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HEATS OF PROTONATION OF AMINES, DIAZACROWN ETHERS AND CRYPTANDS IN METHANOL

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Abstract

The heats of protonation of different amines, diazacrown ethers and cryptands in methanol have been measured using calorimetric titrations. The values of the reaction enthalpies decrease in going from primary over secondary to tertiary amines. The results for the protonation of diazacrown ethers and cryptands are not comparable with those obtained for the alkyl amines. Additional interactions between the proton and the oxygen donor atoms influence the values of the reaction enthalpy for the first protonation. The results for the second protonation reaction indicate that this proton is located outside the cavities of the macrocyclic and macrobicyclic ligands.

Keywords: amines, azacrown ethers, cryptands, heat of protonation

Introduction

The protonation of amino groups containing organic molecules has been studied over a long period and an enormous number of results have been reported in the literature [1]. Since the first quantitative measurements of the complex formation between amine and cations by a pH-metric method [2] this method has been used up until now to determine the stability constants of complexes with ethylene diamine tetraacetic acids (EDTA) and other amino groups containing ligands in aqueous solution [3–5]. pH-metric titrations can further be used to study the complex formation between cations and polyamines [6].

The selective complexation of alkali and alkaline earth cations in aqueous solution by macrobicyclic ligands (cryptands) was first measured using the protonation reaction of these ligands [7, 8]. In the meantime several authors published the protonation constants of diazacrown ethers and cryptands in aqueous solution [9–11]. Recently the protonation reactions of amines, diazacrown ethers and cryptands in aqueous solution have been studied again in detail [12, 13].

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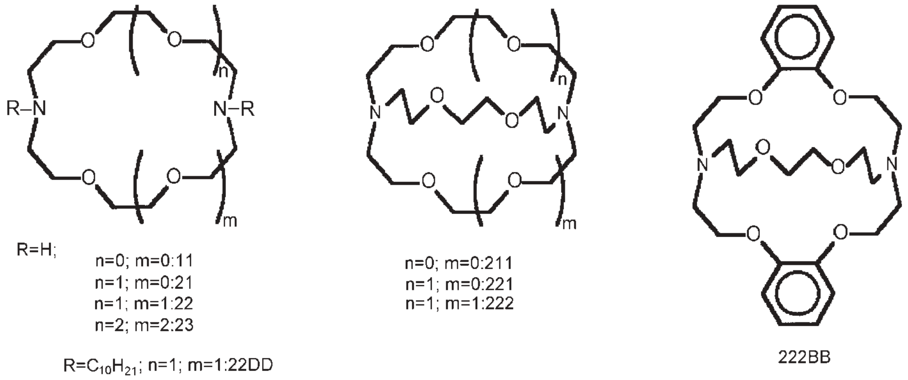

Fig. 1 Possible conformations of diprotonated cryptands

Surprisingly only very few results about the protonation reactions of diazacrown ethers and cryptands in non-aqueous solution have been reported. To our knowledge only two articles have been published on this topic [14, 15]. In both articles the protonation reactions of diazacrown ethers and cryptands in methanol have been examined. No thermodynamic data for comparison are available. Thus we have studied the protonation reaction of different amines and diamines in methanol.

Experimental

All aliphatic amines used (Table 1) were commercial samples and used as purchased. 1,4-Diazabicyclo[2.2.2]octane (DABCO, Fluka), 1,8-diamino-3,6-dioxaoctane (DAOO, Merck) and the diazacrown ethers and cryptands (Fig. 1, all Merck, purity >99%) were used without further purification. The purity of the amines has been measured in course of pK_a determinations in aqueous solution [12, 13].

All solutions were prepared using anhydrous methanol (H_2O content less than 0.005%, Merck).

Table 1 Stability constants $\log K_1$ and $\log K_2$ (K in L mol^{-1}) for the protonation of diazacrown ethers and cryptands in methanol at 25°C [14] together with the calculated concentrations of the monoprotonated (LH^+) and diprotonated ligand (LH_2^{2+}) (in mol L^{-1}) at a given acid ($c_H=1.0\cdot10^{-5}$ mol L^{-1}) and ligand concentration ($c_L=7.0\cdot10^{-3}$ mol L^{-1})

Ligand	$\log K_1$	$\log K_2$	LH^+	LH_2^{2+}
21	10.31	9.11	$9.99\cdot10^{-6}$	$9.02\cdot10^{-10}$
22	10.64	9.14	$9.99\cdot10^{-6}$	$4.52\cdot10^{-10}$
211	12.65	8.46	$1\cdot10^{-5}$	$>4\cdot10^{-12}$
221	11.50	9.48	$9.99\cdot10^{-6}$	$1.37\cdot10^{-10}$
222	10.72	9.03	$1\cdot10^{-5}$	$>4\cdot10^{-12}$

