

Effect of Solvent on the Complexation and Dediazonation of Benzenediazonium Tetrafluoroborate in the Presence of Acyclic Polyethers

Toivo Kuokkanen and Simo Sarpola

Department of Chemistry, University of Oulu, SF-90570 Oulu, Finland

Kuokkanen, T. and Sarpola, S., 1994. Effect of Solvent on the Complexation and Dediazonation of Benzenediazonium Tetrafluoroborate in the Presence of Acyclic Polyethers. – Acta Chem. Scand. 48: 258–264 © Acta Chemica Scandinavica 1994.

The complexation and the kinetics of the thermal decomposition of benzenediazonium tetrafluoroborate in the presence of acyclic polyethers such as pentaglyme, PEG 1000 and PEG 2000 in dichloromethane, 1,2-dichloroethane, methanol, 2,2,2-trifluoroethanol and dimethyl sulfoxide (DMSO) have been studied by UV spectrophotometry. Solid 1:1 complexes were prepared. The 1:1 complex benzenediazonium ion–pentaglyme was identified in the gas phase by fast atom bombardment (FAB) mass spectrometry.

When the degree of homolysis did not increase with increasing polyether concentration (the case in all solvents except dichloromethane), the complexation of the benzenediazonium ion with acyclic polyether increased the thermal stability in solution. Only in 1,2-dichloroethane was this increase in stability significant. No stabilizing effect was observed in the solid state. The complexation caused a hypsochromic shift in the UV spectrum of the benzenediazonium salt and this shift was much larger in only weakly polar and basic solvents such as 1,2-dichloroethane and dichloromethane than in polar and basic methanol and 2,2,2-trifluoroethanol. The values of the complexation equilibrium constant K were strongly dependent on the solvent, being the smallest in polar and basic solvents. The benzenediazonium ion did not form complexes with acyclic polyethers in DMSO, the most basic solvent in the study.

The investigation of macrocyclic polyethers, crown ethers, began in 1967 when Pedersen¹ published his pioneering work on their synthesis and his observations that crown ethers can form stable complexes with many metal cations of an appropriate size, e.g., alkali- and alkaline-earth metal ions. Since then, the host–guest complexation of crown ethers with various species has been enthusiastically studied owing to the broad and versatile application of these complexes in synthesis, in phase-transfer catalyses and in increasing the solubility and stability of guest compounds.^{2–4}

The host–guest complexation of crown ethers with arenediazonium ions has also been widely studied by various kinetic, spectroscopic and calorimetric methods.^{3–8} The insertion-type complex has generally been assumed to be the only type of complexation for the crown ether–arenediazonium ion system. We have recently shown, however, that arenediazonium ions in 1,2-dichloroethane form weak charge-transfer complexes⁶ with 15-crown-5,⁷ the cavity diameter of which is too small for insertion-type complexation.

Acyclic polyethers like glymes also form charge-transfer complexes with alkali- and alkaline-earth metal ions

and can be used as phase-transfer catalysts in the reactions of these cations.⁹ In agreement with other workers, we have shown that acyclic polyethers such as pentaglyme [pentaethylene glycol dimethyl ether, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3$] and PEGs [polyethylene glycols, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$], form stable charge-transfer complexes with arenediazonium ions in 1,2-dichloroethane.^{10,11} Bartsch¹² has noted that it might be possible to use commercially available and inexpensive PEGs instead of expensive crown ethers as solubilizing agents and phase-transfer catalysts in the reactions of arenediazonium salts in solvents of low polarity. Small changes in the reaction system, i.e., the character of the substituent and its position, the solvent, atmosphere, pH and the presence of other substrates, etc., may drastically affect the rate of the dediazonation, the product composition and the mechanism.⁷ When using the unsubstituted benzenediazonium ion as a model compound to eliminate steric effects on the complexation, we recently studied the effect of solvent on the complexation and thermal stability of benzenediazonium tetrafluoroborate in the presence of crown ethers.⁸ The results indicated that the complexation of the benzenediazonium ion with crown ethers

strongly depends on the character of the solvent. Continuing these studies we have now investigated the effect of solvent on the complexation and the thermal decomposition of benzenediazonium tetrafluoroborate in the presence of acyclic polyethers using kinetic and spectroscopic methods. As model polyethers we used pentaglyme, PEG 1000 and PEG 2000. Pentaglyme, like the corresponding cyclic 18-crown-6, contains six oxygen atoms, which makes it possible to study the macrocyclic effects on complexation. The solvents in our study were dichloromethane, 1,2-dichloroethane, methanol, 2,2,2-trifluoroethanol and dimethyl sulfoxide (DMSO); only 1,2-dichloroethane has previously been used.^{10,11} In all solvents of this investigation the dediazonation of unsubstituted benzenediazonium tetrafluoroborate in the absence of complexing agent is solely a heterolytic process.⁷

