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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE

Effect of Solvent on the Reaction Rate. Part. III
Role of Macrocyclic Ethers on the S_N2 Reactions in Water-Dioxane Solutions.

by

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21

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

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ABSTRACT

Effect of some macrocyclic ethers have been investigated in the reaction of di or tri nitro phenoxides with some alkil halides in water-dioxane mixtures. It has been found that in most cases heptaoxa oligomer has more influence although the fact that the such compounds are more pronounced on the S_N1 type of reactions with respect to S_N2 reactions so that the ehters seem to capable to bind the carbonium intermediates even in water-dioxane mixtures.

INTRODUCTION

In our previous studies we have deeply investigated the role of some macrocyclic ethers in water-dioxane mixtures The systems how-ever are discussed previously was choosen to investigate the contribution of the macrocyclic ether in water-dioxane-crownether tertiary system (1). The systems of reported studies of similar effects rather consider on methanol, DMSO (2) disregarding the role of hydrogen bonding in water. We partly isolate the water molecules keeping the dielectricity of the system at a certain level which infliuence the role of macrocyclic ether, and makes it more apparent.

As it is figured out the breakage of hydrogen bonds simply reduce the role of water in creasing efficency of dipolar power which is main effect of Crown ether as it acts as a ligand or complexing agent consisting both hydrophobic and hydrophilic sites on the some molecule. However it is an interesting and still open to discussion result that we observed is the role of macrocyclic ethers in water-dioxane system in which the S_N2 reaction is not so infliuenced as the S_N1 type of reactions.

RESULTS

The present study was basicly concerned on the substutition reaction of alkaline salts of nitrophenols with h-buthyl halides.

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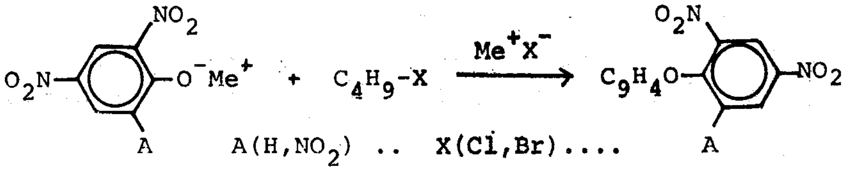
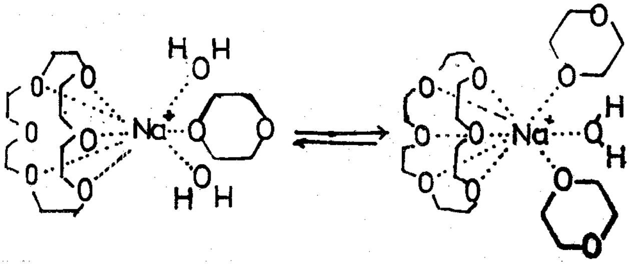


