JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 10, 67–75 (1997)

EFFECT OF RING SIZE ON THE COMPLEXATION AND DECOMPOSITION OF BENZENEDIAZONIUM ION IN THE PRESENCE OF CROWN ETHERS IN 1,2-DICHLOROETHANE AND THE GAS PHASE

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The host–guest complexation and the kinetics of the thermal dediazoniation of benzenediazonium tetrafluoroborate in the presence of unsubstituted and (di)benzene- and dicyclohexane-substituted crown ethers containing 4–10 oxygen atoms were studied by UV spectrophotometry in 1,2-dichloroethane at 40°C. The complexation equilibrium constants K and the stabilizing ability of the complexation (k_2/k_1) were calculated by a kinetic method. Complexation in the gas phase was observed and characterized by fast atom bombardment mass spectrometry (FAB-MS). All complexing agents except 12-crown-4 formed 1:1 complexes [crown ether–PhN_2]$^+$ under FAB conditions. The complexation caused a hypsochromic shift $\Delta\lambda_{max}$ in the UV spectrum of the benzenediazonium salt, which was largest for hosts containing six oxygen atoms. The thermodynamic and kinetic stability were much greater for insertion-type complexes containing six or more oxygen atoms in the host molecule than for the charge-transfer complexes formed with 15-crown-5. In contrast, 12-crown-4 destabilized benzenediazonium ion owing to the increase in homolytic dediazoniation. 21-Crown-7 was the strongest complexing and stabilizing agent for benzenediazonium ion; with a larger hole size in the host the effects weakened. The effects of benzene and cyclohexane substituents in crown ethers on the thermodynamic and kinetic stability were small compared with the effects of the number of oxygen atoms. © 1997 by John Wiley & Sons, Ltd.

J. Phys. Org. Chem. **10**, 67–75 (1997) No. of Figures: 3 No. of Tables: 4 No. of References: 27
Keywords: benzenediazonium ion; host–guest complexation; dediazoniation; crown ethers; ring size
Received 11 June 1996; accepted 6 September 1996

INTRODUCTION

Macrocyclic polyethers, or crown ethers, have unique chemical properties associated with their ability to form stable host–guest complexes with metal cations such as alkali and alkaline earth ions and with other appropriately sized species.[1–4] In insertion-type complexes the basic oxygen atoms of the crown ether surround the guest, each engaging in an apparently similar electrostatic interaction with it. Host–guest complexation has been investigated with great interest in recent decades, mostly, however, crown ether–metal ion systems, owing to their many possible applications: synthetic chemistry, phase-transfer reactions, enhancement of the solubility and stability of compounds and studies of naturally occurring compounds. A diversity of techniques, including absorption spectrometry, calorimetry, conductometry, kinetic methods, NMR spectrometry and potentiometry, have been used to determine the complexation behaviour in solution.[1–6] In addition, it is observed that fast atom bombardment mass spectrometry (FAB–MS) is a rapid and good method for the characterization of complexation in the gas phase.[7–10]

Arenediazonium salts possess considerable importance in the chemical industry, which has initiated a great number of the studies.[11] According to Bunnett,[12] all reactions, independent of their mechanism, where the two nitrogen atoms of azo or diazo compounds are replaced by any other group, are dediazoniation reactions. The dediazoniation method has broad and versatile applications in synthetic chemistry in the preparation of widely different compounds.[11] Investigations on the host–guest complexation of arenediazonium ions with crown ethers began in 1973 when Gokel and Cram[13] reported that crown ethers of suitable dimensions solubilize arenediazonium ions in non-polar solvents where they otherwise are insoluble and that the complexation changes the ^{1}H NMR spectra of the polyethers. Bartsch *et al*.[14] reported in 1976 that the complexation of 4-*tert*-butylbenzenediazonium tetrafluoroborate with 18-membered crown ethers in 1,2-dichloroethane markedly stabilizes the diazonium salt against thermal dediazoniation. Subsequently many investigations have been published on the host–guest complexation between crown ethers and arenediazonium ions but only a few considered both the thermodynamic and kinetic stability of the com-

CCC 0894–3230/97/020067–09 $17.50

plexes.[5, 6, 15–18] Zollinger *et al.*[6] have studied the dediazoniation of arenediazonium ions complexed with crown ethers in 1,2-dichloroethane using as complexing agents 18-crown-6, 21-crown-7 and dicyclohexano-24-crown-8. We have studied by kinetic and spectroscopic methods, in solution, the complexation of crown ethers (15-crown-5, 18-crown-6 and 21-crown-7) with arenediazonium ions.[5, 15–18] Continuing our studies on the interaction between crown ethers and stable organic cations, we have recently[10, 19] reported the complexation of crown ethers with tropylium ions in solution and in the gas phase under FAB conditions.

With the benzenediazonium ion, whose diazonium group has a cylindrical diameter of about 0·24 nm, 18-crown-6 and 21-crown-7 can form insertion-type complexes[5, 6] (**1**, Figure 1), but 15-crown-5,[17] with its cavity diameter[2] of only 0·17–0·22 nm, forms only much weaker charge-transfer complexes Zollinger *et al.*[6] argued that in the charge-transfer complex the acceptor center of the arenediazonium ion is either the *β-N*-atom and/or the combined π-electron system of the aryl part and the diazonio group, while the donor centers are one or several of the oxygen atoms in the crown ether.

