

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.

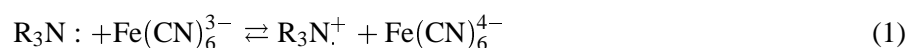
Key words: crown ether, triethylamine, ferricyanide ion, kinetics, retardation, pH.

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

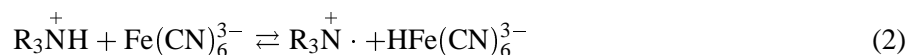
Interest in the chemistry of crown ethers arises from their ability to complex with a wide range of cations; alkali, alkaline earth, transition metals, ammonium and neutral compounds [1–8]. It has been established that stable complexes form when the relative sizes of the cation and the ligand cavity 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 mechanistically 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)



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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).



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 3×10^{-4} M $\text{K}_3\text{Fe}(\text{CN})_6$ 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.

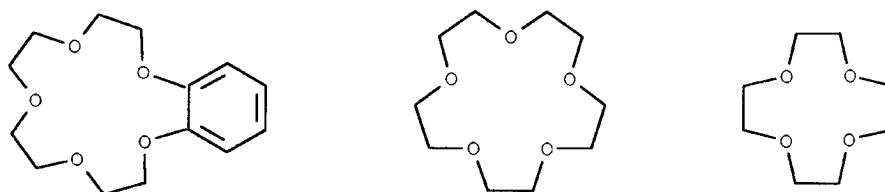


Figure 1. Structures of the ligands.

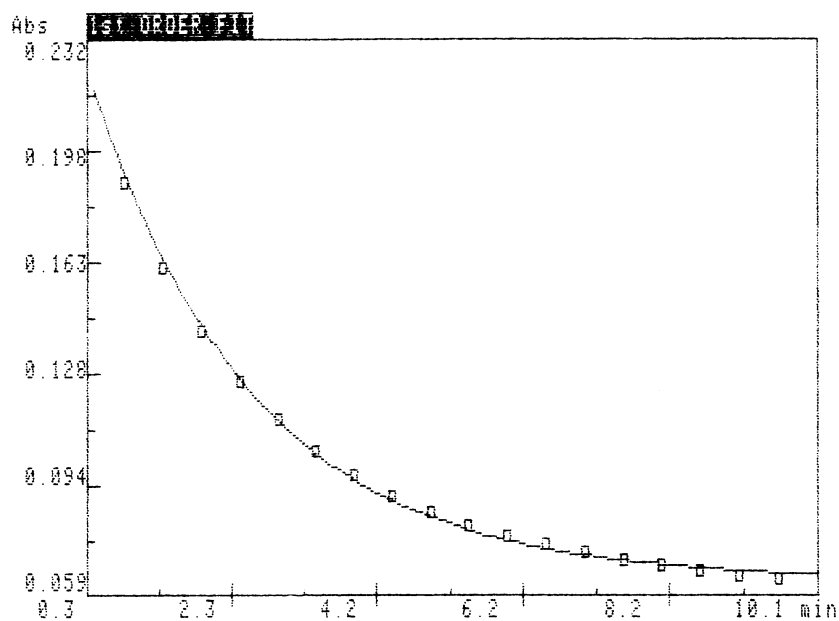


Figure 2. The variation of absorbance versus time for the oxidation of triethylamine by hexacyanoferrate (III) ion in aqueous solution.

Under the conditions used in this study, the reaction follows the simple kinetic relationship

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = 2k_2[\text{amine}] [\text{Fe}(\text{CN})_6^{3-}] \quad (3)$$

where k_2 is the second order rate constant and the above equation takes into account the consumption of a second equivalent of ferricyanide ion in a fast reaction. At relatively high amine concentration the above relation can be transformed into

$$\frac{-d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = k_{\text{obs}}[\text{Fe}(\text{CN})_6^{3-}] \quad (4)$$

where $k_{\text{obs}} = 2k_2[\text{amine}]$.

Table I. The dependence of the pseudo-first order rate constants for oxidation of triethylamine (0.21 M) by ferricyanide ion on the 15-crown-5-concentration.

