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MOLECULAR COMPLEXES IN SOLUTION CONTAINING BENZENE-SUBSTITUTED CROWN ETHERS AND TROPYLIUM IONS

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The interaction of benzo-15-crown-5, benzo-18-crown-6, dibenzo-18-crown-6, dibenzo-24-crown-8, and dibenzo-30-crown-10 with tropylium tetrafluoroborate in 1,2-dichloroethane was studied by spectroscopic methods. The stoichiometries of the complexes in the gas phase were investigated by fast atom bombardment mass spectrometry. The crown ethers formed 1 : 1 molecular complexes with the acceptors, apparently by a charge-transfer mechanism. The stability constant K and the molar absorptivity of the complex ε_c were determined by the method of Rose and Drago. The magnitudes of the thermodynamic parameters of complexation were calculated. A discussion of the thermodynamic parameters is included.

INTRODUCTION

Macrocyclic polyethers, or crown ethers, have unique chemical properties associated with their ability to form complexes with metal cations and other species. Complexation has been demonstrated with ammonium (NH_4^+), diazonium (N_2^+), hydronium (H_3O^+), acylium ($C{=}O^+$), hydrazinium ($N_2H_5^+$), and many other species.[1] In all these cases, stabilization takes place with a dipolar interaction with cationic species which may also involve direct hydrogen bonding. Much less attention has been paid to carbonium ions, which are singly charged organic cations containing even numbers of electrons.

Vaskuri and Virtanen[2] have studied stable carbonium ions in solution. Cycloheptatrienylium (tropylium) ions are stable aromatic carbonium ions, whose chemistry has been extensively developed since Doering and Knox[3] prepared tropylium bromide salt over 40 years ago. Dauben and Honnen[4] were the first to discover that, under appropriate conditions, tropylium cation can form cycloheptatriene – metal sandwich compounds (where the metal is molybdenum, chromium or tungsten). In these compounds, the seven ring carbons are symmetrically bonded to metal by means of the six π-electrons. Feldman and Winstein[5] found that tropylium ion forms 1 : 1 charge-transfer complexes with a variety of aromatic hydrocarbons. Several groups have developed model chemical systems for the study of the intramolecular charge-transfer interaction, in which the positively charged tropylium ring is incorporated in a system such as cyclophanes.[6,7] The ring expansion of toluene and related aromatic compounds to form tropylium ions is a much studied reaction in mass spectrometry.[8]

The relative stability of an aromatic tropylium ion is due to the resonance resulting from the presence of six π-electrons in the conjugated unsaturated seven-membered ring.[9] The symmetrical nature of the tropylium ion has been established beyond doubt: it exists as a planar regular heptagon with D_{7h} symmetry. The cation is an effective π-acceptor with full positive charge, and since donor capacity is usually dependent on electron density, and acceptor capacity on electron deficiency, tropylium ions together with polyethers offer a model system for the study of the complexation of stable organic cations.

The complexation behaviour of crown ethers and metal cations in solution has most often been investigated by calorimetry, potentiometry and absorption spectroscopy. However, the stoichiometry of a complex must be known before the definition and evaluation of equilibrium constants. Fast atom bombardment mass spectrometry (FAB-MS) offers a unique and rapid method for examining the complexation in the gas phase between crown ethers and alkaline metal cations[10–12] or aromatic diazonium ions[13] and, as recently shown, between polyethers and tropylium ions.[14] The advantage of this technique for the exploration of complexation is that the complexes tend to retain their integrity in the gas phase and can thus be observed directly. Maleknia and Brodbelt[15] have found that the trends observed in the gas phase between crown ethers and alkali metal ions closely parallel those seen in non-polar solvent environments.

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Recently, we reported[14] the weak complexation of polyethers with tropylium ions in the gas phase, in the absence of the complicating effect of solvation. We have also studied widely by kinetic and spectroscopic methods the host–guest complexation of cyclic and acyclic polyethers with aryldiazonium ions, an important class of stable organic cations.[16] Continuing our studies on the interaction between polyethers and stable organic cations in solution, we report here the complexation of benzene-substituted crown ethers with tropylium tetrafluoroborate in 1,2-dichloroethane (DCE). The benzene-substituted crown ethers are an obvious choice, not only because of the wealth of information on them and related molecules, but also because they contain aromatic moieties. These ethers provide both n- and π-donor sites for interaction with π-acceptors.

