

Complexation and Decomposition of Benzenediazonium Tetrafluoroborate in the Presence of Acyclic Polyethers in 1,2-Dichloroethane and in the Gas Phase

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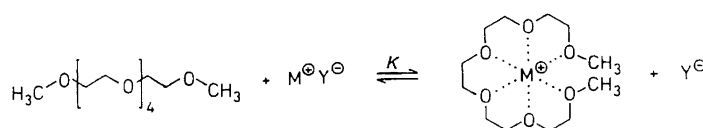
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The complexation and the kinetics of the thermal decomposition of benzenediazonium tetrafluoroborate in the presence of short polyethylene glycols $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ($n \leq 6$) and their dimethyl ethers (or glymes) $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n \leq 5$) have been studied by UV spectrometry in 1,2-dichloroethane. The complexation in the gas phase was observed and characterized by fast atom bombardment mass spectrometry (FAB MS).

The complexation increased the thermal stability of the benzenediazonium ion in 1,2-dichloroethane and caused a hypsochromic shift $\Delta\lambda_{\text{max}}$ in the UV spectrum of the benzenediazonium salt. The complexation equilibrium constant K and the stabilization ability of the complexation k_2/k_1 were calculated by a kinetic method. The values of $\Delta\lambda_{\text{max}}$ and k_2/k_1 were the smallest for the smallest complexing agents but were largely independent of the host when the chain was long enough fully to wrap the polyether chain around the diazonium group. The value of K clearly increased with the number of oxygen atoms and, in accordance with earlier results, linearly when the host was capable of being fully wrapped around the guest. Macrocyclic thermodynamic and kinetic effects were determined. In the gas phase, in the absence of the complicating effect of solvation, the peak of the 1:1 complex $[\text{polyether}-\text{PhN}_2]^+$ did not increase with the number of oxygen atoms. The complexes in the FAB mass spectra were not observed unless the number of oxygen atoms was at least four.

Over the last quarter of a century the host–guest complexation of macrocyclic polyethers, the crown ethers, has been extensively investigated and numerous books and reviews have been published on their synthesis, binding phenomena, complex structures and applications.^{1–5} Macrocyclic polyethers have been successfully used for diverse processes, such as separation of ions by transport through artificial and natural membranes, liquid–liquid or solid–liquid phase-transfer reactions, synthetic applications, dissolution of metal and organic salts in apolar solvents, preparation of ion-selective electrodes, isotope separations, and for the understanding of certain natural processes through mimicry of metalloenzymes.

Though much less studied, the complexation of acyclic polyethers is of considerable interest because macrocyclic polyethers can be synthesised through the complexation of metal cations with acyclic polyethers of the appropriate size in concentrated solution.^{3–5} Acyclic polyethers are flexible molecules. The preorganization that occurs during the fast complexation process, presented for penta-glyme in Scheme 1, is now widely known as the template effect.⁵ The cavity of the open-chain polyether, the podand, is built up during the complexation process. While the outside of the cationic complexes is lipophilic, the cations are held inside the hydrophilic cavity of the organic host component. Yet another source of interest in



Scheme 1.

acyclic polyethers is that it may be possible to use commercially available and inexpensive polyethylene glycols (PEGs) instead of expensive crown ethers as solubilizing agents and phase-transfer catalysts in the synthesis of arenediazonium salts in solvents of low polarity.⁶ The complexing ability of acyclic polyethers, whose complexation equilibrium constants K are about 10^2 – 10^4 M^{-1} , is much weaker than that of the corresponding cyclic crown ethers with K values about 10^4 – 10^5 M^{-1} . Not surprisingly, then, in contrast with crown ethers, there are no books or wide reviews dealing exclusively with the complexation of acyclic polyethers, but rather these compounds are considered in conjunction with the crown ethers.^{3–5}

Numerous experimental techniques have been used to determine complexation behaviour in solution, including absorption spectroscopy, calorimetry, conductimetry, potentiometry, NMR spectroscopy, ion-selective electrodes and kinetic methods.^{1–9} Fast atom bombardment mass spectrometry (FAB MS) offers a rapid method for screening host–guest complexation in the gas phase.^{9,10} We have recently⁹ observed and characterized by the FAB MS technique the strong 1:1 complex [18-crown-6–PhN₂]⁺ and the weak 1:1 complex [pentaglyme–PhN₂]⁺ and very recently,¹⁰ the weak complexes formed between tropylium or 4-methoxyphenyltropylium ion and crown ethers [crown ether–Tr]⁺ or acyclic polyethers [acyclic polyether–Tr]⁺. Complexation of polyethers with tropylium salts has not previously been reported.

