COMPLEXATION OF TROPYLIUM IONS WITH CROWN ETHERS AND ACYCLIC POLYETHERS EXAMINED BY FAST ATOM BOMBARDMENT MASS SPECTROMETRY

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The molecular complex formation of six macrocyclic and six acyclic polyethers with tropylium and 4-methoxyphenyltropylium tetrafluoroborates was observed and characterized in the gas phase by fast atom bombardment mass spectrometry (FABMS), to obtain information on intrinsic molecular interactions in the absence of the complicating effect of solvation. The stoichiometry of the complexes was assessed on the basis of corresponding peaks in FAB mass spectra. In addition to the expected 1 : 1 complexes between polyether and tropylium ion, some 2 : 1 complexes were also formed. The stability order of selected complexes was studied in competition experiments. The complexation equilibrium constant and thermodynamic parameters for the interaction of dibenzo-18-crown-6 with tropylium ion were determined in 1,2-dichloroethane solution by UV-visible spectrophotometry. Complexation of polyethers with tropylium salts has not been reported previously.

INTRODUCTION

Since their discovery by Pedersen[1,2] in 1967, crown ethers have generated a tremendous amount of interest because of their ability to selectively bind alkali and alkaline earth metal ions. In complexation[3] with appropriately sized metal cations, the basic oxygen atoms of crown ether surround the cation, each engaging in an apparently similar electrostatic interaction with it. The ability of these ethers to act as hosts towards a variety of hydrogen-donating molecules such as ammonium cations has also been investigated.[4] Crown ethers are also capable of interacting with organic guests.[5] The forces that govern the interaction of two molecules in a given geometry arise from dipole–dipole, dipole–induced dipole, and other long-range electrostatic effects. Another general type of complexation exists, which most properly may be termed molecular inclusion.[6] In these complexes the macrocycles pack in the lattice with the voids filled by smaller molecular species.

Numerous experimental techniques, including calorimetry,[7,8] potentiometry,[4,9,10] conductometry,[11] absorption spectrometry,[12,13] NMR spectrometry[14] and kinetic methods,[15,16] have been employed to determine the complexation behaviour in solution. Fast atom bombardment mass spectrometry (FAB) is unique in offering a rapid method for examining the complexation

between crown ethers and, for example, alkali metal cations or aromatic diazonium ions in the gas phase.[17–22] We have recently[16] observed and characterized by FABMS the 1:1 complexes between 18-crown-6 and benzenediazonium ion and between pentaglyme and benzenediazonium ion in the gas phase. Investigations of host–guest chemistry have shown that the intrinsic nature of binding interactions and the size selectivity of complexation can be clarified in these solvent-free conditions.[23] Maleknia and Brodbelt[24] reported that the trends observed between crown ethers and alkali metal ions in the gas phase closely parallel those seen in nonpolar solvent environments.

The studies of Doering and Knox[25] in the 1950s aroused interest in the tropylium ions and their aromatic character. In our laboratory, Virtanen and co-workers[26] intensively studied tropylium ions and their stability and reactivity in solution. The ring expansion of toluene and related aromatic compounds to form tropylium ion is a much studied reaction in mass spectrometry.[27] The tropylium ion represents an aromatic system where the relative stability is due to resonance resulting from the presence of six π-electrons in the conjugated unsaturated seven-membered ring.[28] The $C_7H_7^+$ cyclic cation is a planar regular heptagon with D_{7h} symmetry possessing considerable resonance energy.[29,30] The ion is assumed to have the symmetry of a cylinder with a radius of the carbon ring of 0·165 nm (C—C bond 0.141 nm).[31]
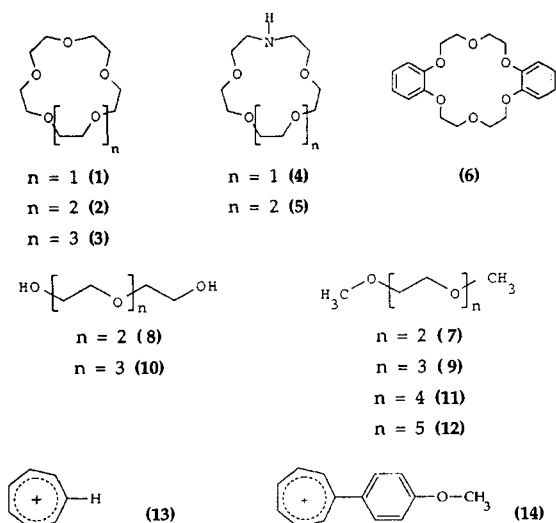
Figure 1. Structures of the compounds studied