pH 4									
Total [15C5]M × 10 ²	0.00	0.500	1.800	4.000	8.000	9.330	12.000	14.66	20.000
$k_{\text{obs}} \text{ s}^{-1} \times 10^3$	8.757	8.678	8.225	7.891	6.523	6.182	5.776	5.288	5.023
Complexed [15C5]M × 10 ^{2*}	0.00	0.190	1.280	2.080	5.360	6.180	7.150	8.320	8.960
pH 7									
Total [15C5]M × 10 ²	0.000	0.500	1.800	4.000	8.000	9.330	12.000	14.660	20.000
$k_{\text{obs}} \text{ s}^{-1} \times 10^3$	9.881	9.694	8.939	8.302	7.521	7.176	7.058	6.753	6.232
Complexed [15C5]M × 10 ^{2*}	0.000	0.400	2.001	3.355	4.990	5.750	6.000	6.650	7.754
pH 11									
Total [15C5]M × 10 ²	0.000	0.500	1.800	4.000	8.00	9.330	12.000	14.660	20.000
$k_{\text{obs}} \text{ s}^{-1} \times 10^3$	10.987	10.866	10.365	9.619	8.597	8.404	8.248	8.078	7.470

* Complex ratio is 1 : 1 amine to crown.

The results are recorded in Tables I–III and displayed in Figures 3–5. The results show the variation of the observed rate constant (k_{obs}) with the concentration of crown ether. However, in each case, substantial retardation of k_{obs} was observed at all pH values in this study. Inspection of the data indicates that the behavior of the crown ethers at pH 4 and 7 is different from that at pH 11 and the behavior of the different crown ethers is different at the same pH.

At pH 4 and 7, the first addition of crown ether to the reaction mixture causes a slight decrease in the observed rate constant. Further addition of the crown causes further decrease of k_{obs} which then tends to level off. The slope of the corresponding k_{obs} vs crown ether concentration plots changes at the point where the concentration of 15C5 is 0.1 M and the B15C5 and 12C4 concentrations are about 0.06 M. The point at which the slope changes is taken as indication of a complexation process between the crown ether and the cations existing in solution. As previously reported [16] at these pH values, the complexation is mainly occurring with the triethylammonium cation. Therefore, the retardation is due to the complexation between the triethylammonium ion and the crown ether.

To explain the above results, the mechanism suggested by Smith *et al.* [14], who proposed that a reductive process involving protonated amine is the important rate determining step, will be used here as follows



Table II. The dependence of the pseudo-first-order rate constants for oxidation of triethylamine (0.21 M) by ferricyanide ion on the benzo-15-crown-5 concentration.

pH 4										
Total [B-15C5]M × 10 ²	0.000	0.670	1.550	2.120	3.980	5.600	6.050	7.260	10.090	11.823
$k_{\text{obs}} \text{ s}^{-1} \times 10^3$	8.757	8.087	7.768	7.0854	5.979	5.637	5.403	5.321	5.293	5.213
Complexed [B-15C5]M × 10 ^{2*}	0.000	0.610	2.370	4.010	6.660	7.480	8.040	8.240	8.310	8.500
Complexed [B-15C5]M × 10 ²⁺	0.000	0.805	1.185	2.005	3.330	3.740	4.020	4.120	4.155	4.250
pH 7										
Total [B-15C5]M × 10 ²	0.000	0.670	1.550	2.120	3.980	5.600	6.050	7.260	10.090	11.823
$k_{\text{obs}} \text{ s}^{-1} \times 10^3$	9.881	9.375	8.929	8.256	7.006	6.754	6.282	5.989	5.606	5.424
Complexed [B-15C5]M × 10 ^{2*}	0.000	1.070	2.020	3.450	6.110	6.650	7.650	8.270	9.090	9.470
Complexed [B-15C5]M × 10 ²⁺	0.000	0.535	1.010	1.725	3.005	3.325	3.825	4.135	4.545	4.735
pH 11										
Total [B-15C5]M × 10 ²	0.000	0.670	1.550	2.120	3.980	5.600	6.050	7.260	10.090	11.823
$k_{\text{obs}} \text{ s}^{-1} \times 10^3$	10.987	9.703	9.453	9.258	8.950	8.702	8.250	7.987	7.273	6.998

* Complex ratio 1 : 1 amine to crown.

+ Complex ratio 2 : 1 amine to crown.

Table III. The dependence of the pseudo-first-order rate constants for oxidation of triethylamine (0.21 M) by ferricyanide ion on the 12-crown-4 concentration.