The complexation of arenediazonium ions by acyclic polyethers has received relatively little attention.^{6–9,11,12} Using as host component a long polyether (pentaglyme; PEG 2000), for which full wrapping of the polyether chain around the diazonium group is possible (cf., Scheme 1), we have earlier investigated the effects of the chain length of the polyether, the character of the substituent of the arenediazonium ion and the polarity of the solvent on the thermodynamic and kinetic stability of the complex. In addition, some values of the activation parameters ΔH^\ddagger , ΔS^\ddagger and ΔV^\ddagger for the decomposition of the complexes have been determined. Bartsch *et al.*^{6,12} have studied, in 1,2-dichloroethane, the complexation of 4-*tert*-butylbenzenediazonium tetrafluoroborate with polyethylene glycols and glymes from diglyme to decaglyme but using only the ratio [polyether]/[ArN₂⁺] = 10. Because of the excess of polyether they were wrongly led to assume that the complex is unreactive (see below).^{7–9}

Continuing these investigations of the effect of acyclic polyethers I have now studied, by spectroscopic and kinetic methods, the complexation of benzenediazonium tetrafluoroborate with short polyethylene glycols and glymes where the chain length of the complexing agent is too short fully to wrap the polyether chain around the diazonium group (cf., Scheme 1). The effect of the length of the polyether chain on the thermodynamic and kinetic stability of the benzenediazonium ion was investigated in solution by UV spectrometry and the weak complexation in the gas phase was characterized by the FAB MS tech-

nique. The results obtained in these two phases are compared.

Experimental

Materials. Benzenediazonium tetrafluoroborate was earlier synthesised from aniline by diazotization with sodium nitrite at 0–4°C in tetrafluoroboric acidic aqueous solution and was crystallized before use from about 25% aqueous tetrafluoroboric acid.⁹ Polyethylene glycols HO(CH₂CH₂O)_{*n*}H where *n* = 3–6 and glymes, or polyethylene glycol dimethyl ethers, CH₃O(CH₂CH₂O)_{*n*}CH₃ where *n* = 2–4, were commercial reagents from Fluka and were used as received or after distillation. Ethylene glycol from Baker and pentaglyme from Riedel–de Haen were used as received. 1,2-Dichloroethane, Merck, *reinst.*, was purified, dried and distilled.⁷

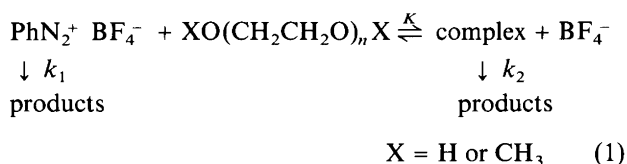
Measurements. UV spectra were recorded with a Philips PU 8740 or Shimadzu UV 160 A spectrophotometer. The longest wavelength maximum λ_{\max} in the UV was accurate to within ± 1 nm. Kinetic measurements were carried out with a Perkin-Elmer 139 spectrophotometer equipped with a Hitachi Perkin-Elmer 139-0880 temperature-controlled cell attachment, keeping the temperature constant to within $\pm 0.03^\circ\text{C}$. After thermostating, usually 6–8 values of the absorbance A , were read at suitable time intervals up to about two half-lives, and the observed rate constant of the decomposition k_{obsd} was calculated by plotting the values of $\ln(A_t - A_\infty)$ vs. t . The absorbance after the reaction A_∞ was determined after about ten half-lives. All reactions were found to obey first-order kinetics within the intervals investigated: the standard deviation for k_{obsd} was usually $\pm (0.5\text{--}2.0)\%$ and the correlation constant about 0.9997. Generally only one kinetic run was carried out at each concentration for each polyether. The reproducibility of the rate constants was tested to be better than 2%. The small amounts of benzenediazonium tetrafluoroborate and polyethers were weighed with a Perkin-Elmer AD-2 autobalance.

The complexation and decomposition of benzenediazonium tetrafluoroborate in the presence of polyethers in the gas phase were investigated under the fast atom bombardment conditions with a Kratos MS 80 autoconsole mass spectrometer. The atom gun was operated at 8 KeV and argon was employed as the bombarding gas with pressure around 1×10^{-6} Torr in the collision region. The liquid matrix for FAB studies has recently¹³ been optimized and 3-nitrobenzyl alcohol (NBA) proved to be the best solvent tested owing to its electron scavenging nature. For this reason NBA was used as the liquid matrix also in this study. The stainless steel tip of the FAB probe was coated with a thin layer of the mixture of benzenediazonium tetrafluoroborate, liquid acyclic polyether in excess and the matrix NBA. The spectrum was recorded immediately after the sample had been installed.

Results

The spectral and stabilization effects of complexation of benzenediazonium tetrafluoroborate with polyethylene glycols HO(CH₂CH₂O)_nH (*n* ≤ 6) and their dimethyl ethers (glymes) CH₃O(CH₂CH₂O)_nCH₃ (*n* ≤ 5) in 1,2-dichloroethane (DCE) were studied by UV spectroscopy by determining the longest wavelength maximum λ_{max} and dediazonation rate constant *k*_{obsd}. The system hexaethylene glycol-PhN₂⁺BF₄⁻ was also investigated in methanol to obtain information about the effect of solvent on the complexation. The kinetic measurements were carried out for the uncomplexed benzenediazonium ion as well as in the presence of at least five concentrations of each acyclic polyether. The total initial concentration of the benzenediazonium salt was kept constant in each solvent ([PhN₂⁺]_{total} = [PhN₂⁺] + [complex] = 1.0 × 10⁻⁴ M in DCE). The experimental results for the studies in solution are presented in Table 1. The hypsochromic shift is a measure of the degree of complexation.

