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Source / Izvornik: **Journal of Coordination Chemistry, 2006, 59, 1537 - 1539**

Journal article, Accepted version
Rad u časopisu, Završna verzija rukopisa prihvaćena za objavljivanje (postprint)

https://doi.org/10.1080/00958970500537788

Foretić B., Lovrić J., Burger N. (2006) ***Reaction of 1-benzoylethylpyridinium-4-aldoxime chloride with aquapentacyanoferrate(II).*** **Journal of Coordination Chemistry, 59 (13). pp. 1537-1539. ISSN 0095-8972**

http://www.informaworld.com/smpp/title~content=t713455674~link=cover

http://dx.doi.org/10.1080/00958970500537788

Journal of Coordination Chemistry
Vol. 59, No. 13. 10 September 2006, 1537-1 539

Reaction of 1-benzoylethylpyridinium-4-aldoxime chloride with aquapentacyanoferrate(II)

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The results of a spectrophotometric investigation of the reaction of the biologically active salt 1-benzoylethy1pyridinium-4-aldoxime chloride with aquapentacyanoferrate(II) ion are presented. In spite of the presence of two donor sites only the carbonyl group of the ligand coordinates to the iron centre. Reaction kinetics is consistent with a dissociative mechanism.

Keywords: Spectrophotometry; l-Benzoylethylpyridinium-4-aldoxime chloride; Aquapentacyanoferrate(II); Equilibrium constant; Kinetics

1. Introduction

Oximes having different chemical structures are known to form coloured complexes with a great number of metal ions [1] including aquapentacyanoferrate(II) [2]. Reactions of ketones with $[Fe(CN)_5OH_2]^{3-}$ are less investigated. An examination of the reactions of napthaquinone oximes with $[Fe(CN)_5OH_2]^{3-}$ indicated that both the carbonyl and the oxime group participate in complex formation [3]. Recently, some newly synthesized ketones of the phenacyl- and benzoylethylpyridinium type were also found to react with $[Fe(CN)_5OH_2]^{3-}$ [4]. A detailed spectrophotometric investigation of the reaction of 1-benzoylethylpyridinium chloride (BEP) was undertaken and the kinetics and mechanism of this substitution reaction established. Results were consistent with a dissociative mechanism [4]. The carbonyl group was recognized as a σ-donor ligand which can form complexes with $[Fe(CN)_5OH_2]^{3-}$. Its reactive form is the enolate ion.

1-Benzoylethylpyridinium-4-aldoxime chloride (BEPA-4) has been synthesized by introducing an aldoxime group to the position 4 of the pyridine ring of 1-benzoylethylpyridinium chloride (BEP) with the primary aim of establishing if and how this compound with two potential donor sites reacts with aquapentacyanoferrate(II).

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2. Experimental

1-Benzoylethylpyridinium-4-aldoxime chloride (BEPA-4) was prepared by mixing equimolar solutions of chloropropiophenone and pyridine-4-aldoxime [5, 6]. Solutions of $[Fe(CN)_5OH_2]^{3-}$ were obtained by aquation of $[Fe(CN)_5NH_3]^{3-}$ [7] and were freshly prepared. Ionic strength was maintained constant with sodium chloride. The pH of the reaction mixtures was adjusted using Britton and Robinson buffers [8] and measured by a pH-meter equipped with a combined calomel-glass electrode accurate to ± 0.05 pH units. Redistilled water was used throughout.

