

COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 26

ANNÉE 1980

**Effect of Macrocyclicethers on the Reaction Rate
Role of 1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane and
1, 4, 7, 10, 13, 16, 19-hepta oxacycloheneicosane in
Water-dioxane mixtures. Part II.**

by

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

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Received, 21 January, 1980 and accepted, 6 March, 1980

ABSTRACT

The effect of cyclic hexamer and heptamer of macrocyclic ethers on the reaction rate of K^+ picrate and t-butyl chloride in water-dioxane mixtures was studied at various temperatures. The results obtained showed the role of the size of cavity complexed with the cation which are quite in accordance with our earliler studies and the works reported.

INTRODUCTION

The earliler evidence from the work of Ugelstad and his coworkers on the complexation ability of dimethylethers of polyethylene glycoles as coordinating agents pointed out that such a behavior mostly depends on the number of atoms arranged around the cation(1) and also several studies of Cram led us to work(2) on the effect of macrocyclic ethers on the reaction rate. The coordination of glymes or crown ethers with alkaalin ions which is not a purely donor-acceptor type and there is no reason, for instance, to from tetrahedral arrangement of oxygen atoms, so the macrocyclics of planar structure are of the strong coordinating agents. The behavior of ions and ion pairs were deeply dicsussed by Szwarc(3) and the role of macrocyclic ethers were explained by Smid(4). However, it is known that in powerful cation solveting media such as dimethyl sulfoxide, dimethyl formamide most of the salts form only seperated ion pairs(5). In one of our recent study the quarterner amonium salts were observed to form complexed ion pairs

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**To be submitted for the partial fulfillment of Ph.D.degree in Physical Chemistry, University of Diyarbakır.

of similar nature of solvent separated ion pairs as they are indicated in their optical spectra(6).

Accordingly in the previous study we have already reported the role of 1, 4, 7, 10-tetraoxocyclododecane on the reaction rate of potassium picrates. Now we report the behaviour of larger oligomers under similar conditions(7).

RESULTS AND DISCUSSIONS

The observed results as they are exhibited on table 1-3 very much in accordance with the earlier considerations on the cation solvation tendency of the macrocyclic ethers.

Table-1. Rate of reaction of K⁺ picrate with t-butyl chloride on water-dioxane (80:20, V/V) at various temperatures in the presence of 12-Crown-4.

Conc.K ⁺ Picrate. 10 ⁴	Conc. t-but. Chl. 10 ³	12-Crown-4	70°C K. 10 ² (hr ⁻¹)	40°C K.10 ⁴ (hr ⁻¹)
1.34	5.46	0.1	5.55	7.9
1.37	"	0.4	18.40	28.6
1.36	"	0.7	12.40	36.8
1.32	"	1.0	14.40	59.5

Table-2. Rate of reaction of K⁺ picrate with t-butyl chloride in Water-dioxane (80:20, V/V) at 70°C in the presence of 18-Crown-6.

Conc.K ⁺ picrate.10 ⁵	Conc. t-but.Chl.10 ³	Conc. 18-Crown-6	K.10 ² (hr ⁻¹)
13.40	5.46	0.1	9.6
9.65	"	0.4	20.0
8.65	"	0.7	26.8
6.65	"	1.0	43.2

Table-3. Rate of reaction of K⁺ picrate with t-butyl chloride in water-dioxane (80:20, V/V) at 40°C in the presence of 21-Crown-7.

Conc. K ⁺ pic- rate. 10 ⁴	Conc. t-but. chl. 10 ²	Conc. 21-Crown-7	K.10 ³ (hr ⁻¹)
1.32	1.82	0.1	1.9
1.35	"	0.4	6.8
1.30	"	0.7	15.6

Mainly observed effect of 12-Crown-4 is almost similar to that of 18-Crown-6 where as the 21-Crown-7 exhibited remarkable effect of selectivity depending on the diameter of the hole of macrocyclic ether with respect to the cation hole.