Experimental

Materials. Benzenediazonium tetrafluoroborate was synthesized from aniline by diazotization with sodium nitrite at 0–4°C in aqueous solution acidified with tetrafluoroboric acid and was crystallized twice from tetrafluoroboric acidic aqueous solution. The polyethers were commercial reagents and were used as received. Pentaglyme (pentaethylene glycol dimethyl ether) was from Riedel-de Haen AG, Seelze-Hannover, FRG, and PEG 1000 [polyethylene glycol, HO(CH₂CH₂O)_nH, the molar mass about 1000], PEG 2000 and 18-crown-6 were from Fluka AG, Buchs, Switzerland. Crystalline, white 1:1 C₆H₅N₂⁺BF₄⁻/polyether complexes, the polyether being pentaglyme or 18-crown-6, were synthesized in 1,2-dichloroethane and were purified as described by Zollinger.⁶ The corresponding 1:1 C₆H₅N₂⁺BF₄⁻/polyether complexes from PEG 1000 and PEG 2000 were synthesized by the method of Gokel.⁵ Dichloromethane, Merck, BRD, *p.a.*, and 1,2-dichloroethane, Merck, *reinst.*, were purified as described earlier and kept under a nitrogen atmosphere.¹³ Methanol (Merck, *p.a.*) was dried with molecular sieves 4 Å, treated with magnesium activated with iodine and distilled. Dimethyl sulfoxide (Fluka AG, *purum*) was distilled from calcium hydride at reduced pressure. 2,2,2-Trifluoroethanol (Fluka AG, *puriss.*) was used as received.

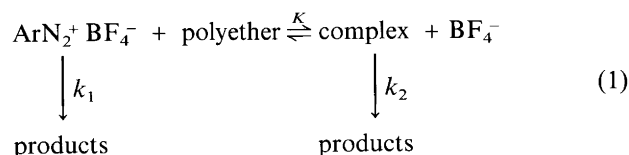
Measurements. UV spectra were recorded with a Philips PU 8740 spectrophotometer. Kinetic measurements were carried out with a Perkin-Elmer 139 spectrophotometer equipped with a Hitachi Perkin-Elmer 139-0880 temperature-controlled cell attachment. The temperature was kept constant to within ±0.03°C. The products of decomposition in dichloromethane were identified with a Kratos MS 80 RF Autoconsole mass spectrometer using a capillary gas chromatographic sample inlet system, and were determined quantitatively on a Hewlett-Packard 5720A gas chromatograph equipped with a Merck-Hita-

chi D-2500 Chromato-Integrator. The 1:1 host-guest complexes of the benzenediazonium ion with pentaglyme and 18-crown-6 in the gas phase were identified by fast atom bombardment (FAB) mass spectrometry. The liquid matrix for the FAB mass spectrometric study has recently been optimized and 3-nitrobenzyl alcohol (NBA) proved to be the best solvent owing to its electron scavenging nature.¹⁴ Fourier transform infrared spectra of the synthesized 1:1 complexes were obtained with a Bruker IFS-66 FTIR spectrophotometer using KBr tablets. The longest wavelength maximum in UV λ_{max} was accurate to within ±1 nm while ν_{NN} in IR was accurate to within ±1 cm⁻¹. The decomposition temperatures of the solid salts were determined using a Thermopan microscope (Reichert, Wien). The small amounts of the benzenediazonium salt and the polyethers were accurately weighed with a Perkin-Elmer AD-2 autobalance.

Results

The stabilization and spectral effects of complexation of benzenediazonium tetrafluoroborate with pentaglyme, PEG 1000 and PEG 2000 in dichloromethane, methanol, 2,2,2-trifluoroethanol, dimethyl sulfoxide and 1,2-dichloroethane were studied by UV spectrometry by determining the dediazonation rate constant *k*_{obs} and the longest wavelength maximum λ_{max}. The experiments with pentaglyme and PEG 1000 in 1,2-dichloroethane have been reported earlier.^{10,11} The progress of the thermal decomposition reaction was followed for about two half-lives. The kinetic measurements were carried out for the uncomplexed benzenediazonium ion and in the presence of at least five suitable polyether concentrations. The total initial concentration of benzenediazonium tetrafluoroborate was kept constant in each solvent. All reactions were found to obey first-order kinetics within the intervals studied: the correlation constant *r* for *k*_{obs} was about 0.9996 and its standard deviation was usually within ±(0.5–2.0)%. The experimental results, presented in Table 1, indicate clearly the solvent effects.

As reported earlier,^{10,11} the data can be interpreted in terms of 1:1 complexation according to reaction (1)



where *k*₁ and *k*₂ are the rate constants for the thermal decomposition of the uncomplexed and complexed ions, respectively, and *K* is the complexation equilibrium constant. When the decomposition of the complex cannot be ignored, the values of *K*, *k*₁ – *k*₂ and *k*₂ can be calculated from the kinetic data by an iteration method using eqns. (2)–(5) where *k*_{obs} is the observed rate constant in the presence of the free polyether concentration [polyether]

Table 1. Effect of complexation on the thermal decomposition of benzenediazonium tetrafluoroborate in the presence of acyclic polyethers in solution.