The reactions of benzenediazonium salt in the presence of acyclic polyether in solution can be interpreted by eqn. (1) where complex denotes a 1:1 complex, *K* is the complexation equilibrium constant and *k*₁ and *k*₂ are the rate constants for the thermal decomposition of the uncomplexed and complexed benzenediazonium ion, respectively. The complexation is assumed to be very fast.^{3,4}



If the complex is unreactive (*k*₁ >> *k*₂), as Bartsch *et al.*^{6,12} have assumed, the value of *K* can be calculated by eqn. (2) where *k*_{obsd} is the observed dediazonation

$$K = \frac{k_1 - k_{\text{obsd}}}{k_{\text{obsd}} \times [\text{XO}(\text{CH}_2\text{CH}_2\text{O})_n\text{X}]} \quad (2)$$

rate constant in the presence of the free polyether concentration [XO(CH₂CH₂O)_nX]. The kinetic results in Table 1 indicate, however, that the values of *K* calculated by eqn. (2) decrease with increasing polyether concentration [XO(CH₂CH₂O)_nX]; e.g., the value of *K* calculated for PhN₂⁺-HO(CH₂CH₂O)₃H decreases from 27.1 M⁻¹ to 6.3 M⁻¹ and that for PhN₂⁺-HO(CH₂CH₂O)₅H from 323 M⁻¹ to 144 M⁻¹. The decrease indicates (cf., the values of *k*₂/*k*₁ in Table 2) that the assumption of unreactivity of the complex is incorrect. The values of *K*, *k*₁-*k*₂, *k*₂ and the stabilizing ability of complexation *k*₂/*k*₁ were therefore calculated from the kinetic data as previously presented⁷⁻⁹ by the iteration method by eqn. (3).

Table 1. Effect of complexation on the thermal decomposition of benzenediazonium tetrafluoroborate ([PhN₂⁺] = 1.0 × 10⁻⁴ M) in the presence of polyethylene glycols and polyethylene glycol demethyl ethers (glymes) in 1,2-dichloroethane.

Conditions	T/°C	[Host]/ 10 ⁻² M	λ _{max} / nm	<i>k</i> _{obsd} / 10 ⁻⁴ s ⁻¹
Ethylene glycol	40.0	0	266	3.55
	40.0	5.00	265	3.30
Diglyme	40.0	1.00	265	3.15
	40.0	7.80	262	2.97
Triglyme	40.0	0.59	266	3.16
	40.0	1.18	265	2.95
	40.0	5.34	261	2.67
	40.0	9.27	259	2.66
Triethylene glycol	40.0	0.624	266	3.02
	40.0	0.936	265	2.84
	40.0	1.62	265	2.67
	40.0	3.25	263	2.49
	40.0	8.00	261	2.36
Tetraglyme	40.0	0.435	262	1.86
	40.0	0.653	261	1.65
	40.0	1.03	258	1.33
	40.0	2.16	257	1.04
	40.0	4.53	256	0.813
Tetraethylene glycol	40.0	0.45	265	2.89
	40.0	0.599	265	2.74
	40.0	1.20	264	2.47
	40.0	2.40	263	2.23
	40.0	4.79	260	1.90
Pentaethylene glycol	40.0	0.126	264	2.53
	40.0	0.196	264	2.24
	40.0	0.393	261	1.87
	40.0	0.812	257	1.48
	40.0	1.53	255	1.11
Hexaethylene glycol	40.0	0.109	258	1.63
	40.0	0.163	256	1.31
	40.0	0.386	255	0.992
	40.0	0.451	254	0.834
	40.0	0.902	253	0.584
Hexaethylene glycol in methanol ^a	35.0	0	260	4.15
	35.0	1.71	259	3.89
	35.0	3.16	259	3.70
	35.0	7.15	258	3.47
	35.0	11.2	257	3.15
12-Crown-4	40.0	0.155	266	3.09
	40.0	0.329	266	3.30
	40.0	0.658	266	3.80
	40.0	1.32	265	4.59
	40.0	2.47	265	5.36
	40.0	4.00	264	5.82

^aIn 1.0 × 10⁻³ M H₂SO₄, [PhN₂⁺] = 1.3 × 10⁻⁴ M.

$$\frac{1}{k_1 - k_{\text{obsd}}} = \frac{1}{(k_1 - k_2)K} \times \frac{1}{[\text{XO}(\text{CH}_2\text{CH}_2\text{O})_n\text{X}]} + \frac{1}{k_1 - k_2} \quad (3)$$

Table 2. Complexation and decomposition of benzenediazonium tetrafluoroborate with glymes and polyethylene glycols at 40 °C, unless otherwise shown.