The ring size of the host molecule is an important and widely studied factor for the strength of the host–guest complexation, but more difficult to predict for flexible organic molecules than for ‘rigid’ metal cations. As seen above, the effects of the ring size and substituents of crown ether on the thermodynamic and kinetic stability of the complexes between arenediazonium ions and crown ethers have not been studied systematically. In this work, the effect of ring size on the thermodynamic and kinetic stability of benzenediazonium ion complexed with crown ethers containing 4–10 oxygen atoms was investigated systematically by kinetic and spectroscopic methods in solution and by FAB-MS in the gas phase. It is considered that this complexation is a good model to understand the corresponding host–guest complexation of other organic cations. Since unsubstituted crown ethers with 8–10 oxygen atoms were not available, benzo- and cyclohexano-substituted complexing agents were used instead. The results are compared with the corresponding values obtained for acyclic polyether–PhN$_2^+$ systems.

EXPERIMENTAL

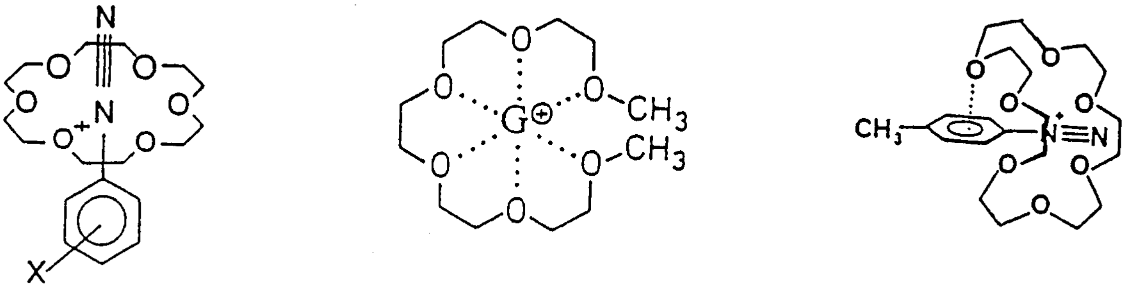
Materials

Benzenediazonium tetrafluoroborate was synthesized previously[5] from aniline by diazotization with sodium nitrite at 0–4 °C in tetrafluoroboric acid aqueous solution and was crystallized before use from about 25% aqueous tetrafluoroboric acid. The unsubstituted crown ethers 12-crown-4 (Fluka), 15-crown-5 (Fluka), 18-crown-6 (Fluka) and 21-crown-7 (Pfaltz & Bauer), the benzene-substituted crown ethers benzo-15-crown-5 (Fluka), benzo-18-crown-6 (Fluka), dibenzo-18-crown-6 (Parish Chemical) and dibenzo-30-crown-10 (Aldrich-Chemie) and the dicyclohexane-substituted compounds dicyclohexano-18-crown-6 (Fluka) and dicyclohexano-24-crown-8 (Fluka) were used without further purification. Dibenzo-24-crown-8 (Fluka) was purified as described previously.[19] 1,2-Dichloroethane (Fluka) was purified, dried, distilled and used as the solvent in all solution measurements.[20]

Apparatus and measurements

The complexes of crown ethers with benzenediazonium tetrafluoroborate and their fragments in the gas phase under FAB conditions were identified on a Kratos MS 80 autoconsole mass spectrometer operating with a DART data system. The atom gun was operated at 8 eV and argon was used as the bombarding gas with pressure of about 1×10^{-6} Torr in the collision region. 3-Nitrobenzyl alcohol (NBA) was earlier shown, owing to its electron-scavenging nature, to be the best solvent for the FAB experiments.[10] NBA was also used as the liquid matrix in this study. The stainless-steel tip of the FAB probe was coated with a thin layer of a mixture of benzenediazonium salt, crown ether ([crown ether]$\approx$[PhN$_2^+$]) and the matrix NBA. The spectrum was recorded immediately after the sample had been inserted.

UV spectra were recorded with a Shimadzu UV 160 A or



1 **2** **3**

Figure 1. Structures of the insertion-type complex of 18-crown-6 (**1**), the ‘pseudo-insertion-type’ complex of pentaglyme (**2**) and the modified insertion-type complex[17] of 21-crown-7 including σ-base–π-acid interactions (**3**)

Philips PU 8740 spectrophotometer. Kinetic measurements were carried out with a Shimadzu UV 160 A spectrophotometer, a double-beam apparatus. The cells were held at 40·0 ± 0·1 °C by circulating water from an electrically thermostated water bath into the self-constructed temperature attachment. 1,2-Dichloroethane was used as a reference in studies of unsubstituted and dicyclohexano-substituted crown ethers. Because benzo-substituted crown ethers are UV absorbing, a similar concentration of the host compound was used in the two cells in the investigations of benzo- and dibenzo-substituted crown ethers in solution. After thermostating, about 10 values of the absorbance A_t were read at suitable time intervals up to about two half-lives. The observed rate constant of the decomposition k_{obs} was calculated by plotting the values of $\ln(A_t - A_\infty)$ vs time t. The absorbance after the reaction A_∞ was determined by reading the absorbance after about 10 half-lives. All reactions investigated were found to obey first-order kinetics within the intervals studied: the standard deviation for k_{obs} was usually 0·5–2·0% and the correlation constant r was about 0·9997.

Small amounts of crown ethers and benzenediazonium salt were weighed with a Perkin-Elmer AD-2 autobalance.

