

# Environmental Effect of Macrocyclic Molecules on the Oxidation of Triethylamine by Ferricyanide Ion in Aqueous Solution

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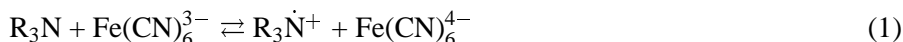
**Abstract.** The effect of 18-crown-6 and kryptofix (2,2,1) on the oxidation of triethylamine by aqueous ferricyanide ion has been studied at pH 4, 7, and 9. The macrocycle retarded the normal oxidation process at all pH values, the effect depending on the macrocyclic ligand concentration. Kryptofix (2,2,1) had a greater effect than 18-crown-6 at all pH values in this study. For 18-crown-6, retardation decreases in the order pH 9 > 4 > 7 while for kryptofix it follows the order pH 9 > 7 > 4.

**Key words:** Macrocyclic molecules, triethylamine, potassium hexacyano ferrate, buffer, rate, retardation.

## 1. Introduction

The discovery [1–3] that cations form stable complexes with macrocyclic polyethers and polyamines has opened the door to several broad and fruitful areas of chemical investigation. Interest in these macrocycles was stimulated when it was found that some of them formed stable complexes with alkali and alkaline earth metal ions and that preferential cation complexation resulted, provided the relative sizes of the cation and ligand cavity were matched [4]. 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 [5].

It is well known that ferricyanide ion reacts with electron-rich organic compounds in a one-electron abstraction process [6]; the oxidation of a variety of trialkylamines has been investigated mechanistically in a series of papers by Smith and coworkers [7]. Recently, Burrows *et al.* [8] investigated the oxidation of a number of trialkylamines by ferricyanide ion in aqueous solutions and reported that the reaction was reversible (Equation 1).



Evidence for reversibility came from the retardation effect caused by the added ferrocyanide over the pH range 3.7–13.4 used in their study.

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In addition, a mechanism was proposed involving two rate determining steps, the first being an electron transfer from the free amine, which predominates at high pH (Equation 1), the second being hydrogen transfer from trialkylammonium cation, which predominates at lower pH (Equation 2)



The present study was undertaken to investigate the effect of the water soluble 18-crown-6 ( $L_1$ ) and kryptofix (2,2,1) ( $L_2$ ) on the course of the reaction of ferricyanide and triethylamine at different pH values. The retardation caused by 18-crown-6 and kryptofix (2,2,1) and the mechanism of the oxidation are discussed.

## 2. Experimental

### 2.1. MATERIALS

Potassium ferricyanide (analytical reagent BDH) and triethylamine (Fischer) were used as received. Standard buffer solutions (Metrohm Herisau), pH 4, 7 and 9, were used. Deionized water was used throughout. Kryptofix (2,2,1) (Merck) was used without further purification. 18-Crown-6 (Merck) was recrystallized from acetonitrile by a standard procedure [9] before use.

### 2.2. GENERAL PROCEDURE FOR KINETICS

The kinetics were followed by measuring the absorbance of ferricyanide at 420 nm with a 616-photometer (Metrohm) using an optic fibre. In each experiment, a 10 mL solution of  $8 \times 10^{-4}$  M  $K_3Fe(CN)_6$  and 10 mL of buffer were placed in a universal titration vessel. This was followed by the addition of the appropriate amount of crown or kryptofix. The solution was stirred until the ligand dissolved, then the initial absorption was recorded by placing the optic fibre in the solution. An appropriate amount of triethylamine was then added and the solution was stirred for 30 s. The absorbance of the solution was then measured at appropriate intervals. The temperature of the solution was kept constant ( $25 \pm 0.02$  °C) by circulating (Julabo F3) water around the titration vessel. Only the initial portion of the reaction ( $0.7t_{1/2}$ ) was followed in order to exclude any retarding effect of ferrocyanide formed which might interfere with the macrocyclic effect. Pseudo-first order rate constants ( $k_{obs}$ ) for these reactions were obtained by a least squares program.