Solvent	T/°C	Polyether	[Polyether]/M	λ_{\max}/nm	$k_{\text{obs}}/\text{s}^{-1}$
Dichloromethane [ArN ₂ ⁺]= 1.0 × 10 ⁻⁴ M	40.0	Pentaglyme	0	265	2.25 × 10 ⁻⁴
	40.0	Pentaglyme	4.00 × 10 ⁻⁴	264	1.96 × 10 ⁻⁴
	40.0	Pentaglyme	6.67 × 10 ⁻⁴	264	1.85 × 10 ⁻⁴
	40.0	Pentaglyme	1.00 × 10 ⁻³	263	1.81 × 10 ⁻⁴
	40.0	Pentaglyme	2.50 × 10 ⁻³	260	1.67 × 10 ⁻⁴
	40.0	Pentaglyme	5.00 × 10 ⁻³	258	1.66 × 10 ⁻⁴ ^a
	40.0	Pentaglyme	1.00 × 10 ⁻²	255	1.88 × 10 ⁻⁴ ^a
	40.0	Pentaglyme	2.00 × 10 ⁻²	254	2.07 × 10 ⁻⁴ ^a
	40.0	PEG 1000	3.00 × 10 ⁻⁴	262	2.50 × 10 ⁻⁴
	40.0	PEG 1000	6.00 × 10 ⁻⁴	261	2.62 × 10 ⁻⁴
	40.0	PEG 1000	1.50 × 10 ⁻³	259	3.04 × 10 ⁻⁴
	40.0	PEG 1000	2.50 × 10 ⁻³	257	4.01 × 10 ⁻⁴
	40.0	PEG 1000	4.00 × 10 ⁻³	255	4.94 × 10 ⁻⁴
	40.0	PEG 1000	6.00 × 10 ⁻³	255	5.44 × 10 ⁻⁴
	40.0	PEG 2000	3.00 × 10 ⁻⁴	262	2.42 × 10 ⁻⁴
	40.0	PEG 2000	6.00 × 10 ⁻⁴	261	2.51 × 10 ⁻⁴
	40.0	PEG 2000	2.50 × 10 ⁻³	256	2.84 × 10 ⁻⁴
	40.0	PEG 2000	4.00 × 10 ⁻³	256	3.31 × 10 ⁻⁴
	40.0	PEG 2000	6.00 × 10 ⁻³	256	4.03 × 10 ⁻⁴
	Methanol ^b [ArN ₂ ⁺]= 1.3 × 10 ⁻⁴ M	35.0	Pentaglyme	0	260
35.0		Pentaglyme	4.33 × 10 ⁻³	260	3.90 × 10 ⁻⁴
35.0		Pentaglyme	1.30 × 10 ⁻²	260	3.75 × 10 ⁻⁴
35.0		Pentaglyme	5.20 × 10 ⁻²	260	3.30 × 10 ⁻⁴
35.0		Pentaglyme	7.80 × 10 ⁻²	260	3.10 × 10 ⁻⁴
35.0		PEG 1000	7.80 × 10 ⁻⁴	260	3.95 × 10 ⁻⁴
35.0		PEG 1000	1.95 × 10 ⁻³	259	3.82 × 10 ⁻⁴
35.0		PEG 1000	6.50 × 10 ⁻³	259	3.58 × 10 ⁻⁴
35.0		PEG 1000	1.30 × 10 ⁻²	258	3.33 × 10 ⁻⁴
35.0		PEG 1000	2.60 × 10 ⁻²	258	2.77 × 10 ⁻⁴
35.0		PEG 2000	3.25 × 10 ⁻³	259	3.58 × 10 ⁻⁴
35.0		PEG 2000	4.68 × 10 ⁻³	259	3.49 × 10 ⁻⁴
35.0		PEG 2000	6.50 × 10 ⁻³	259	3.34 × 10 ⁻⁴
35.0		PEG 2000	1.30 × 10 ⁻²	258	2.79 × 10 ⁻⁴
35.0		PEG 2000	2.34 × 10 ⁻²	258	2.33 × 10 ⁻⁴
2,2,2-Trifluoroethanol [ArN ₂ ⁺]= 1.3 × 10 ⁻⁴ M		35.0	PEG 1000	0	261
	35.0	PEG 1000	4.33 × 10 ⁻³	261	3.86 × 10 ⁻⁴
	35.0	PEG 1000	6.50 × 10 ⁻³	261	3.81 × 10 ⁻⁴
	35.0	PEG 1000	1.30 × 10 ⁻²	261	3.74 × 10 ⁻⁴
	35.0	PEG 1000	2.60 × 10 ⁻²	261	3.60 × 10 ⁻⁴
	35.0	PEG 1000	7.80 × 10 ⁻²	259	2.97 × 10 ⁻⁴
	35.0	PEG 2000	3.25 × 10 ⁻³	261	3.85 × 10 ⁻⁴
	35.0	PEG 2000	9.75 × 10 ⁻³	261	3.72 × 10 ⁻⁴
	35.0	PEG 2000	2.60 × 10 ⁻²	260	3.36 × 10 ⁻⁴
	35.0	PEG 2000	3.90 × 10 ⁻²	260	3.21 × 10 ⁻⁴
	35.0	PEG 2000	7.80 × 10 ⁻²	258	2.40 × 10 ⁻⁴
	1,2-Dichloroethane [ArN ₂ ⁺]= 1.2 × 10 ⁻⁴ M	50.0	PEG 2000	0	267
50.0		PEG 2000	2.40 × 10 ⁻⁴	258	5.74 × 10 ⁻⁴
50.0		PEG 2000	3.60 × 10 ⁻⁴	257	4.80 × 10 ⁻⁴
50.0		PEG 2000	6.00 × 10 ⁻⁴	256	3.93 × 10 ⁻⁴
50.0		PEG 2000	1.20 × 10 ⁻³	256	3.24 × 10 ⁻⁴
50.0		PEG 2000	2.40 × 10 ⁻³	256	2.86 × 10 ⁻⁴
DMSO [ArN ₂ ⁺]= 1.3 × 10 ⁻⁴ M	35.0	PEG 1000	0	262	2.00 × 10 ⁻⁴
	35.0	PEG 1000	1.3 × 10 ⁻²	261	2.13 × 10 ⁻⁴
	35.0	PEG 1000	2.6 × 10 ⁻²	261	2.15 × 10 ⁻⁴

