.02 *M* and the pH range was between 8.60–9.60. The ionic strength was adjusted to 1.0. The rate law for a reaction was determined from about 50 reaction mixtures of different compositions. One rate value was taken from the mean of 3 or more parallel runs.

The applied conditions are summarized in Table II. Some reaction/time curves are shown in Figs. 1, 2 and 3.

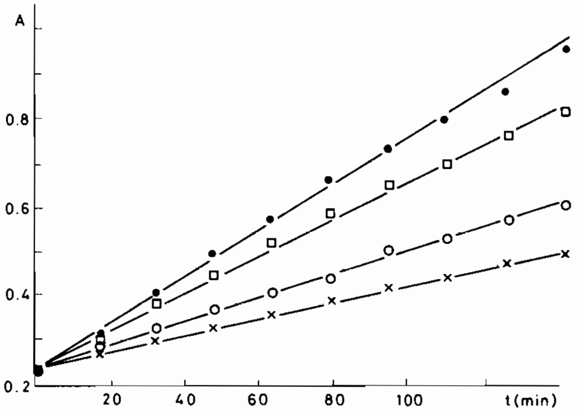


Fig. 1. Change of absorbance in the reactions of ethylamine at different amine concentrations. 1 cm cell length, 395 nm, pH = 9.0, 25 °C, concentration of complex: 0.01 mol dm^{-3}, concentration of ethylamine: ××× 0.05; ○○○ 0.1; □□□ 0.15; ●●● 0.2 mol dm^{-3}.

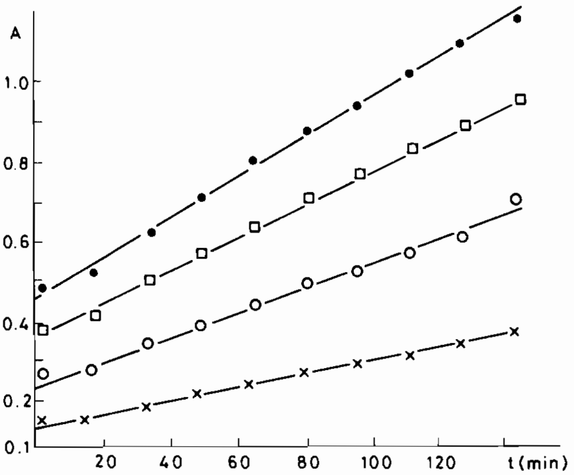


Fig. 2. Change of absorbance in the reactions of ethylamine at different complex concentrations. Concentration of ethylamine: 0.1 mol dm^{-3}, concentration of complex: ××× 0.005; ○○○ 0.01; □□□ 0,015; ●●● 0.02 mol dm^{-3} (for the other conditions see Fig. 1).

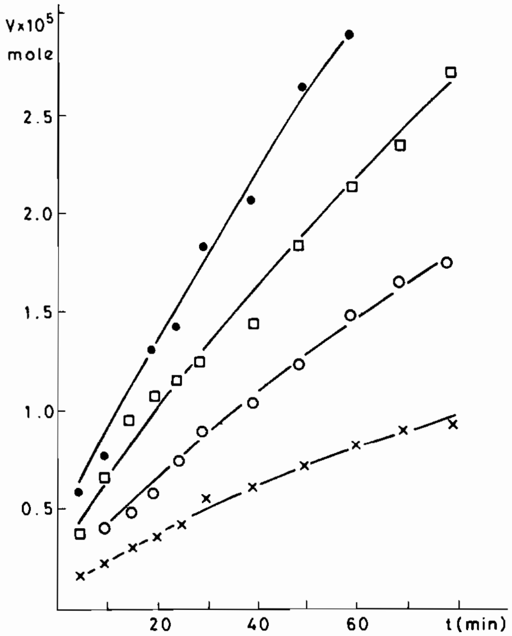


Fig. 3. Amount of evolved N_2 as a function of time. pH = 9.6, concentration of complex: 0.01 mol dm^{-3}, concentration of ethylamine: ××× 0.1; ○○○ 0.2; □□□ 0.3; ●●● 0.4 mol dm^{-3}.

TABLE III. The Reaction Orders.

Amine		Order in amines	Order in complex
Ethyl-	sp	0.95 ± 0.06	0.91 ± 0.05
	g	0.96 ± 0.15	0.85 ± 0.15
n-Propyl-	sp	1.00 ± 0.05	1.05 ± 0.06
	g	0.96 ± 0.14	1.25 ± 0.15
n-Butyl-	sp	1.12 ± 0.06	1.12 ± 0.05
	g	1.00 ± 0.15	0.72 ± 0.15
Cyclohexyl–	sp	1.05 ± 0.05	0.96 ± 0.05
	g	0.85 ± 0.15	0.88 ± 0.12
Benzyl-	sp	1.1 ± 0.05	0.89 ± 0.05
	g	0.86 ± 0.15	1.03 ± 0.13

sp: spectrophotometry. g: gas volumetry.