Tropylium ion forms 1 : 1 charge-transfer complexes with a variety of aromatic hydrocarbons.[32] It is an effective π-acceptor with full positive charge, and as the donor capacity is usually dependent on electron density and the acceptor capacity on electron deficiency, tropylium ions together with polyethers offer a new model system for the study of complexation of stable organic cations.

Continuing with our earlier studies on the interaction between polyethers and stable organic cations, such as aryldiazonium ions, we report here on the complexation of cyclic and acyclic polyethers with tropylium or cycloheptatrienylium and 4-methoxyphenyltropylium tetrafluoroborates in the gas phase under FAB conditions.

The cyclic and acyclic ether compounds 1–12 and donor compounds 13 and 14 used in this study are shown in Figure 1.

EXPERIMENTAL

FAB mass spectra were obtained on a Kratos MS 80 mass spectrometer operating with a DART data system. The atom gun was operated at 8 keV and argon was employed as the bombarding gas with pressures of about 1×10^{-6} Torr (1 Torr = 133·3 Pa) in the collision region. The liquid matrix for FAB studies has recently been optimized and 3-nitrobenzyl alcohol (NBA) proved to be the best solvent for our experiments owning to its electron-scavenging nature.[23,33] The stainless steel tip of the FAB probe was coated with a thin layer of the matrix solution, after which a solution of an ether and a tropylium fluoroborate salt in 1,2-dichloroethane (DCE) was carefully added to NBA and the probe introduced into the ion source.

The competition experiments were carried out by mixing equimolar concentrations of two polyethers in DCE, each in excess of the tropylium tetrafluoroborate concentration. The mixture was added to the NBA matrix and the resulting spectra of the two crown complexes formed were observed. The relative complex stabilities were estimated from the ion intensities.

Materials. The following chemicals were obtained from the indicated suppliers: 15-crown-5 (1) (Fluka), 18-crown-6 (2) (Fluka), 21-crown-7 (3) (Pfaltz & Bauer), 1-aza-15-crown-5 (4) (Aldrich-Chemie), 1-aza-18-crown-6 (5) (Fluka), dibenzo-18-crown-6 (6) (Parish Chemical Co), diethylene glycol dimethyl ether (diglyme) (7) (Fluka), triethylene glycol (triglycol) (8) (Fluka), triethylene glycol dimethyl ether (triglyme) (9) (Fluka), tetraethylene glycol (tetraglycol) (10) (Fluka), tetraethylene glycol dimethyl ether (tetraglyme) (11) (Fluka) and pentaethylene glycol dimethyl ether (penta-glyme) (12) (Riedel-de Haën). The ethers were used as received.

Tropylium tetrafluoroborate (13) (EGA-Chemie) was purified by dissolving it in a minimum amount of acetonitrile, followed by precipitation with the addition of ethyl acetate.

4-Methoxyphenyltropylium fluoroborate (14) was synthesized by converting tropylium fluoroborate into 7-methoxytropylidene, which was used for syntheses of substituted phenyltropylidines by the method of Jutz and Voithenleitner.[34] These were converted to tropylium ions with trityl fluoroborate. 4-Methoxy-phenyltropylidene was treated in acetonitrile with excess of trityl fluoroborate and the mixture was refluxed for 45 min on a steam bath. After cooling, 4-methoxyphenyltropylium tetrafluoroborate was precipi-tated three times from mixtures of acetonitrile and ethyl acetate: m.p. 159–160 °C, $\lambda_{max} = 459$ nm ($\varepsilon = 2·54 \times 10^4$ l mol^{-1} cm^{-1}), and $\lambda_{max} = 240$ nm ($\varepsilon = 2·74 \times 10^4$ l mol^{-1} cm^{-1}), in DCE.

1,2-Dichloroethane (Fluka) was purified, dried and distilled. 3-Nitrobenzyl alcohol (Aldrich-Chemie) was used without further purification.