^aNot used in calculating the constants of eqn. (2). ^b1.0 × 10⁻³ M H₂SO₄ (cf. ref. 7).

and $[\text{ArN}_2^+]$ is the concentration of the uncomplexed arenediazonium ion. In eqns. (3)–(5), x denotes the concentration of the complex.^{6–8,10,11}

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

$$K = x/([\text{ArN}_2^+] \times [\text{polyether}]), \quad x = [\text{complex}] \quad (3)$$

$$[\text{polyether}] = [\text{polyether}]_{\text{total}} - x \quad (4)$$

$$[\text{ArN}_2^+] = [\text{ArN}_2^+]_{\text{total}} - x \quad (5)$$

The reactions for which the complexation has a stabilizing effect (the case in all solvents except dichloromethane and DMSO) obeyed eqn. (2) with a correlation coefficient r of about 0.994 in the final plot. Table 2 shows the calculated values of the complexation equilibrium constant K and the stabilization ability of the complexation against the thermal decomposition, $k_2/k_1(\%)$, together with the values of the maximum hypsochromic shift in UV $\Delta\lambda_{\text{max}}$.

Under comparable experimental conditions homolytic rates are faster than the corresponding rates of heterolysis.¹⁵ We have previously¹¹ observed that after a minimum at $[\text{PEG 1000}]/[\text{PhN}_2^+] \approx 2.5$ the rate of the thermal decomposition of 4-cyanobenzenediazonium tetrafluoroborate in 1,2-dichloroethane increases with increasing concentration of PEG 1000. Zollinger *et al.*⁶ have reported a similar destabilization and have observed an increase of homolytic arene products during the de-

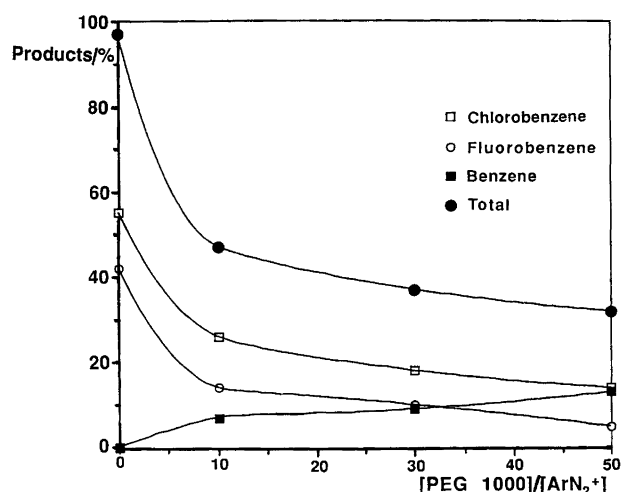


Fig. 1. Effect of [PEG 1000] on the products of the thermal decomposition of benzenediazonium tetrafluoroborate (usually 4×10^{-3} M) in dichloromethane at 40 °C after about ten half-lives.

diazonation of 4-chloro- and 3-cyano-benzenediazonium ion in the presence of crown ethers in 1,2-dichloroethane. The observed decrease in the stability of benzenediazonium tetrafluoroborate with increasing concentration of PEG 1000 and PEG 2000 in dichloromethane, cf. Table 1, can be attributed to the change from the heterolytic to the homolytic dediazonation mechanism. This complexation caused a decrease in λ_{max} with increasing concentration of PEG 1000 and PEG 2000. The degree

Table 2. Solvent effect on the complexation and stabilization of benzenediazonium tetrafluoroborate in the presence of acyclic polyethers at 35 °C.

