

KINETICS AND MECHANISM OF OXIDATION OF DIALLYLAMINE BY ALKALINE HEXACYANOFERRATE (III)

BY

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ملخص

يتناول هذا البحث أكسدة مركب ثنائي أليل أمين $[(C_3H_5)_2NH]$ بواسطة مركب حديدي سيانات البوتاسيوم $K_3Fe(CN)_6$ في محلول قاعدي مكون من ماء وكحول ايثيلي على درجة أيونية ثابتة ، وقد تبين أن تركيز العامل المؤكسد لا يؤثر على سرعة التفاعل المذكور في حين أن سرعة التفاعل تتناسب طردياً مع تركيز الأمين وتتحسن مع زيادة قيمة الـ pH للمحلول المستعمل .

هذا وتم أيضاً دراسة تأثير كل من إضافة $K_4Fe(CN)_6$ الى محلول التفاعل ، درجة أيونية المحلول ، تغير الشق السالب لأملاح مختلفة مضافة للمحلول وكذلك التركيب الكيميائي لوسط التفاعل . وبناء على نتائج الدراسة تم اقتراح ومناقشة ميكانيكية مناسبة للتفاعل المذكور .

Abstract

The kinetics of oxidation of diallylamine by hexacyanoferrate (III) in alkaline aqueous ethanol at constant ionic strength has been studied . The rate of the reaction was dependent on the first power of the concentration of diallylamine , but was independent of hexacyanoferrate (III) concentration . The rate was enhanced by an increase in the pH value

The effects of added hexacyanoferrate (II) , ionic strength , types of anion and cation , and the solvent composition have also been investigated . The activation parameters were evaluated . A mechanism consistent with the kinetic results is proposed and discussed .

Introduction

The oxidation of amines by hexacyanoferrate (III) has been studied extensively by several investigators⁽¹⁻⁹⁾ . However , most of these studies were done on tertiary amines with only very few on the oxidation of primary or secondary amines⁽⁸⁻⁹⁾ . Furthermore , it has been reported by Lindsay Smith⁽³⁾ that secondary amines are not oxidizable by hexacyanoferrate (III) . Although Dasgupta and Mahanti⁽⁸⁻⁹⁾ , reported the oxidation of aniline and substituted anilines by alkaline

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hexacyanoferrate (III) , a survey of the literature revealed that the oxidation of open-chain aliphatic amines has not been reported . The mechanisms proposed by Dasgupta and Mahanti involve the formation of an aminium radical cation , and a radical intermediate . An interesting feature of the oxidation of diallylamine is the presence of the allyl groups . The present work demonstrates the usefulness of hexacyanoferrate (III) as a reagent for the oxidation of secondary , open-chain amines .

Experimental

Materials – Diallylamine, obtained from Aldrich Chemical Co., was refluxed and fractionated over solid KOH no more than two days before use and stored over size 3A molecular sieves . All other materials were purchased from Aldrich Chemical Co. in the purest form and used as such . Buffers were prepared from sodium hydroxide and potassium chloride in 20 % ethanol (V/V) . Doubly distilled water was used throughout .

Kinetics – Kinetics were followed by monitoring the absorbance of hexacyanoferrate (III) at 414 nm vs. time . The required amounts of diallylamine and hexacyanoferrate (III) were dissolved in portions of the buffer in separate flasks

Sodium chloride was added to adjust the ionic strength of the reaction mixture to the required value . The contents of the flasks were mixed , and then a small portion of the reaction mixture was pipetted into a 1cm spectrophotometer cell . The cell was then stoppered and returned to the sample compartment of the spectrophotometer for continuous measurements of absorbance vs. time . In a similar manner , the effect of each of added hexacyanoferrate (II) and other salts on the reaction rate was studied ; in each case adjusting the amount of buffer to keep a constant total volume .

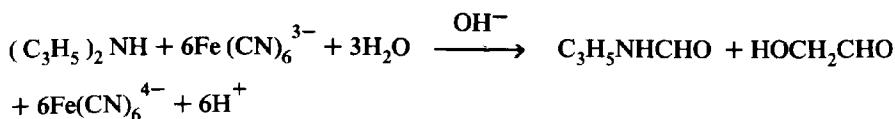
Stoichiometry and product analysis – A reaction mixture containing ten-fold molar excess of hexacyanoferrate (III) over diallylamine at pH 13.0 was allowed to stand for three days . The molar stoichiometry was calculated spectrophotometrically . On evaporation of the reaction solution and addition of ether , a solid precipitated which was recrystallized from ether to give 2,5- dihydroxy -1,4-dioxane (mp 82 ° C)

The filtrate was evaporated to a small volume and the residue was identified by I.R as N-allylformamide .