System	K/M^{-1} ^a	$\Delta\lambda_{\max}/nm$ ^{b,c}	$(k_1 - k_2)/s^{-1}$ ^a	k_2/s^{-1}	k_2/k_1 ^{a,c}
Solvent: 1,2-Dichloroethane					
Ethylene glycol	<i>d</i>	1	<i>d</i>	<i>d</i>	<i>d</i>
Diglyme	<i>d</i>	5	<i>d</i>	<i>d</i>	<i>d</i>
Triglyme	$1.1(1) \times 10^2$	7	1.03×10^{-4}	2.52×10^{-4}	0.71
Triethylene glycol	$1.0(1) \times 10^2$	6	1.38×10^{-4}	2.17×10^{-4}	0.61
Tetraglyme	$3.2(2) \times 10^2$	12	2.89×10^{-4}	0.66×10^{-4}	0.19
Tetraethylene glycol	$1.3(1) \times 10^2$	8	1.80×10^{-4}	1.75×10^{-4}	0.49
Pentaglyme ^e	$1.2(1) \times 10^3$	14	2.95×10^{-4}	0.60×10^{-4}	0.17
Pentaethylene glycol	$5.2(4) \times 10^2$	11	2.61×10^{-4}	0.94×10^{-4}	0.27
Hexaethylene glycol	$1.6(2) \times 10^3$	13	3.09×10^{-4}	0.46×10^{-4}	0.13
Solvent: Methanol, at 35 °C					
Hexaethylene glycol	$1.1(2) \times 10^1$	4	1.71×10^{-4}	2.44×10^{-4}	0.59

^aCalculated by eqn. (3). ^b[Host]=0.1 M. ^cIn the absence of the host, see Table 1. ^dThe stabilizing effect of complexation is too small for the use of eqn. (3). ^eFrom Ref. 7.

Table 2 shows the calculated values of K and k_2/k_1 , together with the values of the hypsochromic shift in the UV, $\Delta\lambda_{\max}$, determined when the ratio $[XO(CH_2CH_2O)_nX]_{\text{total}}/[PhN_2^+]_{\text{total}}$ was 1000.

In earlier work,^{9,13} the strong 1:1 insertion complex of crown ethers with arenediazonium ions in the gas phase was observed by FAB mass spectrometry when $[polyether]_{\text{total}} \approx [PhN_2^+]_{\text{total}}$, but under the same conditions the weaker 1:1 complex between pentaglyme and benzenediazonium ion was not observed because the de-

gree of complexation was too low. Acyclic polyethers were therefore used in excess here, for the observation and characterization of the complexation between acyclic polyethers and benzenediazonium tetrafluoroborate in the gas phase. Fig. 1 shows as an example the positive ion FAB spectrum of benzenediazonium tetrafluoroborate in the presence of triglyme in NBA matrix. Formation of the ion at m/z 283 in relative abundance 2.9%, confirms that the 1:1 complexation between triglyme and benzenediazonium ion does occur in the FAB conditions, and the