System	$\lambda_{\text{max}}/\text{nm}^a$	$\Delta\lambda_{\text{max}}/\text{nm}$	$K/\text{dm}^3\text{mol}^{-1b}$	$(k_1 - k_2)/\text{s}^{-1b}$	$k_1/k_2 (\%)^b$
Solvent: $\text{CH}_2\text{Cl}_2^{c,d}$					
Pentaglyme	254	11	$(2.0 \pm 0.3) \times 10^3$	6.9×10^{-5}	69
PEG 1000	255	10	$> 2 \times 10^{3e}$	<i>f</i>	<i>f</i>
PEG 2000	256	9	$> 2 \times 10^{3e}$	<i>f</i>	<i>f</i>
Solvent: CH_3OH^c					
Pentaglyme	259	1	$(4.1 \pm 1.6) \times 10^1$	1.03×10^{-4}	75
PEG 1000	256	4	$(1.3 \pm 0.3) \times 10^2$	1.21×10^{-4}	70
PEG 2000	256	4	$(6.6 \pm 2.4) \times 10^1$	2.60×10^{-4}	36
Solvent: $\text{CF}_3\text{CH}_2\text{OH}^c$					
PEG 1000	259	2	$(2.4 \pm 0.8) \times 10^1$	1.05×10^{-4}	73
PEG 2000	258	3	$(2.3 \pm 1.1) \times 10^1$	1.55×10^{-4}	61
Solvent: $\text{ClCH}_2\text{CH}_2\text{Cl}^{c,g}$					
Pentaglyme ^h	253	14	$(1.17 \pm 0.03) \times 10^3$	9.93×10^{-4}	17
PEG 1000 ⁱ	253	14	$(6.32 \pm 0.20) \times 10^3$	9.72×10^{-4}	19
PEG 2000	255	12	$(1.23 \pm 0.02) \times 10^4$	9.42×10^{-4}	21

^aPolyether in excess. ^bCalculated by eqn. (2). ^c λ_{max} and k_1 for the uncomplexed ion, see Table 1. ^dAt 40.0 °C. ^eCf. the text. ^fCould not be determined by the kinetic method owing to the increase in homolysis. ^gAt 50.0 °C. ^hFrom Ref. 10. ⁱFrom Ref. 11.

Table 3. Data for solid benzenediazonium tetrafluoroborate-polyether complexes.

Compound	$\lambda_{\max}/\text{nm}^a$	$\nu_{\text{NN}}/\text{cm}^{-1b}$	$T_{\text{decomp}}/^\circ\text{C}$
$\text{C}_6\text{H}_5\text{N}_2^+\text{BF}_4^-$	267	2296	108–110
$\text{C}_6\text{H}_5\text{N}_2^+\text{BF}_4^-$ -PEG 1000	265	2298	35–39 ^c
$\text{C}_6\text{H}_5\text{N}_2^+\text{BF}_4^-$ -PEG 2000	261	2297	52–55 ^d
$\text{C}_6\text{H}_5\text{N}_2^+\text{BF}_4^-$ -pentaglyme	266	2298	98–99
$\text{C}_6\text{H}_5\text{N}_2^+\text{BF}_4^-$ -18-crown-6	253	2314	88–90

^aIn 1,2-dichloroethane. ^bBy the KBr tablet technique. ^cDecomposition temp. of PEG 1000. ^dDecomposition temp. of PEG 2000.

of the hypsochromic shift is a measure of the degree of complexation. The results in Table 1 indicate that the dediazonium rate of the benzenediazonium ion in dichloromethane increases with increasing concentration of pentaglyme after a minimum at $[\text{pentaglyme}]/[\text{PhN}_2^+] \approx 50$. By plotting λ_{\max} vs. $[\text{polyether}]$ we observe that in dichloromethane the decrease of λ_{\max} is much stronger and more rapidly approaches the maximal hypsochromic shift in the presence of PEG 1000 and PEG 2000 than in the presence of pentaglyme. These spectral results indicate that PEG 1000 and PEG 2000 are stronger complexing agents for arenediazonium ions than is pentaglyme, as, indeed, is expected from the K -values calculated by the kinetic method in 1,2-dichloroethane.^{10,11} It is interesting to observe that no spectral effect of the change in mechanism can be seen for the benzenediazonium-pentaglyme system in dichloromethane, although the change from heterolysis to homolysis has a clear effect on the kinetic behaviour. In agreement with this, Zollinger⁶ has noted that no conclusions regarding the kinetic or thermodynamic stability of the host-guest complexation of arenediazonium with crown ethers can be drawn from the spectroscopic data.