RESULTS AND DISCUSSION

Crown ethers

Figure 2 presents the positive-ion FAB mass spectrum of tropylium ion in the presence of 18-crown-6 (18C6) in NBA matrix. The spectrum includes a base peak at m/z 265 and peaks at m/z 354 and 356 assigned to complexation between tropylium cation (Tr$^+$) and 18C6. In addition, there are ions at m/z 133, 131, 117, 115, 91, 89, 87, 77 and 45, indicating the fragmentation of both crown ether and tropylium ion. For all crown ethers, the fragmentation pattern consists of a series of losses of protonated $(C_2H_4O)_n$ structural units. Thus,
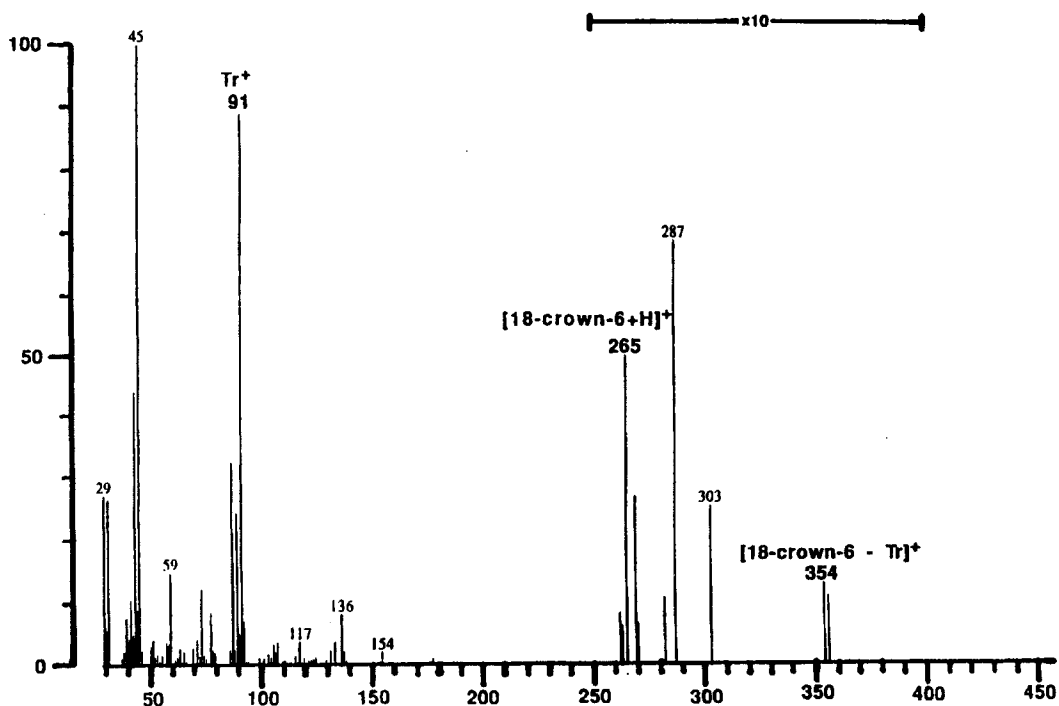
Figure 2. Mass spectrum of tropylium tetrafluoroborate in the presence of an excess of 18-crown-6 recorded by the FAB technique in NBA as matrix

the fragmentation ions consistently observed include m/z 45, 89, 133, 177, ..., depending on the size of the initial parent ion. The peaks at m/z 154, 136 and 107 are due to the fragmentation of 3-nitrobenzyl alcohol matrix.

Possible fragmentation pathways for 18-crown-6 and tropylium tetrafluoroborate are proposed in Scheme 1. Since fragmentation mechanisms furnished with structural formulae have been presented in the literature,[35–38] suggested structures are given without mechanistic interpretation. Other peaks at m/z 287 and 303 indicate that alkali metal cations Na^+ and K^+ compete effectively in complex formation with tropylium cation. The mass peak at m/z 282 is suggested to be $[18C6 + H_3O]^+$ ion.