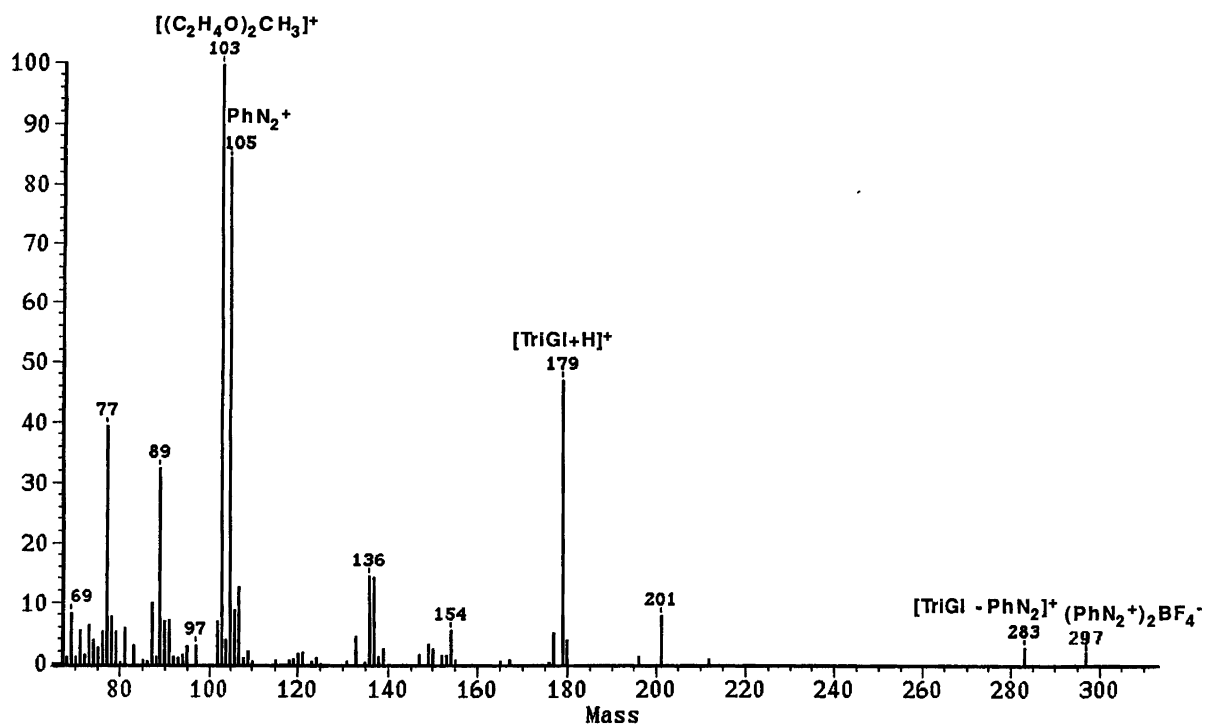


Fig. 1. Mass spectrum of benzenediazonium tetrafluoroborate in the presence of an excess of triglyme (TriGI) recorded by the FAB technique in NBA as the matrix.

Table 3. Partial positive ion FAB mass spectra of benzenediazonium tetrafluoroborate in the presence of acyclic polyether.

Polyether	Ion (m/z) and relative abundance (%) in parentheses
Diglyme	89 (33.7) [(C ₂ H ₄ O) ₂ +H] ⁺ ; 105 (100.0) PhN ₂ ⁺ ; 239 (0.0) [diglyme-PhN ₂] ⁺ ; 297 (9.6) (PhN ₂ ⁺) ₂ BF ₄ ⁻
Triglyme (TriGI)	103 (100.0) [(C ₂ H ₄ O) ₂ CH ₃] ⁺ ; 105 (84.7) PhN ₂ ⁺ ; 179 (47.5) [TriGI+H] ⁺ ; 283 (2.9) [TriGI-PhN ₂] ⁺ ; 297 (2.1) (PhN ₂ ⁺) ₂ BF ₄ ⁻
Triethylene glycol (TriEG)	89 (81.8) [(C ₂ H ₄ O) ₂ +H] ⁺ ; 105 (39.1) PhN ₂ ⁺ ; 151 (100.0) [TriEG+H] ⁺ ; 255 (2.5) [TriEG-PhN ₂] ⁺ ; 297 (1.0) (PhN ₂ ⁺) ₂ BF ₄ ⁻
Tetraglyme (TetraGI)	103 (100.0) [(C ₂ H ₄ O) ₂ CH ₃] ⁺ ; 105 (27.3) PhN ₂ ⁺ ; 223 (20.7) [TetraGI+H] ⁺ ; 297 (1.0) (PhN ₂ ⁺) ₂ BF ₄ ⁻ ; 327 (1.8) [TetraGI-PhN ₂] ⁺
Tetraethylene glycol (TetraEG)	89 (100) [(C ₂ H ₄ O) ₂ +H] ⁺ ; 105 (59.6) PhN ₂ ⁺ ; 195 (88.9) [TetraEG+H] ⁺ ; 297 (1.2) (PhN ₂ ⁺) ₂ BF ₄ ⁻ ; 299 (2.6) [TetraEG-PhN ₂] ⁺
Pentaglyme (PentaGI)	103 (100.0) [(C ₂ H ₄ O) ₂ CH ₃] ⁺ ; 105 (43.4) PhN ₂ ⁺ ; 267 (13.1) [PentaGI+H] ⁺ ; 297 (2.9) (PhN ₂ ⁺) ₂ BF ₄ ⁻ ; 371 (2.3) [PentaGI-PhN ₂] ⁺
Pentaethylene glycol (PentaEG)	89 (100.0) [(C ₂ H ₄ O) ₂ +H] ⁺ ; 105 (28.1) PhN ₂ ⁺ ; 239 (45.6) [PentaEG+H] ⁺ ; 297 (0.8) (PhN ₂ ⁺) ₂ BF ₄ ⁻ ; 343 (1.7) [PentaEG-PhN ₂] ⁺
Hexaethylene glycol (HexaEG)	89 (100.0) [(C ₂ H ₄ O) ₂ +H] ⁺ ; 105 (46.0) PhN ₂ ⁺ ; 283 (38.8) [HexaEG+H] ⁺ ; 297 (3.7) (PhN ₂ ⁺) ₂ BF ₄ ⁻ ; 387 (1.4) [HexaEG-PhN ₂] ⁺

ion at m/z 297 (2.1%) indicates the presence of a two cation–one anion cluster (PhN₂⁺)₂BF₄⁻. Partial FAB mass spectra for the investigated systems polyethylene glycol–PhN₂⁺ and glyme–PhN₂⁺ are presented in Table 3.