pH 4										
Total [12C4]M × 10 ²	0.000	1.600	2.270	4.800	6.040	6.670	9.800	15.330	18.830	26.670
$k_{\text{obs}} \text{ s}^{-1} \times 10^3$	8.757	8.169	7.662	6.550	6.045	5.432	4.906	4.422	4.322	3.867
Complexed [12C4]M × 10 ^{2*}	0.000	1.410	2.630	5.290	6.504	7.970	9.230	10.400	10.640	11.730
Complexed [12C4]M × 10 ²⁺	0.000	0.705	1.315	2.645	3.252	3.985	4.615	5.200	5.320	5.865
pH 7										
Total [12C4]M × 10 ²	0.000	1.600	2.270	4.800	6.040	6.670	9.800	15.330	18.930	26.670
$k_{\text{obs}} \text{ s}^{-1} \times 10^3$	9.881	8.785	8.334	7.511	6.633	6.231	5.513	4.923	4.757	4.318
Complexed [12C4]M × 10 ^{2*}	0.000	2.330	3.290	5.040	6.900	7.760	9.280	10.540	10.890	11.820
Complexed [12C4]M × 10 ²⁺	0.000	1.165	1.645	2.520	3.450	3.880	4.640	5.270	5.445	5.910
pH 11										
Total [12C4]M × 10 ²	0.000	1.600	2.270	4.800	6.040	6.670	9.800	15.330	18.930	26.670
$k_{\text{obs}} \text{ s}^{-1} \times 10^3$	10.987	9.921	9.220	8.859	8.242	8.076	7.892	6.532	5.657	4.889

* Complex ratio 1 : 1 amine to crown.

+ Complex ratio 2 : 1 amine to crown.

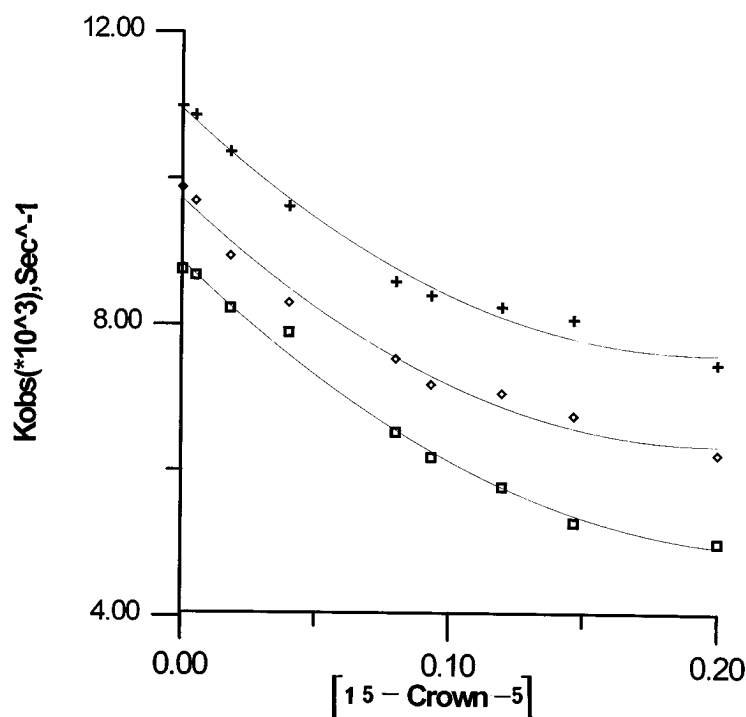
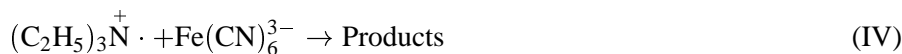
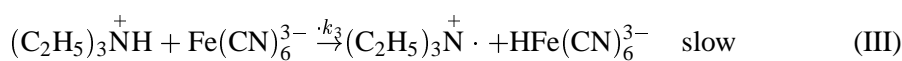


Figure 3. k_{obs} vs. [15-crown-5] at 25 °C. \square , pH 4; \diamond , pH 7; +, pH 11.



The rate law derived from the above mechanism is

$$\text{Rate} = k[(\text{C}_2\text{H}_5)_3\text{NH}^+]_{\text{free}}[\text{Fe}(\text{CN})_6^{3-}]$$

where $[(\text{C}_2\text{H}_5)_3\text{NH}^+]_{\text{free}}$ is the concentration of triethylammonium undergoing oxidation which equals $[(\text{C}_2\text{H}_5)_3\text{NH}^+]_{\text{initial}} - [(\text{C}_2\text{H}_5)_3\text{NH}^+]_{\text{complexed}}$. From step I in the mechanism, the initial concentration of the triethylammonium ion equals the concentration of triethylamine. Taking into account that k (specific rate constant) at a certain pH is the same through all readings, therefore, the change in the values of k_{obs} is due to the change in the concentration of free triethylammonium ion. From the relation $k_{\text{obs}} = 2k[\text{amine}]_{\text{free}}$ and since the k specific rate constant is known, 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 the amine which was constant at all points and equal to 0.21 M.