To be able to confirm the conclusions drawn from the kinetic data, the effect of [PEG 1000] on the dediazonium products in dichloromethane was studied by GLC. The results, presented in Fig. 1, support the kinetic measurements and the conclusion that, when dichloromethane is the solvent, the homolytic dediazonium mechanism (the amount of benzene) increases in importance with increase in the acyclic polyether concentration. A similar decrease in the amount of fluorobenzene and in the total amount of the known products has previously^{6,7,16} been found in 1,2-dichloroethane in the presence of all polyethers studied, and is evidently due to the reactions of the intermediate phenyl cation with the polyether.

In addition to the investigations in solution, we studied the complexation of the benzenediazonium ion with acyclic polyethers in the solid state. For comparison, we also synthesized the corresponding insertion complex $\text{PhN}_2^+\text{BF}_4^-/18\text{-crown-6}$. The results are presented in Table 3.

For identification of the host-guest complex between the arenediazonium ions and polyethers we investigated, by FAB mass spectrometry, the complexation of

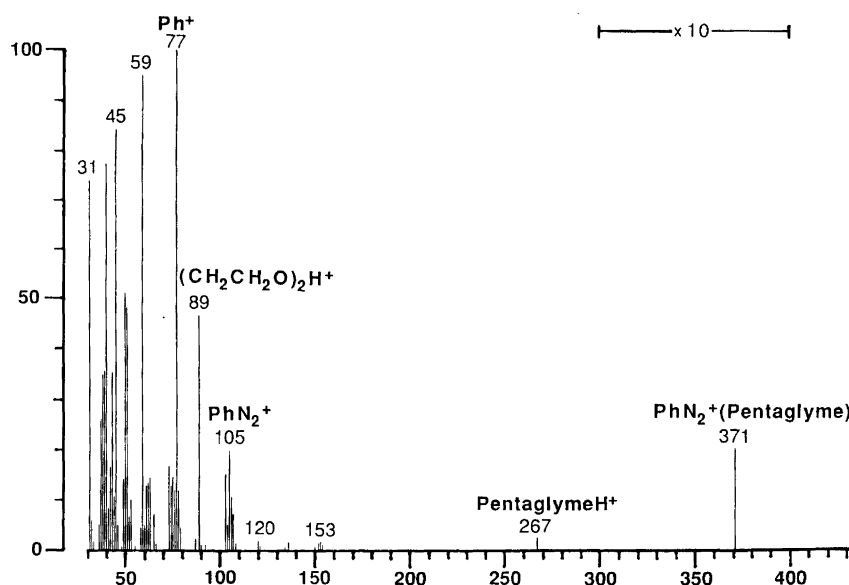


Fig. 2. Mass spectrum of the benzenediazonium tetrafluoroborate in the presence of an excess of pentaglyme recorded by the fast atom bombardment (FAB) technique in 3-nitrobenzyl alcohol as the matrix.

benzenediazonium tetrafluoroborate with pentaglyme and the corresponding cyclic polyether, 18-crown-6, in the gas phase. Under conditions where $[\text{PhN}_2^+]_{\text{total}} \approx [\text{polyether}]_{\text{total}}$, the FAB mass spectrum of the benzenediazonium ion/18-crown-6 complex showed an PhN_2^+ ion (m/z 105), a two cation–one anion cluster $(\text{PhN}_2^+)_2\text{BF}_4^-$ (m/z 297), and a 1:1 complex ion $\text{PhN}_2^+/\text{18-crown-6}$ (m/z 369), in good accord with the earlier studies.^{14,17} The complex between benzenediazonium tetrafluoroborate and pentaglyme was not observed when $[\text{PhN}_2^+]_{\text{total}} \approx [\text{pentaglyme}]_{\text{total}}$ because, in this case, the degree of complexation was too low. Use of pentaglyme in excess, however, allowed us to identify a 1:1 complex ion $\text{PhN}_2^+/\text{pentaglyme}$ (m/z 371), Fig. 2.

Discussion

The results of our investigation show, in accordance with earlier work,^{9–12,16} that arenediazonium salts form 1:1 complexes with acyclic polyethers. This complexation can be detected in the gas phase by fast atom bombardment mass spectrometry (FAB MS). As far as we know, no mass spectrum for a host–guest complex from an acyclic polyether and an arenediazonium salt has been reported. The complexation causes a hypsochromic shift in the UV spectrum of the arenediazonium salt in solution. When the proportion of homolysis does not increase with increasing polyether concentration, this complexation increases the stability of the arenediazonium ion in solution but not in the solid state (Table 3). This stabilizing effect and the hypsochromic shift are strongly dependent on the solvent and are discussed below. In contrast with the much stronger insertion-type complexation with cyclic crown ethers, only a slight shift, about 2 cm^{-1} , in the stretching frequency of the N–N bond is observed in the IR spectrum, cf. Table 3. 18-Crown-6, used for comparison in this study, is known to produce the maximal spectral shift in both IR and UV spectra.^{5,6,8} The hypsochromic shift indicates a more localized π -electron system in the complexed arenediazonium ion than in the uncomplexed ion. The observed complexation effects can be explained in terms of electrostatic interactions between the diazonium group carrying a positive charge and the electron donors, the oxygen atoms of the polyethers.