Discussion

The results suggest that benzenediazonium ion forms weak 1:1 complexes with flexible acyclic polyethers both in 1,2-dichloroethane solution and in the gas phase under FAB conditions. The complexation in the gas phase can be observed when the number of the oxygen atoms in polyethylene glycol or glyme is at least four. This is in good accord with a recent failure to find the ion [diglyme–tropylium]⁺ in the FAB mass spectrum.¹⁰ Evidently when the number of oxygen atoms is less than four the acyclic polyether is too short and is unable to wrap itself around the tropylium ion or the diazonium group of benzenediazonium ion (see Scheme 1) and therefore the interaction between the oxygen atoms and the cations is very weak. As far as we know, the host–guest complexation between acyclic polyethers and arenediazonium salts in the gas phase has been reported earlier only for the system pentaglyme–benzenediazonium ion.⁹

The present study, together with earlier work,^{7–9,11} indicates that the complexation with acyclic polyethers in solution causes a hypsochromic shift in the UV spectrum of the arenediazonium salt and increases the stability of the arenediazonium ion in solution but not in the solid state. The stabilizing effect of complexation and hypsochromic shift are much larger in weakly polar and basic solvents such as 1,2-dichloroethane than in polar and basic solvents such as methanol.⁹ The solvent effects were

discussed earlier for benzenediazonium ion in the presence of pentaglyme, PEG 1000 or PEG 2000 in various solvents and were determined in this work (Table 2) for hexaethylene glycol–PhN₂⁺ using 1,2-dichloroethane and methanol as model solvents. The hypsochromic shift indicates a more localized π -electron system in the complexed benzenediazonium ion than in the corresponding uncomplexed ion. The maximum value of λ_{\max} for crown ether–PhN₂⁺ and acyclic polyether–PhN₂⁺ is shown to be sensitive to solvent effects.^{9,14} The values of λ_{\max} presented in Table 2, taken together with the earlier results,¹⁴ show that when the polyether chain is too short to wrap fully around the diazonium group (see below) the maximum hypsochromic shift in the UV spectrum of the benzenediazonium salt increases with chain length of acyclic polyether; for longer acyclic hosts, however, it is independent of the length of polyether, $\lambda_{\max} = 13 \pm 1$ nm. The stabilizing effect of complexation k_1/k_2 shows a similar dependence on the length of the polyether chain (see below). The values of λ_{\max} and K for short polyethylene glycols with two terminal OH groups are a little lower than those for the corresponding glymes with two terminal OCH₃ groups. This indicates a weaker complexation ability of the oxygen atoms of PEG towards the diazonium group (see below, cf., the structure of glyme in Scheme 1). Correspondingly, Haymore *et al.*¹⁵ have observed that the complexation equilibrium constant for pentaethylene glycol–K⁺ in 99% methanol, $1.12 \times 10^2 \text{ M}^{-1}$, is a little lower than that for pentaglyme–K⁺, $1.86 \times 10^2 \text{ M}^{-1}$. The complexation effects in solution can be explained in terms of electrostatic interactions between the diazonium group, which carries a positive charge, and the electron donor oxygen atoms in the polyether (see Scheme 1). The cylindrical diameter of the diazonium group is about 0.24 nm and thus the full wrapping of the polyether chain around the diazonium group

of the benzenediazonium ion can be assumed to be possible when the number of oxygen atoms in a flexible acyclic polyether is at least six.^{9,14}

The FAB mass spectra show, in accordance with earlier investigations,^{10,16} that acyclic polyethers dissociate in the gas phase to several series of ions separated by 44 u, the molar mass of CH₂CH₂O. The observed protonated ions include *m/z* 45, 89, 133, 177... for polyethylene glycols and glymes, and in addition 103, 147... for glymes. The following ions include the benzenediazonium ion and were present in the FAB mass spectra: the uncomplexed ion PhN₂⁺, the 1:1 complex [polyether-PhN₂]⁺ and the two cation-one anion cluster (PhN₂⁺)₂BF₄⁻. The relative abundances of the complex peaks (Table 3), determined under similar conditions in the presence of an excess of acyclic polyether, were 1.4–2.9%. The results show that the host-guest complexation between an acyclic polyether and the benzenediazonium ion in the gas phase, in the absence of the complicating effect of solvation and in contrast with the effects in solution (see the discussion below), does not increase with the number of the oxygen atoms in the polyether chain. The effect of chain length seems rather to be the opposite.

The stabilization of benzenediazonium tetrafluoroborate with pentaglyme, PEG 1000 and PEG 2000 was recently shown to be significant in 1,2-dichloroethane but not in polar and basic solvents like methanol and 2,2,2-trifluoroethanol.⁹ The values of *k*₂/*k*₁ of this work (Table 2) together with the earlier results show there to be three different groups of acyclic polyethers according to their stabilizing effect on PhN₂⁺: (i) short polyethylene glycols and glymes with 2–3 oxygen atoms have no significant effect on the stability of PhN₂⁺, (ii) the value of *k*₂/*k*₁ decreases with the chain length when the host molecule is too short to wrap fully around the diazonium group, and (iii) the stabilizing effect is more or less independent of the acyclic polyether, *k*₂/*k*₁ = 0.17 ± 0.04, when the host molecule is long enough to wrap fully around the cation (see above and Scheme 1). The stabilizing abilities of tetraethylene glycol and pentaethylene glycol are less than those of the corresponding glymes and one can try to use the same reasoning as for the comparative strength of complexation, by the intramolecular or intermolecular hydrogen bonding of two terminal OH groups.¹⁵ Further speculation is unwarranted until the structures of these complexes can be ascertained. We are planning to investigate the structures of the complexes [crown ether-PhN₂]⁺ and [acyclic polyether-PhN₂]⁺ by NMR and IR spectroscopy and X-ray crystallography.

