The Effect of Crown Ethers on the Oxidation of Triethylamine by Ferricyanide Ion in Aqueous Solutions at Different pH Values

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Abstract. The effect of benzo-15-crown-5, 15-crown-5 and 12-crown-4 on the oxidation of triethylamine by aqueous ferricyanide ion has been studied at pH 4, 7 and 11. The crown ethers retard the normal oxidation process at all pH values, the effect depending on the crown ether concentration. The three crown ethers show the same retardation effect at pH 4 and 7, while at pH 11 the retardation decreases in the order B15C5 > 12C4 > 15C5.

Key words: crown ether, triethylamine, ferricyanide ion, kinetics, retardation, pH.

Supplementary Data relevant to this publication have been deposited with the British Library, Boston Spa, Wetherby, Yorkshire, U.K., as Supplementary Publication No. SUP 82234 (3 pp.).

1. Introduction

Interest in the chemistry of crown ethers arises from their ability to complex with a wide range of cations; alkali, alkaline earth, transition metals, ammonium and neutral compounds [1–8]. It has been established that stable complexes form when the relative sizes of the cation and the ligand cavity are matched. However, various studies showed that crown ethers can complex with large cations such as ammonium and triethylammonium cation [9–11]. In addition, these synthetic ligands are similar in their structures and reactions to many naturally occurring macrocyclic compounds, which are known to exhibit selective cation complexation [12].

It is well known that ferricyanide ion reacts with electron-rich organic compounds by a one electron abstraction process [13]. The oxidation of a variety of trialkylamines was investigated mechanismically in a series of papers by Smith and coworkers [14]. Burrows et al. [15] investigated the oxidation of a number of trialkylamines by ferricyanide ion in aqueous solution and reported the reversibility of the reaction (Equation 1)

\[ \text{R}_3\text{N} + \text{Fe(CN)}_6^{3-} \rightleftharpoons \text{R}_3\text{N}^+ + \text{Fe(CN)}_6^{4-} \]  

Equation 1

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A mechanism was proposed involving two rate determining steps, the first being an electron transfer from the free amine which predominates at high pH and the second, hydrogen transfer from the trialkylammonium cation which predominates at low pH (Equation 2).

\[
R_3NH + Fe(CN)_6^{3-} \rightleftharpoons R_3N^+ + HFe(CN)_6^{3-}
\]  

(2)

A recent study showed that 18-crown-6 retards the oxidation of triethylamine by aqueous ferricyanide ion [16].

The present study was undertaken to investigate the effects of benzo-15-crown-5, 15-crown-5 and 12-crown-4 on the course of reaction of ferricyanide and triethyl amine at different pH values. The retardation caused by the crown ethers and the mechanism of oxidation are discussed.

2. Experimental

2.1. MATERIALS

Benzo-15-crown-5, 15-crown-5 and 12-crown-4 (Merck) were used as received. Deionized water was used throughout. Standard buffer solutions (Metrohm Herisau) of pH 4, 7 and 11, were used.

2.2. GENERAL PROCEDURE FOR KINETICS

The kinetics were followed by measuring the absorbance of ferricyanide at 420 nm. The absorbance spectra were recorded using a Varian-Cary 2390 spectrophotometer connected to a data station (Varian DS-15). In each experiment, 1 mL of the buffered solution of \(3 \times 10^{-4} \text{ M K}_3\text{Fe(CN)}_6\) was placed in an optical cell, and the initial absorbance was measured. This was followed by the addition of the appropriate solution of triethylamine and crown ether. The solution was stirred for 30 s. The absorbance of the solution was then measured at appropriate intervals. The results were stored by using the kinetic storage program (Varian 85-180080-00). The temperature of the optical cell was kept constant at 25 ± 0.5 °C by circulating (Julabo F3) water around the cell. Only the initial portion of the reaction (0.7t_1/2) was followed to exclude any retarding effect of the ferrocyanide formed which might interfere with the crown ether effect. Pseudo-first order rate constants (k_{obs}) were obtained by a least squares program.

3. Results and Discussion

A number of runs with constant initial concentrations of amine, ferricyanide ion and different concentrations of crown ethers were studied at a temperature of 25 ± 0.5 °C and at pH values of 4, 7 and 11 in aqueous solutions. Figure 2 displays a typical run showing the variation of the absorbance of the ferricyanide ion with time.