EXPERIMENTAL

Materials. The benzene-substituted crown ethers (Figure 1) benzo-15-crown-5 (**1**) (Fluka), benzo-18-crown-6 (**2**) (Fluka), dibenzo-18-crown-6 (*3*) (Fluka), and dibenzo-30-crown-10 (**5**) (Aldrich-Chemie) were used without further purification. Dibenzo-24-crown-8 (**4**) (Fluka) was purified by dissolving it in DCE, shaking the solution with a mixture of methanol and water and separating the organic layer. The solvent was evaporated under vacuum and the solid residue was dissolved in methanol. The mixture was cooled and dibenzo-24-crown-8 was precipitated by addition of water. The fine white crystals were dried (m.p. 104 °C). Tropylium tetrafluoroborate (EGA-Chemie) was purified by dissolving it in a minimum amount of acetonitrile, followed by precipation with the addition of ethyl acetate. 1,2-Dichloroethane (Fluka) was purified, dried, distilled[17] and used as the solvent in all measurements. 3-Nitrobenzyl alcohol (Aldrich-Chemie) was used without further purification.

Apparatus. The complexes of the benzene-substituted crown ethers with tropylium ion in the gas phase were identified by FAB-MS with a DART data system. Argon was used as the bombarding gas with an atom gun energy of 8 keV. The stainless-steel probe was coated with a thin layer of 3-nitrobenzyl alcohol matrix solution, and samples of crown ether and tropylium salt ($[\text{crown ether}] \approx [\text{Tr}^+]$) dissolved in 1,2-dichloroethane were deposited on the probe tip for insertion. The spectrum was recorded immediately after the sample had been inserted.

Spectral measurements were carried out with a Phillips PU 8740 spectrophotometer and matched glass or quartz cells of 10 mm path length. The cell containing the solution was maintained at a temperature set to within ±0·05 °C by circulating water from a thermostated bath through a double-walled cell insert. The temperature inside the cell was monitored with a digital thermometer.

Small amounts of the tropylium salt were accurately weighed with a Perkin-Elmer AD-2 autobalance. The melting temperature of the solid compounds was determined using a Thermopan microscope (Reichert, Vienna).

Procedure. A $2{\cdot}0 \times 10^{-3}$ M stock solution of tropylium tetrafluoroborate was prepared by dissolving an appropriate quantity of tropylium salt in a 25 ml volumetric flask and diluting to volume with dried 1,2-dichloroethane at 20 °C. Solutions containing a constant

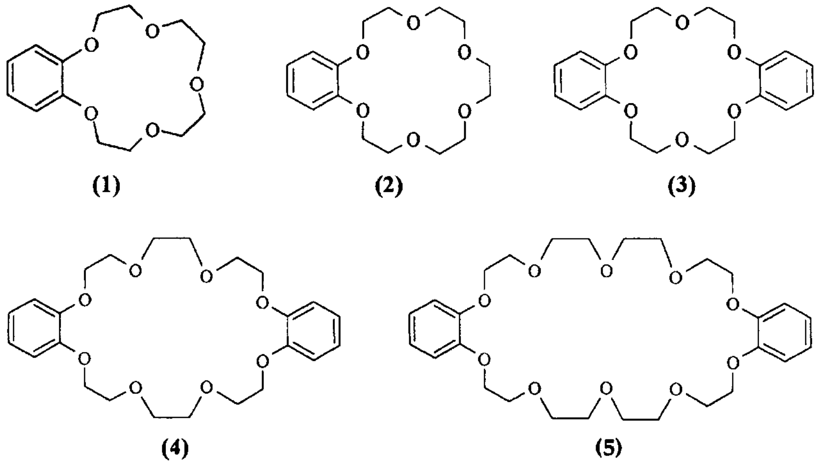

Figure 1. Structural formulae of benzene-substituted crown ethers

amount ($2{\cdot}0 \times 10^{-4}$ or $4{\cdot}0 \times 10^{-4}$ M) of tropylium salt and different amounts of crown ether ($[\mathrm{Cr}]_0/[\mathrm{Tr}^+]_0 = 5$–$150$, see below) in 1,2-dichloroethane were prepared in a 10 ml volumetric flask. The spectrum was recorded in the region 330–600 nm. The benzene-substituted crown ethers and tropylium tetrafluoroborate in 1,2-dichloroethane have negligible absorbance in the visible region. The equilibrium constant of the molecular complex was determined from the absorbance value of the new band having maximum absorbance.