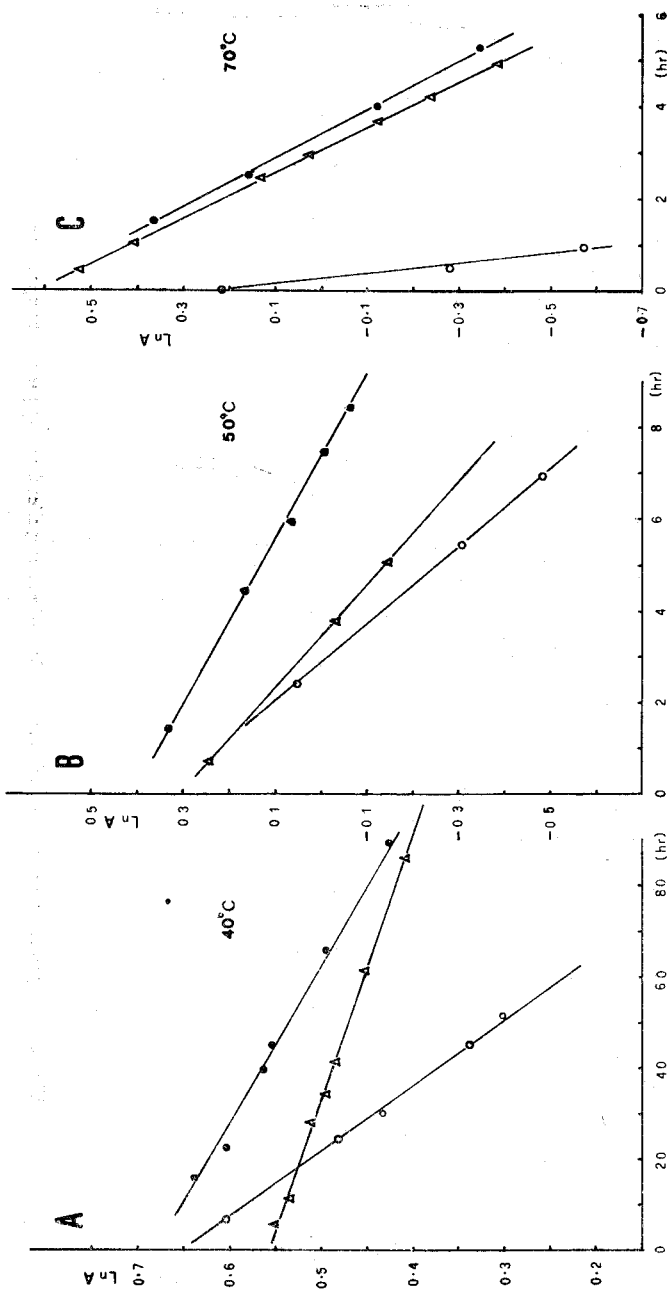


Figure-1. Dependence of ln of absorbance on the time at A) 40°C B) 50°C C) 70°C degrees in presence of (●) 12-Crown-4 (○) 18-Crown-6 (△) 21-Crown-7 of the reaction of potassium picrate with t-butyl chloride in water-dioxane