The orders in the amines and in the complex determined by the van't Hoff method were found to be one for both reactants (Table III).

The rate law is described by the form:

$$v_0 = k' c_A c_C \tag{4}$$

where c_A and c_C are the concentrations of the amines and that of the complex. The graphically-determined k′ values at 25 °C are summarized in Table IV.

These data show that k′ is a function of pH. The reaction of $Fe(CN)_5NO^{2-}$ with OH^- ions only plays a role [10, 11] above pH 11, so this is neglected and the pH dependence is interpreted by the protonation equilibria of the amines:

$$RNH_2 + H^+ \overset{K}{\rightleftharpoons} RNH_3^+ \tag{5}$$

Assuming that RNH_2 is the reactive form and RNH_3^+ is the unreactive form the rate law is:

$$v = k[RNH_2]c_C \tag{6}$$

Taking into account that:

$$[RNH_2] + [RNH_3^+] = c_A \tag{7}$$

the function of pH is expressed as follows

$$v = k \frac{1}{1 + K[H^+]} c_A c_C \tag{8}$$

TABLE IV. k' Rate Constants ($v = k' c_A c_K$).

Amine	$k' \times 10^5$ M^{-1} s^{-1}	pH = 8.6	pH = 8.8	pH = 9.0	pH = 9.2	pH = 9.4	pH = 9.6	
		sp					sp	g
Ethyl-	a	4.5	7.15	11.0	16.8	26.3	41.3	46.8
	b	–	–	11.6	–	–	–	49.9
n-Propyl-	a	4.81	–	11.1	16.6	–	45.0	48.1
	b	–	–	12.3	–	–	–	36.2
n-Butyl-	a	4.48	–	11.6	16.8	–	43.3	47.8
	b	–	–	11.6	–	–	–	43.6
Cyclohexyl-	a	1.83	2.31	3.67	6.46	9.2	14.7	13.5
	b	–	–	4.17	–	–	–	16.5
Benzyl-	a	9.16	–	18.3	25.0	–	35.0	35.3
	b	–	–	20.1	–	–	–	43.3

sp: spectrophotometry; g: gas volumetry. [a]From measurements at constant complex concentration. [b]From measurements at constant amine concentration.

TABLE V. k Rate Constant Values at 25 °C ($v = k[RNH_2][Fe(CN)_5NO^{2-}]$).

Amine	$k \times 10^3$ M^{-1} s^{-1}	pH = 8.6	pH = 8.8	pH = 9.0	pH = 9.2	pH = 9.4	pH = 9.6	
		sp					sp	g
Ethyl-	a	5.21	5.25	5.14	5.10	5.10	5.15	5.84
	b	–	–	5.42	–	–	–	6.23
n-Propyl-	a	6.69	–	6.21	5.92	–	6.66	7.12
	b	–	–	6.88	–	–	–	5.36
n-Butyl-	a	5.68	–	5.92	5.48	–	5.88	6.49
	b	–	–	5.92	–	–	–	5.92
Cyclohexyl-	a	2.00	1.62	1.64	1.90	1.69	1.76	1.61
	b	–	–	1.86	–	–	–	1.97
Benzyl-	a	0.77	–	0.72	0.72	–	0.61	0.62
	b	–	–	0.79	–	–	–	0.75

(See Table IV about the meaning of a, b, sp, g).

TABLE VI. Activation Enthalpy and Entropy Values (pH = 9.2).

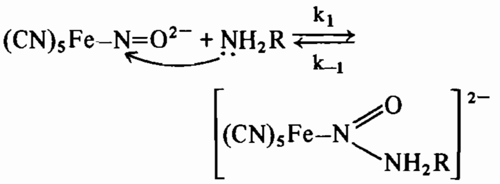
Amine	$\Delta H^{\neq}_b$ kJ mol^{-1}	$\Delta S^{\neq}_b$ J mol^{-1} K^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}
Ethyl-	69.6 ±4.2	−81.6 ±12.6	14.6	−239
n-Propyl-	78.7 ±4.5	−52.7 ±13.0	20.0	−218
n-Butyl-	87.0 ±5.0	−25.0 ±14.0	20.2	−219
Cyclohexyl-	95.3 ±4.2	−2.8 ±12.6	34.3	−179
Benzyl-	106.1 ±4.1	40.6 ±12.6	68.2	−77

Using the K values from the literature [12] k values are determined. The data at 25 °C are reported in Table V. As k is independent of pH, this proves our assumption to be correct.

The rates and the rate constants were determined at 15, 20, 25, 30 and 35 °C. From k′ values 'brutto' ($\Delta H_b^{\neq}$) activation parameters were found which contains the thermodynamic parameters for amine protonation. When these are substracted the 'real' activation enthalpy and entropy ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) were obtained (Table 6). (It must be remembered that the data for protonation belong to I = 0.5, except for cyclohexylamine where I = 0, and the kinetic experiments were at I = 1.0; however this may not cause large deviations).

