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Note

## Kinetics of Oxidation of Benzylamines by Alkaline Hexacyanoferrate(III)

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The reaction of benzylamine with alkaline hexacyanoferrate(III), at constant ionic strength, in aqueous methanol, has been investigated. The rate of the reaction was first order in each, substrate and oxidant, but was independent of the concentration of alkali, in the range studied (0.01 M to 0.1 M). The mechanistic pathway involved the formation of a radical intermediate, which was characterized by a value of  $\rho = -1.0$ ,  $k_H/k_D = 6.3$ , and by ESR spectroscopy as four sets of 1:2:1 triplets.

### INTRODUCTION

Primary aromatic amines have been oxidized by phenyl iodosoacetate<sup>1,2</sup>, lead tetracetate<sup>3</sup>, manganese dioxide<sup>4</sup>, cupric chloride<sup>5,6</sup>, potassium permanganate<sup>7</sup>, and by pyridine chlorochromate<sup>8</sup>; the major product obtained being an azobenzene. In continuation of our work on the oxidation reactions of amines<sup>9</sup>, we now report the kinetics of oxidation of benzylamines by alkaline hexacyanoferrate(III), at constant ionic strength, in aqueous methanol, under a nitrogen atmosphere.

### EXPERIMENTAL

#### (a) Materials, Methods and Stoichiometry

Benzylamine and substituted benzylamines were E. Merck samples, and were distilled before use. All other materials were E. Merck samples, and were used as such. The deuterated compound, benzylamine- $\alpha$ -d<sub>2</sub>, was obtained from Isotopes Inc., and the NMR spectrum of the sample, in CCl<sub>4</sub> (EM 390, 90 MHz, Varian), did not show any absorption for the methylene protons. The methods used for the preparation of solutions, and for the kinetic determinations for the disappearance of hexacyanoferrate(III) at 420 nm (UV-26, Beckman), have been described earlier<sup>9</sup>. The reaction was followed up to 60% disappearance of hexacyanoferrate(III), the plot of  $\log k_{\text{obs}}$  against  $t$  being linear in this range. The stoichiometry of the reaction was determined<sup>9</sup> to be:



#### (b) Product Analysis

Using the same experimental conditions that were used for the kinetic determinations, solutions of substrate and oxidant, taken in aqueous methanol (60% v/v), containing NaOH (0.10 M), and KCl (ionic strength adjusted to 0.1 M), were mixed and kept at 60 °C for 24 h, under nitrogen.

- (i) The evolution of ammonia was shown by partial distillation of the aqueous reaction mixture, and titration of the distillate with standard base.
- (ii) The reaction mixture was treated with chloroform, the organic layer washed with water, dried over anhydrous  $MgSO_4$ , and then concentrated. Spotting on TLC plates gave a single spot. IR analysis (IR-297, Perkin Elmer) exhibited a carbonyl band at  $1700\text{ cm}^{-1}$  and other bands that were characteristic of benzaldehyde.
- (iii) The reaction mixture was treated with an acidic solution of sodium bisulfite, and cooled in an ice bath. 25 ml of 2,4-dinitrophenyl hydrazine solution (0.05 M) was added, and the mixture allowed to stand overnight at  $0^\circ\text{C}$ . The solid compound which was formed was filtered, dried and weighed as the 2,4-dinitrophenyl hydrazone derivative of benzaldehyde (mp.  $237^\circ\text{C}$ ; yield  $\sim 80\%$ ).

