

Kinetics and Equilibrium Constants of Some Pentacyanoferrate(II) Complexes of Nitrogen and Sulfur Containing Heterocycles

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ABSTRACT: The kinetics of the substitution reactions of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ ion with a series of nitrogen and sulfur containing heterocycles were studied in aqueous media. In the presence of excess ligand, varied over a large range of concentrations, second-order rate constants were calculated at $\mu = 0.100 \text{ M NaClO}_4$. Activation parameters for the formation reactions were found, ΔH^* and ΔS^* , $28 \pm 6 \text{ kJ/mol}$ and $135 \pm 20 \text{ J/mol}$, respectively. The results are interpreted as being consistent with dissociative, SN_1 mechanism. The kinetics of formation and dissociation were studied by stopped-flow technique at several temperatures. An investigation of the kinetics of exchange of coordinated heterocycles for 1,3,5-triazine, yielded rate saturation that is typical of a limiting SN_1 mechanism. Activation parameters of the limiting first-order specific rate of dissociations were found with ΔH^* and ΔS^* $53 \pm 2 \text{ kJ/mol}$ and $105 \pm 5 \text{ J/mol}$, respectively. From the specific rates of formation and dissociation reactions the equilibrium constants were calculated. © 1998 John Wiley & Sons, Inc. *Int J Chem Kinet*: 30 :415–418, 1998

INTRODUCTION

The ligand substitution reactions of pentacyanoferrate(II) complexes, $\text{Fe}(\text{CN})_5\text{L}^{3-}$, has been the subject of considerable interest recently [1–5]. An extensive series of complexes have been synthesized from $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ with N, O, and S donor ligands. These complexes exhibit well-defined metal to ligand charge-transfer (MLCT) absorption, due to electron

transfer from the **d** orbital of iron(II) to π^* orbitals of the heterocycles [6,7]. It has been demonstrated that the complexation reactions of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ with a variety of ligands L and the dissociation reactions of $\text{Fe}(\text{CN})_5\text{L}^{3-}$, in the presence of excess triazine, follow a dissociative mechanism. The interest in the reactions of heterocycles with $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ ion is mainly associated with the fact that this ion typically coordinates with only one additional ligand and can be used as a probe for the binding properties of several functional groups. $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ easily loses water and forms stable complexes with heterocyclic ligands.

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In this article we report the kinetics of formation and dissociation, spectral properties, and equilibrium constants of pentacyanoferrate(II) complexes of 1,3,5-triazine(tri), isoxazole (isox), pyridinecarbonitrile(pyCN), indoline(ind), 1,2-bis(4-pyridyl)etan(bpe), 3-mercapto-1,2,4-triazole(mtr), 2-tiazoline-2-thiol(tt), picoline(pcl), and pyrazine(pz) in aqueous solution. The complete dissociation of the ligand from the metal center can be accomplished by the addition of an excess of a strongly coordinating ligand such as 1,3,5-triazine. We have extended the preceding study to examine the kinetic properties of some heterocycle complexes of pentacyanoferrate(II).

EXPERIMENTAL METHOD

Materials

$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$, NaClO_4 , and all the heterocyclic compounds were supplied from Merck. Some of them were recrystallized and purified before use. The salt $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ was prepared from $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$ following the conventional procedure [8] and recrystallized several times from concentrated ammonia.