Discussion

The following pathways are suggested for the interpretation of the kinetic law. The first step is the attack of the nucleophilic amine group on the electrophilic NO^+:



$$(CN)_5Fe{-}N{=}O^{2-} + NH_2R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[(CN)_5Fe{-}N\begin{smallmatrix}{=}O\\ NH_2R\end{smallmatrix}\right]^{2-} \quad (9)$$

$$[(CN)_5Fe{-}NONH_2R]^{2-} \xrightarrow{k_2} [(CN)_5Fe{-}N{\equiv}N{-}R]^{2-} + H_2O \quad (10)$$

which decomposes to a dinitrogen complex and alcohol. The last step is the aquation of the dinitrogen complex.

$$[(CN)_5Fe{-}N{\equiv}N{-}R]^{2-} + OH^- \xrightarrow{k_3} [(CN)_5Fe{-}N{\equiv}N]^{3-} + ROH \quad (11)$$

$$[(CN)_5FeN_2]^{3-} + H_2O \xrightarrow{k_4} [Fe(CN)_5H_2O]^{3-} + N_2 \quad (12)$$

Naturally, these steps are not necessarily elementary steps. The intermediates were not detected, but their postulated role is very likely on the basis of analogous reactions. In the reactions of $Ru(bipy)_2NO(Cl)^{2+}$ with aromatic amines Bowden *et al.* [13] showed the formation of a diazo complex and Guengerich and Schug [14] separated the dinitrogen complex from the reaction of $Ru(NH_3)_5NO^{2+}$ with aliphatic amines and suggested a similar mechanism. Earlier in the reaction of PNF with NH_3 Yatsimirskii *et al.* prepared the dinitrogen complex [15] and we also observed its formation in this reaction [16].

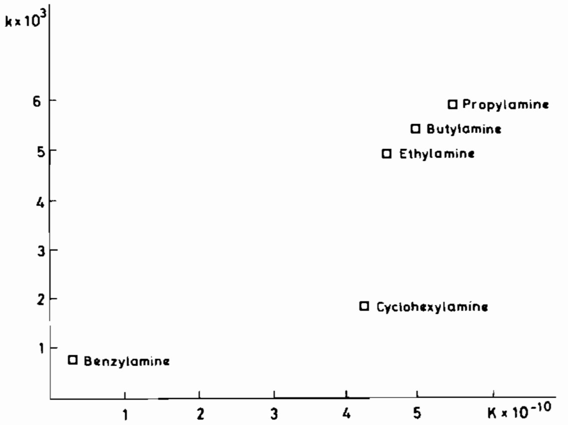
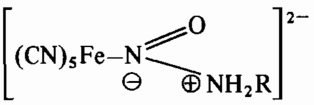


Fig. 4. Rate constants (k) at 25 °C as a function of amine basicity K ($v = k\,[RNH_2]\,[complex]$; $RNH_2 + H^+ \overset{K}{\rightleftharpoons} RNH_3^+$).

The fact that k is a monotonous function of the basicity of amines (Fig. 4) supports the important role of the reaction (9). The parallelism between k_1 and the proton affinity of amines characterized by protonation constants looks plausible. This can affect the measured rate in two ways. If $k_1 \ll k_{-1}, k_2, k_3, k_4$, then k is equal to k_1. The other case is $k_1, k_{-1} \gg k_2, k_3, k_4$. In this case the reaction (9) is a pre-equilibrium and if $k_2 \ll k_3, k_4$ (which is probable because intermediates are not detectable) then, $k = k_2k_1/k_{-1}$ *i.e.* k contains a real bimolecular rate constant and an equilibrium constant, $K_9 = k_1/k_{-1}$.

The activation parameters support this latter concept. The small activation enthalpy (15–70 kJ mol⁻¹) and the high negative activation entropy ((–80) – (–240) J K⁻¹ mol⁻¹) values suggest that k does not belong to a single elementary reaction. The high negative activation entropy may be interpreted by a rigid structure of the transition state which is due to the steric hindrance of CN^- ions for a nucleophilic attack. In addition to this the change in solvation will also produce an effect in this direction if the transition state has a polar structure:



$$\left[(CN)_5Fe{-}\overset{\ominus}{N}\begin{smallmatrix}{=}O\\ \oplus NH_2R\end{smallmatrix}\right]^{2-}$$

The steric restriction may cause the reactivity of cyclohexylamine to be less than one would expect from its basicity. The bulky cyclohexyl group bonded directly to the reaction center possibly hinders the bond formation of the amine with another bulky $Fe(CN)_5NO^{2-}$ group.

The trend in the activation entropies may be explained by the increasing hydrophobic effect of the alkyl groups in the series from ethyl to benzyl which causes an increasing disorder of the solvent.

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