RESULTS AND DISCUSSION

Theoretical equations for evaluation of parameters

The equilibrium reaction between a benzene-substituted crown ether and tropylium ion can be represented as follows:

$$\text{Crown ether} + \text{Tropylium ion} \rightleftharpoons [\text{Crown ether} - \text{tropylium}] \qquad (1)$$

The equilibrium constant K for 1 : 1 association between the crown ether and tropylium ion is given by

$$K = \frac{[\mathrm{C}]}{([\mathrm{Cr}]_0 - [\mathrm{C}])([\mathrm{Tr}]_0 - [\mathrm{C}])} \qquad (2)$$

where $[\mathrm{C}]$ = concentration of the complex [crown ether – Tr^+] at equilibrium, $[\mathrm{Cr}]_0$ = initial concentration of the crown ether and $[\mathrm{Tr}]_0$ = initial concentration of tropylium ion. Rearrangement of equation (2) gives

$$[\mathrm{C}] = \frac{[\mathrm{Tr}]_0 + [\mathrm{Cr}]_0 + \dfrac{1}{K} \pm \sqrt{\left([\mathrm{Tr}]_0 + [\mathrm{Cr}]_0 + \dfrac{1}{K}\right)^2 - 4[\mathrm{Tr}]_0[\mathrm{Cr}]_0}}{2} \qquad (3)$$

When the crown ether does not absorb at the selected wavelength, the total absorbance, A, for the 10 mm cell is given by

$$A = \varepsilon_c[\mathrm{C}] + \varepsilon_{\mathrm{Tr}}[\mathrm{Tr}] \qquad (4)$$

where ε_{C} = molar absorptivity for the complex, $\varepsilon_{\mathrm{Tr}}$ = molar absorptivity for the tropylium salt and $[\mathrm{Tr}]$ = concentration of the uncomplexed tropylium ion at equilibrium. We assume that all species obey the Beer–Lambert law. When only one complex is formed, the concentration of the tropylium ion obeys the equation

$$[\mathrm{Tr}]_0 = [\mathrm{C}] + [\mathrm{Tr}] \qquad (5)$$

and $A = [\mathrm{C}]\,(\varepsilon_{\mathrm{C}} - \varepsilon_{\mathrm{Tr}}) + \varepsilon_{\mathrm{Tr}}[\mathrm{Tr}]_0$ or $A = [\mathrm{C}](\varepsilon_{\mathrm{C}} - \varepsilon_{\mathrm{Tr}}) + A_0$. Combining these equations with equation (3) gives

$$\frac{1}{K} = \frac{A - A_0}{\varepsilon_{\mathrm{C}} - \varepsilon_{\mathrm{Tr}}} - [\mathrm{Tr}]_0 - [\mathrm{Cr}]_0 + \frac{[\mathrm{Cr}]_0[\mathrm{Tr}]_0(\varepsilon_{\mathrm{C}} - \varepsilon_{\mathrm{Tr}})}{A - A_0} \qquad (6)$$

This is called the Rose – Drago equation[18] and can be employed in cases where the crown ether can be assumed to have essentially zero molar absorptivity in the region of the measurement.

By assuming the simplification $[(A - A_0)/(\varepsilon_{\mathrm{C}} - \varepsilon_{\mathrm{Tr}})] - [\mathrm{Tr}]_0 \ll \{[\mathrm{Cr}]_0[\mathrm{Tr}]_0(\varepsilon_c - \varepsilon_{\mathrm{Tr}})\}/A - A_0) - [\mathrm{Cr}]_0$, equation (6) reduces to the form of the Ketelaar equation:[19]

$$\frac{[\mathrm{Tr}]_0}{A - A_0} = \frac{1}{K(\varepsilon_{\mathrm{C}} - \varepsilon_{\mathrm{Tr}})}\,\frac{1}{[\mathrm{Cr}]_0} + \frac{1}{(\varepsilon_{\mathrm{C}} - \varepsilon_{\mathrm{Tr}})} \qquad (7)$$

When A_0 and $\varepsilon_{\mathrm{Tr}}$ are zero and the terms $A/\varepsilon_{\mathrm{C}} - [\mathrm{Tr}]_0$ can be neglected, equation (7) reduces to a form of the Benesi–Hildebrand equation:[20]

$$\frac{[\mathrm{Tr}]_0}{A} = \frac{1}{K\varepsilon_{\mathrm{C}}}\,\frac{1}{[\mathrm{Cr}]_0} + \frac{1}{\varepsilon_{\mathrm{C}}} \qquad (8)$$