RESULTS

Complexation in the gas phase under FAB conditions

FAB-MS has proved to be a rapid and good method for studying the host–guest complexation of crown ethers, acyclic polyethers and glymes with benzenediazonium ion and the fragmentation of the complexes in the gas phase.[7–9] The same method was used in this work for the observation and characterization of the host–guest complexation between crown ethers containing 4–10 oxygen atoms and benzenediazonium ion. The mass spectrum of benzenediazonium tetrafluoroborate in the presence of 15-crown-5 was recently presented in connection with our investigations of polyether–tropylium ion systems.[10] In the present work, the FAB mass spectrum of 15-crown-5–benzenediazonium ion ($15C5–PhN_2^+$) showed an abundant PhN_2^+ ion (*m/z* 105), the two cation–one anion cluster $(PhN_2^+)_2BF_4^-$ (*m/z* 297) and the 1:1 complex $[15C5–PhN_2]^+$ (*m/z* 325). Data on the partial positive ion FAB mass spectra are presented in Table 1. It is widely assumed that insertion-type complexation (IC) is the only type of complexation occurring between crown ethers and arenediazonium ions.[1, 21] Our FAB results, in good accordance with kinetic measurements,[17] have shown, however, that 15-membered crown ethers, whose cavity diameter[2] of 0·17–0·22 nm is too small for an insertion-type complex with the diazonium group, form charge-transfer 1:1 complexes (CT) with benzenediazonium ion, the diazonium group of which has a cylindrical diameter of about 0·24 nm. It is interesting that the peak of the ion $[12C4–PhN_2]^+$ was not detected in the mass spectrum, which means that complexation between 12-crown-4 and benzenediazonium ion under FAB conditions is at the most very weak. For all crown ethers, in agreement with an earlier investigation,[10] the fragmentation pattern consisted of a series of losses of protonated $(C_2H_4O)_n$ structural units and thus the fragmentation ions consistently observed

Table 1. Partial positive ion FAB mass spectra of benzenediazonium tetrafluoroborate in the presence of crown ethers,[a] $[PhN_2^+]_{total} \approx [\text{crown ether}]_{total}$

Crown ether[b]	Ion (*m/z*) with relative abundance (%) in parentheses
15-Crown-5 (15C5)	105 (100) PhN_2^+; 221 (59) $[15C5]^+$; 297 (4·2) $(PhN_2^+)_2BF_4^-$; 325 (9) $[15C5\text{-}PhN_2]^+$
Benzo-15-crown-5 (B15C5)	105 (100) PhN_2^+; 268 (84) $[B15C5]^+$; 297 (1·9) $(PhN_2^+)_2BF_4^-$; 373 (2·9) $[B15C5\text{-}PhN_2]^+$
18-Crown-6 (18C6)	105 (100) PhN_2^+; 265 (0) $[18C6]^+$; 297 (16) $(PhN_2^+)_2BF_4^-$; 369 (13) $[18C6–PhN_2]^+$
Benzo-18-crown-6 (B18C6)	105 (100) PhN_2^+; 297 (3·1) $(PhN_2^+)_2BF_4^-$; 312 (7·1) $[B18C6]^+$; 417 (6·3) $[B18C6–PhN_2]^+$
Dibenzo-18-crown-6 (DB18C6)	105 (100) PhN_2^+; 297 (8·1) $(PhN_2^+)_2BF_4^-$; 360 (12) $[DB18C6]^+$; 465 (2·0) $[DB18C6–PhN_2]^+$
Dicyclohexano-18-crown-6 (DCH18C6)	105 (100) PhN_2^+; 297 (3·6) $(PhN_2^+)_2BF_4^-$; 373 (1·5) $[DCH18C6]^+$; 477 (1·8) $[DCH18C6–PhN_2]^+$
21-Crown-7 (21C7)	105 (100) PhN_2^+; 297 (22) $(PhN_2^+)_2BF_4^-$; 309 (0) $[21C7]^+$; 413 (12) $[21C7–PhN_2]^+$
Dibenzo-24-crown-8 (DB24C8)	105 (100) PhN_2^+; 297 (4·3) $(PhN_2^+)_2BF_4^-$; 448 (4·5) $[DB24C8]^+$; 554 (2·7) $[DB24C8–PhN_2]^+$
Dicyclohexano-24-crown-8 (DCH24C8)	105 (100) PhN_2^+; 297 (1·0) $(PhN_2^+)_2BF_4^-$; 461 (0) $[DCH24C8]^+$; 565 (4·0) $[DCH24C8–PhN_2]^+$
Dibenzo-30-crown-10 (DB30C10)	105 (100) PhN_2^+; 297 (2·9) $(PhN_2^+)_2BF_4^-$; 537 (5·2) $[DB30C10]^+$; 642 (1·7) $[DB30C10\text{-}PhN_2]^+$

[a] Fragmentations of crown ether and benzenediazonium ions are omitted; see Results.
[b] In the presence of 12-crown-4 the peak of $[12C4–PhN_2]^+$ at *m/z* 281 was not detected.

included m/z 45, 89, 133, etc., depending on the size of the initial parent ion. In addition, the ion $[PhOC_2H_4O]^+$ at $m/z = 136$ is typical in the FAB mass spectra of benzene-substituted crown ethers.