Measurements – All spectra and kinetics were recorded using a UV/visible SP8 – 100 recording spectrophotometer equipped with 1 cm cells and a thermostated cell holder . IR spectra were recorded on a Pye Unicam SP 200 infrared spectrophotometer . All pH measurements were made with a Fisher Accumet model 230A pH /Ion Meter .

Results and Discussion

Stoichiometry – The experiments , carried to establish the stoichiometry of the oxidation of diallylamine by hexacyanoferrate (III) at alkaline pH , showed that six moles of $\text{Fe}(\text{CN})_6^{3-}$ were reduced for each mole of diallylamine oxidized . Thus the overall reaction stoichiometry may be written as



Kinetics – The results of oxidation of diallylamine by hexacyanoferrate (III) showed that the rate of the reaction is independent of $[\text{Fe}(\text{CN})_6^{3-}]$, as shown in Table (1). The plot of $\log(\text{initial rate})$ vs . $\log[\text{diallylamine}]$ was linear with a slope of

Table I : Effect of varying [hexacyanoferrate (III)]

$[\text{Fe}(\text{CN})_6^{3-}] \times 10^3 \text{ M}$	0.50	0.70	1.00	1.30	1.50
$k_{\text{obs}} \times 10^2 \text{ sec}^{-1}$	1.00	1.00	1.00	1.05	1.10

[Amine] = 0.20 M ; pH = 13.0 , $\mu = 0.1$; temperature 25 °C .

about unity , establishing a first order dependence with respect to diallylamine , (Fig 1) . Thus the rate determining step involves a proton loss rather than an electron

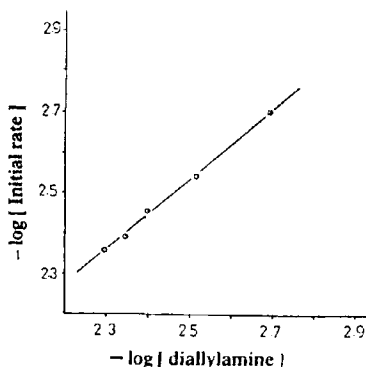


Figure 1 : Plot of $-\log(\text{initial rate})$ versus $-\log[\text{diallylamine}]$ at 25 °C ; $[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{ M}$; pH = 13.0 ; $\mu = 0.1$

transfer as supported by the results of the effect of changing the pH on the reaction rate . This effect indicates a faster rate at higher pH values (Fig. 2) . The rate law in consonance with the results can be written as :

$$\frac{-d [\text{Fe}(\text{CN})_6^{3-}]}{dt} = K_{\text{obs}} [\text{Diallylamine}]$$

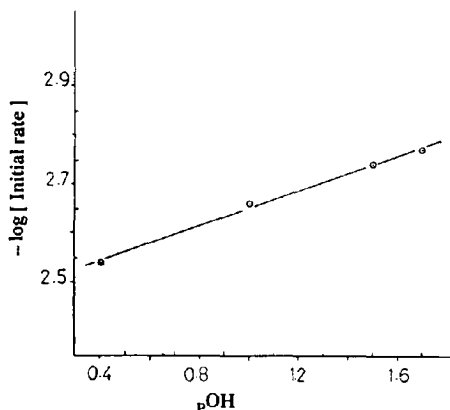


Figure 2 : Plot of $-\log$ (initial rate) versus pOH at 27 °C ; $[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{ M}$; [diallylamine] = 0.20 M ; $\mu = 0.1$

Effect of added salts : Addition of $\text{Fe}(\text{CN})_6^{4-}$ up to $1.0 \times 10^{-3} \text{ M}$, caused a slight increase in the rate . However , at higher concentrations a very slight negative effect on the rate was observed , (Table II) . The effect of ionic strength was studied by

Table II : Effect of [hexacyanoferrate (II)]

