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Note

Complex formation between the macrocyclic ligand 18-crown-6 and unprotonated amines in methanol

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Abstract

The complexation reactions between different amines and the macrocyclic ligand 18-crown-6 have been studied in methanol. Calorimetric titrations have been performed in order to obtain the stability constants and the reaction enthalpies and entropies for these reactions. The stability constants of all amines studied are within the same order of magnitude. However, alkyl and aryl substituents strongly influence the values of the reaction enthalpies and entropies. In contrast, for all secondary and tertiary amines examined nearly identical values for the reaction enthalpies and entropies are observed. As a result, the number of hydrogen bonds formed between the crown ether and these amines is not the most important factor.

INTRODUCTION

The main interest in complex chemistry during recent years has focused on the complexation of ions by crown ethers and cryptands [1, 2]. In addition, the complex formation of alkylammonium ions with macrocyclic ligands has been investigated [3–5]. Even the complexation of amino acids with crown ethers, cryptands and calixarenes has been reported [6–8].

From the crystallographic structures of complexes between ammonium ions and the crown ether 18C6, it is known that hydrogen bonds are formed between ammonium ions and the ligand [9, 10]. In contrast, complex formation between uncharged amines and macrocyclic ligands has been reported in only a few cases [11–13]. Most of these results discuss the crystal structures of such complexes [13]. No thermodynamic data for the reaction of uncharged amines with macrocyclic ligands have been reported

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in the literature so far. For a better understanding of these processes, the complexation of uncharged amines by crown ethers was measured using calorimetric titrations.

This experimental technique is very useful for the study of reactions between neutral ligands and amines because no charged species are involved in the complex formation. However, if some heat is produced during the complexation then the stability constant and the reaction enthalpy can be calculated from the experimental data [14, 15].

EXPERIMENTAL

All the amines examined were commercial samples. They were of the highest purity available. The crown ether 18-crown-6 (18C6, Merck) was used without further purification. All solutions were prepared using anhydrous methanol (Merck, max. 0.01% H_2O).

The adiabatic calorimetric titrations were performed using a Tronac calorimeter (Model 450). Solutions of the crown ether (0.06–0.08 mol l^{-1}) were titrated continuously into solutions containing the amines (5×10^{-3} mol l^{-1}).

The reaction between the amines (A) and the crown ether (C) is given by

$$A + C \rightleftharpoons AC$$

and the equilibrium constant K by

$$K = \frac{[AC]}{[A][C]}$$

The reaction enthalpy ΔH is calculated from the heat Q produced during the titration after the correction of all non-chemical heat effects

$$Q_t = \Delta H \, \Delta n_t$$

The number of moles of the complex formed at any time during the titration is given by Δn_t. Using a non-linear least-squares method, both unknown parameters, i.e. the stability constant and the reaction enthalpy, can be fitted to the experimental data [14, 15].

RESULTS AND DISCUSSION

The values of the stability constants, reaction enthalpies and reaction entropies for the complex formation between different amines and the crown ether 18C6 in methanol as solvent are summarized in Table 1.

The values of the stability constants for the crown ether complexes formed with different amines are nearly identical. However, large variations in the reaction enthalpies and entropies are observed. Comparing the results for *n*-butyl-, *sec*-butyl- and *tert*-butyl amines, the values of the reaction enthalpies decrease and the reaction entropies increase. This effect cannot be

TABLE 1

Stability constants log K, and thermodynamic parameters ΔH and $T\Delta S$ for the complexation of different amines by the crown ether 18-crown-6 in methanol at 25°C

Amines	$\log(K/\mathrm{M}^{-1})$	$-\Delta H/\mathrm{kJ\ mol}^{-1}$	$T\Delta S/\mathrm{kJ\ mol}^{-1}$
n-$C_4H_9NH_2$	2.60 ± 0.05	31.5 ± 0.3	-16.7 ± 0.6
sec-$C_4H_9NH_2$	2.40 ± 0.01	19.2 ± 0.2	-5.6 ± 0.3
$tert$-$C_4H_9NH_2$	2.46 ± 0.05	12.7 ± 1.3	1.3 ± 1.0
$(n\text{-}C_4H_9)_2NH$	2.51 ± 0.06	2.0 ± 0.3	12.3 ± 0.6
$(n\text{-}C_4H_9)_3N$	2.58 ± 0.04	2.3 ± 0.4	12.4 ± 0.7
$C_6H_5NH_2$	2.52 ± 0.02	1.6 ± 0.7	12.7 ± 0.6
$C_6H_5CH_2NH_2$	2.46 ± 0.02	22.5 ± 0.3	-8.6 ± 0.3
$4\text{-}CH_3C_6H_5CH_2NH_2$	2.54 ± 0.01	23.8 ± 0.4	-9.4 ± 0.4
$C_6H_5CH_2NHCH_3$	2.47 ± 0.04	1.2 ± 0.3	12.8 ± 0.9
$C_6H_5CH_2N(CH_3)_2$	2.51 ± 0.01	2.1 ± 0.9	12.2 ± 0.9

explained by the number of hydrogen bonds formed between the amines and the crown ether because they should be constant for these amines. The different substituents, however, influence the electron density at the nitrogen atom. This interpretation can easily be confirmed from the data for the reaction of aniline with 18-crown-6. Due to the delocalization of the lone electron pair at the nitrogen atom, the interactions between this amine and the ligand 18-crown-6 are not strong and consequently the value of the reaction enthalpy is low.

Comparable observations are made in the case of secondary and tertiary amines. The chemical structures of the substituents at the nitrogen atom examined do not show any great influence on the measured reaction enthalpies. In this case, sterical reasons may be the most important factor that influences the strength of the interactions between the ligand and the amines.

Different factors may be responsible for the observed values of the reaction entropies. Thus, the differences in the solvation of the various amines contribute to the values of the reaction entropies. Sterical factors also play a dominant role in achieving optimal interactions between the amines and 18-crown-6. For all secondary and tertiary amines studied, the complex formation is favored by the reaction entropy, indicating the absence of special sterical requirements for the complex formation. The presence of the different amines in the solvent influences the structure of the solvent itself. Therefore positive entropic changes during the complex formation may be caused by a structure increase of the solvent due to the complexation of the amine.

More experimental evidence is necessary for a better understanding of all factors influencing the complex formation of amines with neutral ligands in solution.

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