Heller *et al.*[21] have described a method for evaluating K and ε_{C} for a weak complex. Their treatment is useful when deviation from linearity in plots of the donor vs acceptor is slight or when the equilibrium constants are small. The first differential of equation (4) with respect to $[\mathrm{Cr}]_0$ gives

$$\left(\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}[\mathrm{Cr}]_0}\right)_0 = \frac{K[\mathrm{Tr}]_0}{1 + K[\mathrm{Tr}]_0} \qquad (9)$$

The slope of the plot of A vs $[\mathrm{Cr}]_0$ is related to K and ε_{C} as expressed in the equation

$$\left(\frac{\mathrm{d}A}{\mathrm{d}[\mathrm{Cr}]_0}\right)_0 = \frac{\varepsilon_{\mathrm{C}}K[\mathrm{Tr}]_0}{1 + K[\mathrm{Tr}]_0} \qquad (10)$$

It must be noted that measurements of the slopes of $(\mathrm{d}A/\mathrm{d}[\mathrm{Cr}]_0)_0$ from the plots of A vs $[\mathrm{Cr}]_0$ will not be reliable if the deviations from linearity are prominent. In the case of weak complexation, a careful choice of method is essential.

Measurement of stability constants

In earlier work, we used FAB-MS to screen the stoichiometry of stable polyether–tropylium complexes in the gas phase.[14] The results showed the 1 : 1 complex to predominate under FAB conditions. In the same connection, we discovered that, in 1,2-dichloroethane solution, dibenzo-18-crown-6 forms a coloured complex with tropylium ion. In order to obtain reliable values for the equilibrium constant of complexations of this type, we tested the four different treatments described in equations (6)–(10). Tropylium tetrafluoroborate in DCE exhibits a maximum absorption at 279 nm and the benzene-substituted crown ethers have no absorptions at wavelengths over 290 nm in the UV and visible regions. Addition of a benzene-substituted crown ether to DCE solutions containing tropylium salt resulted in the appearance of a new absorption band around 430 nm, indicating the formation of a molecular complex between the tropylium ion and the crown ether. It can be seen in Figure 2 that the spectrum of 2B-18-crown-6-tropylium salt is a charge-transfer spectrum with bathochromic shift absorption. The occurrence of a good or at least satisfactory isosbestic point in all plots implies that only one association complex is significant under the conditions used. Figure 3(a) shows a typical double-reciprocal plot for the 2B-18-crown-6-tropylium ion complex. A linear relationship was obtained for the entire range of concentrations tested, indicating that the stoichiometry of the complex in solution is 1 : 1. These results were expected after the observations in FAB-MS experiments in the gas phase (Table 1). The method of continuous variations, or Job's method,[22] was used to confirm the composition of the complex. Where the complex was weak, however, a very curved absorbance vs mole fraction plot resulted and the stoichiometry of the complex could not be determined by this method alone. The values of the stability constant K and the molar absorptivities of the complex ε_C calculated by four different methods for 2B-18-crown-6 and tropylium ion are collected in Table 2. Ketelaar and Rose–Drago plots are presented in Figure 3(b) and (c) and Heller *et al.* plots in Figure 3(d).

In all these studies, the benzene-substituted crown ethers were found to have essentially zero molar absorptivity in the region of the measurement. The concentrations of crown ethers were maintained at a level at least five times as high as the concentration of tropylium ion. Changes in concentration of the tropylium ion did not influence the values of the stability constants. The differences between the values