The effect on the complexation of a substituent of the tropylium ring was studied with H- and 4-methoxyphenyl-substituted tropylium ion. 4-Methoxyphenyltropylium fluoroborate is one of the most stable tropylium ions used in our studies.[26] The larger substituent did not cause any marked change in the intensity of the complex peak, which means that it did not have much effect on the strength of the complexation between crown ethers and tropylium ions in the gas phase. This is in accordance with our earlier observations in the complexation of polyethers with

aryldiazonium ions, where the sensitivity to changes in the character of the substituent in the benzene ring decreased with decreasing value of the complexation equilibrium constant K in solution.[16]

Cluster ions are also seen in the mass spectra. For example, ions corresponding to $(Tr^+)_2BF_4^-$ (m/z 269) and $(TrPhOMe^+)_2BF_4^-$ (m/z 354) clusters are observed in the positive-ion FAB mass spectra of tropylium ions in the presence of 15-crown-5 (15C5). The mass spectra of tropylium ions in the presence of different crown ethers are compiled in Table 1, with data for the main peaks being shown.

All the crown ethers studied exhibited clearly detectable [crown + H]$^+$ species. For 15-crown-5, 18-crown-6, 21-crown-7, 1-A-18-crown-6 and 2B-18-crown-6, 1 : 1 complexes between the crown ether and tropylium ions were observed. In the spectra of 1-A-15-crown-5 and tropylium, a peak at m/z 527 was observed instead of the peak indicating 1 : 1 complex. Evidently reaction with a second ligand occurred to form 2 : 1 complexes, corresponding to the ion $[(1A-15C5)_2-Tr - 2H]^+$. In the case of 1-A-15C5 with TrPhOMe$^+$, no ions corresponding to a 2 : 1 complex were observed. This suggests that the bulkiness of the side group affects the steric interference between 1-A-15C5 and substituted tropylium cation, and 1:1 complex formation is preferred.

Table 1. Partial positive-ion FAB mass spectra of tropylium ions in the presence of cyclic polyethers

