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Kinetics of *N*-Alkyl Side Chain Oxidations. Oxidation of *N*,*N*-Dimethylaniline by Alkaline Hexacyanoferrate(III)

*Gopa Dasgupta and Mahendra K. Mahanti**

Department of Chemistry
North-Eastern Hill University, Shillong 793003, India

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The oxidation of *N*,*N*-dimethylaniline by alkaline hexacyanoferrate(III), at constant ionic strength, gave *N*-methylformanilide. The rate of the reaction was dependent on the first powers of the concentrations of substrate and oxidant, but was independent of the concentration of alkali in the range studied (0.01 M to 0.10 M). The mechanistic pathway involved an electron abstraction from the amine, giving a radical intermediate which was detected by ESR spectroscopy as a three-line spectrum with a peak height of 1 : 2 : 1.

INTRODUCTION

The mechanism by which a one-electron oxidizing agent such as potassium hexacyanoferrate(III) reacts with aromatic tertiary amines is of continuing interest. Aromatic tertiary amines have been oxidized by ceric ions[1], chromium trioxide,[2,3] lead tetraacetate,[4] and manganese dioxide.[5] Potassium hexacyanoferrate(III) is an efficient one-electron oxidant, and has been observed to be a substitution-inert transition metal complex.[6] The mechanism of oxidation by hexacyanoferrate(III) is *via* an outer sphere process,[6] the transfer of an electron occurring from the substrate to the metal ion through the cyano ligand. In alkaline medium, there is a distinct possibility of the formation of a radical intermediate, as a result of the abstraction of an electron, by hexacyanoferrate(III), from the substrate. In the present investigation, we report the kinetics of oxidation of *N*,*N*-dimethylaniline by alkaline hexacyanoferrate(III), at constant ionic strength, in aqueous methanol, under a nitrogen atmosphere. A mechanistic pathway, consistent with the kinetic results, has been suggested.

EXPERIMENTAL

Materials and Methods

N,*N*-dimethylaniline (E. Merck) was distilled before use (bp 193 °C). Methanol (E. Merck) was distilled before use. All other materials were E. Merck samples, and were used as such. The substrate was weighed, and the solution was prepared in methanol and water. Potassium hexacyanoferrate(III) was weighed and dissolved in a small volume of water. Sodium hydroxide of known concentration was added, the required amount of KCl introduced to maintain a constant ionic strength, and the solution was made up with methanol and water. The solutions were equilibrated at 35 °C for 1 h under nitrogen. 1 ml aliquots of the substrate and oxidant solutions were syringed into the spectrophotometric cell, and the reaction was followed by observing the disappearance of hexacyanoferrate(III) at 420 nm, spectrophotometrically (Uv-26, Beckman), at the required temperature. IR spectra were recorded on an IR-297 (Perkin Elmer) spectrophotometer, UV spectra on an Uv-26 (Beckman) spectrophotometer, NMR spectra on an EM-390 (Varian) 90 MHz spectrometer, and ESR spectra on an E-4 (Varian) EPR spectrometer. All values of rate constants were the average of two or more experiments, the agreement being ± 3%.

Stoichiometry

Reaction mixtures containing the substrate and an excess of the oxidant solution were allowed to react to completion at 35 °C (time period 24 hours), under nitrogen, and then analyzed, spectrophotometrically, for the remaining hexacyanoferrate(III). The rseults gave a ratio of substrate to oxidant consistent with the equation:

$$C_8H_{11}N + 4\,Fe\,(CN)_6^{3-} + H_2O \rightarrow C_8H_9NO + 4\,Fe\,(CN)_6^{4-} + 4\,H^+.$$

Product Analysis

Using the same experimental conditions as used for the kinetic determinations, the substrate and oxidant solutions, taken in aqueous methanol (60%, v/v), containing NaOH (0.01 M) and KCl (ionic strength adjusted to 0.1 M), were mixed and kept at 35 °C for 24 hours, under a nitrogen atmosphere. The solvent was removed, and the residue was washed with dilute HCl, and then concentrated. The residue was distilled (yield ~75%), and identified as the *N*-acyl derivative, *N*-methyl formanilide, *I* (b. p 243 °C; IR bands at 2940, 1670, 1590, 1490, 1450, 1350, 1270, 1110, 1090, 1030, 980 and 760 cm^{-1}; UV spectrum taken in methanol, absorption at 235 nm; NMR spectrum taken in CCl_4, peaks at δ 6.8 (aromatic protons), 2.8 (methyl protons) and 9.5 (formyl proton), with relative signal intensities of 5 : 3 : 1, respectively.

ESR Experiments

Using the same experimental conditions as used for the kinetic determinations, the substrate and oxidant solutions were mixed in an ESR tube. The mixture was placed under vacuum to expel dissolved oxygen, and the ESR sample tube was placed in the cavity of the spectrometer. The conditions for obtaining the spectrum were as follows: scan range 4000 G, field set 3300 G, modulation amplitude 5.0 G, microwave frequency 9.50 GHz, time constant 0.3 s, scan time 240 s.

RESULTS AND DISCUSSION

Kinetic Results

The rate of the reaction was dependent on the first powers of the concentrations of substrate and oxidant, but was independent of the concentration of alkali in the range studied (Table I). The oxidation of *N*,*N*-dimethylaniline was also possible with neutral hexacyanoferrate(III), but the reaction was very slow, as seen from the relative rate constants (Table I). An alkaline medium is thus necessary for the facile oxidation of the substrate. Though there is no dependence on the alkali over the pH range studied, it is not independent of pH in the wider sense.