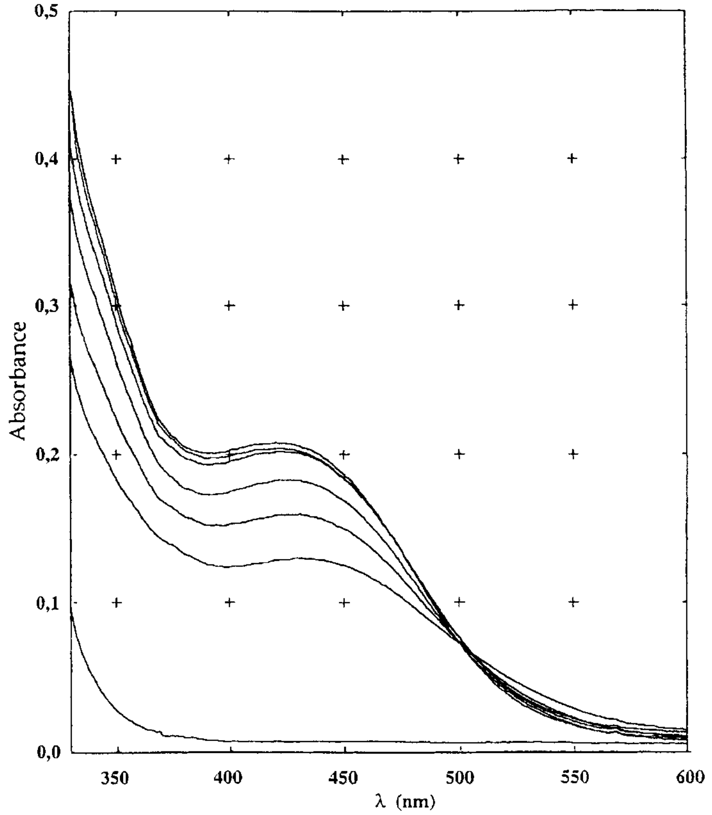

Figure 2. Visible absorption spectra of tropylium tetrafluoroborate (2.0×10^{-4} mol dm^{-3}) in 1,2-dichloroethane solutions at 25.0 °C in the presence of increasing amounts of dibenzo-18-crown-6: (1) 0, (2) 0.005, (3) 0.010, (4) 0.020, (5) 0.030, (6) 0.040 and (7) 0.050 mol dm^{-3}

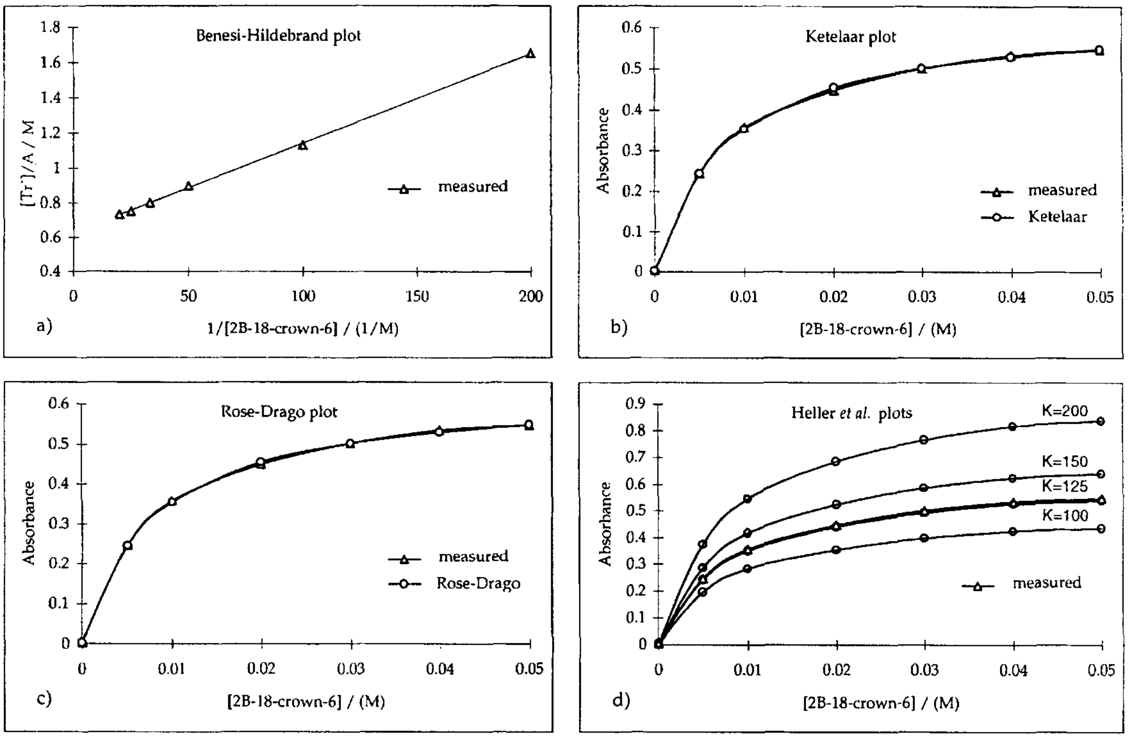

Figure 3. Plots obtained in experiments carried out for evaluation of the stability constants in the complexation of dibenzo-18-crown-6 with tropylium tetrafluoroboraten 1,2-dichloroethane solutions at 25.0 °C: (a) Benesi–Hildebrand plot; (b) Ketelaar plot; (c) Rose–Drago plot; (d) Heller *et al.* plots with four curves (O) calculated with *K* values of 100, 125, 150, and 200 mol dm^{-3}. The concentration of tropylium ion was 4.0×10^{-4} mol dm^{-3}

of *K* and ε_c were within experimental error, based on the maximum and minimum values obtained. In this work, the plots of absorbance vs concentration of the crown ether deviated considerably from linearity. Also, if two assumptions can be made, i.e. that the molar absorptivity is independent of temperature and the absorbance is directly proportional to the concentration of the complex, the method of Rose and Drago is the most suitable for the benzene-substituted crown ethers–tropylium ion systems.