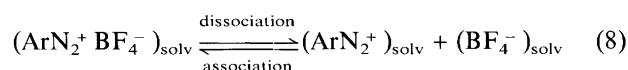
We observed recently⁸ that the complexation equilibrium constant K for a benzenediazonium tetrafluoroborate–crown ether complex, where insertion-type complexation is possible, varies strongly with the solvent and depends on the polarity and/or basicity of the solvent.^{15,18} A correlation between the values of $\log K$ and the polarity or the Koppel and Paju's basicity parameter was observed. There are too few values in this study for an exact mathematical treatment, but the results indicate that the value of $\log K$ for the complex benzenediazonium tetrafluoroborate–acyclic polyether is similarly dependent on the character of the solvent, e.g., one arrives at the

following correlations for $\text{PhN}_2^+\text{BF}_4^-$ –pentaglyme [eqns. (6) and (7)], where $E_T(30)$ is the polarity parameter of

$$\log K = -0.11 E_T(30) + 7.87, \quad r = 0.997, n = 3 \quad (6)$$

$$\log K = -0.0085B + 3.45, \quad r = 0.999, n = 3 \quad (7)$$

the solvent and B is Koppel and Paju's basicity parameter of the solvent.^{8,15,18} Because the hypsochromic shift is also a measure of the strength of the complexation, the values of the hypsochromic shift for ArN_2^+ –polyether are much larger in only weakly polar and basic solvents such as 1,2-dichloroethane and dichloromethane than in polar and basic solvents such as methanol and 2,2,2-trifluoroethanol.^{8,15,18} We note, however, that it is not possible to measure the maximal hypsochromic shift for ArN_2^+ –acyclic polyether in methanol and 2,2,2-trifluoroethanol because in these solvents the K -values are very small (Table 2). This also means that it is not possible to measure λ_{max} in conditions where the benzenediazonium ion is totally in the complexed form. Both kinetic and spectral results as listed in Table 1 show that the benzenediazonium ion does not form complexes with acyclic polyethers in DMSO, the most basic solvent used in our study. In solvents of low permittivity ϵ ($\epsilon < 10$ – 15), salts exist as solvated ion pairs, here as $(\text{ArN}_2^+\text{BF}_4^-)_{\text{solv}}$, whereas in solvents of high permittivity ($\epsilon > 40$) they dissociate into solvated ions.¹⁸ The effect of the solvent on the complexation of benzenediazonium tetrafluoroborate, as observed in this study with acyclic polyethers and recently⁸ with cyclic crown ethers, may therefore be explained by the ability of the arenediazonium ion to be more effectively stabilized by solvation, $(\text{ArN}_2^+)_{\text{solv}}$, in a solvent of higher polarity and basicity [eqn. (8)].

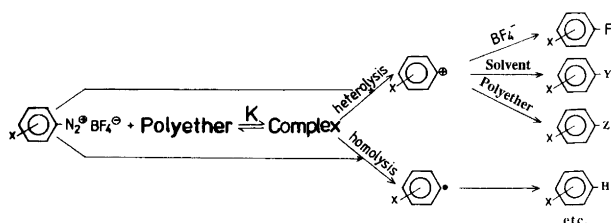


The macrocyclic effect on the complexation, determined by the ratio $K(\text{ArN}_2^+/\text{18-crown-6})/K(\text{ArN}_2^+/\text{pentaglyme})$,⁸ clearly varies with the solvent: the ratio is 23.6 in 1,2-dichloroethane, 5.1 in dichloromethane, 3.5 in methanol and 1.5 in 2,2,2-trifluoroethanol. We have earlier reported for 4-*tert*-butyl- and 3-chloro-benzenediazonium ions that the value of the complexation equilibrium constant K in 1,2-dichloroethane increases linearly with the number of $\text{CH}_2\text{CH}_2\text{O}$ groups in the polyethylene glycol chain.¹¹ The values of K for the complexation of 3- and 4-substituted benzenediazonium ions with pentaglyme¹⁰ and PEG 1000¹¹ in 1,2-dichloroethane were observed to be only slightly sensitive to the character of the substituent in the benzene ring and to obey the Hammett equation, with ρ -values of 0.68 and 1.12, respectively. These results indicate that the value of K increases with increasing electron-withdrawing power of the substituent in the benzene ring and agree well with the proposal that the interaction between arenediazonium ion and the oxy-

gen atoms of the polyether is electrostatic. The difference in the reaction constants agrees with the differences calculated above for the macrocyclic effect on K , and the results show that the sensitivity to changes decreases with decreasing K value. It can be assumed that the values of K in other solvents obey correlations similar to those observed in 1,2-dichloroethane.