21-Crown-7 is the strongest stabilizing crown ether for PhN₂⁺BF₄⁻ against the thermal decomposition in 1,2-dichloroethane: the values of *k*₂/*k*₁ for 15-crown-5,¹⁷ 18-crown-6,¹⁴ 21-crown-7¹⁴ and dicyclohexano-24-crown-8¹⁸ are 0.26, 0.01, 0.0012 and 0.048, respectively. 15-Crown-5 is assumed to form a charge-transfer complex with benzenediazonium ion, whereas the others form insertion-type complexes. Table 2, together with the earlier

results^{7–9} suggests that hexaethylene glycol, including also seven oxygen atoms, is the most effective stabilizing acyclic agent for benzenediazonium salt: *k*₂/*k*₁ = 0.13 in 1,2-dichloroethane. Table 1 shows that the value of *k*_{obsd} increases with the concentration of 14-crown-4 in 1,2-dichloroethane. Under comparable conditions, homolytic dediazonation reactions are faster than the corresponding heterolytic reactions,^{8,9,19} and thus the destabilization with increasing concentration of 12-crown-4 can be assumed to be due to the increase of homolytic dediazonation reactions. The finding that acyclic polyether tetraglyme is a stronger stabilizing agent than cyclic 15-crown-5 can be explained by the greater flexibility of acyclic polyethers than crown ethers.

The complexation with polyethers stabilizes significantly benzenediazonium ions in 1,2-dichloroethane when the number of the oxygen atoms is at least four, and the equilibrium constants *K* can be calculated by the kinetic method. The effect of the chain length and the type of the complexing agent on the strength of the complexation between polyethers and benzenediazonium ion can be seen in Table 4 and Fig. 2. The results indicate that the value of *K* for acyclic polyether-PhN₂⁺ increases with the number of oxygen atoms and, in contrast with the other effects of complexation studied in this work, over the whole range studied, up to PEG 2000 with about 45 oxygen atoms. *K*-values for glymes are a little larger than those for corresponding PEGs, perhaps due to the hydrogen bonding of two terminal OH groups of PEGs (see above). The results in Fig. 2 suggest a small but clear difference in the complexation strength between hosts that are long enough for the polyether chain to wrap fully around the diazonium group (see above) and those with chains that are too short. Therefore, the straight line in Fig. 2 was calculated using only the first group of the hosts. In the gas phase, electrostatic interactions are strong and will dominate the interactions. In solution, the entropy contribution will be much more important since the electrostatic terms have been scaled down by the dielectric constant of the solvent. The phenomenon that ions in solution form complexes with multidentate ligands

Table 4. Effect of chain length on the complexation and stabilization ability of polyethers

Number of O-atoms	<i>K</i> for PEG	<i>K</i> for glyme	<i>K</i> for crown ether	Macrocyclic effect	
				<i>K</i> -values ^a	<i>k</i> -values ^b
4	104	107	destabilizes	< 1 ^c	< 1
5	133	319	136 ^d	1.0	1.9
6	524	1170	27 700 ^d	53	27
7	1600		506 000 ^d	316	108
22.3	6320 ^e				
45.0	12 300 ^e				

^aThe ratio of the values of *K*(PhN₂⁺-crown ether) and *K*(PhN₂⁺-polyethylene glycol). ^bThe ratio of *k*₂/*k*₁ (PhN₂⁺-polyethylene glycol) and *k*₂/*k*₁ (PhN₂⁺-crown ether), see Ref. 14. ^cConcluded from the effect of complexation on λ_{max}. ^dFrom Ref. 14, 17 or 18. ^eFrom Ref. 9.