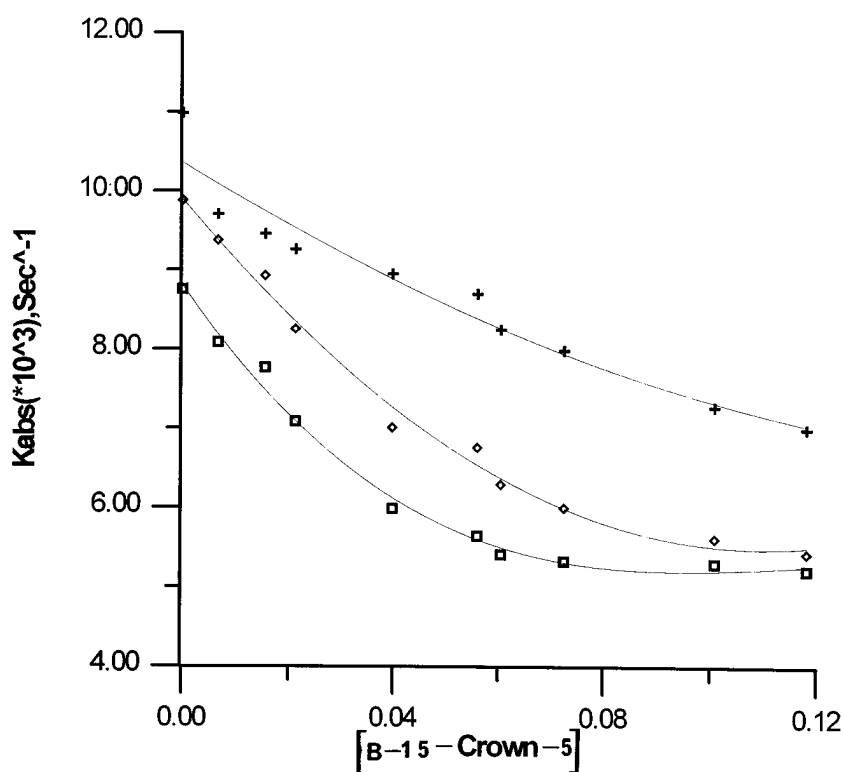


Figure 4. k_{obs} vs. [benzo-15-crown-5] at 25 °C. □, pH 4; ◇, pH 7; +, pH 11.

Knowing the concentration of complexed amine, the concentration of complexed crown is also known.

Assuming the complexing ratio is 1 : 1 amine to crown, 15C5 satisfies this relation. But in the case of benzo 15-C-5 and 12C4 the supposed complexed crown concentration based on a 1 : 1 complexing ratio is more than the total crown concentration. Therefore, we assume the complexing ratio is 2 : 1 amine to crown for the case of 12C4 and B15C5. Support for this conclusion exists in Figures 3–5, where the slope changes at about 0.1 M concentration for 15C5 and about 0.06 M for 12C4 and B15C5. In addition, detailed examination of the data in Tables I–III, indicates that the decrease in the values of k_{obs} by B15C5 and 12C4 is more than that caused by the same concentration of 15C5.

When 12C4 and B15C5 are used, the addition of either crown causes retardation but it does not show a minimum point as in the case of 15C5. This does not mean that the complexation is not occurring but that the equilibrium state is not reached within the range of crown concentrations used. It also might indicate that the nature of the complexes of these two crowns is different from that of 15C5.