The Rose–Drago equation contains two unknown constants, *K* and ε_C, which were evaluated by an iteration method with a personal computer implementing a SigmaPlot program.[23] The program relies on a least-squares procedure with the Marquardt–Levenberg algorithm. For each solution, initial guesses are made for *K* and ε_C, from which new values of *K* and ε_c are obtained. For crown ethers, the enthalpies of association $\Delta H°$, were evaluated by means of a least-squares fit of ln *K* vs $1/T$ to give $\Delta H°$ and the corresponding standard deviation (the small temperature dependence of the density of the solvent has been ignored). The values of *K*, ε_C and $\Delta H°$ together with the values of $\Delta S°$ are given in Table 3.

Examination of the data in Table 3 shows that the *K* values increase with increasing ring size of the benzene-substituted crown ether. The effect on the cooperative interaction of oxygen atoms with tropylium ion is clearly seen in Fig. 4, where the magnitude of *K* varies linearly with the number of oxygen atoms in the polyether. A study of 1B-18-crown-6 and 2B-18-crown-6 allows a comparison of two molecules of similar ring size and ion binding properties but with different structural properties. The presence of the second benzene ring enhances the *K* value, and this adds to the strength of complexing by 42 mol dm^{-3}, indicating the participation of the aromatic ring in the electron donation to tropylium ion. Thus, both n–π and π–π interactions (lone electron pairs from oxygen atoms and π-electrons from benzene rings, respectively) contribute to the values of *K*.

Now the question arises of whether unsubstituted crown ethers, such as 18-crown-6, form complexes with tropylium ion. Our FAB-MS studies have shown that

Table 1. Partial positive ion FAB mass spectra of tropylium ions in the presence of benzene-substituted crown ethers[a]

Crown ether	Ion (m/z) with relative abundance (%) in parentheses
1B-15-crown-5	91 (100·0) Tr+, 154(5·7) $[\mathrm{NBA+H}]^+$, 268 (45·3) $[\mathrm{1B{-}15C5}]^+$, 269 (25·2) $(\mathrm{Tr}^+)_2\mathrm{BF}_4^-$, 359 (1·9) $[\mathrm{1B{-}15C5{-}Tr}]^+$
1B-18-crown-6	91 (100·0) Tr^+, 154 (9·0) $[\mathrm{NBA+H}]^+$, 312 (11·2) $[\mathrm{1B{-}18C6}]^+$, 313 (7·1) $[\mathrm{lB{-}18C6+H}]^+$, 335 (0·7) $[\mathrm{1B{-}18C6{-}Na}]^+$, 403 (1·1) $[\mathrm{1B{-}18C6{-}Tr}]^+$
2B-18-crown-6	77 (100·0) $\mathrm{C_6H_5^+}$, 91 (94·3) Tr^+, 154 (23·0) $[\mathrm{NBA+H}]^+$, 269 (1·3) $(\mathrm{Tr}^+)_2\mathrm{BF}_4^-$, 360 (6·2) $[\mathrm{2B{-}18C6}]^+$, 383 (1·2) $[\mathrm{2B{-}18C6{-}Na}]^+$, 451 (0·9) $[\mathrm{2B{-}18C6{-}Tr}]^+$
2B-24-crown-8	91 (100·0) Tr^+, 154 (3·0) $[\mathrm{NBA+H}]^+$, 269 (3·4) $(\mathrm{Tr}^+)_2\mathrm{BF}_4^-$, 448 (2·1) $[\mathrm{2B{-}24C8}]^+$, 449 (0·8) $[\mathrm{2B{-}24C8+H}]^+$, 471 (0·4) $[\mathrm{2B{-}24C8{-}Na}]^+$, 539 (0·2) $[\mathrm{2B{-}24C8{-}Tr}]^+$
2B-30-crown-10	91 (100·0) Tr^+, 154 (3·0) $[\mathrm{NBA+H}]^+$, 269 (1·9) $(\mathrm{Tr}^+)_2\mathrm{BF}_4^-$, 536 (1·9) $[\mathrm{2B{-}30C10+H}]^+$, 627 (0·4) $[\mathrm{2B{-}30C10{-}Tr}]^+$

[a] B = benzo; Tr^+ = tropylium ion; NBA = 3-nitrobenzyl alcohol.