Kinetic Measurements

Kinetic measurements were made by using both stopped-flow (High-Tech, SF-11) and Baush-Lomb spectronic 2000 spectrophotometer, modified with a cell block thermostated to within $\pm 0.1^\circ\text{C}$ by means of an external water bath. Complex formation reactions were followed by monitoring at λ_{MLCT} of the $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complex. The ligand dissociation reactions were followed by monitoring at λ_{MLCT} of the $\text{Fe}(\text{CN})_5\text{L}^{3-}$ reactant or $\text{Fe}(\text{CN})_5\text{tri}^{3-}$ product species [9]. Pseudo-first-order conditions of excess ligand concentrations (at least 10 fold) were employed and the reactions were monitored for 3–4 half lives. The dependence of the rate of formation of $\text{Fe}(\text{CN})_5\text{tri}^{3-}$ on the tri concentration gave saturation behavior. This rate of saturation behavior was established for each dissociation reaction at the beginning of each kinetic run then the kinetics of dissociation reactions were studied. Infinity absorbance readings were recorded after 8 half-lives. First-order rate constants were determined from the least-squares plot of $\ln(A_\infty - A_t)$ or $\ln(A_t - A_\infty)$ against time. k_{obs} values given in this work are the mean values of three measurements. Ionic strength of the solution was kept constant with added NaClO_4 ($\mu = 0.100 \text{ M}$). All the ligands used were neutral and pH change was not observed during kinetic

runs, therefore no buffer solution was needed during the kinetic runs.

RESULTS AND DISCUSSION

Rate Studies

The rates of formation of the heterocycle-substituted pentacyanoferrate(II) were measured spectrophotometrically by stopped-flow technique at wavelengths corresponding to λ_{MLCT} of the complexes. The aquapentacyanoferrate(II) ion, $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$, may be generated in solution by the aquation of $\text{Fe}(\text{CN})_5\text{NH}_3^{3-}$ ion. The pale yellow $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ ion has an absorption maximum at 442 nm with $\epsilon = 3100 \text{ cm}^{-1}\text{M}^{-1}$. At higher concentrations $> 10^{-4} \text{ M}$, $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ ion is observed to undergo a slow dimerization to yield $\text{Fe}_2(\text{CN})_{10}^{6-}$ [10,11]. 10^{-4} M solution of pentacyanoferrate(II) gave well-defined and reproducible first-order kinetic plots, linear over at least 3 half-lives. From the slopes of these plots we have calculated the pseudo-first-order rate constants at several ligand concentrations. Each second-order rate constant reported in the result was obtained as the slope of a plot of k_{obs} vs. $[\text{L}]$ at four or more ligand concentrations. Temperature dependence of the rate constants of the formation reactions was studied in the range of $15.0\text{--}35.0^\circ\text{C}$. The kinetics of ligand exchange in $\text{Fe}(\text{CN})_5\text{L}^{3-}$ by 1,3,5-triazine shows typical rate saturation curves expected for processes where the loss of a coordinated ligand completely determines the rate of substitution. We have calculated the equilibrium constants, K , from the limiting rates of the loss of coordinated heterocycles measured, (k_d) and from the rate of formation, (k_f) of the same complexes with respect to $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ and the free ligand using equation $K = k_f/k_d$.

UV-Visible Spectrum

The addition of an excess of a ligand to a dilute solution of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ ion results in a shift in λ_{MLCT} in the UV-Visible spectrum, ascribed to the formation of a complex, $\text{Fe}(\text{CN})_5\text{L}^{3-}$. The absorption in the visible region is assigned to a metal to ligand charge transfer transition. An additional band in the UV region is assigned as an inter ligand $\pi\text{-}\pi^*$ transition, centered on coordinated ligand. The values of λ_{MLCT} and $\log \epsilon$ for a series of these complexes where L specified are listed in Table I. The UV-vis absorption spectra of the $\text{Fe}(\text{CN})_5\text{L}^{3-}$ complexes (L: Nitrogen donor ligands) are similar to those of corresponding complexes of ammonia, indicating coordination through

Table I MLCT Absorption of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ Complexes

Ligand	λ_{MLCT}	$\log \epsilon$
bpe	366	3.55
pz	458	3.49
tri	449	3.38
pcl	361	3.49
ind	315	3.24
pyCN	485	3.78
isox	329	3.42
mtr	693	3.37
tt	375	3.51

