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Effect of 1, 4, 7, 10-Tetraoxacyclododecane on the Reaction Rate

Part. I,

by

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Effect of 1, 4, 7, 10-Tetraoxocyclododecane on the Reaction Rate*

Part. I.

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ABSTRACT

Effect of 12-Crown-4 on the reaction rate of potassium picrate with *t*-butyl chloride in water-dioxan was studied. Result obtained exhibited that crown ether with that cavity as effective as the larger oligomers.

INTRODUCTION

The crown ethers have been shown to have a tremendous ability to complex metal salts, especially those of alkaline and alkaline earth metals, and aid by solvation of the cation the dissolution of these salts in non-polar aprotic solvents. The reactive behavior of these salts in solution have shown unusual properties (1,2). The work of Sam adn Simmons have showed that potassium halides and potassium hydroxide in benzene possesses strong nucleophilic and basic properties (3). The observations of Liotta on the reactivity of KF and KCH_2COO in non-polar aprotic solvents using 18-Crown-6 as the catalyst has shown that anions become reactive in solution when their cations are complexed with crown ethers (4).

The stability of these complexes depends on the size of the cation relative to that hole of macrocyclic polyether; the charge of the ion, the number of ring oxygen atoms, their basicity, coplanarity, and symmetrical placement, steric hinderance in the polyether ring, and the extent of ion association with the solvent (5)

RESULTS

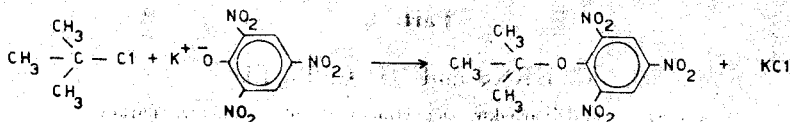
However we recently observed that in some cases the behavior of crown ethers might be differet than what has so far been re-

* Submitted in I. Thermodynamics meeting, Bursa, 1978, Turkey

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ported. 12-crown-4 could complexed with some of the heavy metals disregarding the cavity and the ionic radius (6). We now report the similar results in connecte dwith the effect of the smaller rings on the reaction rate.



In our study we investigated the role of 12-crown-4 in water-dioxan solutions for a nucleophilic substitution reaction and found out that it was almost as effective, as larger rings despite the fact that DMSO and DMF did not play any role under similar conditions.

As a kinetic system we tried the ether formation from potassium picrate under pseudo first order conditions.

Without the crown ether, the formation of t-butylpicryl ether was not observed even after heating for a long time in DMSO. However kinetic results are displayed in Table-1, exhibiting the effect of crown ethers.

Complexing of cations with smaller cavity are very rare although the fact that in our earlier study we found that the 12-Crown-4 could form stable complexes with actinides by inverting the conformation (6).

Regarding Table-1 in lower amount of crown ether shows lower effect because of the hydrogen bonding of water-crown ether molecules which increase the viscosity of respective liquid.

Table 1 Pseudo first order rates of potassium picrate reaction with t-butylchloride in % 20 dioxane-water mixtures at 70° C in the presence of 1,4,7,10-tetraoxocyclododecane.

Conc. of K ⁺ dicrate x 10 ⁻¹ M	Conc. of t-but. Cl. x 10 ⁻¹ M	Conc. of 12C4 M	Rate Cons. x 10 ⁻¹ min ⁻¹
7,5	3,6	0,1	5,10
7,5	3,6	0,4	6,90
7,5	3,6	0,7	8,50
7,5	3,6	1,0	9,40

Table 2 Pseudo first order rates of potassium picrate reaction with t-butylchloride in % 20 dioxan-water mixtures at 40° C in the presence of 1,4,7,10-tetraoxocyclododecane.

Conc. of K ⁺ picrate x 10 ⁻¹ M	Conc. of t-but. Chl. x 10 ⁻¹ M	Conc. of 12C4 M	Rate Cons. x 10 ⁻¹ min. ⁻¹
7,5	4,6	0,1	0,90
7,5	4,6	0,4	1,10
7,5	4,6	0,7	1,30
7,5	4,6	1,0	2,80

Table 3 Pseudo first order rates of potassium picrate reaction with t-butylchloride in % 20 dioxan-water mixtures at 70° C in the presence of tetramethyl-1,4,7,10-tetraoxocyclododecane.