Table 2. Stability constants and molar absorptivities for the 1 : 1 complex of dibenzo-18-crown-6 and tropylium ion at 25 °C, calculated by four different methods

Method	K ($\mathrm{dm^3\,mol^{-1}}$)	ε_c ($\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$)
Benesi–Hildebrand	124·3 ± 2·5	1574 ± 14
Ketelaar	124·1 ± 3·8	1582 ± 13
Rose–Drago	128·5 ± 4·2	1575 ± 13
Heller *et al*·	127·2[a]	1354[a]

[a] Standard deviations were not calculated.

Table 3. Stability constants, molar absorptivities and thermodynamic parameters for the interaction of benzo-substituted crown ethers with tropylium ion in 1,2-dichloroethane solution at different temperatures[a]

Crown ether	T (°C)	$\lambda_{\max}$ (nm)	K ($\mathrm{dm^3\,mol^{-1}}$)	ε_c ($\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$)	$-\Delta H^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	$-\Delta S^\circ$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
1B-15-crown-5	25·00	432	24·2 ± 3·9	553·6 ± 47	20·8 ± 0·4	43·2 ± 2·7
	35·00		18·3 ± 3·5	626·6 ± 69		
	45·00		14·3 ± 2·9	731·8 ± 93		
1B-18-crown-6	25·00	420	86·3 ± 6·2	557·7 ± 13	25·1 ± 2·7	47·2 ± 9·8
	35·00		67·4 ± 5·6	542·0 ± 16		
	45·00		45·6 ± 4·9	588·2 ± 27		
2B-18-crown-6	25·00	435	128·5 ± 4·1	1574·5 ± 14	18·3 ± 1·2	21·0 ± 4·2
	35·00		98·6 ± 3·9	1399·8 ± 16		
	45·00		80·1 ± 4·3	1194·8 ± 21		
2B-24-crown-8	25·00	425	273·5 ± 13·8	1060·1 ± 13	26·8 ± 0·5	43·2 ± 2·0
	35·00		194·6 ± 9·9	997·1 ± 14		
	45·00		138·6 ± 7·5	942·4 ± 17		
2B-30-crown-10	25·00	419	417·6 ± 18·4	914·5 ± 9	27·1 ± 1·6	40·6 ± 5·8
	35·00		292·0 ± 10·9	825·2 ± 8		
	45·00		210·3 ± 8·3	743·4 ± 8		

[a] Values were calculated from the absorbance at selected wavelength by method of Rose and Drago.

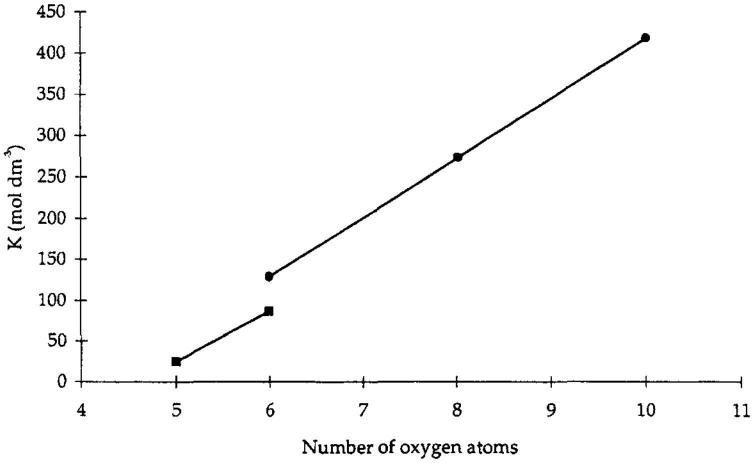

Figure 4. Plots of the values of stability constants vs the number of oxygen atoms in the crown ethers: (●) dibenzo-substituted crown ethers and (■) monobenzo-substituted crown ethers