Kinetic data

The stabilizing effect of the complexation of benzenediazonium tetrafluoroborate with the crown ethers 12-crown-4, benzo-18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6, dibenzo-24-crown-8, dicyclohexano-24-crown-8 and dibenzo-30-crown-10 in 1,2-dichloroethane at 40 °C was studied by UV spectrophotometry. The corresponding effects in the presence of 15-crown-5, 18-crown-6 and 21-crown-7 have been reported.[6, 17] Measurements were made of the uncomplexed benzenediazonium salt and of the salt in the presence of at least five host concentrations, where the total concentration of the salt was kept constant: $[PhN_2^+]_{total} = 1{\cdot}0\times 10^{-4}$ M. The kinetic data are presented in Table 2. In the presence of benzo-substituted crown ethers the value of λ_{max} for benzenediazonium ion cannot be determined exactly, owing to the absorption of the benzene ring (see Apparatus and measurements) and therefore any values of λ_{max} are not included in Table 2. All measurements showed, however, that the complexation causes a hypsochromic shift in the UV spectrum of benzenediazonium salt, e.g. in the presence of 0, $1{\cdot}54\times 10^{-4}$, $2{\cdot}02\times 10^{-4}$, $4{\cdot}04\times 10^{-4}$ and $1{\cdot}13\times 10^{-3}$ M dicyclohexano-18-crown-6 the values of λ_{max} for benzenediazonium tetrafluoroborate in 1,2-dichloroethane were 266, 250, 248, 247 and 247 nm, respectively.

Calculation of thermodynamic and kinetic stability

The complexation and decomposition reactions of benzenediazonium salt in the presence of a crown ether or any other complexing agent in solution can be interpreted by the equation

$$\begin{array}{ccc} PhN_2^+BF_4^- + \text{crown ether} & \overset{K}{\rightleftharpoons} & \text{complex} \\ \downarrow k_1 & & \downarrow k_2 \\ \text{products} & & \text{products} \end{array} \qquad (1)$$

where ‘complex’ denotes a 1:1 complex (insertion or charge-transfer complex), k_1 and k_2 are the rate constants for the thermal decomposition of the uncomplexed and complexed benzenediazonium ion, respectively, and K is the complexation equilibrium constant.[5, 6, 15–18] The complexation and decomposition reactions are very fast, the complexation process being in effect diffusion controlled.[1, 6] When the decomposition of the complex cannot be ignored, the values of K and $k_1 - k_2$ can be calculated from the kinetic data by iteration method using the equations

$$\frac{1}{k_1 - k_{obs}} = \frac{1}{(k_1 - k_2)K} \times \frac{1}{[\text{crown}]} + \frac{1}{k_1 - k_2} \qquad (2)$$

$$K = [\text{complex}]/([PhN_2^+]\,[\text{crown}]) \qquad (3)$$

$$[PhN_2^+] = [PhN_2^+]_{total} - [\text{complex}] \qquad (4)$$

$$[\text{crown}] = [\text{crown}]_{total} - [\text{complex}] \qquad (5)$$

$$[\text{complex}] = (\text{sum} - \surd(\text{sum}^2 - 4[PhN_2^+][\text{crown}]))/2 \qquad (6)$$

Table 2. Effect of complexation on the thermal decomposition of benzenediazonium tetrafluoroborate ($[PhN_2^+] = 1{\cdot}0\times 10^{-4}$ M) in the presence of crown ethers in 1,2-dichloroethane at 40 °C

Crown ether	[Crown] (M)	k_{obs} (s^{-1})	[Crown] (M)	k_{obs} (s^{-1})
12-Crown-4	0	$3{\cdot}10\times 10^{-4}$	$1{\cdot}55\times 10^{-3}$	$3{\cdot}09\times 10^{-4}$
	$6{\cdot}58\times 10^{-3}$	$3{\cdot}80\times 10^{-4}$	$1{\cdot}32\times 10^{-2}$	$4{\cdot}58\times 10^{-4}$
	$2{\cdot}47\times 10^{-2}$	$5{\cdot}36\times 10^{-4}$	$4{\cdot}00\times 10^{-2}$	$5{\cdot}82\times 10^{-4}$
Benzo-18-crown-6	$1{\cdot}23\times 10^{-4}$	$1{\cdot}15\times 10^{-4}$	$2{\cdot}01\times 10^{-4}$	$7{\cdot}13\times 10^{-5}$
	$4{\cdot}02\times 10^{-4}$	$3{\cdot}42\times 10^{-5}$	$6{\cdot}55\times 10^{-4}$	$2{\cdot}66\times 10^{-5}$
	$9{\cdot}83\times 10^{-4}$	$1{\cdot}79\times 10^{-5}$		
Dibenzo-18-crown-6	$1{\cdot}51\times 10^{-4}$	$1{\cdot}23\times 10^{-4}$	$2{\cdot}02\times 10^{-4}$	$1{\cdot}00\times 10^{-4}$
	$4{\cdot}04\times 10^{-4}$	$5{\cdot}85\times 10^{-5}$	$6{\cdot}55\times 10^{-4}$	$4{\cdot}13\times 10^{-5}$
	$1{\cdot}13\times 10^{-3}$	$2{\cdot}35\times 10^{-5}$		
Dicyclohexano-18-crown-6	$1{\cdot}54\times 10^{-4}$	$7{\cdot}78\times 10^{-5}$	$2{\cdot}02\times 10^{-4}$	$5{\cdot}43\times 10^{-5}$
	$4{\cdot}05\times 10^{-4}$	$2{\cdot}50\times 10^{-5}$	$6{\cdot}06\times 10^{-4}$	$1{\cdot}93\times 10^{-5}$
	$1{\cdot}00\times 10^{-3}$	$1{\cdot}36\times 10^{-5}$		
Dibenzo-24-crown-8	$1{\cdot}24\times 10^{-4}$	$8{\cdot}30\times 10^{-5}$	$1{\cdot}85\times 10^{-4}$	$5{\cdot}23\times 10^{-5}$
	$3{\cdot}71\times 10^{-4}$	$2{\cdot}42\times 10^{-5}$	$6{\cdot}66\times 10^{-4}$	$1{\cdot}28\times 10^{-5}$
	$9{\cdot}99\times 10^{-4}$	$1{\cdot}03\times 10^{-5}$		
Dicyclohexano-24-crown-8	$1{\cdot}46\times 10^{-4}$	$7{\cdot}45\times 10^{-5}$	$2{\cdot}19\times 10^{-4}$	$4{\cdot}76\times 10^{-5}$
	$4{\cdot}37\times 10^{-4}$	$2{\cdot}99\times 10^{-5}$	$6{\cdot}56\times 10^{-4}$	$2{\cdot}49\times 10^{-5}$
	$1{\cdot}11\times 10^{-3}$	$2{\cdot}00\times 10^{-5}$		
Dibenzo-30-crown-10	$1{\cdot}51\times 10^{-4}$	$1{\cdot}43\times 10^{-4}$	$2{\cdot}26\times 10^{-4}$	$1{\cdot}10\times 10^{-4}$
	$4{\cdot}53\times 10^{-4}$	$7{\cdot}37\times 10^{-5}$	$7{\cdot}05\times 10^{-4}$	$5{\cdot}98\times 10^{-5}$
	$1{\cdot}00\times 10^{-3}$	$3{\cdot}71\times 10^{-5}$		