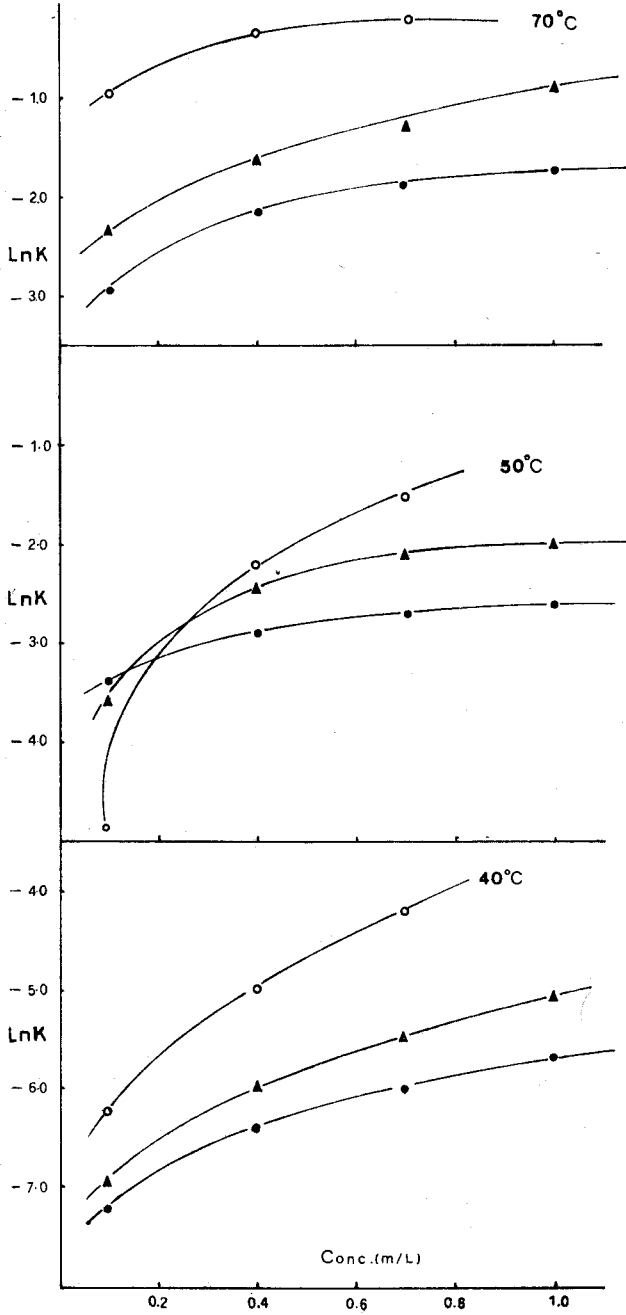


Figure-2. Dependence of LnK on the concentration of macrocyclicethers at various temperatures.

Table-4. Thermodynamic data for the pseudo first order reaction of K^+ picrate with *t*-butyl chloride in water-dioxane (80:20, V/V).

Poly. et. Conc.	0.1		0.4		0.7		1.0	
Poly. eth. (**)	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
12-Crown-4	30473.5	83.9	29825.6	84.4	25381.6	70.9	22926.6	63.9
18-Crown-6	34796.4	97.6	34123.4	96.7	33579.8	96.2	34734.8	99.8
21-Crown-7	37208.4	105.5	34035.2	99.0	28118.5	81.9	—	—
Glyme-6 (*)	29467.9	81.5	27375.3	77.1	21400.4	59.8	26151.2	75.0

(*) Hexaethylene glycol dimethyl ether.

(**) Given in Cal/mol.

It is also interesting that the observed small increments of reaction rates by the temperature indicates the role of Crown separated ion pairs involved in the reactions where the complexed ions cause the smaller loss of entropy due to the effectiveness as compare to solvents like pure dioxane.

In our work we particularly tried in dioxane-water mixtures as a solvent because of very low dielectric constant which give ion pair aggregation and this could naturally effect the ion pair solvation in an unfavourable way. In the other hand dioxane itself could take part among the water molecules although such a inclusion break the intra molecular hydrogen bonds which mainly compute with the dipolar power of macrocyclic ether tried to bind the cation in the media. This computation mostly influenced from the nature of solvent however such a system seems rather suitable media with respect to alcohols to observe the main effect.

It has been also pointed out that the dielectric saturation makes the effective dielectric constant much smaller than the macroscopic one therefore external solvation of a contact ion pair is more effective in polar solvents. On the coordination with the macrocyclic ethers part of solvents should be removed and this process requires more energy for methanol than for dioxane. That could also explain the closeness of the the role of 12-Crown-4 with compare to 18-Crown-6. The both cases are expected to cause from fast exchange rates of low cation solvation energy and ligand flexibility(8).

21-Crown-7 therefore seems more capable to bind the cation due to the ring flexibility which release the cation rather slowly.

EXPERIMENTAL

Kinetic studies were run in a thermostated bath of $\pm 0.05^\circ\text{C}$ temperature variety. Concentrations were determined by the absorbances measured at appropriate wavelengths by the UV-VIS spectrometer model JASCO-UVIDEC-4 as soon as they are quenched in a ice cooled bath.

Potassium picrate were obtained from picric acid (Merck) and purified by crystallisation from ethanol.

1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane (18-Crown-6) was obtained according to Cram and his coworkers. from 1,8-dichloro-3,6-dioxooctane and triethyleneglycole in THF in the presence of KOH. We modified the method in a way that the ether was obtained in 99 % purity of 35-45 % in yield (GLC) so that it could be tried without complexing with CH_3CN .(9)

1, 4, 7, 10, 13, 16, 19-heptaoxacycloheneicosane (21-Crown-7) was obtained according to the method given above starting from 1, 8-dichloro-3,6-dioxooctane and tetraethylene glycol in n-buthanol. However several distilations gave only 85-90 % purity of the products in 15-20 % yields.

1, 4, 7, 10-tetraoxacyclododecane was obtained by one of the authors from ethyleneoxide according to earliler work(10).

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ÖZET

Bu çalışmada, 12-Crows-4, 18-Crown-6 ve 21-Crown-7 gibi makrosiklik eterlerin K^+ pikratın verdiği bir yer değiştirme reaksiyonunun hızına olan etkisi incelenmiştir. Su-dioksan karışımında yapılan çalışmalar halkadaki oksijen sayısı ile reaksiyon hızının bağıntılı olduğunu ve 21-Crown-7 nin maksimum etkiyi gösterdiğini ortaya koymuştur.

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