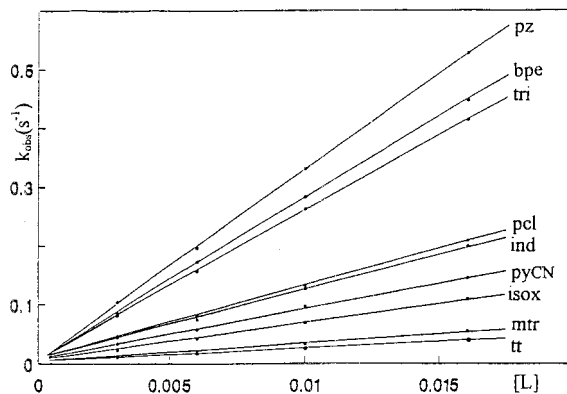
nitrogen atom, except **mtr**. **Mtr** is bound to metal center through sulphur donor atom therefore MLCT band shifted to lower energy. For $\text{Fe}(\text{CN})_5\text{mtr}^{3-}$ complex $\text{M}(\text{d} \pi) - \text{S}(\text{d} \pi)$ back bonding is possible and this bond is observed at low energy region [12–15].

Kinetics of Formation

The rate of formation of the $\text{Fe}(\text{CN})_5\text{L}^{3-}$ with the heterocyclic ligands was measured spectrophotometrically by the stopped-flow technique at λ_{MLCT} . The concentration of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ was 10^{-4} M and the concentration of ligands varied in the range of 0.001–0.016 M ensuring a substantial excess of ligand. The second-order rate constants and activation parameters for the complex formation reactions studied are presented in Table II. A plot of k_{obs} vs ligand gave a straight line which passes through the origin Figure 1. This indicates that there is no significant dissociation. A relative invariance among the specific rate of attack of a number of entering ligands upon a given aqueous $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ is considered as indicative of a common SN_1 mechanism [15,16]. The positive activation entropies, ΔS^\ddagger , fall into a range that is usually interpreted as indicating a dissociative pathway but pentacoordinate intermediate of different configura-

Table II Rate and Activation Parameters for the Formation Reactions of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ Complexes in Aqueous Media

Ligand	$k_f(\text{M}^{-1} \text{s}^{-1})$ 25.0°C	$\Delta H^\ddagger(\text{kJ/mol})$	$\Delta S^\ddagger(\text{J/mol})$
pz	33.5 ± 0.4	31	121
bpe	27.9 ± 0.3	29	102
tri	27.2 ± 0.3	28	121
pcl	12.4 ± 0.2	27	154
ind	12.2 ± 0.1	24	142
pyCN	9.1 ± 0.1	27	137
isox	6.8 ± 0.2	31	152
mtr	3.0 ± 0.1	22	155
tt	2.9 ± 0.1	34	123

**Figure 1** Dependence of k_{obs} on ligand concentrations for the complex formation reactions of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ at 25°C, $\mu = 0.100$ M NaClO_4 .

tions are involved. For octahedral complexes, dissociative pathways involving trigonal-bipyramidal intermediate give positive ΔS^\ddagger while square-pyramidal intermediates give more negative values [17,18]. The rate law is,

$$\frac{d[\text{Fe}(\text{CN})_5\text{L}^{3-}]}{dt} = k_f[\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}][\text{L}]$$

From the variation of k_f with temperature, the activation parameters were calculated.

Kinetics of Ligand Exchange

Ligand exchange reactions given below were studied in order to determine the rate of dissociation of $\text{Fe}(\text{CN})_5\text{bpe}^{3-}$ complexes.