## RESULTS AND DISCUSSION

The rate of the reaction was dependent on the first powers of the concentration of both, substrate and oxidant, but was independent of the concentration of alkali in the range studied (Table I). The oxidation of benzylamine by neutral hexacyanoferrate(III) was very slow, as seen from the value of the rate constant (Table I). An alkaline medium was thus necessary for

TABLE I  
Rate Data for the Oxidation of Benzylamine at  $60^\circ\text{C}$

| Benzylamine<br>M | $[K_3Fe(CN)_6]$<br>$10^2 \times M$ | $[NaOH]$<br>$10^2 \times M$ | $10^6 \times k_{obs}$<br>$s^{-1}$ |
|------------------|------------------------------------|-----------------------------|-----------------------------------|
| 0.10             | 1.0                                | 1.0                         | 7.0                               |
| 0.25             | 1.0                                | 1.0                         | 17.0                              |
| 0.50             | 1.0                                | 1.0                         | 35.0                              |
| 1.0              | 1.0                                | 1.0                         | 69.0                              |
| 1.5              | 1.0                                | 1.0                         | 108.0                             |
| 1.0              | 2.5                                | 1.0                         | 68.0                              |
| 1.0              | 5.0                                | 1.0                         | 70.0                              |
| 1.0              | 10.0                               | 1.0                         | 69.0                              |
| 1.0              | 0.5                                | 1.0                         | 68.0                              |
| 1.0              | 1.0                                | 2.5                         | 67.0                              |
| 1.0              | 1.0                                | 5.0                         | 70.0                              |
| 1.0              | 1.0                                | 10.0                        | 68.0                              |
| 1.0              | 1.0                                | 1.0                         | 37.0*                             |
| 1.0              | 1.0                                | 1.0                         | 51.0†                             |
| 1.0              | 1.0                                | 1.0                         | 91.0‡                             |
| 1.0              | 1.0                                | 1.0                         | 118.0‡‡                           |
| 1.0              | 1.0                                | 0.0                         | 0.3 (neutral<br>medium)           |

Aqueous methanol = 60% (v/v);  $\mu = 0.10\text{ M}$ .

\* $50^\circ\text{C}$ ; † $55^\circ\text{C}$ ; ‡ $65^\circ\text{C}$ ; ‡‡ $70^\circ\text{C}$  (all temperature corrections were  $\pm 0.1^\circ\text{C}$ ). All values of rate constants were the average of three experiments, agreement being  $\pm 3\%$ .

the facile oxidation of the substrate. A plot of  $k_{obs}$  versus a 15-fold range of concentration of substrate gave a straight line passing through the origin, indicating that the rate was first order with respect to the [substrate]. At constant substrate concentration (large excess), the pseudo first order rate constant ( $k_{obs}$ ), did not change, with changing hexacyanoferrate(III) concentration (20-

-fold range), which indicated a first order dependence of the rate on the concentration of the oxidant.

Variations in the ionic strength of the medium using KCl ( $\mu = 0.01$  M to 0.10 M), and the addition of hexacyanoferrate(II) ions in the concentration range,  $1 \times 10^{-4}$  M to  $1 \times 10^{-3}$  M, did not have any effect on the rate of the reaction.

The rate of the reaction was influenced by changes in the temperature (Table I), and the activation parameters were evaluated:  $E = 53.0 \pm 4$  kJmol<sup>-1</sup>,  $A = 2 \times 10^4$  s<sup>-1</sup>,  $\Delta H^\ddagger = 50 \pm 4$  kJmol<sup>-1</sup>,  $\Delta S^\ddagger = -170 \pm 7$  JK<sup>-1</sup> mol<sup>-1</sup>. The favourable enthalpy for electron abstraction may be partly due to the release of energy on solvation of charges created in the transition state. Values of  $\Delta S^\ddagger$  in this range for radical reactions have been ascribed<sup>10</sup> to the nature of electron-pairing and electron-unpairing processes, and to the loss of degrees of freedom, formerly available to the reactants, on the formation of a rigid transition state.