Tropylium ion	Crown ether	Ion (m/z) with relative abundance (%) in parentheses
Tr^+	15C5	45 (100·0) $C_2H_5O^+$, 91 (25·4) Tr^+, 221 (4·8) $[15C5+H]^+$, 269 (0·6) $(Tr^+)_2BF_4^-$, 311 (0·6) $[15C5-Tr]^+$
$TrPhOMe^+$	15C5	45 (100·0) $C_2H_5O^+$, 91 (1·1) Tr^+, 197 (41·9) $TrPhOMe^+$, 221 (23·9) $[15C5+H]^+$, 418 (0·5) $[15C5-TrPhOMe]^+$, 482 (0·8) $(TrPhOMe^+)_2BF_4^-$
Tr^+	18C6	45 (100·0) $C_2H_5O^+$, 91 (89·0) Tr^+, 265 (5·1) $18C6+H]^+$, 269 (0·1) $(Tr^+)_2BF_4^-$, 354 (1·3) $[18C6-Tr-H]^+$, 356 (1·1) $[18C6-Tr+H]^+$
$TrPhOMe^•$	18C6	45 (78·0) $C_2H_5O^+$, 91 (2·8) Tr^+, 197(100·0) $TrPhOMe^+$, 265 (8·9) $[18C6+H]^+$, 462 (0·3) $[18C6-TrPhOMe+H]^+$, 482 (3·1) $(TrPhOMe^+)_2BF_4^-$
Tr^+	21C7	45 (100·0) $C_2H_5O^+$, 91 (71·1) Tr^+, 399 (0·7) $[21C7-Tr]^+$
$TrPhOMe^+$	21C7	45 (100·0) $C_2H_5O^+$, 91 (1·5) Tr^+, 197 (47·8) $TrPhOMe^+$, 310 (4·8) $[21C7+2H]^+$, 482 (1·2) $(TrPhOMe^+)_2BF_4^-$, 506 (0·2) $21C7-TrPhOMe^+$
Tr^+	2B-18C6	91 (95·4) Tr^+, 269 (1·3) $(Tr^+)_2BF_4^-$, 360 (2·2) $[2B-18C6]^+$, 451 (0·9) $2B-18C6-Tr^+$
$TrPhOMe^+$	2B-18C6	91 (4·5) Tr^+, 197 (100·0) $TrPhOMe^+$, 361 (0·9) $[2B-18C6+H]^+$, 482 (1·6) $(TrPhOMe)_2BF_4^-$, 558 (0·1) $[2B-18C6-TrPhOMe+H]^+$
Tr^+	1-A-15C5	91 (17·9) Tr^+, 220 (100·0) $[1-A-15C5+H]^+$, 527 (1·2) $[(1A-15C5)_2-Tr-2H]^+$
$TrPhOMe^+$	1-A-15C5	197 (6·0) $TrPhOMe^+$, 220 (100·0) $[1-A-15C5+H]^+$, 417 (0·4) $[1-A-15C5-TrPhOMe]^+$
Tr^+	1-A-18C6	91 (100·0) Tr^+, 264 (30·5) $[1-A-18C6+H]^+$, 269 (0·6) $(Tr^+)_2BF_4^-$, 352 (1·1) $[1-A-18C6-Tr-2H]^+$
$TrPhOMe^+$	1-A-18C6	91 (6·3) Tr^+, 197 (28·4) $TrPhOMe^+$, 264 (100·0) $[1-A-18C6+H]^+$, 459 (0·1) $[1-A-18C6-TrPhOMe-2H]^+$
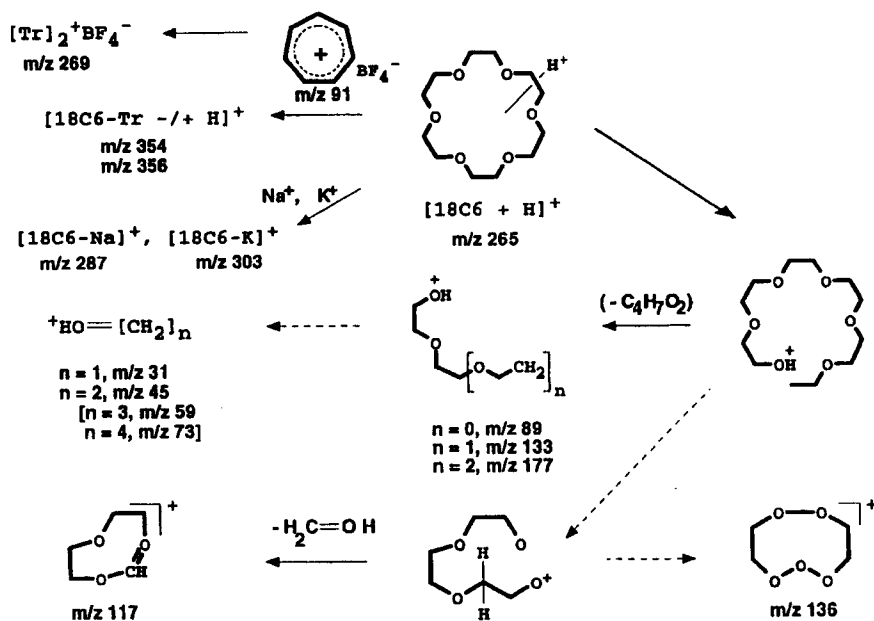
Scheme 1

Acyclic polyethers

With both structural and electronic similarities, glycols and glymes serve as important acyclic analogues of the crown ethers. The formation of the ion at m/z 357 indicates that the complex between the tropylium cation and PEG is stable in the gas phase. The FAB mass spectra of polyglycols have shown that the glycols dissociate into several ions separated by 44 u, to protonated ions at m/z 45, 89, 133, 177, ... etc., depending

on the size of the polyglycol molecule.[39] Partial FAB mass spectra of tropylium ions in the presence of acyclic polyethers are shown in Table 2. No [complex]$^+$ ions at all were observed for diglyme, which suggests that the chain of diethylene glycol is too short and rigid to interact readily with a tropylium ion. In other words, the oxygen atoms of diglyme cannot form strong interactions with tropylium ion, and no complex is observed in the gas phase. In contrast to diglyme, the other acyclic polyethers, triglycol (TriG), triglyme (TrEG), tetraglycol (TeEG), tetraglyme (TEG) and pentaglyme (PEG), show detectable complex peaks with tropylium ion. In the case of 4-methoxy-phenyltropylium ion, a tiny complex peak at m/z 420 is observed with TEG but not with PEG. The peaks at m/z 269 and 389 in the spectrum of tetraglycol–tropylium indicate the formation of cluster ions, here corresponding to $(Tr^+)_2BF_4^-$ or $(TrBF_4)Tr^+$ and $[(TeEG)_2 + H]^+$ clusters. Likewise, the spectrum of 4-methoxy-phenyltropylium ion with TEG shows the cluster ion $(TrPhOMe^+)_2BF_4^-$ at m/z 482.