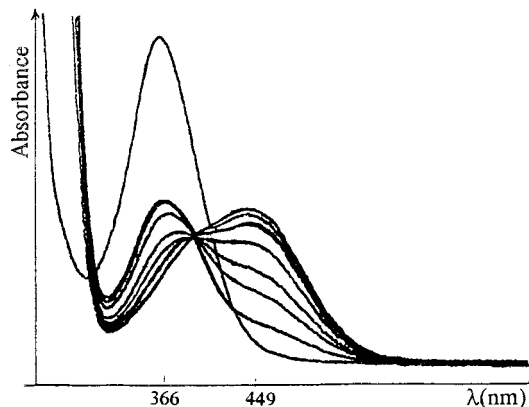
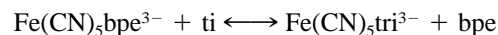
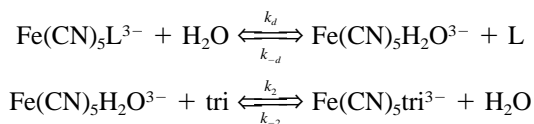
**Figure 2** Variation of UV-Visible spectrum of the $\text{Fe}(\text{CN})_5\text{bpe}^{3-}$ with 1,3,5-triazine.

Table III Rate, Activation Parameters, and Equilibrium Constants for Ligand Substitution of L by 1,3,5-Triazine in $[\text{Fe}(\text{CN})_5\text{L}]^{3-}$ ($\mu = 0.100 \text{ M}$)

Ligand	$k_d(\text{s}^{-1})10^4$ 25.0°C	$\Delta H^\ddagger(\text{kJ/mol})$	$\Delta S^\ddagger(\text{J/mol})$	$K(\text{M}^{-1})10^{-4}$
bpe	1.42 ± 0.02	51.4	118	19.65 ± 0.04
pcl	1.50 ± 0.03	52.6	109	8.27 ± 0.03
pyCN	1.86 ± 0.02	52.2	111	4.89 ± 0.02
isox	2.06 ± 0.01	54.3	103	3.30 ± 0.02
mtr	4.63 ± 0.02	53.7	117	0.65 ± 0.01
tt	4.94 ± 0.01	54.8	103	0.59 ± 0.01

The rates of ligand exchange were measured as a function of triazine concentration. Reactions were monitored by following the appearance of the product λ_{MLCT} band or disappearance of the reactant, $\text{Fe}(\text{CN})_5\text{bpe}^{3-}$, λ_{MLCT} band. The reactions of $\text{Fe}(\text{CN})_5\text{bpe}^{3-}$ in the presence of an excess of **tri** resulted in a first-order formation of $\text{Fe}(\text{CN})_5\text{tri}^{3-}$ or loss of $\text{Fe}(\text{CN})_5\text{bpe}^{3-}$ (Fig. 2). The dissociation rate constants, k_d , and the corresponding activation parameters for the complexes are presented in Table III. Dissociative mechanism, SN_1 , of ligand substitution is proposed for the exchange of the L and triazine in the ligand-pentacyanoferrate(II) complexes, on the basis of the saturation of k_{obs} at high concentration of triazine, the dependence of k_d on the nature of L, and the lack of a dependence of k_d on the nature of triazine.



By steady-state approximation, The observed rate constants may be expressed as,

$$k_{\text{obs}} = \frac{k_d k_2 [\text{tri}] + k_{-2} k_{-d} [\text{L}]}{k_2 [\text{tri}] + k_{-d} [\text{L}]}$$

As the concentration of tri is increased with [L] held constant, k_{obs} will increase until the condition of $k_2[\text{tri}] \gg k_{-d}[\text{L}]$ is met. At this point, k_{obs} will approach to k_d , where k_d is the rate of dissociation of [L] from the $\text{Fe}(\text{CN})_5\text{L}^{3-}$.

Equilibrium Constants

The calculated values of K decrease slightly on moving down the series of complexes in Table III. This decrease reflects the relative independence on ligand properties of both k_d and k_f . Increase in k_d on moving down is accompanied by a decrease in the ligand's π -acceptor capacities [19] and is consistent with a de-

crease in stabilization of the complexes by $d\pi\text{-p}\pi^*$ backbonding. Backbonding caused by σ donation from cyanide ligands to iron(II) in $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ ion should lead to an accumulation of negative charge on the metal that is probably removed by backbonding. This would weaken the $\text{Fe}-\text{OH}_2$ bond, prompting SN_1 mechanism. Observed ordering of k_d and K values is caused by backbonding capabilities of ligands.

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