The Macrocyclic and Cryptate Effect.
6. Complexation of Protons by Noncyclic Polyethers and Crown Ethers in Acetonitrile

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Abstract

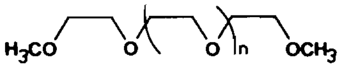
The complex formation of H^+ with glymes and crown ethers has been studied in acetonitrile by means of calorimetric titrations With the exception of 18C6 and DC18C6 the observed thermodynamic data for the reaction of monocyclic and bicyclic ligands are comparable. The observed macrocyclic effect is caused only by favourable entropic contributions.

Introduction

The complexation properties of crown ethers towards different metal ions in solution have been studied by many authors. These results were recently compiled by Izatt and co-workers [1]. In contrast, less attention was paid to the complexation reaction of H^+ with crown ethers.

The low solubility of the H_3O^+-complex of the *syn* isomer of DC18C6 in an aqueous solution was used to separate it from the *anti* isomer [2]. It has taken ten years to a general procedure for the preparation of other solid hydronium ion crown ether complexes to be described [3].

The formation constant for the reaction of HBr with DC18C6 in chloroform [4] and for the reaction of organic acids with 15C5, B15C5, 18C6 and DC18C6 in 1,2-dichloroethane have also been estimated [5] by means of conductivity measurements. The same experimental method was used to study the complexation of H^+ and H_3O^+ with crown ethers in acetonitrile [6]. In a recent paper the possibility of the complex formation between crown ethers and H_3O^+ in aprotic solvents was discussed in detail [7]. However, any values of the reaction enthalpies are very rare [4]. Under these circumstances it is impossible to make a definite statement about the origin of the macrocyclic effect on these reactions. In order to change this we decided, as a continuation of our previous work in connection with the macrocyclic and cryptate effect [8], to study the reaction between H^+ and several noncyclic and monocyclic polyethers in acetonitrile solutions by means of calorimetric titrations.



n=1 : TG
n=2 : TeG
n=3 : PG
n=4 : HG

Fig. 1. Noncyclic ligands used in this work.

Experimental

Materials

The noncyclic ligands (see Fig. 1) 2,5,8,11-tetraoxadodecane (TG; Merck), 2,5,8,11,14-pentaoxapentadecane (TeG; Riedel-de Haën), 2,5,8,11,14,17-hexaoxaoctadecane (PG; Riedel-de Haën), and 2,5,8,11,14,17,20-heptaoxaheneicosan (HG; Riedel-de Haën) were commercial samples. If the purity of these ligands was not high enough they were distilled under reduced pressure prior to use.

All crown ethers (see Fig. 2) 12-crown-4 (12C4; Merck), 15-crown-5 (15C5; Merck), cyclohexano-15-crown-5 (C15C5; Merck), benzo-15-crown-5 B15K5; Merck), 18-crown-6 (18C6; Merck), dicyclohexano-18-crown-6 (DC18C6; Merck), dibenzo-18-crown-6 (DB18C6; Ega), dicyclohexano-24-crown-8 (DC24C8; PCR), and dibenzo-24-crown-8 (DB24C8; Ventron) were used without further purification.

Trifluoromethanesulfonic acid (Ega) was used as purchased. Under experimental conditions the dissociation of trifluoromethanesulfonic acid is complete [9]. The water content of the solvent acetonitrile (Merck) was less than 0.3%.

Procedure

All stability constants and reaction enthalpies were determined by titration calorimetry using a Tronac Model 450 calorimeter. The procedure of evaluation of the measured thermograms has already been described elsewhere [10].

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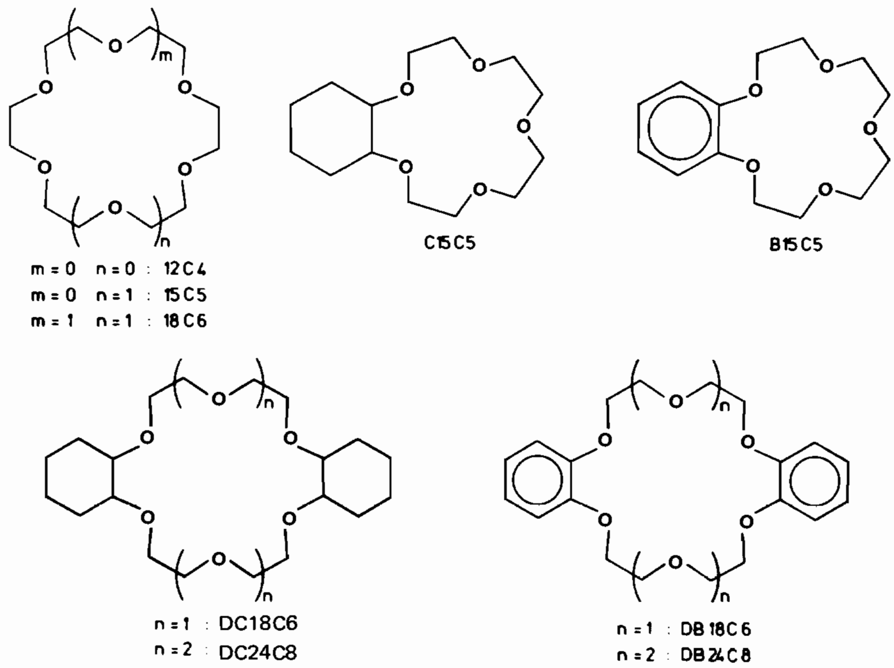

Fig. 2. Monocyclic ligands used in this work.