The calorimetric titrations were performed using a Tronac calorimeter (Model 450). In order to measure only the monoprotonation in the case of diaza compounds a solution of trifluoromethane sulfonic acid (0.02–0.03 mol L^{-1}) is titrated into the amine solution (5–9·10^{-3} mol L^{-1}). After a titration time of 1 min (burett rate=0.333 mL min^{-1}) the total concentration of the acid in the reaction vessel is lower than c_{H}=1·10^{-5} mol L^{-1}. Under these experimental conditions one only expects the formation of 1:1-complexes.

The following reactions between the ligand L and protons take place in solution:

$$\mathrm{L}+\mathrm{H}^{+}\leftrightarrow\mathrm{LH}^{+} \tag{1}$$

and

$$\mathrm{LH}^{+}+\mathrm{H}^{+}\leftrightarrow\mathrm{LH}_2^{2+} \tag{2}$$

The protonation constants K_1 and K_2 are given by:

$$K_1=\frac{[\mathrm{LH}^{+}]}{[\mathrm{L}][\mathrm{H}^{+}]} \tag{3}$$

$$K_2=\frac{[\mathrm{LH}_2^{2+}]}{[\mathrm{LH}^{+}][\mathrm{H}^{+}]} \tag{4}$$

Using the mass balances for the total ligand c_{L} and total proton concentration c_{H}

$$c_{\mathrm{L}}=[\mathrm{L}]+[\mathrm{LH}^{+}]+[\mathrm{LH}_2^{2+}] \tag{5}$$

$$c_{\mathrm{H}}=[\mathrm{H}^{+}]+[\mathrm{LH}^{+}]+2[\mathrm{LH}_2^{2+}] \tag{6}$$

and the equations for the protonation constants it becomes possible to calculate the concentration of each species present in solution:

$$c_{\mathrm{H}}=[\mathrm{H}^{+}]+\frac{K_1[\mathrm{H}^{+}]+2K_1K_2[\mathrm{H}^{+}]^2}{1+K_1[\mathrm{H}^{+}]+K_1K_2[\mathrm{H}^{+}]^2} \tag{7}$$

$$[\mathrm{LH}^{+}]=c_L\frac{K_1[\mathrm{H}^{+}]}{1+K_1[\mathrm{H}^{+}]+K_1K_2[\mathrm{H}^{+}]^2} \tag{8}$$

$$[\mathrm{LH}_2^{2+}]=c_L\frac{K_1K_2[\mathrm{H}^{+}]^2}{1+K_1[\mathrm{H}^{+}]+K_1K_2[\mathrm{H}^{+}]^2} \tag{9}$$

With the known protonation constants, Table 1, and the experimentally used concentrations one calculates the concentration of the mono- and diprotonated ligands also given in Table 1. Even if the values of the protonation constants differ only by one order of magnitude the concentration of the diprotonated ligand is at least four orders of magnitude lower compared with the monoprotonated ligand. Thus, no corrections for the experimentally measured values of the reaction enthalpies are necessary.

Titrating a solution of the diaza compound (0.02–0.03 mol L^{-1}) into the acid solution (5–9·10^{-3} mol L^{-1}) results in its simultaneous diprotonation. From this sum of the reaction enthalpies for the mono- and diprotonation the value of the second protonation can be calculated using the separately measured value of the reaction enthalpy for the monoprotonation.

Results and discussion

The reaction enthalpies for the protonation of amines, diazacrown ethers and cryptands in methanol are given in Table 2. The highest values of the reaction enthalpies are observed for the primary amines (pentylamine, DAOO). These values decrease for secondary and even more for tertiary amines. From the results obtained for the protonation of dipentylamine, piperidine and pyrrolidine one clearly sees that the reaction enthalpy is not influenced by the structure of these secondary amines. This behaviour changes in the presence of a further amino group. The values of the reaction enthalpies for the first protonation of piperazine and DABCO are significantly smaller than that of the other secondary amines. The second amino group obviously influences the protonation of the first group. Due to electrostatic repulsion the value of the reaction enthalpy for the second protonation reaction is smaller than for the first one.

Surprisingly the results for the protonation of diazacrown ethers and cryptands are not comparable with the data of the other amines. The reaction enthalpies for the first protonation step are nearly identical for all macrocyclic and macrobicyclic diamines. The monoprotonation of (22) and (22DD) gives identical results although these ligands contain secondary and tertiary amino groups. The same is true for diazacrown ethers and cryptands. The later possesses even tertiary amino groups.