Conc. of K ⁺ picrate x 10 ⁻¹ M	Conc. of t-but. Chl. x 10 ⁻¹ M	Conc. of Cr. Et M	Rate Cons. x 10 ⁻¹ min. ⁻¹
7,5	3,6	0,1	0,40
7,5	3,6	0,4	1,50
7,5	3,6	0,7	4,45
7,5	3,6	1,0	7,75

Table 4 pseudo first order rate of potassium picrate reaction with t-butylchloride in % 20 dioxan-water mixtures at 40° C in the presence of tetramethyl-1,4,7,10-tetraoxocyclododecane.

Conc. of K ⁺ picrate x 10 ⁻¹ M	Conc. of t-but. Chl. x 10 ⁻¹ M	Conc. of Cr. Et M	Rate Cons. x 10 ⁻¹ min. ⁻¹
7,5	4,5	-	0,04
7,5	4,5	0,1	0,95
7,5	4,5	0,4	0,06
7,5	4,5	0,7	0,09
7,5	4,5	1,0	0,16

However dissolved ions break the structure and disorganize locally the solvent and decrease its local viscosity (7). By increasing the concentration of 12-Crown-4 (8) the rate of reaction was observed to be increased with a higher slope (Figure-1) proving

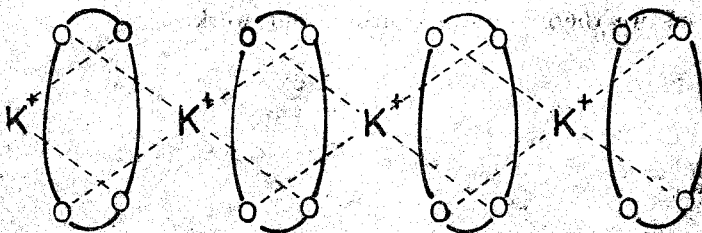


Figure. 1 Sandwiches from 12-crown-4 with K⁺ ion

the above conclusions. Steric role is clearly seen in the presence of tetramethyl-12-Crown-4 (8) of lower effect with respect to 12-Crown-4. In the other hand, under the conditions given on the tables rate of reaction for 18-Crown-6 was found to be $1,0 \cdot 10^{-4} \text{ min}^{-1}$ which indicates the minimum role of the cavity size of the ring in the aqueous dioxane solutions.

DISCUSSIONS

The results of this study suggest that the rate of reaction modified by addition of catalytic amounts of crown ethers to the medium. In the presence of crown ether, the species that reacts might be the crown ethers-separated ion pair in which the coordinating sites of potassium are occupied neither by the hydroxide ion nor solvent molecules. This species resembles in properties the more ordinary solvent separated ion pairs.

However, the behavior of electrolytes in mixed solutions is even complex. The composition of mixtures in the vicinity of ions, or ion pairs may deviate from its average position, therefore, the local dielectric constant may differ from that of the bulk of the mixtures (9).

The role of 12-Crown-4 could be best explained by formation of gaint sandwiches (Figure-2) which does not allow the cation to interact with its accompanied anion more like solvent separated ion pairs. In that respect the role is the similar with compare of larger rings which tightly bonds the cation in the center of cavity forming "Crown Complexed" ions (10).

It is now understood that for the ions in solutions smaller size of crown compounds of lower cost may be applied in ionic reactions we therefore still continue our work.