where sum $= [PhN_2^+]_{total} + [crown]_{total} + 1/K$ and k_{obs} is the dediazoniation rate constant observed in the presence of the free crown ether [crown]. If the complex is unreactive, or $k_1 \gg k_2$, the value of K can be calculated much easier from

$$K = \frac{k_1 - \mathrm{k_{obs}}}{k_{obs}[\mathrm{crown}]} \qquad (7)$$

For all systems we used equations (2)–(6). The dediazoniation reactions, for which the complexation has a stabilizing effect (cf. 12-crown-4), obeyed equation (2) with a correlation coefficient $r \approx 0{\cdot}998$. Table 3 presents the calculated values of K (thermodynamic stability) and k_2/k_1, a measure of the effect of complexation on the kinetic stability of benzenediazonium ion, together with the values of the maximum hypsochromic shift in the UV spectrum, $\Delta\lambda_{max}$.

DISCUSSION

The kinetic and spectroscopic measurements and product analyses in this and earlier studies[5–8, 13–18, 21] in solution and in the gas phase show that crown ethers form host–guest complexes with arenediazonium ions. In the presence of a crown ether with at least an 18-membered ring, the complex is of insertion type (IC) (**1**, Figure 1), while the smaller hosts form weaker charge-transfer (CT) complexes. The complexation causes a hypsochromic shift in the UV spectrum of arenediazonium salt in solution and causes an unusual positive stretching frequency shift $\Delta\nu_{NN}$ in its IR spectrum; it also increases the thermal stability of the salt in solution, though not in the solid state.[6, 17, 18, 21, 22] The complex [crown ether–PhN_2]$^+$ can be detected under FAB conditions when the number of the oxygen atoms is five or more, whereas the complex [acrylic polyether–PhN_2]$^+$ can be detected when the number of oxygen atoms is only four. This difference can be assumed to be due to the greater flexibility of the acyclic polyether than the corresponding crown ether by allowing more optimized geomeries of the electrostatic bonds. In contrast, the insertion-type complexes are much stronger than those of the corresponding acyclic polyethers, even though acyclic polyethers form pseudo-cyclic complexes (**2**, Figure 1), when the chain of the acyclic polyether, PEG or glyme, is long enough to wrap fully around the diazonium group (thermodynamic and kinetic macrocyclic effects, see below). Maleknia and Brodbelt[23] found that the trends observed in the gas phase between crown ethers and alkaline metal ions closely parallel those seen in non-polar solvents. The results for complexation between crown ethers and arenediazonium ions are in good accordance with this observation.

12-Crown-4 does not form a stabilizing charge-transfer complex with benzenediazonium ion in solution and the peak of the ion [12C4–PhN_2]$^+$ cannot be detected by FAB-MS. Indeed, the rate of decomposition increases with the concentration of 12-crown-4 in 1,2-dichloroethane. Under comparable conditions, homolytic decomposition reactions are faster than the corresponding heterolysis reactions, and thus the increasing destabilization with increasing concentration of 12-crown-4 can be explained as being due to the increase in homolysis (see Scheme 1).[6, 18]

In accordance with Laali and Lattimer's[8] observation, and in contrast to crown ether–metal ion systems, sandwich complexes[1, 7] were not detected by FAB-MS; only 1:1 complexes were observed under FAB conditions. Using field desorption mass spectrometry (FD-MS), Laali and Lattimer[8] also observed the 2:1 complex [(18-crown-6)$_2$–PhN_2]$^+$ (m/z 633). The results in Table 1 suggest that in the gas phase, in the absence of the complicating effects of solvation and counterion, benzo and cyclohexano sub-

Table 3. Complexation and decomposition of benzenediazonium tetrafluoroborate with crown ethers in 1,2-dichloroethane at 40 °C

Crown ether	K (M^{-1})[a]	k_2/k_1 (%)[b]	$\Delta\lambda_{max}$ (nm)[b, c]
12-Crown-4	–[d]	–[d]	2
15-Crown-5[e]	$(1{\cdot}4 \pm 0{\cdot}2) \times 10^2$	26	17
18-Crown-6[f]	$4{\cdot}7 \times 10^4$	1·4	19
Benzo-18-crown-6	$(3{\cdot}1 \pm 0{\cdot}1) \times 10^4$	2·6	–[g]
Dibenzo-18-crown-6	$(1{\cdot}9 \pm 0{\cdot}1) \times 10^4$	4·7	–[g]
Dicyclohexano-18-crown-6	$(4{\cdot}2 \pm 0{\cdot}2) \times 10^4$	1·5	19
21-Crown-7[f]	$5{\cdot}1 \times 10^5$	0·1	14
Dibenzo-24-crown-8	$(5{\cdot}8 \pm 0{\cdot}2) \times 10^4$	1·8	–[g]
Dicyclohexano-24-crown-8	$(6{\cdot}2 \pm 0{\cdot}2) \times 10^4$	5·1	13
Dibenzo-30-crown-10	$(1{\cdot}6 \pm 0{\cdot}1) \times 10^4$	9·1	g