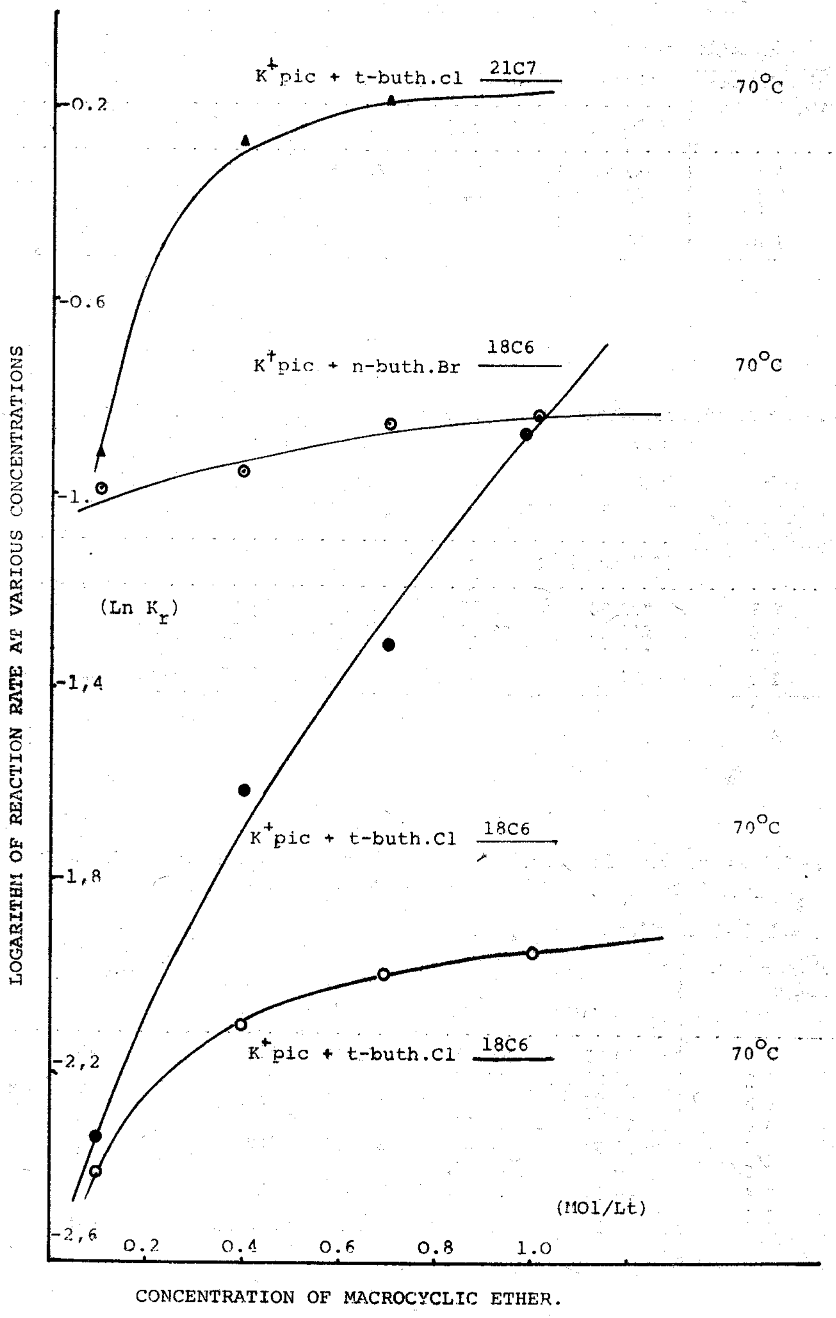
The increases of concentration of macrocyclic ether in some cases give rise to lower the rate of reaction in the water-dioxane-Crown ether system which is quite contrary to the fact that, nonpolar and anhydrous solutions remarkably increase the effect of macrocyclic ethers. We here ascribe such a result to the role of hydration of water molecules to the ions which are rather accelareted by the crown ether and lower the rate as dioxane simply changes the dipolar role. So that displacement is mostly determined by the more hydrated alkaline ions which relase the OH^- ion to react (3-7).



As they were performed on Fig-1. Bromides react more readily then chlorides which is usual for S_N2 pathway. However the role of size of macrocyclic ether is still proving the hexaoxa ring in such a system. This might be most probabely due to the lower number of oxygen in solvation shell in the case that of larger ether ring. Most important case is that of the fact that tert-halides react much more readily then that of the n-halides depending on the S_N1 pathway which seems more practical regarding the role of ether in similar aquous systems.

We therefore conclude that the in aquous media carbonium centers are more attracted and therefore easily solvated.

Experimental conditions and chemicals were used almost the similar to that of reported in our previous studies.


K⁺pic + t-buth.cl 21C7
70°C
K⁺pic + n-buth.Br 18C6
70°C
K⁺pic + t-buth.Cl 18C6
70°C
K⁺pic + t-buth.Cl 18C6
70°C
-0.2
-0.6
-1.
-1,4
-1,8
-2,2
-2,6
0.2
0.4
0.6
0.8
1.0
(Ln K_r)
(MOl/Lt)
LOGARITHM OF REACTION RATE AT VARIOUS CONCENTRATIONS
CONCENTRATION OF MACROCYCLIC ETHER.

