

KINETICS OF OXIDATION OF TRIMETHYLAMINE BY HEXACYANOFERRATE(III) IN AQUEOUS MEDIUM

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The reaction of trimethylamine with aqueous hexacyanoferrate(III) gave formyl-dimethylamine. The rate depends on the first powers of the concentrations of substrate and oxidant; the activation parameters were: $E = 57.0 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -154 \text{ JK}^{-1} \text{ mol}^{-1}$. The mechanism involves abstraction of the proton attached to the α -carbon, yielding a radical, whose ESR spectrum gave 9 spectral lines.

Реакция триметиламина с водным гексацианоферратом(III) привела к образованию формилдиметиламина. Скорость реакции зависит от концентрации субстрата и оксиданта в первой степени, $E = 57,0 \text{ кДж. моль}^{-1}$, $\Delta S^\ddagger = -154 \text{ Дж. К}^{-1} \text{ моль}^{-1}$. Механизм реакции - отрыв водорода от α -СН связи с образованием свободного радикала. Спектр ЭПР содержит 9 линий.

INTRODUCTION

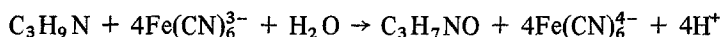
Aliphatic amines have been oxidized by Mn(III) /1/, RuO₄ /2/, V(V) /3/, and by alkaline KMnO₄ /4/. The present study reports the kinetic features of the oxidation of trimethylamine by aqueous potassium hexacyanoferrate(III).

EXPERIMENTAL

(a) *Materials, methods and stoichiometry*

Trimethylamine solution (30%, w/v) was an SD's sample. K₃Fe(CN)₆ was an E. Merck sample. Aqueous solutions of substrate and oxidant were separately thermostated for 3 h at 35 °C. 1 ml aliquots of each solution were syringed into the spectrophotometric cell, and the reaction followed by observing the disappearance

of $\text{Fe}(\text{CN})_6^{3-}$ at 420 nm, spectrophotometrically (UV-26, Beckman), at the required temperature /5/. The stoichiometry of the reaction was determined /5/ to be:



(b) *Product analysis*

Stoichiometric amounts of substrate (1 mol) and oxidant (4 mol) solutions were mixed and heated for 3 h at 60°C. The reaction mixture was cooled, extracted with ether, concentrated and dried over anhydrous MgSO_4 , to give the product in about 75% yield. This product, I, was characterized by bp (154 °C) and by IR analysis (absorptions at 2940, 1670, 1490, 1430, 1390, 1250, 1090 cm^{-1}) to be the N-acyl derivative, formyldimethylamine.

RESULTS AND DISCUSSION

The rate of the reaction was dependent on the first powers of the concentrations of substrate and oxidant (Table 1). The rate was enhanced with an increase in temperature, and the activation parameters were: $E = 57.4 \pm 1.2 \text{ kJ mol}^{-1}$, $A = 1.4 \times 10^5 \text{ s}^{-1}$, $\Delta S^\ddagger = -154 \pm 3 \text{ JK}^{-1} \text{ mol}^{-1}$.

Table 1
Rate data for oxidation of trimethylamine
at 35.0 °C

[Substrate] ($10^2 \times \text{M}$)	$[\text{K}_3\text{Fe}(\text{CN})_6]$ ($10^3 \times \text{M}$)	$10^5 \times k_{\text{obs}}$ (s^{-1})
5.0	5.0	2.8
25.0	5.0	14.3
50.0	5.0	29.0
5.0	2.5	2.8
5.0	1.0	3.0
5.0	0.5	2.7
5.0	5.0	3.3*
5.0	5.0	5.5*
5.0	5.0	7.4 [‡]

Temp.: *40.0 °C; †45.0 °C; ‡50.0 °C; all values of rate constants were the average of two or more experiments, with agreement being $\pm 1.5\%$ or better