[a] Calculated by equation (2).
[b] $k_1 = 3{\cdot}10 \times 10^{-4}\ s^{-1}$ and $\lambda_{max} = 266$ nm for the uncomplexed ion.
[c] The maximum hypsochromic shift due to the complexation.
[d] Could not be determined by the kinetic method owing to the increase in homolysis.
[e] From Ref. 9.
[f] From Ref. 6; tested also in this work.
[g] Not determined owing to the absorption of the host.

stituents decrease the complexation, i.e. the intensity of [crown ether–PhN_2]$^+$. These bulky groups reduce the flexibility of crown ethers to allow more optimized geometries of the electrostatic bonds. In addition, the electron-withdrawing power of the benzene group(s) weakens the electron-donor ability of the oxygen atoms.[3] It was observed recently[9] that the host–guest complexation between an acyclic polyether and the benzenediazonium ion in the gas phase, in contrast to the effects in solution, does not increase with increasing number of oxygen atoms in the polyether chain. Correspondingly, and in contrast with the strength of the complexation in solution (see below), the values of the relative abundances of the complexes [18-crown-6–PhN_2]$^+$ and [21-crown-7–PhN_2]$^+$, 13% and 12% in Table 1, respectively, were closely similar.

In agreement with Zollinger *et al.*'s results,[6] but in contrast with the effects of complexation on the thermodynamic and kinetic stabilities (K and k_2/k_1 values, see below), the complexation with 18-crown-6 was recently[5] found to produce, in all solvents studied, the maximum hypsochromic shift $\Delta\lambda_{max}$ in the UV spectrum. Zollinger *et al.* noted that no conclusions regarding the kinetic or thermodynamic stability of the host–guest complexation of arenediazonium ion with crown ethers can be drawn from the spectroscopic data. Leaving aside the benzo-substituted crown ethers, since they themselves exhibit strong UV absorption, the results in Table 3 suggest for $\Delta\lambda_{max}$ of the crown ether–PhN_2^+ system in 1,2-dichloroethane the order 18-crown-6 ≈ dicyclohexano-18-crown-6 > 15-crown-5 > 21-crown-7 ≈ dicyclohexano-24-crown-8 ≫ 12-crown-4.

Excluding 12-crown-4 ($\Delta\lambda_{max} = 2$ nm), the changes of 13–19 nm in $\Delta\lambda_{max}$ in 1,2-dichloroethane show that the maximum hypsochromic shift is not sensitive to the ring size of crown ether. For the acyclic polyether–PhN_2^+ system the corresponding hypsochromic shift in 1,2-dichloroethane is smallest for the smallest complexing agents but independent of the host ($\Delta\lambda_{max} = 13 \pm 1$ nm) when the polyether chain is long enough to wrap fully around the diazonium group (see structure **2**, Figure 1).[9]

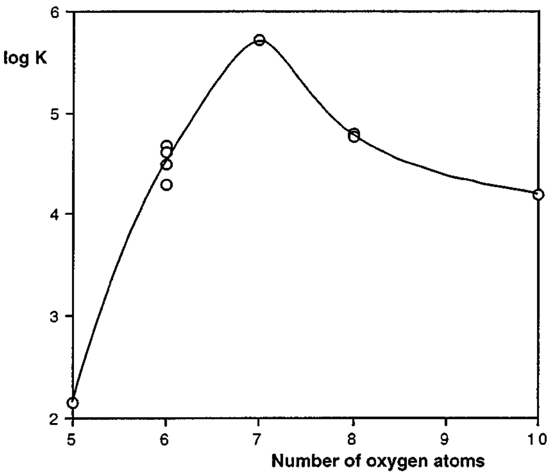


Figure 2. Effect of the number of oxygen atoms of unsubstituted and benzo-(mono- or di-) and dicyclohexano-substituted crown ethers on the thermodynamic stability of the complexed benzenediazonium ion in 1,2-dichloroethane

The K values in Table 3 and Figure 2 show that the thermodynamic stability of benzenediazonium ion complexed with crown ether in solution varies markedly with the ring size of the host but relatively little with the benzo or cyclohexano substituent(s) of the host molecule. The K values of the IC complexes containing six or more oxygen atoms in the host are clearly larger than those of CT complexes of hosts containing five or less oxygen atoms. It might be assumed that the cavity of 21-crown-7, with its diameter[2] of 0·34–0·43 nm is slightly too large for the diazonium group, which has a cylindrical diameter of about 0·24 nm. However, the greater ring flexibility, compared with 18-crown-6 with its cavity diameter[2] of 0·26–0·32 nm, may allow for the relief of steric interactions between the macrocyclic ring and the 2-hydrogens or other 2-substituents[18] in the arenediazonium cation. On the basis of their examination of C–P–K molecular structures, Beadle *et al.*[21] suggested that an important difference between 18-crown-6 and 21-crown-7 is the inability of the latter to assume the planar D_{3d} conformation, which is well documented for 18-crown-6 and its derivatives. It seems reasonable to assume that one of the CH_2—O—CH_2 units in 21-crown-7 will turn upwards and away from the mean plane of the other oxygen atoms, or else inwards over the benzene ring, as shown in the modified insertion-type complex structure **3** (Figure 1)[8, 21] with σ-base–π-acid interactions. Both modified IC structures will present to the diazonium group a cavity of essentially the same size as that found in 18-crown-6, but the extra oxygen donor atom of 21-crown-7 can now interact with other electrophilic center to provide additional stabilization to the overall complex. Correspondingly, the larger crown ethers can be suggested to be capable in solution of wrapping around the cation to form a three-dimensional cavity with all oxygen atoms coordinated to the cation.[3] The relatively large K values found for the complexation between 24- and 30-membered crown ethers and benzenediazonium ion in this work (see Fig. 2) are in good accord with this suggestion.