Acyclic ethers 7–12 have several oxygen atoms, which provide multiple binding sites for tropylium ions. Although the glycols and glymes possess different terminal groups (hydroxy/hydroxy or methoxy/methoxy), all are flexible molecules in which either the terminal or internal oxygen atoms may interact with the guest molecule in complexation. For example, the larger ethers in our study have three to five internal oxygen atoms which may participate in binding, thereby stabilizing the complexes.

Type of complexation and stability

The insertion complex has generally been assumed to be the only type of complexation between crown ethers and arenediazonium ions (I) in solution. We have recently studied the FAB mass spectra of crown ethers

in the presence of these ions. As the spectrum of 15-crown-5 with arenediazonium tetrafluoroborate in NBA matrix in Figure 3 shows, the complex is stable under FAB conditions. In addition, we have demonstrated, through several approaches (UV spectra, stabilizing effect of complexation against the thermal decomposition, activation parameters ΔH^*, ΔS^*, ΔV^*, product analyses), that in DCE, arenediazonium ions form weak charge-transfer complexes with 15-crown-5, the cavity of which is too small for insertion-type complexation.[40]

In all FAB mass spectra recorded in this study, the peaks of complexes were small with relative abundance less than 1·5%, indicating that the complexation was weak. Evidently no insertion complex ions are formed with these large tropylium cations. The hole sizes of crown ethers, ranging from 0·17 nm to 0·32 nm,[30] are simply too small to allow the insertion of tropylium ions. Some other kind of stable complex, e.g. II, must be involved. It is difficult to say what effect ring size has on the stabilization of the complexes since the complexes with all the ethers were weak. In addition, the small quantities of alkali metal impurities with 15-crown-5, 18-crown-6 and dibenzo-18-crown-6 produced strong alkali ion adduct peaks at m/z 243 (15C5–Na$^+$), 259 (15C5–K$^+$), 287 (18C6–Na$^+$), 303 (18C6–K$^+$) and 383 (2B-18C6–Na$^+$), and these may be interpreted to mean that complexation between crown ethers and acyclic polyethers with tropylium ions is relatively weak. Since complexes were observed in the presence of crown ethers and acyclic polyethers (except diglyme) in every case in this study, the steric requirement for complex formation must be far less important in the gas phase than in solution, and all this suggests that ion–dipole interaction is the preferred complexation mode.

In competition reactions the intensities of complex peaks closely parallel the relative complex stability. In this study we determined the stability order of 18C6,

Table 2. Partial positive-ion FAB mass spectra of tropylium ions in the presence of acyclic polyethers