## 3. Results and Discussion

A number of runs with constant initial concentrations of ferricyanide ion, amine and different concentrations of macrocyclic ligand were studied at a constant temperature of  $25 \pm 0.02$  °C and pH values 4, 7 and 9. The results are recorded in Tables I and II and displayed in Figures 1 and 2. The results show the variation of

Table I. The dependence of pseudo-first order rate constants for oxidation of triethylamine [0.141 M] by ferricyanide ion on 18-crown-6-concentration.

pH 4							
Total [Crown] M $\times 10^2$	0.000 <sup>a</sup>	0.930	3.281	6.192	7.290	8.760	
$K_{\text{obsd.min}}^{-1} \times 10^2$	9.87	9.011	7.471	5.640	4.832	3.583	
Complexed [Crown] M $\times 10^2$	–	1.230	3.40	6.00	7.200	9.000	
pH 7							
Total [Crown] M $\times 10^2$	0.000 <sup>a</sup>	1.370	2.012	5.201	6.002	7.801	
$K_{\text{obsd.min}}^{-1} \times 10^2$	9.87	9.630	9.165	6.770	6.360	5.210	
Complexed [Crown] M $\times 10^2$	–	0.300	1.010	4.430	5.040	6.640	
pH 9							
Total [Crown] M $\times 10^2$	0.000 <sup>a</sup>	2.010	4.592	7.501	12.382	15.780	
$K_{\text{obsd.min}}^{-1} \times 10^2$	16.92	5.550	5.221	4.653	3.531	3.410	

<sup>a</sup> Data taken from Ref. [8].

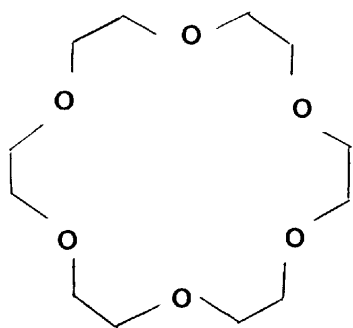
Table II. The dependence of pseudo-first-order rate constants for oxidation of triethylamine [0.141 M] by ferricyanide ion on kryptofix (2,2,1) concentration.

pH 4							
Total [Kryptofix (2,2,1)] M $\times 10^2$	0.000 <sup>a</sup>	1.590	2.501	3.142	5.892	7.103	
$K_{\text{obsd.min}}^{-1} \times 10^2$	9.87	7.781	6.752	6.081	5.352	4.902	
Complexed [Kryptofix] M $\times 10^2$	–	1.490	2.225	2.70	3.225	3.550	
pH 7							
Total [Kryptofix (2,2,1)] M $\times 10^2$	0.000	1.641	2.660	3.951	4.083	5.102	
$K_{\text{obsd.min}}^{-1} \times 10^2$	9.87	6.221	5.581	4.202	3.652	2.301	
Complexed [Kryptofix] M $\times 10^2$	–	2.60	3.050	4.00	4.45	5.40	
[Kryptofix(2,2,1)] M $\times 10^2$	0.000	1.800	2.501	3.902	5.103	6.500	
$K_{\text{obsd.min}}^{-1} \times 10^2$	16.92	4.560	4.302	3.781	2.621	1.751	

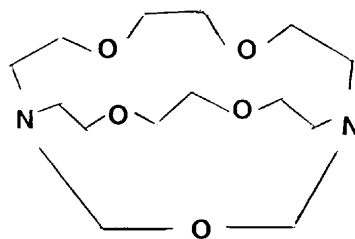
<sup>a</sup> Data taken from Ref. [8].

the observed rate constants ( $k_{\text{obs}}$ ) with the concentration of macrocyclic ligands, where  $k_{\text{obs}} = 2k_2[\text{amine}]$ ,  $k_2$  being the second order rate constant and the equation takes account of the consumption of a second equivalent of ferricyanide ion in a rapid reaction [8]. However, in each case, substantial retardation of  $k_{\text{obs}}$  was observed at all pH values in this study.

Inspection of the data in Tables I and II indicates that the behavior of the macrocycles at pH 4 and 7 is different from that at pH 9. At pH 4 and 7, the first addition of 18-crown-6 to the reaction mixture causes a slight decrease in the observed rate constant. Further addition of the macrocycle causes greater retardation, as shown in Table I. At pH 4 it is expected that triethylamine will be fully protonated; in addition, the solution contains other cations, such as  $\text{K}^+$  from potassium ferri-