Three different possibilities for the complex formation between crown ethers and H^+ ions have to be taken into account:

(a) In the simplest case only 1:1-complexes (ratio of ligand to complexed ion) are formed. Under these circumstances a solution of the ligand (0.04–0.08 M) is titrated into a solution of trifluoromethanesulfonic acid (5×10^{-3} M). The heat Q produced during titration is related to the reaction enthalpy ΔH, after correction for all non-chemical heat effects by the following equation:

$$Q_t = \Delta H \times \Delta n_t \tag{1}$$

Δn_t is the number of moles of complex formed at the time t. The reaction observed in the reaction vessel of the calorimeter is shown in the eqn. (2).

$$L + H^+ \rightleftharpoons LH^+ \qquad K_1 = \frac{[LH^+]}{[L]\,[H^+]} \tag{2}$$

(b) If the cavity of a crown ether is too small to surround the complexed ion completely, the formation of 2:1-complexes (ratio of ligand to ion) becomes possible. The following reactions take place simultaneously,

$$L + H^+ \rightleftharpoons LH^+ + L \rightleftharpoons L_2H^+ \tag{3}$$

with the individual stability constants

$$K_1 = \frac{[LH^+]}{[L]\,[H^+]} \text{ and } K_2 = \frac{[L_2H^+]}{[LH^+]\,[L]}$$

The corrigated heat Q is related to both reactions as shown in eqn. (4):

$$Q_t = \Delta H_1 \times \Delta n_{1,t} + \Delta H_2 \times \Delta n_{2,t} \tag{4}$$

$\Delta n_{1,t}$ and $\Delta n_{2,t}$ are the number of moles of the 1:1- and 2:1-complexes formed at the time t.

To simplify the evaluations of these thermograms the experimental conditions have to be changed. The stability constants and reaction enthalpies for the formation of 1:1-complexes are measured if the concentration of the ligand in the reaction vessel is much lower in comparison with the concentration of H^+. Under this experimental condition Δn_2 shown in eqn. (4) is nearly zero. The measured thermogram can be treated in the usual way.

Titrating a solution containing H^+ (0.04–0.08 M) into a ligand solution (5×10^{-3} M), the concentration of the ligand is much higher when compared with the H^+ concentration in the reaction vessel. The formation of 1:1-complexes is nearly complete during titration and $\Delta n_{1,t}$ is constant. The observed curvature of the thermogram can only be caused by a variation of $\Delta n_{2,t}$. The calculation of K_2 is therefore possible. However, the calculated value of the reaction enthalpy is the sum of ΔH_1 and ΔH_2. This experimental method has already been tested successfully in the case of the reactions of crown ethers and alkali and alkaline-earth cations [11].

(c) If the cavity of a crown ether is very large it becomes possible that one ligand molecule is able to complex two H^+ cations (1:2-complex).

$$L + H^+ \rightleftharpoons LH^+ + H^+ \rightleftharpoons LH_2^{2+} \qquad (5)$$

$$K_1 = \frac{[LH^+]}{[L][H^+]} \qquad K_2' = \frac{[LH_2^{2+}]}{[LH^+][H^+]}$$

To observe the formation of 1:1-complexes the concentration of the ligand in the reaction vessel has to be much higher than the H^+ concentration. 1:2-complexes can be formed if the concentration of H^+ is higher in comparison with the ligand concentration.

Results and Discussion

The values of $\log K$, ΔH, and $T\Delta S$ for the reaction of H^+ with noncyclic ligands and crown ethers are summarized in Table I and Table II. The published complex stabilities for the reaction of crown ethers with H^+ [6] agree, with few exceptions, very well with our data. No experimental values are obtainable from existing literature for the reaction of glymes with H^+.

With increasing chain length of the noncyclic ligands the measured reaction enthalpies for the complexation of H^+ also increase. More donor atoms are participating in the complex formation. However, due to sterical requirements the values of the reaction entropies change in the opposite direction like the values of the reaction enthalpies. In short, the stability of the complexes formed are nearly constant. The same observations were made for the reactions of polyethylene glycols with alkali and alkaline-earth cations [12].

TABLE I. Stability Constants ($\log K$; K in M^{-1}) and Thermodynamic Parameters (ΔH, $T\Delta S$ in kJ mol^{-1}) for the Reaction of H^+ with Noncyclic Ligands in Acetonitrile at 25 °C.

	TG	TeG	PG	HG
$\log K$	2.50	2.50	2.51	2.60
$-\Delta H$	8.4	29.2	37.7	34.0
$T\Delta S$	5.6	−15.4	−23.4	−19.2

The monocylic crown ethers already possess a certain cavity. They are not as flexible as the noncyclic ligands. The dimensions of these cavities are expected to play an important role in the stability of protonated crown ethers.