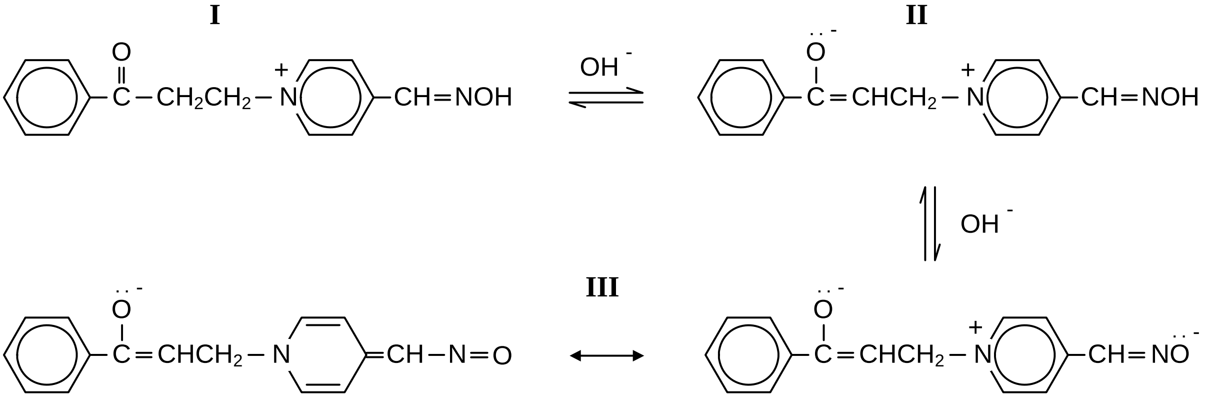
A Pye Unicam SP 600 UV spectrophotometer and 1-cm silica-glass cells were used to make absorption measurements. Kinetic experiments were carried out using a Durrum D-110 stopped-flow spectrophotometer by following the absorbance increase at the band maximum of the formed complex (440 nm). Data were collected under *pseudo*-first order conditions keeping BEPA-4 at a 10 to 70 molar excess. Plots of $\ln(A_\infty - A_t)$ *versus* time were linear for at least two half-lives.

3. Results and discussion

1-Benzoylethylpyridinium-4-aldoxime chloride (BEPA-4) reacts with the aquapentacyanoferrate(II) ion forming a yellow complex in the pH range of 6.0 to 9.5, whose electronic spectrum exhibits a strong MLCT band at 440 nm. Spectrophotometric methods [4] revealed the formation of a complex of 1:1 stoichiometry. The overall reaction may be presented as shown below,

$$[Fe(CN)_5OH_2]^{3-} + \text{BEPA-4}^{(n-1)+} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [Fe(CN)_5\text{BEPA-4}]^{(4-n)-} + H_2O \qquad (1)$$

where n equals 0, 1 or 2. The equilibrium constant of the reaction was derived using the molar ratio method [4] and was found to be $K(25\ °C) = 2 \times 10^5\ M^{-1}$. Aqueous solutions of BEPA-4 display the following acid-base equilibria [5]:



Since the pK_a values of the carbonyl and the oxime groups of BEPA-4 are 6.70 and 9.97 respectively, it is apparent that the carbonyl group, its ionized form, participates in complex formation.

The kinetics of formation of BEPA-4 substituted pentacyanoferrate(II) were investigated at 25 °C, pH 7.9 and I = 0.05 M. Observed rate constants, k_{obs}, linearly depend on the BEPA-4 concentration (figure 1) which is in accordance with (2).

$$k_{obs} = k_f \text{ [BEPA-4]}. \qquad (2)$$

Such behaviour is consistent with a dissociative mechanism for water substitution [9-11]. The formation rate constant, k_f, of $[Fe(CN)_5BEPA\text{-}4]^{(4-n)-}$ was found to be 184 M^{-1} s^{-1}, which is comparable to values found for the formation rates of complexes with zwitterionic forms of a number of ligands [9, 10] as well as of BEP [4]. Moreover, no significant influence of increasing ionic strength on the reaction rate was observed, confirming that the reaction involves the uncharged, zwitterionic ligand. Therefore it can be deduced that the reactive form of BEPA-4 is the form **II.** The appreciably smaller formation rates constants found for the reactions of two oximes with the $[Fe(CN)_5OH_2]^{3-}$ ion [12] support the above statement that in the present case the carbonyl group is the reactive one.

Information and results obtained at this stage of investigation will be further elaborated. Because substituted pentacyanoferrates(II) are useful models for certain biologically active macromolecules, while both carbonyl and oxime compounds of the aralkylpyridinium type show significant and versatile bioactivities, this investigation is also of practical importance.

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Figure 1. Plot of the observed rate constants *vs*. ligand concentrations at 25 °C, pH=7.9 and I=0.05 M.