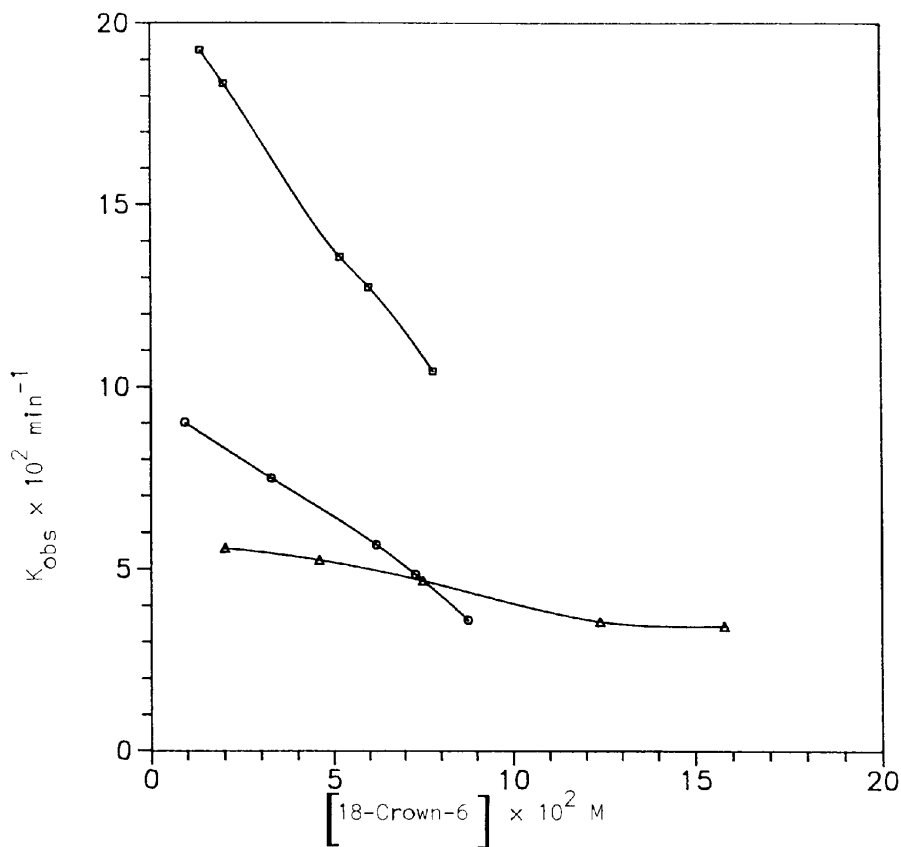
18-crown-6

 $L_1$ 

kryptofix (2,2,1)

 $L_2$ 

Figure 1. Structure of ligands.

Figure 2.  $k_{\text{obs}}$ .vs. [18-crown-6] at 25 °C, ○ pH 4; □ pH 7; △ pH 9.

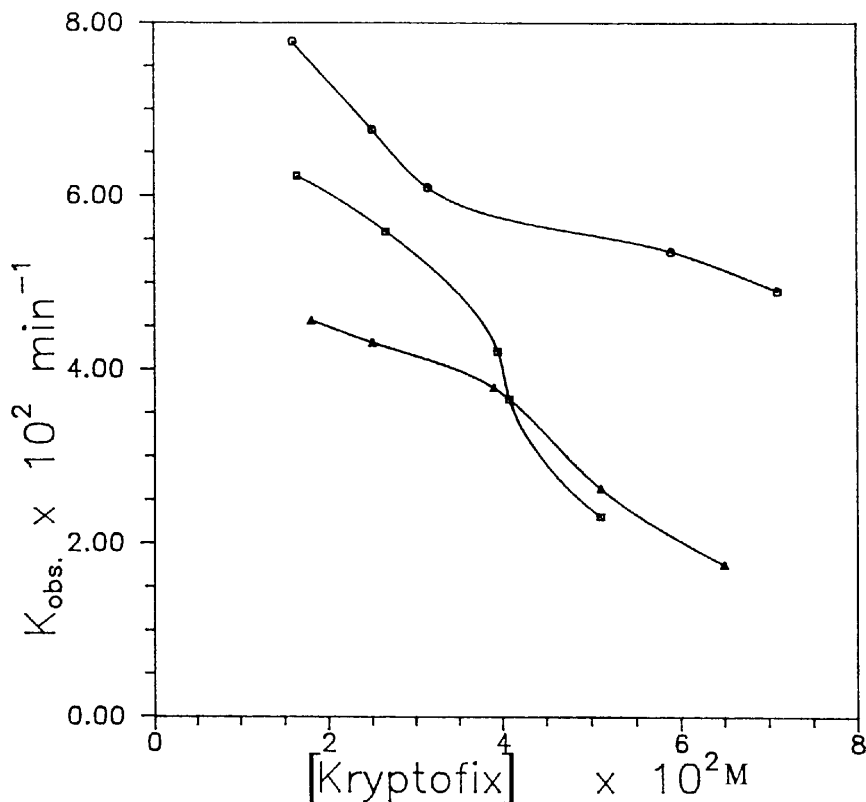
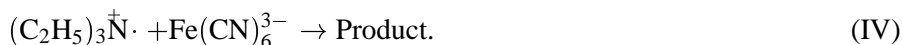
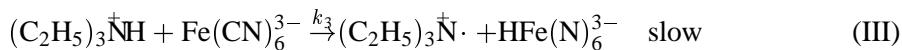


Figure 3.  $k_{\text{obs.}}$  vs. [Kryptofix 2,2,1] at 25 °C, ○ pH 4; □ pH 7; △ pH 9.

cyanide and from the buffer. The macrocycle added to the solution is subjected to complexation with all these cations. It is very difficult to calculate the amount of macrocycle which complexes with each cation. As an approximation we assume that at pH 4 and 7 the complexation mainly occurs with triethylammonium cation.