We observed recently⁸ that the stabilization of benzenediazonium tetrafluoroborate induced by complexation with cyclic crown ethers is insensitive to the solvent but depends on the crown ether used. Table 2 indicates that the value of the stabilization ability against thermal decomposition, k_2/k_1 , in 1,2-dichloroethane is 20% largely independent of the polyether used. In other solvents the complexation with any of the acyclic polyethers studied has much less stabilizing effect. On the contrary, in dichloromethane the stability of the benzenediazonium ion is actually decreased with increasing acyclic polyether concentration. This can be explained in terms of the increasing importance of the homolytic dediazonation. A similar decrease in stability is not observed in basic solvents such as methanol and 2,2,2-trifluoroethanol, in which the values of the complexation equilibrium constant K are small. This can be assumed to be due to the small degree of complexation within the interval that can be used for the measurements.

In accordance with earlier work,^{9-12,16} the results of this study suggest that the thermal decomposition of substituted arenediazonium salts in the presence of acyclic polyethers in solution occurs by an S_N1 -like reaction mechanism (Scheme 1) via two competing but independent pathways: the formation of the highly reactive aryl cation by heterolysis and 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 (anion of the salt, solvent, polyether, etc.) give ArF, ArCl (e.g., in 1,2-dichloroethane and dichloromethane), ArOCH₃,¹⁶ etc.,



Scheme 1.

by the heterolytic mechanism and ArH, ArAr',^{4,12} etc., by the homolytic mechanism.

Conclusion. The present study seems to suggest that one may use inexpensive PEGs in place of expensive crown ethers as phase-transfer catalysts and solubilizing agents in the reaction of arenediazonium salts in a solvent of low polarity and basicity such as 1,2-dichloroethane. In dichloromethane, however, where homolytic dediazonation decreases the stability of the arenediazonium ion, this substitution is not possible.

Acknowledgements. The authors are grateful to Mrs. Päivi Joensuu for the MS spectra and to Mr. Reima Rönkkö for the FTIR spectra.

References

1. Pedersen, C. J. *J. Am. Chem. Soc.* 89 (1967) 2495; *ibid.* 89 (1967) 7017.
2. Knipe, A. C. *J. Chem. Educ.* 53 (1976) 618.
3. Izatt, R. M., Bradshaw, J. S., Nielsen, S. A., Lamb, J. D. and Christensen, J. J. *Chem. Rev.* 85 (1985) 271; Izatt, R. M., Pawlak, K. and Bradshaw, J. S. *ibid.* 91 (1991) 1721; Izatt, R. M., Bradshaw, J. S., Pawlak, K., Brueing, R. L. and Tarbet, B. J. *ibid.* 92 (1992) 1261 and references therein.
4. Bartsch, R. A. *Prog. Macrocycl. Chem.* 2 (1981) and references therein.
5. Beadle, J. R., Khanna, R. K. and Gokel, G. W. *J. Org. Chem.* 48 (1983) 1242.
6. Nakazumi, H., Szele, I., Yoshida, K. and Zollinger, H. *Helv. Chim. Acta* 66 (1983) 1721.
7. Kuokkanen, T. *Acta Chem. Scand.* 44 (1990) 394; Kuokkanen, T., Slotte, T. and Virtanen, V. *ibid.* 45 (1991) 674; Kuokkanen, T. *Acta Univ. Oul. A* 134 (1982) Chem. 16.
8. Kuokkanen, T. and Haataja, A. *Acta Chem. Scand.* 47 (1993) 872.
9. Bartsch, R. A. and Juri, P. N. *Tetrahedron Lett.* (1979) 407 and references therein.
10. Kuokkanen, T. *Finn. Chem. Lett.* (1985) 12.
11. Kuokkanen, T. *Acta Chem. Scand., Ser. B* 39 (1985) 813.
12. Bartsch, R. A., Juri, P. N. and Mills, M. A. *Tetrahedron Lett.* (1979) 2499; Bartsch, R. A. and Yang, I. W. *ibid.* (1979) 2503.
13. Perrin, D. D. and Armarego, W. L. F. *Purification of Laboratory Chemicals*, Pergamon Press, Oxford 1988, p. 131 and p. 145.
14. Jalonen, J., Joensuu, P. and Kuokkanen, T. *19th British Mass Spectrometry Society Meeting*, St. Andrews, Scotland (1992) 124.
15. Szele, I. and Zollinger, H. *Helv. Chim. Acta.* 61 (1978) 1721.
16. Kuokkanen, T. *Finn. Chem. Lett.* 13 (1986) 111.
17. Laali, K. and Lattimer, R. P. *J. Org. Chem.* 54 (1989) 496.
18. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 1st reprint 1990, of the 2nd ed. 1988, Verlag Chemie, Weinheim 1990.

Received September 3, 1993.