Tablel. Second order rate constants of reactions K+ picrate with n-butyl cloride in water-dioxane (30:70, v/v) at various temparatures in the presence of different polyethers.

$k=k_2 . 10^2 .lt.mol^{-1}.hr^{-1}$ $C_{picrate}=1,8.10^{-4}{}_M$ $C_{Cl}=19,15.10^{-2}{}_M$

Poly. et. Conc. mol/lt	70°C	70°C	70 °C	55 °C	40 °C
	18-Crown-6	21-Crown-7	Hexaglyme		
0.1	47.00	88.77	45.59	6.63	– –
0.4	64.23	86.68	44.39	9.82	– –
0.7	71.54	43.34	35.67	11.75	0.54
1.0	73.11	30.81	35.25	13.47	0.92

Table– 2. Rate constants of reactions K+ picrate with n-butyl bromide in water-dioxane (30: 70, v/v) at various temperature in the presence of different polyethers.

$k = k_2.10^2 lt.mol^{-1}.hr^{-1}$ $C_{picrate}=1,8.10^{-4}{}_M$ $C_{Br}=18,62.10^{-2}{}_M$

Poly. et. Conc. mol/lt	70 °C	70 °C	55 °C	55 °C	40 °C
	18-Crown-6	21-Crown-7	Hexaglyme		
0.1	202.74	165.15	145.54	30.08	– –
0.4	205.42	92.05	163.27	32.76	– –
0.7	231.85	– –	192.27	39.64	2.19
1.0	234.69	– –	233.08	45.65	3.04

Table – 3. Rate constants of reaction K+ – 2, 4-dinitrophnolate with n-butyl cloride in water-dioxane (30:70, v/v) at various temperatures in the presence of various polyethers.

$k = k_1.10^1 lt.mol^{-1} hr^{-1}$. Cphenolate$=5,9.10^{-2}{}_M$, $C_{Cl}=0.62_M$

Poly. et. Conc. mol/lt	50 °C		0.1 m 18-Crown-6	non cataıyst	Temp. °C
	12-Crown-4	18-Crown-6			
0.1	110.77	105.69	50.00	18.15	40
0.2	87.92	94.62			
0.3	80.77	– –	105.69	138.46	50
0.4	75.00	78.46			
0.6	55.38	– –	526.15	302.31	60
0.7	– –	489.62			
0.8	44.31	– –	– –	927.62	70
1.0	42.92	– –			

Table – 4. Thermodynamic data for the second order reaction of K^+ picrate with n-butyl -genes 2,4-dinitrophenolate with n-butyl cloride in water-dioxane (30:70, v/v).

Poly. et. Conc.	0.1 m		0.7 m		1.0 m	
Polyethers	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
Glyme-6 (a)	– –	– –	30419	28.5	26451	16.8
Glyme-6 (b)	– –	– –	32389	37.4	31380	34.7
18-Crown-6 (c)	24506	17.8	– –	– –	– –	– –
Noncatalyst (d)	27282	25.4				

(a) K^+ picrate + n-butyl cloride
(b) K^+ picrate + n-butyl bromide
(c,d) K^+ 2,4-dinitrophenolate + n-butyl cloride
ΔH and Δ S are given in cal/mol

ÖZET

n-butil ve t-butil halojebnürlerin polynitro fenolatler ile verdikleri reaksiyonların hız sabitleri üzerine bazı makro halkalı eterlerin etkileri incelenmiş ve heptaoxa halkalı eterin maksimum etkiyi gösterdigi saptanmıştır. Bu sonuç yeni olması bakımından ve mekanizma yönünden de su-Dioksan ortamında etkileşmelerde reaksiyonlarına S_N2 karşılık, S_N1 türünün katalitik etkiye daha çok yer vermesi bakımından önemli bulunmuştur.

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