This retardation is due to the complexation between the triethylammonium ion and the macrocycle, which is more clear in the case of the use of kryptofix (2,2,1), where the minimum point in the curve (Figure 2) is an indication of complexation. The absence of a clear minimum point in the case of the use of 18-crown-6 does not mean that complexation did not occur, but rather that the complexation process is weaker with 18-crown-6 than with kryptofix (2,2,1). Previous studies on the complexation of ammonium ion with these macrocycles confirm the above conclusion [11, 12].

To explain the above results, we used the mechanism suggested by Smith *et al.* [7], which proposed a reductive process involving protonated amine as the important rate determining step, as follows:



The rate law derived from the above mechanism is

$$\text{Rate} = k_3 [(C_2H_5)_3NH^+]_{\text{free}} [Fe(CN)_6^{3-}] \quad (V)$$

where  $[(C_2H_5)_3NH^+]_{\text{free}}$  is the concentration of triethylammonium ion undergoing oxidation. Considering that the concentration of amine is much greater than that of  $Fe(CN)_6^{3-}$  and, in turn, the concentration of triethylammonium ion is much greater than that of ferricyanide ion, the rate law reduces to

$$\text{Rate} = k_{\text{obs}} [Fe(CN)_6^{3-}] \quad (VI)$$

where

$$k_{\text{obs}} = k_3 [(C_2H_5)_3NH^+]_{\text{free}}. \quad (VII)$$

Assuming the ratio of the macrocycle 18-crown-6 to triethylammonium is 1 : 1 in the complex at pH 4, then the concentration of free triethylammonium ion is:

$$[(C_2H_5)_3NH^+]_{\text{free}} = [(C_2H_5)_3NH^+]_{\text{initial}} - [(C_2H_5)_3NH^+]_{\text{complexed}}.$$

From step 1 in the mechanism, the initial concentration of triethylammonium ion is equal to the concentration of triethylamine. Taking into account that  $k_3$ , the rate constant, is the same through all readings, therefore, the change in the values of  $k_{\text{obs}}$  is due to the change in the concentration of free triethylammonium ion. From the relation  $k_{\text{obs}} = 2k_3[\text{amine}]_{\text{free}}$ , and since the specific rate constant  $k_3$  is known ( $0.35 \text{ M}^{-1} \text{ min}^{-1}$ ) [8], the concentration of free amine was calculated at each point, and the complexed amine was calculated by subtracting the free amine at each point from the initial concentration of amine which was constant at all points and equal to 0.141 M. Knowing the concentration of complexed amine, the concentration of complexed crown is also known.

Table III. The correlation of pseudo-first-order rate constants with the concentrations of complexed macrocyclic ligands.

	18-Crown-6		Kryptofix [2,2,1] <sup>+</sup>	
	Slope	Intercept	Slope	Intercept
pH 4	-0.714	0.703	-1.384	0.697
pH 7	-0.697	0.699	-1.397	0.698
pH 9*	-0.164	0.059	-0.371	0.052

<sup>+</sup> The ratio of the complex pH 4 and 7 was taken as 2 : 1 between triethylammonium ion and kryptofix (2,2,1).

\* At pH 9 the correlation was taken between  $k_{\text{obs}}$  vs. total concentration of the macrocyclic ligand.

The values of  $k_{\text{obs}}$  vs. the concentration of reacted (complexed) 18-crown-6 were subjected to a least squares fit which gave a straight line. The results of the analysis are included in Table III.

The same procedure was followed using kryptofix (2,2,1) with a complexing ratio of 2 : 1 triethylammonium ion to kryptofix (2,2,1) at pH 4. This is expected since there are two sites at the nitrogen atoms which can complex with the triethylammonium ion. The results of the analysis are included in Table III.