| Tropylium ion	Ether	Ion (m/z) with relative abundance (%) in parentheses
Tr$^+$	Diglyme	91 (100·0) Tr$^+$, 269 (8·4) (Tr$^+$)$_2$BF$_4^-$
Tr$^+$	Triglycol (TriG)	45 (100·0) C$_2$H$_5$O$^+$, 91 (35·4) Tr$^+$, 151 (73·6) [TriG + H]$^+$, 241 (0·7) [TriG–Tr]$^+$, 269 (0·9) (Tr$^+$)$_2$BF$_4^-$, 301 (3·2) [(TriG)$_2$ + H]$^+$
Tr$^+$	Triglyme (TrEG)	59 (100·0) C$_3$H$_7$O$^+$, 91 (35·4) Tr$^+$, 179 (5·2) [TrEG + H]$^+$, 269 (2·8) TrEG–Tr$^+$, and (Tr$^+$)$_2$BF$_4^-$
Tr$^+$	Tetraglycol (TeEG)	45 (100·0) C$_2$H$_5$O$^+$, 91 27·1) Tr$^+$, 195 (85·1) [TeEG + H]$^+$, 269 (0·9) (Tr$^+$)$_2$BF$_4^-$, 285 (0·7) TeEG–Tr$^+$, 389 (0·7) [(TeEG)$_2$ + H]$^+$
TrPhOMe$^+$	Tetraglyme (TEG)	91 (0·4) Tr$^+$, 197 (5·3) TrPhOMe$^+$, 224 (7·4) [TEG + 2H]$^+$, 420 (0·1) TEG–TrPhOMe$^+$, 482 (0·1) (TrPhOMe$^+$)$_2$BF$_4^-$
Tr$^+$	Pentaglyme PEG	91 (6·7) Tr$^+$, 267 (8·8) [PEG + H]$^+$, 357 (0·6) PEG-Tr$^+$
TrPhOMe$^+$	Pentaglyme (PEG)	91 (1·9) Tr$^+$, 197 (65·3) TrPhOMe$^+$, 268 (3·7) [PEG + 2H]$^+$, 482 (0·5) (TrPhOMe$^+$)$_2$BF$_4^-$
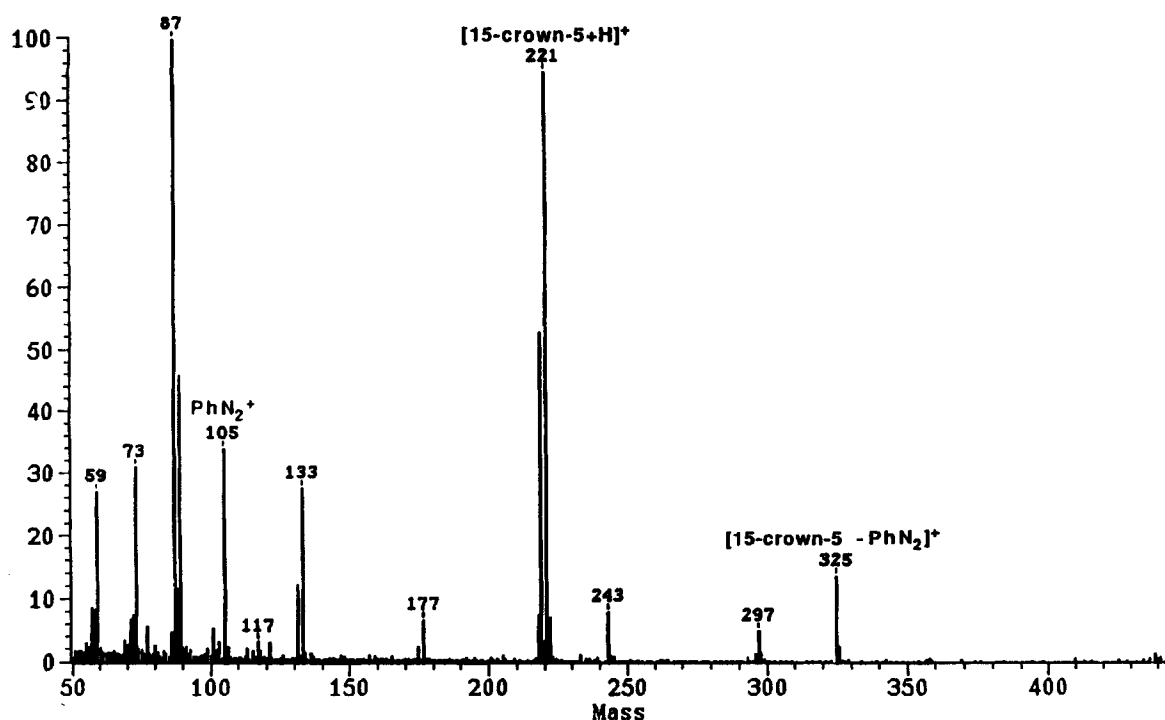
Figure 3. Mass spectrum of benzenediazonium tetrafluoroborate in the presence of an excess of 15-crown-5 recorded by the FAB technique in NBA as matrix