It was found that there was a distance of 2.76 Å between oxygen atoms in an ice crystal Similar distances have only been estimated in the case of 18-crown-6 ethers with cavity diameters of approximately 2.8 Å. Therefore, one can expect that the smaller crown ethers are not able to surround the H^+ ion. The formation of 2:1-complexes becomes possible. Complexes of such composition can be observed in solution. The measured reaction enthalpies for both reaction steps are similar, or the values of ΔH_2 are smaller than the values of ΔH_1. However, the stability constants for the formation of 2:1-complexes of 15-crown-5 ethers are higher when compared with the values for the stability of the 1:1-complexes. This is only caused by favourable entropic contributions. All other crown ethers examined form only 1:1-complexes. Even with the largest ligands no other composition of the complexes could be found. The repulsion between two H^+ ions prevents the formation of 1:2-complexes with the ligands used in this work.

The thermodynamic data for 1:1-complexes of different monocyclic ligands with H^+ show some interesting aspects. As expected from their molecular dimensions 18C6 and DC18C6 form the most stable complexes. All other stability constants have similar values which are nearly identical with those observed in the case of noncyclic ligands. The same behaviour was observed in the reaction enthalpies and also the entropies.

The substitution of the crown ethers does influence the measured reaction enthalpies. One finds the following order in the 18-crown-6 ethers:

TABLE II. Stability Constants ($\log K$; K in M^{-1}) and Thermodynamic Parameters (ΔH, $T\Delta S$ in kJ mol^{-1}) for the Reaction of H^+ with Monocyclic Ligands in Acetonitrile at 25 °C.

	12C4	15C5	C15C5	B15C5	18C6	DC18C6	DB18C6	DC24C8	DB24C8
$\log K_1$	2.54 (2.2)[a]	2.54 (4.1)[a]	2.49	2.56	>5 (6.5)[a]	>5 (8.2)[a]	3.73 (3.7)[a]	3.46	4.03 (3.2)[a]
$-\Delta H_1$	21.0	24.8	30.9	22.5	29.0	42.8	19.8	50.1	27.3
$T\Delta S$	−6.6	−10.4	−16.7	−8.0	7.9	3.8	1.4	−30.4	−4.4
$\log K_2$	2.10 (2.10)[a]	3.57	3.87	3.26	–	–	–	–	–
$-\Delta H_2$	22.0	18.9	15.3	14.5					
$T\Delta S_2$	−10.1	1.4	6.7	4.0					

[a] From ref. 6.

DC18C6 > 18C6 > DB18C6

Identical sequences are also obtained in the case of the mono-substituted 15-crown-5 ethers and the remaining crown ethers. The values of the reaction enthalpies give some evidence of an electron withdrawal effect of the two benzo groups as was used to explain the difference in the stability constants of 18C6 and DB18C6 [6].

The measured reaction enthalpies for the complexation of mono- and bivalent cations by different ligands give no definite proof of the electron withdrawal effect of benzo groups. For the reactions of Na^+ with 15C5, C15C5, and B15C5, almost identical reaction enthalpies are observed [11, 13]. The measured reaction enthalpies decrease if K^+ ions are complexed by 15-crown-5 ethers

15C5 > B15C5 > C15C5

and by 18-crown-6 ethers

18C6 > DC18C6 > DB18C6.

It is possible to give more examples showing sequences which are quite different.

However, another effect may overcompensate this prediction. The benzo and cyclohexano groups already cause a similar ordered conformation of the uncomplexed ligands [14]. During the complex formation these ligands have to undergo fewer structural changes than the unsubstituted ligands. As a result the measured values of the reaction enthalpies for the substituted crown ethers are higher when compared with those of the unsubstituted ligands. Structural influences of the ligand on the reaction enthalpy for the reaction of 12C4 with H^+ have been revealed in a theoretical study [15]. The bond energy between a proton and the crown ether reaches a maximum value if the ligand possesses a planar conformation. This can explain the experimental results for the reactions of the different 15-crown-5 ethers.

The measured reaction enthalpies do support the given explanation. The observed values of the reaction entropies decrease in the following order:

DB-crown ether > crown ether > DC-crown ether.

The complex formation is favoured by the reaction entropy if the uncomplexed ligand already possesses a rigid geometry, as in the case of the dibenzo crown ethers.

The structural changes of the unsubstituted and cyclohexano crown ethers during the complex formation are reflected in the values of the found reaction entropies. Unfortunately, the measured reaction entropies do not support the given explanation. In contrast to the reaction enthalpies, no general order can be deduced from the data. For the ligands 18C6 and DC18C6 the complex formation is favoured by the reaction entropy. Negative values were found in the reaction entropies of all other ligands examined, which were within the same range as the values of the noncyclic ligands.

A more detailed discussion does not seem to be possible yet. However, from the experimental data an important result can be obtained. The macrocyclic effect observed in the case of the proton complexes with 18C6 and DC18C6 is only achieved with favourable entropic contributions.

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