With the presence of benzene or cyclohexano groups in crown ethers, there is a small reduction in the K value. Our results for 18-membered crown ethers in Table 3 and Fig. 2 show that the effect of benzo and cyclohexano substituents on the thermodynamic stability of crown ether-complexed benzenediazonium ion in solution is relatively small, but the following order is suggested: 18-crown-6 ≈ dicyclohexano-18-crown-6 > benzo-18-crown-6 > dibenzo-18-crown-6. The effect of these groups on the K value may be attributed to a combination of ligand bulkiness leading to the isolation of the cation from the solvent molecules, which strengthens the thermodynamic stability of a complex, and the electron-withdrawing power of the benzene group(s), which weakens the electron-donor ability of the oxygen atoms. The aliphatic cyclohexano substituents do not alter the binding properties to any measurable extent.[3] In addition, the benzene and cyclohexano groups reduce the flexibility of crown ethers. It is interesting that the K value for the complexation of the more flexible acyclic polyethers (PEGs and glymes) with benzenediazonium ion increases with increasing number of oxygen atoms over the whole range studied, up to PEG 2000 with about 45 oxygen atoms.[9]

Table 3 shows, in accordance with earlier work,[5, 6, 17] that 21-crown-7 is a very strong stabilizing agent ($k_2/k_1 = 0{\cdot}1\%$) in 1,2-dichloroethane, and clearly the best stabilizing crown ether against the thermal decomposition of benzenediazonium ion in all solvents studied. The stabilizing effect is much weaker for 15-crown-5, which forms a CT complex with benzenediazonium ion, than it is for crown ethers forming IC complexes, but it seems to be weaker still for the large host dibenzo-30-crown-10 ($k_2/k_1 = 9\%$ in 1,2-dichloroethane). The kinetic stability of benzenediazonium ion complexed with 18-membered crown ethers seems to obey a similar order to the thermodynamic stability K given above. We observed recently[9] that, in the presence of flexible acyclic polyethers, the value of k_2/k_1 is more or less independent of the acyclic polyether: $k_2/k_1 = 17 \pm 4\%$, when the host molecule is long enough to wrap fully around the cation (**2**).

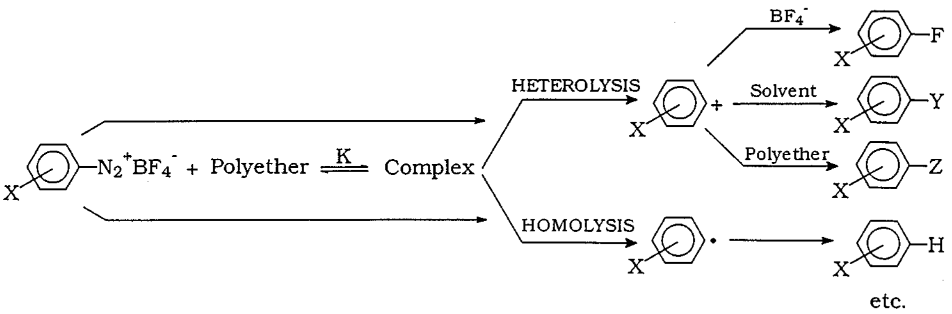
The increased stability, thermodynamic or kinetic, observed for a complex with a cyclic host over that with an open chain of similar composition is called the macrocyclic effect. The calculated values of the thermodynamic and kinetic macrocyclic effects, presented in Table 4, vary widely with the number of oxygen atoms ($n = 4$–10), both being clearly largest for the host containing seven oxygen atoms. The variation can be explained by the greater flexibility of the long chains of the acyclic polyethers. It is interesting that the values of the corresponding thermodynamic and kinetic macrocyclic effects are clearly similar, even though thermodynamic and kinetic stability depend on different factors: the K value on differences in the Gibbs free energy between the solvated products and the corresponding initial state [$\Delta G° = RT\ln(K/\mathrm{M}^{-1})$] and the k value on differences between the solvated transition and initial state. The greater stability of complexes formed by ions in solution with multidentate ligands than with the corresponding monodentate ligands is called the chelate effect. The chelate effect has been concluded to be an entropy effect.[24] Depending on the system studied, enthalpic and/or entropic origins have been identified for the thermodynamic macrocyclic effect.[1–4, 25] Izatt *et al.*[26] studied by calorimetric titration the complexation of arenediazonium ions with 18-crown-6 in methanol and observed that these complexes are enthalpy stabilized: for 18-crown-8–PhN$_2^+$ $K = 3{\cdot}2 \times 10^2\ \mathrm{M}^{-1}$, $\Delta H° = -35{\cdot}2\ \mathrm{kJ\ mol}^{-1}$ and $T\Delta S° = -20{\cdot}9\ \mathrm{kJ\ mol}^{-1}$ at 25 °C. The thermodynamic macrocyclic effect has been shown in the literature to be depend on a number of factors, including the host and its size, the number and type of donor atoms, the guest and the solvent.