The effect of substitution in the aryl ring was studied (Table II). A Hammett plot gave a value of  $\rho = -1.0$  (correlation coefficient = 0.993), indicating that the rate determining step involved the formation of a radical intermediate. Earlier investigations had shown that reactions yielding radicals, gave values of  $\rho$  between  $-0.5$  and  $-1.8$ .<sup>11-13</sup>

TABLE II  
Effect of Substituents ( $60.0 \pm 0.1$  °C)

| Substituent       |  |
|-------------------|--|
| 1.0 M             | $10^6 \times k_{\text{obs}}/\text{s}^{-1}$ |
| <i>p</i> -methoxy | 412  |
| <i>p</i> -methyl  | 148  |
| <i>m</i> -methyl  | 83   |
| H (unsubstituted) | 69   |
| <i>m</i> -methoxy | 62   |
| <i>p</i> -chloro  | 54   |
| <i>m</i> -chloro  | 28   |
| <i>m</i> -nitro   | 15   |
| <i>p</i> -nitro   | 11   |

$[\text{K}_3\text{Fe}(\text{CN})_6] = 0.01$  M; aq. methanol = 60% (v/v);  $\mu = 0.10$  M;  $[\text{NaOH}] = 0.01$  M. All values of rate constants were the average of three experiments, agreement being  $\pm 3\%$ .

The oxidation of benzylamine- $\alpha$ -d<sub>2</sub> exhibited a kinetic isotope effect, with  $k_{\text{H}}/k_{\text{D}} = 6.3$ , indicating that there was the cleavage of the C—H bond of the methylene group attached to the aryl ring, resulting in the formation of a radical intermediate. In the oxidation of organic substrates, similar  $k_{\text{H}}/k_{\text{D}}$  values had indicated a cleavage of the C—H bond, giving a radical.<sup>13-16</sup>

The ESR spectrum (E-4, Varian) of the radical, generated in a flow system,<sup>9</sup> from the oxidation of benzylamine, contained four sets of 1:2:1 triplets. This splitting pattern was attributed to the interaction of the unpaired electron spin with the nitrogen atom, the hydrogen atom attached to the carbon atom, and the two hydrogen atoms at ortho positions in the aryl ring.

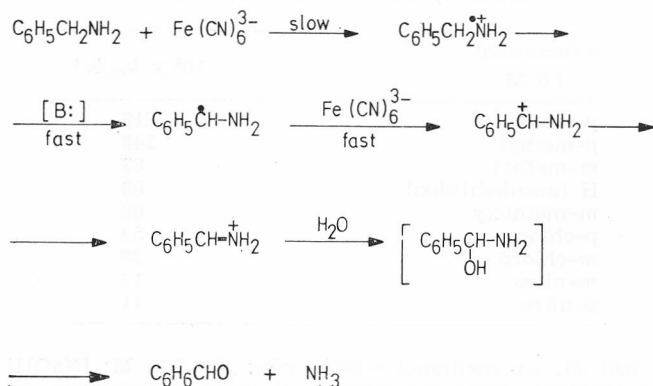
The mechanism of the reaction involved the cleavage of the carbon-hydrogen bond, resulting in the formation of a radical intermediate. This was supported by the following experimental observations:

- the rate of the reaction was dependent on the first powers of the concentrations of substrate and oxidant;
- the lack of any effect on the rate of the reaction by the addition of hexacyanoferrate(ii) ions; and
- the favourable enthalpy and entropy factors.

The radical intermediate was characterized by the value of  $\rho = -1.0$ , the kinetic isotope effect ( $k_H/k_D = 6.3$ ), and by ESR spectroscopy which showed four sets of 1:2:1 triplets. The hydrogen abstraction reaction shown in the SCHEME, leading to the formation of  $C_6H_5CH-NH_2$ , is a two-step process. First, the electron is lost (rate limiting), and then the proton is abstracted by  $OH^-$  (fast). This is the function of the required, but kinetically invisible base. This mechanism has been demonstrated for a related system.<sup>17</sup> The radical intermediate thus formed, is subject to immediate further oxidation, via the imine conjugate acid, to give the products, benzaldehyde and ammonia, which have been characterized.

The sequence of reactions is shown in the Scheme.

#### SCHEME



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### SAŽETAK

#### **Kinetika oksidacije benzilamina s alkalnim heksacijanoferat(III) ionom**

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Nađeno da je oksidacija benzilamina s alkalnim heksacijanoferat(III) ionom prvog reda s obzirom na svaki reaktant, neovisna je o koncentraciji lužine u vodenoj otopini metanola. Raspravlja se o mehanizmu reakcije.