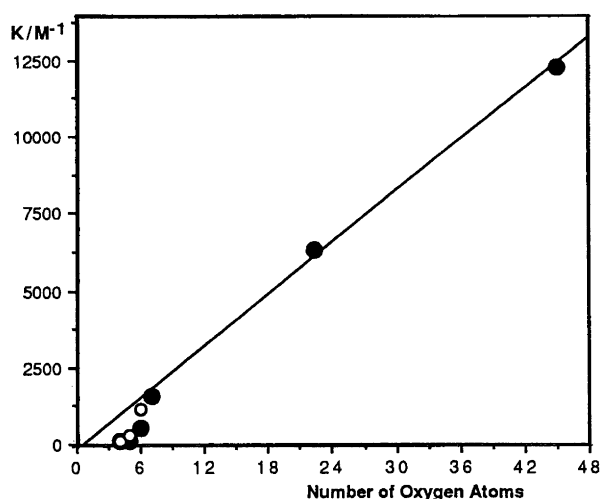


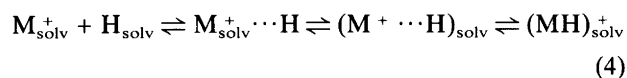
Fig. 2. The effect of chain length on the complexation equilibrium constant K for the host-guest complexation of benzenediazonium tetrafluoroborate with polyethylene glycols (●) and polyethylene glycol dimethyl ethers (○) in 1,2-dichloroethane at 40°C; — the line is drawn only for polyethers capable of the full wrapping of the polyether chain around the diazonium group, see the text.

which are more stable than those of the corresponding monodentate ligands, is called the chelate effect. The chelate effect is considered to be an entropy effect. The observed effects in this work show that only polyethers with enough oxygens to provide a significant electrostatic interaction can overcome the 'entropy cost' on complexation.

The increased stability observed for the complexes of cyclic hosts over those with an open chain of a similar composition is called the macrocyclic effect. The calculated values of the thermodynamic and kinetic macrocyclic effects, presented in Table 4, differ widely with the number of oxygen atoms ($n=4-7$). The macrocyclic effects can be concluded to be largest when $n=7$ because 21-crown-7 is both the strongest complexing and stabilizing agent for the benzenediazonium ion. Larger crown ethers are too large.¹⁸ It is interesting to observe that the thermodynamic and kinetic macrocyclic effects are clearly similar even though thermochemical stability and kinetic stability depend on different factors: K -values on differences in the Gibbs free energy between the products and the corresponding initial state [$\Delta G^\circ = RT \ln(K/M^{-1})$], and the reaction rate on differences between the activation complex and the corresponding initial state. Attempts to assign just one origin, either enthalpic or entropic, to the thermodynamic macrocyclic effect have been unsuccessful, although many systems have been investigated, especially ones with metal ions as guest components.^{1-3,15} Depending on the system investigated, either or both origins have been identified for the thermodynamic macrocyclic effect. The macrocyclic effect varies with the solvent, the host and its size, the number and type of donor atoms, the guest, etc. Haymore

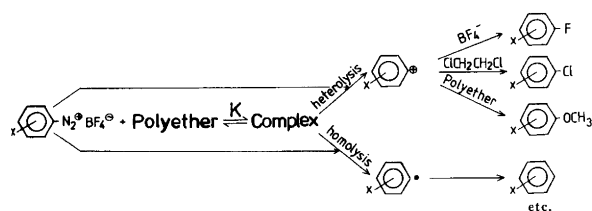
*et al.*¹⁵ have observed for example, that the K -values for 18-crown-6 with Na^+ , K^+ and Ba^{2+} in methanol are 3-4 orders of magnitude higher than those for the corresponding acyclic pentaglyme with the same metal ions. This they mainly attributed to more favourable enthalpic changes. At the same time, they found the macrocyclic effect $K(15\text{-crown-5}/\text{PhN}_2^+)/K(\text{tetraglyme}/\text{PhN}_2^+)$ in acetone to be very small, only about 0.1. This can be explained by the greater flexibility of the acyclic tetraglyme and that the benzenediazonium ion is too large to form a strong insertion-type complex with 15-crown-5.¹⁷ The origin of the macrocyclic kinetic effect for polyether- PhN_2^+ has not been studied.

In accordance with earlier work,^{6-9,11,12} the present investigation suggests that the thermal decomposition of substituted benzenediazonium salt in the presence of acyclic polyether in solution occurs by an $\text{S}_{\text{N}}1$ -like reaction mechanism (Scheme 2) via two competing but independent pathways: the formation of the highly reactive aryl cation by heterolysis and/or the aryl radical by homolysis in the slow rate-determining decomposition step of the uncomplexed ion or the complex. Subsequent fast product-determining reactions with nucleophiles and solvent give the products. The host-guest complexation process is concluded to include a sequence of steps involving both desolvation reactions and rearrangement of the host molecule. The general mechanism can be given by eqn. (4)^{1,2}



where M_{solv}^+ is a solvated guest, H_{solv} is a solvated host, H is a free host, $\text{M}_{\text{solv}}^+ \cdots \text{H}$ is a solvent-separated cation-host pair, $(\text{M}^+ \cdots \text{H})_{\text{solv}}$ is a contact pair and $(\text{MH})_{\text{solv}}^+$ is the final complex. The first step in the complexation is a rapid desolvation of the host molecule followed by a diffusion-controlled bimolecular collision reaction in which solvent molecules around the cation are replaced by donor atoms of the host molecule. The final step is the rearrangement of the host molecule, or the wrapping of the polyether chain around the cation. It is concluded that, in solvents with low polarity and basicity, a rearrangement process rather than cation desolvation is the rate-determining step of the complexation mechanism (4).^{1,2}

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Scheme 2.

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