It has been observed earlier[7, 17] that the activation volume $\Delta V^{\ddagger}$ for the decomposition of benzenediazonium ion complexed with crown ether or acyclic polyether is very large and shows no measurable variation with complexing agents capable of forming IC complexes (**1**) or pseudocyclic complexes (**2**): $\Delta V^{\ddagger} > 15\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ in 1,2-dichloroethane. By comparison, the corresponding value for the uncomplexed ion is much lower, $\Delta V^{\ddagger} = 8{\cdot}4\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$. The changes in polarity during the decomposition step of the uncomplexed and complexed benzenediazonium ion can be assumed to be small and thus the large positive $\Delta V^{\ddagger}$ values for dediazoniation reactions are strong evidence for an S_N1-like reaction mechanism as proposed by Swain *et al.*[27] Correspondingly, the values of the activation enthalpy $\Delta H^{\ddagger}$ and the activation entropy $\Delta S^{\ddagger}$ for the decomposition of the complexed ion are large, and clearly larger than the corresponding values for the dediazoniation of the uncomplexed ion, and suggest an isokinetic relationship for the heterolytic decomposition of an uncomplexed arenediazonium ion and one complexed with crown ethers or acyclic polyethers in various solvents.[16–18] The values of $\Delta H^{\ddagger}$ are much larger than the values of $T\Delta S^{\ddagger}$, e.g. for 18-crown-8–PhN$_2^+$ in 1,2-dichloroethane at 25 °C $\Delta H^{\ddagger} = 157\ \mathrm{kJ\ mol}^{-1}$ and $T\Delta S^{\ddagger} = 46\ \mathrm{kJ\ mol}^{-1}$. The mechanism of the decomposition of complexed benzenediazonium ion in solution is not

Table 4. Effect of the number of oxygen atoms in the host molecule on the thermodynamic and kinetic macrocyclic effect for the polyether–PhN$_2^+$ system in 1,2-dichloroethane

	Number of oxygen atoms					
	4	5	6	7	8	10
Thermodynamic macrocyclic effect[a, b]	$\ll 1$	1	90	316	31[c]	6[c]
Kinetic macrocyclic effect[b, d]	$\ll 1$	2	19	130	3[e]	2[f]

[a] Ratio of the values of K(crown ether–PhN$_2^+$) and K(polyethylene glycol–PhN$_2^+$).
[b] Values for acyclic polyethers from Ref. 13.
[c] K(polyethylene glycol–PhN$_2^+$) is estimated from the values in Ref. 13.
[d] Ratio of k_2/k_1(polyethylene glycol–PhN$_2^+$) to k_2/k_1(crown ether–PhN$_2^+$).
[e] Calculated for dicyclohexano-24-crown-8.
[f] Calculated for dibenzo-30-crown-10.



Scheme 1

known in detail. Zollinger *et al.*[6] have suggested that all decomposition reactions of arenediazonium salts complexed with crown ethers occur via a CT complex, not directly from the unreactive IC complex, and that there is a fast equilibrium between these two types of complexes and the uncomplexed ion.

In accordance with earlier investigations by kinetic and spectroscopic measurements and product analyses by GC and/or GC-MS,[5, 6, 9, 15–18, 21, 22] the present study supports the conclusions that the thermal dediazoniation of arenediazonium salt in the presence of cyclic or acyclic polyether in solution occurs by an S_N-like reaction mechanism[27] (Scheme 1) via two competing but independent pathways, with the formation of a highly reactive aryl cation in the heterolysis and/or an aryl radical in the homolysis in the slow rate-determining decomposition step of the uncomplexed ion or the complex. Subsequent fast product-determining reactions with nucleophiles counterion, solvent and polyether give the products XC_6H_4F, XC_6H_4Y and XC_6H_4Z, respectively, presented in Scheme 1, where X is the substituent of the benzenediazonium ion. The main products of the thermal decomposition of arenediazonium tetrafluoroborate in 1,2-dichloroethane in the absence or presence of polyethers are shown to be fluoroarene XC_6H_4F and chloroarene XC_6H_4Cl from heterolysis as well as arene from homolysis.[5, 6, 16] A general host–guest complexation process is suggested to include a sequence of steps involving both desolvation reactions and preorganization of the host:

$$\begin{aligned} G^+_{solv} + H_{solv} &\rightleftharpoons G^+_{solv} \ldots H \rightleftharpoons (G^+ \ldots H)_{solv} \\ &\rightleftharpoons (GH)^+_{solv} \rightleftharpoons (\text{complex})_{solv} \qquad (8) \end{aligned}$$

where G^+_{solv} and H_{solv} are the solvated guest and host, H is a free host, $G^+_{solv} \ldots H$ is a solvent-separated cation–host pair, $(G^+ \ldots H)_{solv}$ is a solvated contact pair and $(GH)^+_{solv}$ is the solvated complex before the preorganization step of the host molecule around the cation to form the final solvated complex, $(\text{complex})_{solv}$.[3] The first step is a fast desolvation of the host molecule and the second a diffusion-controlled bimolecular collision reaction where solvent molecules around the guest ion are replaced by donor atoms of the host molecule. It is generally proposed that, in a solvent of low polarity and basicity, preorganization of the macrocyclic ligand rather than cation desolvation is the rate-determining step in the host–guest complexation process.[3]

ACKNOWLEDGEMENT

The author is grateful to Mrs. Päivi Joensuu for the mass spectra.

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