$[\text{Fe}(\text{CN})_6^{4-}] \times 10^3 \text{ M}$	1.00	3.00	6.00	10.0	15.0	
$k_{\text{obs}} \times 10^2 \text{ sec}^{-1}$	1.00	1.00	1.10	1.20	1.10	1.05

[Amine] = 0.20M ; $[\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{ M}$; pH = 13.0 ; temperature 25 °C .

following the reaction in the presence of different concentrations of sodium chloride . A small positive salt effect was found , (Table III) . Varying the types of anions and cations has also been noted in Tables IV and V respectively . The rate of the reaction

decreased in the orders $\text{Br}^- > \text{ClO}_3^- > \text{NO}_3^- > \text{I}^-$ and $\text{K}^+ \geq \text{Na}^+ >> \text{NH}_4^+$

Table III : Effect of ionic strength

$[\text{NaCl}] \times 10^2 \text{M}$	3.00	6.00	9.00	12.0	15.0
$k_{\text{obs}} \times 10^2 \text{sec}^{-1}$	1.10	1.20	1.25	1.30	1.40

$[\text{Amine}] = 0.20\text{M}; [\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{M}, \text{pH} = , = 13.0; \text{temperature } 26^\circ\text{C}.$

Table IV : Effect of varying anion

Salt	KF	KBr	KI	KNO_3 .	KClO_3 .
$k_{\text{obs}} \times 10^2 \text{sec}^{-1}$	1.05	1.20	0.85	0.90	1.00

$[\text{Amine}] = 0.20 \text{M}; [\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{M}; [\text{Salt}] = 6.0 \times 10^{-4} \text{M}; \text{pH} = 12.5$
; temperature 25°C .

Table V. : Effect of varying cation

[Salt]	NH_4Cl	NaCl	KCl
$k_{\text{obs}} \times 10^2 \text{sec}^{-1}$	0.95	1.15	1.30

$[\text{Amine}] = 0.20 \text{M}; [\text{Fe}(\text{CN})_6^{3-}] = 1.0 \times 10^{-3} \text{M};$
 $[\text{Salt}] = 6.0 \times 10^{-4} \text{M}; \text{pH} = 13.0; \text{temperature} = 28^\circ\text{C}.$

The sequence found for the anions used reflects their basicity strength . Furthermore , the order found for the relative effect of the cations supports the assumption that the electron abstraction from the amine by the oxidant is not involved in the rate controlling step . Otherwise , the cations should effect the rate by acting as bridges for the electron transfer .

Effect of percent ethanol – The rate dependence on solvent composition was investigated by varying ethanol concentration . No. change in the reaction rate was observed (Table VI) . Thus the transition state in the reaction is nearer to a noncharged species rather than to a charged one .

Table VI : Effect of solvent composition

% EtOH (V/V)	40	50	60	70
$k_{\text{obs}} \times 10^2 \text{ sec}^{-1}$	1.05	1.00	1.05	1.10

[Amine] = 2.20 M ; [Fe(CN)₆³⁻] = 1.0 x 10⁻³ M ; temperature 26° C .

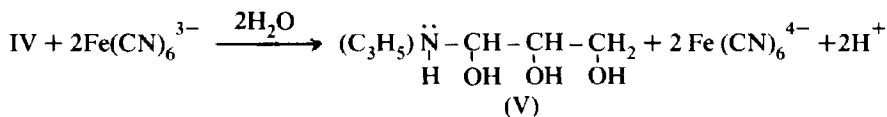
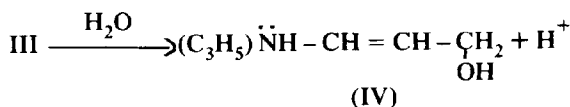
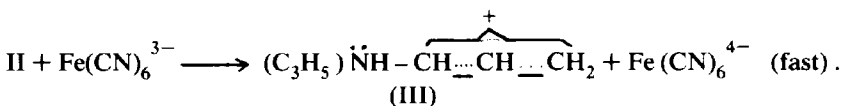
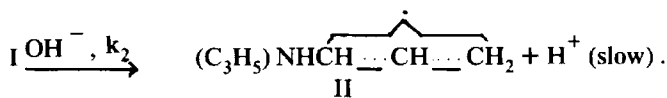
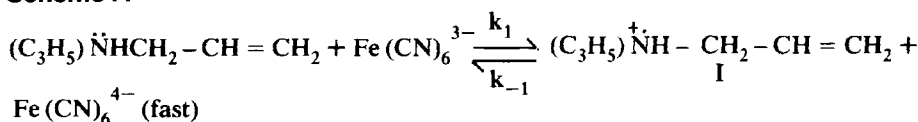
Effect of temperature – The Kinetic data for the reaction were obtained at five different temperatures . The rate constants were calculated and the activation parameters were evaluated (Table VII) .