complexes between crown ethers containing no benzene substituents and tropylium or substituted tropylium ions were formed in the gas phase.[14] The interaction between crown ethers without a benzene ring and tropylium ions depends mainly on oxygen donor atoms and the ring size of the ligand. The values of K in these systems cannot be ascertained by the described approach since no absorption of the complexes is found in the visible region. However, the complex formation results in a decrease in the absorption band of the tropylium ion in the UV region at 279 nm. Preliminary investigations of the complexation of 18-crown-6 with substituted tropylium in DCE likewise showed that the characteristic absorption of 3-methoxyphenyltropylium ion in the visible region at 459 nm decreases with increase in crown ether concentration. Evaluation of a double-reciprocal plot from the Benesi–Hildebrand equation (8) gave a value of about 45 mol dm^{-3} for the stability constant, which is about one third of the corresponding value for 2B-18-crown-6. To obviate the difficulty of determining K values in similar cases, Antonov and Mateeva[24] proposed a spectrophotometric method based on the use of chromoionophore-substituted macrocycles.

A number of other conclusions can be drawn from the thermodynamic results. From the $\Delta H°$ and $T\Delta S°$ contributions to the $\Delta G°$ value, it can be deduced that the complexes are enthalpy stabilized in DCE. The enthalpy stabilization is explained by the expenditure of less energy in the cation desolvation step in a solvent of low dielectric constant. 1,2-Dichloroethane has low dielectric permittivity ($\varepsilon_r = 10.37$), but it is strong enough to dissolve small amounts of tropylium salt. In DCE the overall $\Delta S°$ is negative, as expected for a complexation process. Besides the entropy change occurring when two components are brought together, two other contributions are responsible for the $\Delta S°$ of complexation: the desolvation of the components prior to complexation and the conformational change of the crown ether before complexation. Since the desolvation of tropylium ion will be the same in the formation of all the complexes, the favourable $T\Delta S°$ contribution for the 2B-18-crown-6–tropylium complex must be due to the conformational change of the crown ether prior to complexation. Evidently the ether ring with six oxygen atoms and two structure-stabilized benzene rings allows an effortless match of the tropylium ion.

Our study demonstrates the difficulty of showing quantitatively the individual contributions of the ring size and the donor sites to complexation. In general, the ion whose ionic radius best matches the radius of the cavity in the crown ether ring will form the most stable complex. Interaction of all macrocycle donor atoms with the complexed cation can be expected to give maximum stability to the resulting complex. The hole size of the crown ethers increases from 0.17 nm (15C5) to 0.34 nm (21C7)[25] and to 0.56 nm (30C10) if the ring diameter increases linearly increasing number of ethoxy units in the cyclic ether. Since the molecular diameter of the tropylium ion is a 0.79 nm,[26] clearly no insertion complexes are formed with this acceptor. 2B-30-crown-10 should be representative of large cyclic ethers, which would be expected to be more flexible and have greater ion adaptability upon formation of a complex. In fact, 2B-30-crown-10 has the largest stability constant of the ethers listed in Table 3. The cavities of the crown ethers do not have the same significance in complexation with tropylium ion as in the complexation with metallic cations or diazonium ions. Clearly, the effects of the phenyl rings need to be considered. Many investigations have demonstrated an intramolecular charge-transfer interaction between incorporated tropylium ring and benzene rings in an inflexible molecular framework.[6,7] In the electronic spectra of the complexes there is a broad absorption at 300–550 nm which is not found in the spectra of either tropylium tetrafluoroborate or crown ethers, and this serves as further evidence of the interaction between the tropylium ion and the benzene rings in the complexes. The full nature of the complexation remains to be studied by NMR spectroscopy, x-ray crystallographic analysis and other methods.

CONCLUSIONS

The carbonium ions are singly charged organic cations containing even numbers of electrons on carbon atoms. Their abilities to form complexes with macrocyclic molecules have been little studied, and our investigation is the first to have explored the complexation of tropylium ion in solution. The method of Rose and Drago was found to be the most useful for calculating the stability constants in complexation. The interaction between tropylium ion and the benzene-substituted crown ethers was essentially of the same type, charge-transfer, in all cases studied. From the $\Delta H°$ and $T\Delta S°$ contributions to $\Delta G°$, it can be deduced that the complexes are enthalpy stabilized in 1,2-dichloroethane. The magnitude of the stability constant varied linearly with the number of oxygen atoms in the ethers, and 2B-30-crown-10 exhibited the largest value, $K = 418\ \mathrm{mol\,dm^{-3}}$. The presence of a second benzene ring enhances the value of the stability constant, adding to the strength of complexing by 42 $\mathrm{mol\,dm^{-3}}$, and indicating the participation of the aromatic ring in the electron donation to the tropylium ion.

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