(I)   (II)
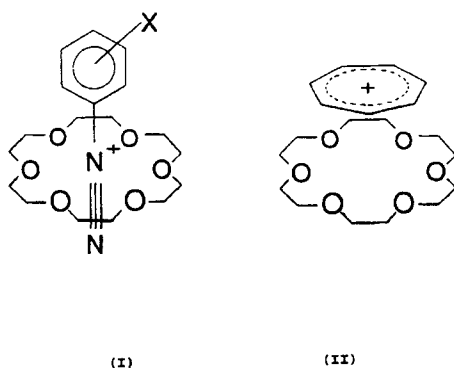
2B-18C6 and PEG towards the tropylium cation under FAB conditions. Equimolar mixtures of 18C6 and another polyether with six oxygen atoms were dissolved with tropylium cation in DCE solution and the stability order of complexation was determined on the basis of the relative intensities of complex ions in mass spectra. We found that 2B-18C6 formed the most stable complex with tropylium, and complexation decreased in the order dibenzo-18-crown-6 > 18-crown-6 > pentaglyme. The competition measurements provide further support for the charge-transfer binding mode, in which the

number of n–π and π–π interactions play an important role. In addition, for the interactions with tropylium to be strong enough, the acyclic PEG chain must be appropriately preorganized, and this is probably achieved by template effect.

Interesting results were obtained in studies of 18C6–tropylium and 2B-18C6–tropylium systems in 1,2-dichloroethane solutions. The complex of 2B-18C6 was orange, which suggests π–π interaction between the tropylium ion and the benzene ring, but no such colour was observed for the complex between 18C6 and tropylium ion. To study the colour formation reaction further, complexation was investigated in DCE solutions in which the tropylium concentration was held constant at $4 \cdot 0 \times 10^{-4}$ M, while the concentration of the 2B-18C6 was varied from $5 \cdot 0 \times 10^{-3}$ to $0 \cdot 05$ M. Both 2B-18C6 and Tr^+ have negligible absorbance in the visible region and the appearance of a new band for the ether–Tr^+ solutions indicates complex formation between the components. The broad band with a maximum at 430 nm (Figure 4) is characteristic of charge-transfer spectra. The formation constant K for the reaction between 2B-18C6 and Tr^+ was determined by use of the Ketelaar equation.[41] The plots are linear, suggesting that the only major species in solution is the 1 : 1 complex. The values obtained are given in Table 3.

Table 3. Measured properties of dibenzo-18-crown-6 interaction with tropylium ion in DCE

Temperature (°C)	K (l mol^{-1})	ε_C (l mol^{-1} cm^{-1})	$\Delta H°$ (kJ mol^{-1})
25·00	124 ± 4	1606 ± 15	−18 ± 2
35·00	96 ± 4	1406 ± 16	$\Delta S°$ (J mol^{-1} K^{-1})[a]
45·00	79 ± 4	1200 ± 21	−20 ± 7

[a] At 25°C.
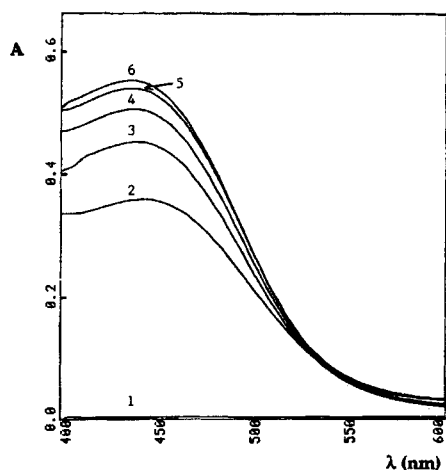
Figure 4. Visible absorption spectra of DCE solutions of TrBF$_4$ (4·0 × 10^{-4} M) with increasing amounts of 2B-18C6: (1) 0; (2) 0·010; (3) 0·020; (4) 0·030; (5) 0·040; (6) 0·050 M (at 25·00 ± 0·05 °C)

These results in the gas phase and solution suggest that the aromatic nuclei of 2B-18C6 and tropylium can occupy parallel planes and are within van der Waals contact. It is equally likely that, in the dibenzo-substituted ethers, both benzene rings are involved in donation to tropylium ion.

CONCLUSIONS

Bombardment with fast atoms promotes the desorption of ionized species directly from the liquid matrix. Thus, FAB mass spectra can be assumed faithfully to reproduce solution chemistry. In fact, our experiments in DCE solution support FABMS results. This being the case, FABMS could provide a rapid means for screening the complexation behaviour of cyclic and acyclic polyethers in the presence of aromatic organic cations and the stoichiometry of the complexes. As far as we

are aware, complexation of crown ethers with tropylium salts has not been reported previously. We shall be extending our complexation studies to solution in the near future.

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