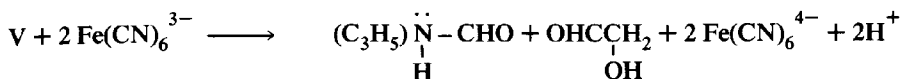
Table VII : Activation parameters

Ea KJ.mol ⁻¹	ΔS^\ddagger J.deg ⁻¹	ΔH^\ddagger KJ.mol ⁻¹	ΔG^\ddagger KJ.mol ⁻¹	A sec ⁻¹
3.0	-0.27	0.53	81.23	3.7×10^2

Mechanism – The mechanism proposed for the reaction of diallylamine with alkaline hexacyanoferrate (III) is shown in Scheme I :

Scheme I :





The first step in the mechanism involves an electron transfer from the nitrogen atom of diallylamine to the oxidant. This results in the formation of the aminium radical cation (I), (a fast step). Similar examples of aminium radical cations have been reported^(3,6,7,10-12). Removal of a proton by the base at α -carbon (a slow step) results in the formation of radical (II). In this radical, the electron is delocalized over the carbon atoms of the allyl group. The formation of the α -amine radical (II) is well established in the literature for similar reactions⁽¹⁻⁹⁾. II is further oxidized by a second hexacyanoferrate (III) to give (III) (a fast step). Oxidation of the α -carbon, although not very common in similar reactions, was reported by several workers^(8,9,13-15). The subsequent steps are fast.

The above mechanism enables us to derive the rate law as follows:

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = k_2[\text{I}][\text{OH}^-] \quad (1)$$

Applying steady state treatment of [I]

$$[\text{I}] = \frac{k_1[\text{amine}][\text{Fe}(\text{CN})_6^{3-}]}{k_{-1}[\text{Fe}(\text{CN})_6^{4-}] + k_2[\text{OH}^-]} \quad (2)$$

but since $k_2 \ll k_{-1}$, then $k_{-1}[\text{Fe}(\text{CN})_6^{4-}] + k_2[\text{OH}^-] \approx k_{-1}[\text{Fe}(\text{CN})_6^{4-}]$

and

$$[\text{I}] = \frac{k_1[\text{amine}][\text{Fe}(\text{CN})_6^{3-}]}{k_{-1}[\text{Fe}(\text{CN})_6^{4-}]} \quad (3)$$

substitution of eqn. (3) in eq. (1) yields

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{k_1 k_2}{k_{-1}} [\text{amine}][\text{OH}^-] \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{CN})_6^{4-}]} \quad (4)$$

The experimentally determined rate follows first order but the derived rate expression does not. However, in any individual experiment, $[\text{OH}^-]$ is constant and present in such excess, $[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]$ is also constant as the first step (equilibrium) is fast. Therefore:

$$\frac{-d [\text{Fe}(\text{CN})_6^{3-}]}{dt} = K_{\text{obs.}} [\text{diallylamine}] \quad (5)$$

The derived rate expression (4), or (5), enables us to explain the observed effects of $[\text{OH}^-]$ and added $[\text{Fe}(\text{CN})_6^{4-}]$ on the experimentally determined rate constant when $[\text{OH}^-]$ or added $[\text{Fe}(\text{CN})_6^{4-}]$ are varied from one experiment to another. Since $[\text{OH}^-]$ and $[\text{Fe}(\text{CN})_6^{3-}] / [\text{Fe}(\text{CN})_6^{4-}]$ are incorporated into the overall rate constant, changing $[\text{OH}^-]$ or $[\text{Fe}(\text{CN})_6^{3-}] / [\text{Fe}(\text{CN})_6^{4-}]$ will change k_{obs} .

The relatively low values of E_a and ΔH^* are presumably due to the resonance stabilization of (II) being an allyl- type radical. The proposed mechanism is consistent with the experimental results and the stoichiometry of the reaction.

Oxidation of other secondary amines, both aliphatic and alicyclic, is under investigation.

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