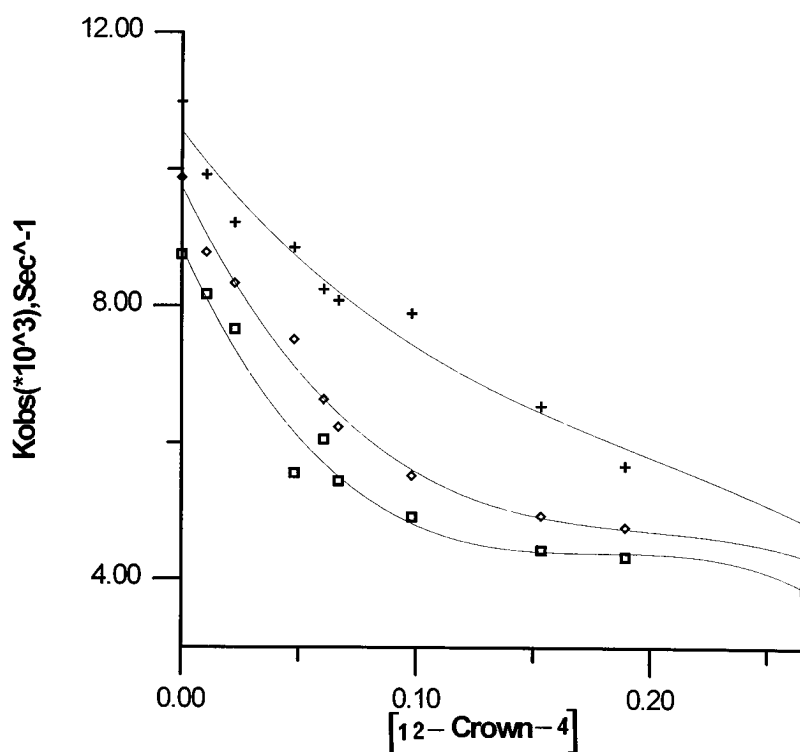


Figure 5. k_{obs} vs. [12-crown-4] at 25 °C. □, pH 4; ◇, pH 7; +, pH 11.

At pH 4 and 7 the values of k_{obs} vs the concentration of reacted (complexed) crown ether were subjected to a least squares fitting which gave a straight line. The results of the analyses are included in Table IV. The slopes are indicative of the retardation caused by the crown ethers. The slopes reported in Table IV reveal that the three crowns have the same retardation power at the same pH and the retardation at pH 7 is greater than that at pH 4. It is expected that the three crown ethers should have the same retardation effect since they have the same type of donor atoms. However, the difference in their behavior regarding the complexation ratio is probably due to their geometry. 12C4 and B15C5 are expected to have a rigid planar geometry which exposes all the oxygen atoms to complexation from both sides, while 15C5 has a twisted geometry and in this case the oxygen atoms are not in the same plane: as a result, not all the oxygen atoms are exposed to complexation. In addition it is possible that the benzo group in B15C5 might enhance the complexation

Inspection of the data at pH 11 indicates that the three crowns cause retardation of the oxidation reaction, and 12C4 and B15C5 causes more retardation than 15C5.

To explain the results at pH 11, a mechanism of oxidation which involves an electron transfer process as proposed by Smith *et al.* [14] was considered here. This

Table IV. The correlation^a of the pseudo-first order rate constants with the concentrations of complexed crown ethers.

	15-crown-5		Benzo-15-crown-5*		12-crown-4*	
	Slope	Intercept	Slope	Intercept	Slope	Intercept
pH 4	-41.690	8.758	-83.410	8.758	-83.387	8.757
pH 7	-47.060	9.881	-94.075	9.880	-94.120	9.882
pH 11	-18.09	10.60	-24.52	10.98	-19.40	10.80

^a The values of the slopes, intercepts and *c*'s are multiplied by 10³.

* The ratio of the complex of pH 4 and 7 was taken to be 2 : 1 between triethylammonium ion and crown ether.

+ At pH 11 the correlation was taken between *k*_{obs} vs. total concentration of the crown ether.

mechanism requires a bridge to transfer the electron, and the cations in this case act as such a bridge. The cationic salt effect [14] was observed in the oxidation of amines and changing the cation from lithium to cesium increases the rate constant 20-fold. Swinehart [17] and others [18] have interpreted cationic effects in these reactions of anions by assuming the cation acts as a bridge for an electron transfer.

In our case, we suggest that the crown ether complexes with the cations (Na⁺, K⁺) mainly coming from the buffer and potassium ferricyanide, therefore the acting bridge is changed from Na_(aq)⁺ and K_(aq)⁺ to complexed Na⁺ and 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.

To compare the effect of crown ethers at pH 11, the data in Tables I–III were subjected to a least squares fit. The results of the analysis are recorded in Table IV. The slopes which represent the decrease of *k*_{obs} by the addition of crown ether indicate the retardation effect and follows the order B15C5 > 12C4 > 15C5. It is expected that the complexation constants of the three crowns with Na⁺ and K⁺ are almost the same, since they have the same cavity radii (0.9 Å 0.9 Å and 0.8 Å) for B15C5, 15C5 and 12C4, respectively. Therefore, the difference in their effect might be due to the difference in their geometry, where B15C5 and 12C4 have rigid planar geometries while 15C5 has a flexible twisted one and this probably affects the complexation ratio. On the other hand, the possibility of complexation of these crown ethers with other amine species exist in solution cannot be ruled out. 18C6 showed less retardation at pH 9 than that at pH 4 and 7 [16] and it is expected that the retardation at pH 11 by 18C6 will be less than by 15C5.

The results in Table IV clearly point out that the three crowns cause retardation and have almost the same retardation power. It is important to emphasize that the pH of the solution was constant and the work was done at low ionic strengths and if there is a slight change in ionic strength it is not expected to introduce any effect on the reaction rate [15].

Further studies in alkaline solution and the effect of ionic strength on the oxidation reaction are currently under investigation to clarify the effect on crown ethers.

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