A plot of k_{obs} *versus* a 10-fold range of concentration of substrate gives a straight line passing through the origin, indicating the rate of oxidation to have a first order dependence on the substrate. At constant substrate concentration (large excess), the pseudo first order rate constant (k_{obs}) did not change, with changing hexacyanoferrate(III) concentration (10-fold range), which indicates a first order dependence on the concentration of the oxidant.

TABLE

Rate Data for the Oxidation of N,N-*Dimethylaniline at 35 °C in Aqueous Methanol (60% v/v), Ionic Strength 0.1 M*

10^2 [Substrate]	10^3 [$K_3Fe(CN)_6$]	10^2 [NaOH]	$10^5 \times k_{obs}/s^{-1}$
1.0	1.0	1.0	9.5
2.5	1.0	1.0	24.1
5.0	1.0	1.0	48.0
10.0	1.0	1.0	96.0
1.0	0.75	1.0	9.5
1.0	0.50	1.0	9.3
1.0	0.25	1.0	9.6
1.0	0.10	1.0	9.5
1.0	1.0	2.5	9.5
1.0	1.0	5.0	9.3
1.0	1.0	10.0	9.4
1.0	1.0	1.0	7.2*
1.0	1.0	1.0	11.8$^+$
1.0	1.0	1.0	14.3$^{\neq}$
1.0	1.0	1.0	17.2$^{\neq \neq}$
1.0	1.0	0.0	0.1 (neutral medium)

* 30 °C; $^+$ 40 °C; $^{\neq}$ 45 °C; $^{\neq \neq}$ 50 °C (temp. corrections ±0.1 °C).

The reaction rate was enhanced by an increase in temperature (Table I), and the activation parameters calculated were: $E_a = 36 \pm 3$ kJmol^{-1}; $A = 135$ s^{-1}; $\Delta S^{\ddagger} = -210 \pm 6$ JK^{-1} mol^{-1}. The low value of the activation energy was due to the resonance stabilization of the intermediate radical by the nitrogen lone pair.

Variation in the ionic strength of the medium using KCl (0.01 M to 0.10 M), and the addition of hexacyanoferrate(II) ions in the concentration range 1×10^{-4} M to 1×10^{-3} M, had no effect on the rate of the reaction.

Radical Intermediate

The ESR spectrum of the radical, generated in a flow system, from the oxidation of *N,N*-dimethylaniline by alkaline hexacyanoferrate(III), gave 3 spectral lines with peak heights 1 : 2 : 1. This is the peak height distribution for an unpaired electron in the environment of two equivalent hydrogen atoms. The following conclusions can be drawn from this spectrum:

(a) the stable radical is formed by the loss of a hydrogen atom from the methyl group adjacent to the amine nitrogen atom;

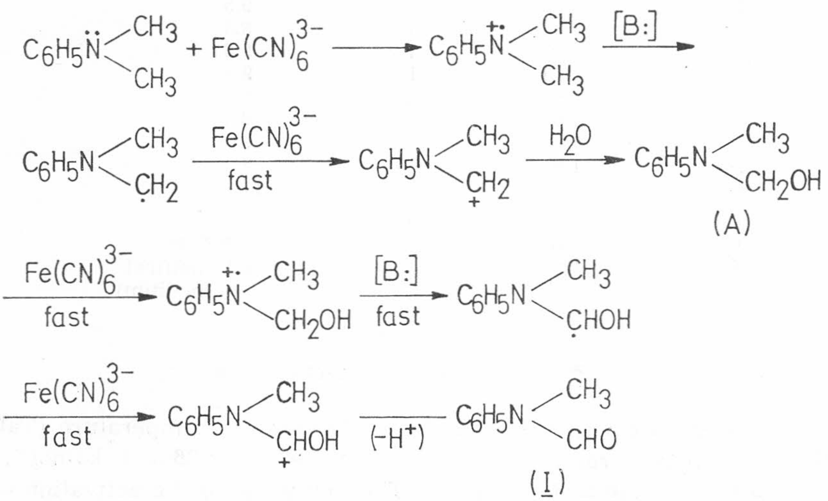
(b) the interaction of the unpaired electron extends to the hydrogen atom on the same carbon atom; and

(c) the methyl group attached to the nitrogen atom does not interact with the unpaired electron to give hyperfine splitting.

Mechanism

The pathway for the reaction can be envisaged as involving the cleavage of the carbon-hydrogen bond, resulting in the formation of a radical intermediate. The hydrogen abstraction reactions shown in the SCHEME, leading to $C_6H_5N(CH_3)CH_2$ and $\dot{C}_6H_5N(CH_3)\dot{C}HOH$, are two-step reactions. 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.[7] The subsequent steps are rapid, and no intermediate product(s) could be isolated from the reaction mixture. Efforts to isolate the carbinolamine, *A*, were not successful. It could be postulated that the carbinolamine, when formed as an intermediate, would be rapidly converted to the *N*-acyl derivative. This mechanism involves the removal of four electrons from the starting compound, which would be in agreement with the stoichiometry of the reaction. The oxidation of *N,N*-dimethylaniline to *N*-methylformanilide, constitutes an example of a reaction wherein the oxidation occurs at the *N*-alkyl side chain, leading to the formation of an *N*-aldehyde. Such products have been isolated and characterized in the oxidation of aromatic amines by manganese dioxide.[5]

Scheme



The reaction sequence is shown in the SCHEME.

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SAŽETAK

Oksidacija *N,N*-dimetilanilina heksacijanoferat(III)-ionom u alkalnom mediju

Gopa Dasgupta i Mahendra K. Mahanti

Određeni su kinetika i mehanizam oksidacije *N,N*-dimetilanilina kalijevim heksacijanoferatom(III)) u alkalnom mediju. Mehanizam reakcije uključuje nastajanje radikalskog intermedijara koji je detektiran ESR spektroskopijom.