The reaction enthalpies for the second protonation of diazacrown ethers and cryptands are higher or equal than for the first protonation. In the case of the second protonation of these ligands comparable results with secondary amines are observed.

Protonated and diprotonated diazacrown ethers and cryptands may exist in three different conformations in solution, Fig. 2. If the first proton is located inside the cavity of the ligand, the value of the reaction enthalpies should be lower than in the case of the protonation of secondary amines due to conformational changes of the ligand. However additional interactions between this proton and the second amino group and oxygen donor atoms of the ligand are possible. Due to the fact that the reaction enthalpies for the second amino groups and secondary amines are of the same order of magnitude the lone pair of electrons of the amino groups in diazacrown ethers and cryptands should be located outside the cavity of these ligands. The measured reaction enthalpies indicate the formation of diprotonated ligands in the exo-endo configuration in methanol.

In Table 3 some values of the reaction entropies for the protonation of diazacrown ethers and cryptands are summarized. All values of the reaction enthalpy for the monoprotonation are positive and for the diprotonation negative. Obviously during the formation of monoprotonated ligands solvent molecules are liberated. During the diprotonation reactions no compensation effects between the entropic contributions from the increase in sterical requirement and the number of solvent molecules released take place. As a result negative values of the reaction enthalpy are observed.

Table 2 Heats for the first and second protonation (ΔH_1, ΔH_2 in kJ mol^{-1}) of amines, diazacrown ethers and cryptands in methanol at 25°C

Ligand	$-\Delta H_1$/kJ mol^{-1}	$-\Delta H_2$/kJ mol^{-1}
Pentylamine	64.5	
Dipentylamine	60.6	
Tributylamine	54.9	
Piperidine	59.0	
Pyrrolidine	59.4	
Piperazine	54.8	53.3
DABCO	40.3	34.5
DAOO	63.5	70.7
(11)	52.5	69.7
(21)	49.2	56.0
(22)	53.0	61.6
(22DD)	52.9	63.2
(23)	57.0	
(111)	44.5	
(211)	54.2 42.2[a]	66.2 58.1[a]
(221)	56.5 55.6[a]	59.6 58.9[a]
(222)	56.5 51.8[a]	55.5 53.9[a]
(222BB)	50.4	59.4

[a] [15]

For the cryptand (222) thermodynamic data for the transfer of the ligand, the mono- and diprotonated ligand from water to methanol are known [16]. The values of the enthalpy of transfer of the cryptand 222 and of the monoprotaned cryptand 222 from water to methanol are both positive and nearly identical. This indicates the loss of hydrogen bonds during the transfer. The interpretation is also supported by the val-

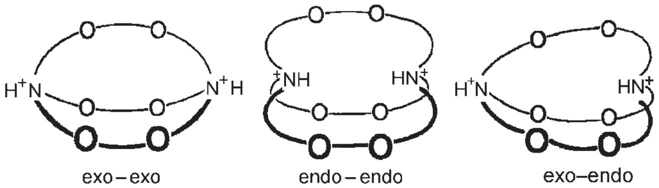

Fig. 2 Chemical structures of the diazacrown ethers and cryptands used in this work

ues of the entropies of transfer. In case of the diprotonated cryptand 222 negative values of the entalpy and entropy of transfer from water to methanol are observed. Thus, the conformations of the diprotonated cryptand (222) in aqueous and methanol solution are different.

Table 3 Stability constants (K in L mol^{-1}) and reaction enthalpies and entropies (in kJ mol^{-1}) for the first and second protonation of diazacrown ethers and cryptands in methanol at 25°C

Ligand	$\log K_1$	$-\Delta H_1$	$T\Delta S_1$	$\log K_2$	$-\Delta H_2$	$T\Delta S_2$
21	10.31[a]	49.2	9.4	9.11[a]	56.0	–4.2
22	10.64[a]	53.0	7.5	9.14[a]	61.6	–9.7
211	12.65[a]	54.2	17.7	8.46[a]	66.2	–18.1
221	11.50[a]	56.5	8.8	9.48[a]	59.6	–5.7
222	10.72[a]	56.5	4.4	9.03[a]	55.5	–4.2

[a] [14]

The crystal structures of the diprotonated cryptand (222) have been published recently with both protons located inside the cavity [17, 18]. This structure is in accordance with the results from molecular dynamic simulation of the diprotonated cryptand (222) [19]. However, in the meantime the exo-exo conformation of the diprotonated cryptand (222) has been reported, too [20].

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