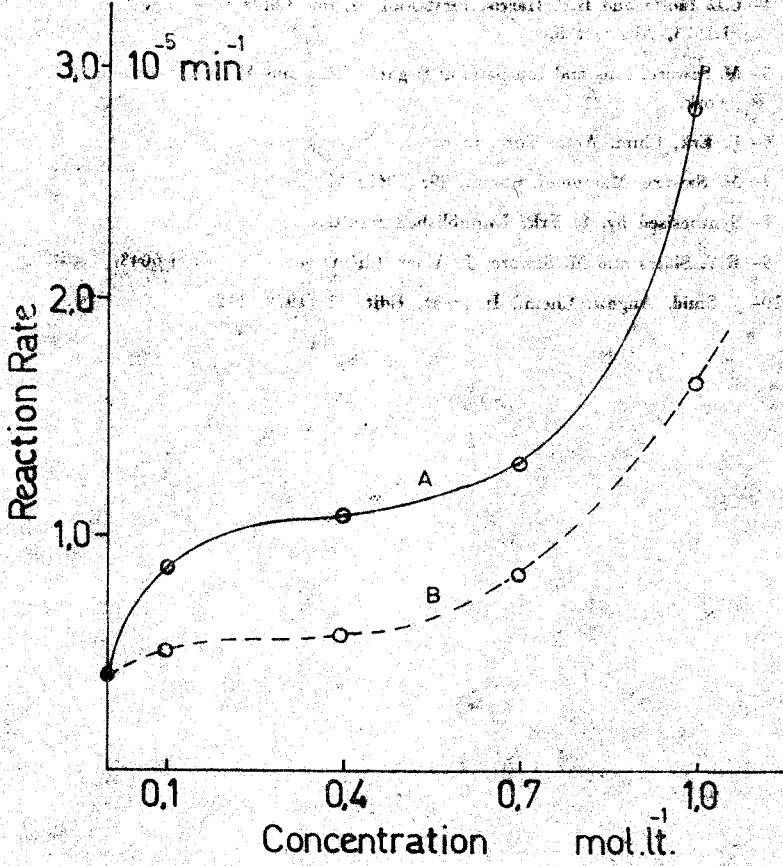


Figure. 2 Dependence of Crown ether concentration on the reaction rate of potassium picrate with *t*-butyl chloride at 40°C a) 12-Crown-4 B) tetramethyl-12-Crown-4.