It is clear from Table III that there is a linear correlation between  $k_{\text{obs}}$  and reacted macrocycle. The slopes of the straight lines are indicative of the retardation effect. It is obvious that the retardation caused by the kryptofix (2,2,1) is much greater than that caused by 18-crown-6. This is expected since the complexation capability of kryptofix (2,2,1) is much greater than that of 18-crown-6.

At pH 7 it is expected that 18-crown-6 complexes with triethylammonium ion in a 1 : 1 ratio and at this pH the triethylammonium ion concentration will be much lower than that at pH 4. For the cryptand case, at pH 7 it showed more retardation than 18-crown-6 after the first addition of kryptofix (2,2,1) and it is expected that the pH of the medium will be more basic since the kryptofix (2,2,1) which is a base, will change the pH of the medium. As a result, we suggest that a mixed mechanism of proton transfer and electron transfer is possible in this case and this might explain the greater retardation at pH 7 caused by the kryptofix (2,2,1) than that caused by 18-crown-6. In addition, careful examination of data in Table II (pH 7) showed that the complexed kryptofix (2,2,1) with triethylammonium ion with ratio 1 : 2 is greater than the total concentration of kryptofix (2,2,1) added. This is explained as follows: if the retardation is due only to the complexation with triethylammonium ion via a proton transfer mechanism, the values of  $k_{\text{obs}}$  should be higher than those obtained.

Since the retardation is greater than that expected due to the complexation of kryptofix (2,2,1) with triethylammonium ion via proton transfer, a mixed mechanism involving proton transfer and electron transfer is suggested, which will be

discussed below. However, the results indicate that retardation at pH 7 caused by kryptofix (2,2,1) is a little greater than that at pH 4 and the kryptofix (2,2,1) causes more retardation than 18-crown-6 at these pHs.

At pH 9 both 18-crown-6 and kryptofix (2,2,1) cause retardation of the reaction. However, both 18-crown-6 and kryptofix (2,2,1) showed different behavior at pH 9 compared with that at pH 4 and 7. The first addition of 18-crown-6 or kryptofix (2,2,1) caused a remarkable decrease in the observed rate constant. In fact  $k_{\text{obs}}$  decreases from  $16.92 \times 10^{-2} \text{ min}^{-1}$  to  $5.55 \times 10^{-2} \text{ min}^{-1}$  when 18-crown-6 is used, and a greater decrease was observed when kryptofix (2,2,1) was used. The addition of more crown or kryptofix produced small changes in the values of  $k_{\text{obs}}$ , this is taken as indication that the complexation process at pH 9 is different from that at pH 4 and 7.

We consider that the mechanism of oxidation at pH 9 occurs via an electron transfer process as proposed by Smith *et al.* [7]. This mechanism requires a bridge to transfer the electron, and the cations in this case act as such a bridge. The cationic salt effect [7] was observed in the oxidation of amines and changing the cation from lithium to cesium increases the rate constant 20-fold. Swinehart [14] and others [15] have interpreted cationic effects in these reactions of anions by assuming that the cations act as a bridge for electron transfer.

In our case, we suggest that the macrocycles complex with the cations ( $\text{Na}^+$ ,  $\text{K}^+$ ) mainly coming from the buffer and potassium ferricyanide, therefore the acting bridge is changed from  $\text{Na}_{(\text{aq})}^+$  and  $\text{K}_{(\text{aq})}^+$  to complexed  $\text{Na}^+$  and  $\text{K}^+$ , which results in a decrease of the charge density of the bridge which, as a result, will hinder the electron transfer and therefore decreases the rate constant. The results in Tables I and II indicate that the kryptofix (2,2,1) is more effective than 18-crown-6 in causing retardation and this is due to the fact that the complexation constant of kryptofix (2,2,1) with  $\text{Na}^+$  and  $\text{K}^+$  is much greater than that with 18-crown-6 [4].

The second and subsequent additions of the macrocycles produced small changes in the values of  $k_{\text{obs}}$  and this could be due to either a change in the environment of the reaction, especially the electron bridge, and/or due to the complexation of the macrocycles with the amine species present in the solution. Other studies in our laboratory of the oxidation reaction at pH 11 with the use of crown ethers support the above conclusions. In addition, we ruled out the retardation observed being due to the changes in pH of the media, since addition of macrocycles to the reaction might increase the pH due to its basic character and, if this happens, it is expected that the rate constant must increase.

The effect of ionic strength was also considered in our study, so we worked under almost constant and low ionic strength. If there is a slight change in ionic strength it is not expected to introduce any effect at these low ionic strengths. Burrows *et al.* confirm this conclusion in their study [8].

Further studies, especially at high pH values, are currently under investigation to clarify the effect of macrocycle on the oxidation reaction.



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