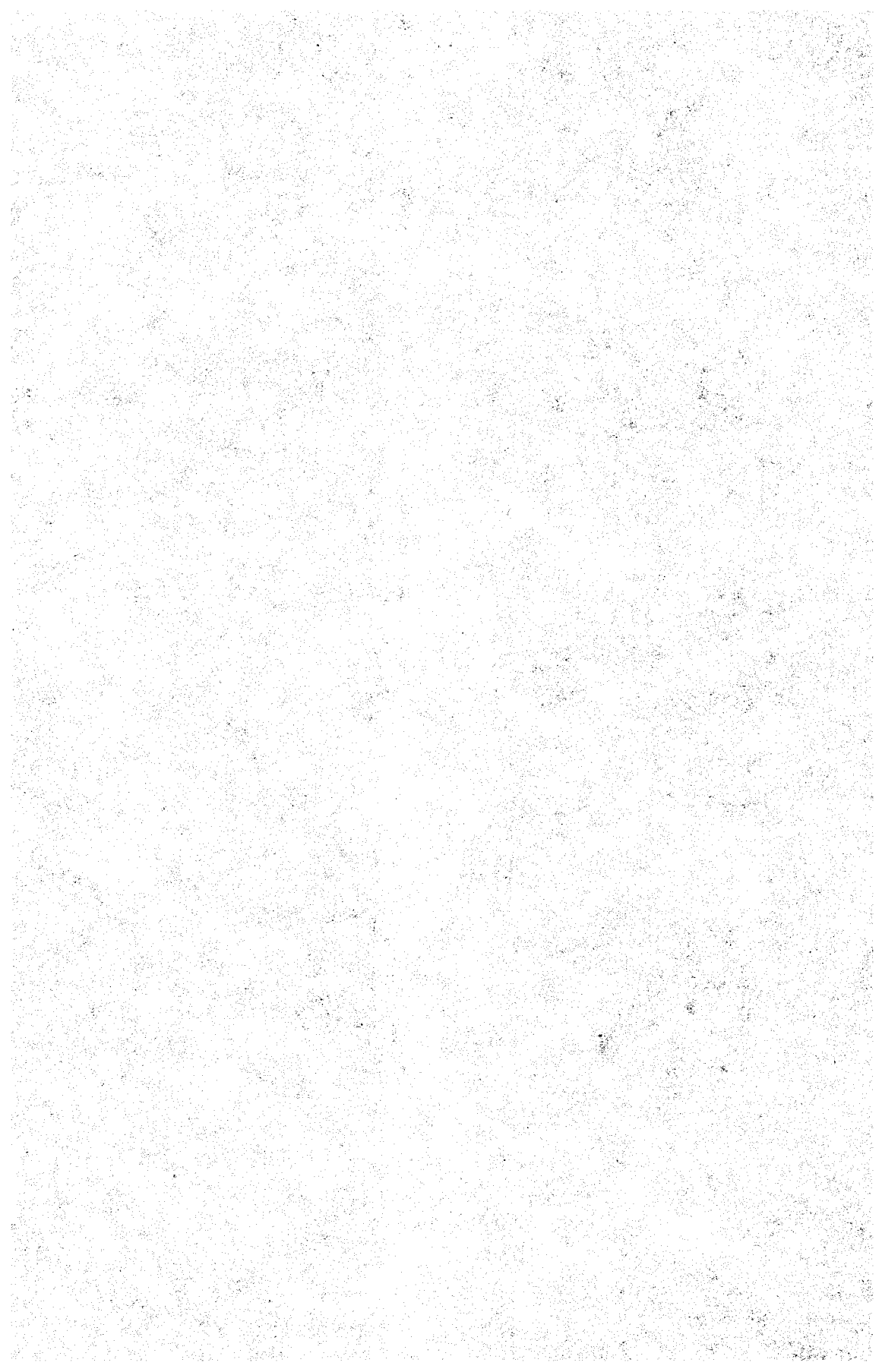
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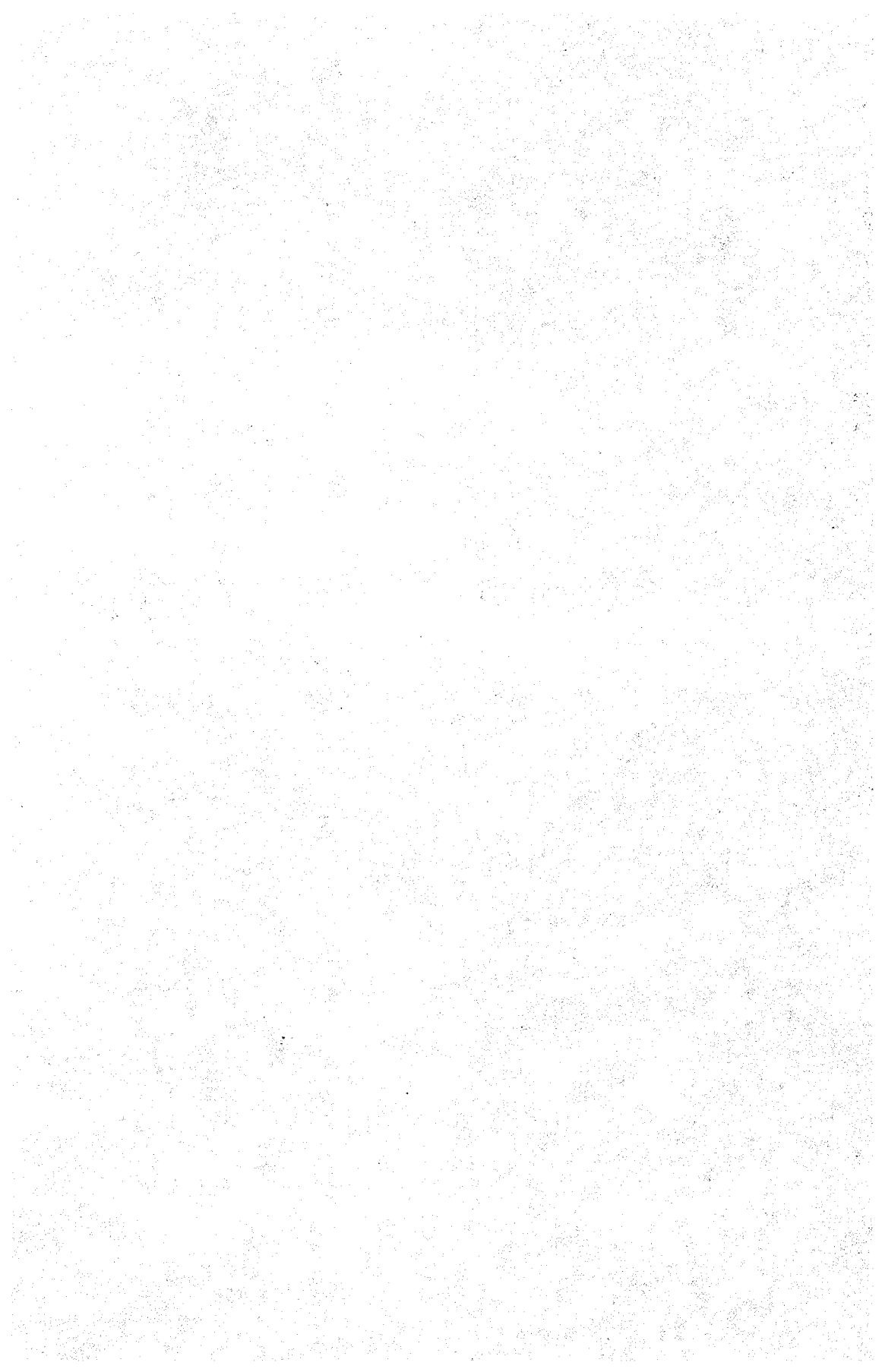
Dört oksijenli bir makro halkalı eter olan 12-Crown-4'ün su-dioksan karışımında potasyum pikrat'ın alkil halojenler ile verdiği yer değiştirme reaksiyonunun hızına olan etkisi incelenmiştir. Bu eter yapısına karşılık su-dioksanlı ortamlarda büyük halkalı eterler kadar etkili bir şekilde kationları bağlamaktadır.

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