

## Effect of Solvent on the Complexation and Thermal Stability of Benzenediazonium Tetrafluoroborate in the Presence of Crown Ethers

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The complexation and the kinetics of the thermal decomposition of benzenediazonium tetrafluoroborate in the presence of crown ethers such as 15-crown-5, 18-crown-6 and 21-crown-7 in dichloromethane, methanol, 2,2,2-trifluoroethanol and dimethyl sulfoxide has been studied by UV spectrophotometry.

The benzenediazonium ion forms only a very weak charge-transfer complex with 15-crown-5. Only in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (measured earlier) does this complexation have a clear stabilizing effect. With the two larger crown ethers the benzenediazonium ion forms stabilizing insertion-type complexes in  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{OH}$  and  $\text{CF}_3\text{CH}_2\text{OH}$ . In DMSO the crown ethers have only a negligible effect up on the stability of the benzenediazonium ion and on its  $\lambda_{\text{max}}$  in UV. The complexation equilibrium constant  $K$  for the benzenediazonium tetrafluoroborate–crown ether complex, the crown ether being 18-crown-6 or 21-crown-7, depends strongly on the solvent and decreases in the order  $\text{ClCH}_2\text{CH}_2\text{Cl} > \text{CH}_2\text{Cl}_2 > \text{CH}_3\text{OH} > \text{CF}_3\text{CH}_2\text{OH}$ . A correlation between the values of  $\log K$  and the polarity or the nucleophilicity values of the solvents has been observed. When a complex is formed, the stabilization ability of the complexation against the thermal decomposition and the hypsochromic shift in the UV spectrum are insensitive to the solvent.

Arenediazonium salts have been known for more than a century and are today of considerable importance to the chemical industry.<sup>1,2</sup> Dediazoniation reactions have broad and diverse applications in synthetic chemistry in the preparation of widely different compounds.<sup>2</sup> The host–guest complexation between arenediazonium ions and crown ethers has been studied extensively over the last two decades by spectroscopic (UV, IR and NMR), kinetic and calorimetric methods.<sup>3–8</sup> It has often been assumed that the insertion complex is the only type of host–guest complexation that may occur. We have recently shown,<sup>7</sup> however, that arenediazonium ions in 1,2-dichloroethane form weak charge-transfer complexes<sup>5</sup> with 15-crown-5. The cavity of this crown ether, 0.18–0.22 nm, is too small for insertion of the diazonium group into the hole of the polyether ring since the cylindrical diameter of this group is about 0.24 nm. The stability of charge-transfer complexes is based on the interaction of the acceptor  $\text{ArN}_2^+$  and the donor component crown ether. Zollinger<sup>5</sup> has argued that the acceptor center of the arenediazonium ion is either the  $\beta$ -N-atom and/or the combined  $\pi$ -electron system of the aryl part and the diazonio group while the donor centers are one or several of the O-atoms.

To be able to exploit the host–guest complexation between arenediazonium ions and crown ethers (increase of the stability and solubility, synthetic chemistry, phase-transfer reactions, etc.) it is important to know the solvent effect on this complexation. Based upon differences in UV spectra, Hashida and Matsui<sup>9</sup> investigated the solvent effect on the complexation equilibrium constant  $K$  and the maximum absorbance  $\lambda_{\text{max}}$ . All other investigations of complexation have been carried out using only one solvent. We have previously used 1,2-dichloroethane as the solvent; being only weakly polar and nucleophilic it is thus ideal for investigations of complexation between arenediazonium salts and crown ethers. Using the unsubstituted arenediazonium ion as a model compound to eliminate steric effects on the complexation<sup>8</sup> we have now studied by kinetic and UV spectroscopic methods the effect of solvent on the complexation and thermal stability of arenediazonium salts in the presence of the crown ethers 15-crown-5, 18-crown-6 or 21-crown-7. The solvents used in the study were dichloromethane, methanol, 2,2,2-trifluoroethanol and dimethyl sulfoxide (DMSO). In all these solvents the dediazoniation of benzenediazonium tetrafluoroborate in the absence of crown ethers is solely a heterolytic process.<sup>10</sup>

Table 1. Complexation and thermal decomposition of benzenediazonium tetrafluoroborate in the presence of a crown ether in solution.

Solvent	$T/^{\circ}\text{C}$	Polyether	[Polyether]/M	$\lambda_{\text{max}}/\text{nm}$	$k_{\text{obsd}}/\text{s}^{-1}$	
Dichloromethane [ArN <sub>2</sub> <sup>+</sup> ] <sub>initial</sub> = $1.0 \times 10^{-4}$ M	50.0	21-crown-7	0	266	$9.38 \times 10^{-4}$	
	50.0	21-crown-7	$1.57 \times 10^{-4}$	254	$1.20 \times 10^{-4}$	
	50.0	21-crown-7	$2.77 \times 10^{-4}$	254	$5.17 \times 10^{-5}$	
	50.0	21-crown-7	$3.14 \times 10^{-4}$	253	$4.67 \times 10^{-5}$	
	50.0	21-crown-7	$1.00 \times 10^{-3}$	253	$8.74 \times 10^{-6}$	
	50.0	21-crown-7	$2.00 \times 10^{-3}$	253	$7.41 \times 10^{-6}$	
	40.0	18-crown-6	0	266	$2.25 \times 10^{-4}$	
	40.0	18-crown-6	$2.50 \times 10^{-4}$	252	$9.28 \times 10^{-5}$	
	40.0	18-crown-6	$3.40 \times 10^{-4}$	249	$6.53 \times 10^{-5}$	
	40.0	18-crown-6	$5.10 \times 10^{-4}$	249	$5.01 \times 10^{-5}$	
	40.0	18-crown-6	$1.25 \times 10^{-3}$	246	$3.84 \times 10^{-5}$	
	40.0	18-crown-6	$2.45 \times 10^{-3}$	246	$2.55 \times 10^{-5}$	
	40.0	15-crown-5	$2.00 \times 10^{-3}$	266	$2.29 \times 10^{-4}$	
	40.0	15-crown-5	$1.00 \times 10^{-2}$	261	$2.36 \times 10^{-4}$	
	40.0	15-crown-5	$4.00 \times 10^{-2}$	255	$2.35 \times 10^{-4}$	
	Methanol [ArN <sub>2</sub> <sup>+</sup> ] <sub>initial</sub> = $1.3 \times 10^{-4}$ M	40.0	21-crown-7	0	260	$8.00 \times 10^{-4}$
		40.0	21-crown-7	$7.83 \times 10^{-4}$	256	$4.27 \times 10^{-4}$
		40.0	21-crown-7	$1.30 \times 10^{-3}$	255	$3.16 \times 10^{-4}$
		40.0	21-crown-7	$2.60 \times 10^{-3}$	255	$2.02 \times 10^{-4}$
		40.0	21-crown-7	$5.48 \times 10^{-3}$	254	$1.07 \times 10^{-4}$
40.0		21-crown-7	$1.37 \times 10^{-2}$	254	$4.82 \times 10^{-5}$	
40.0		18-crown-6	$2.60 \times 10^{-3}$	254	$6.12 \times 10^{-4}$	
40.0		18-crown-6	$3.90 \times 10^{-3}$	252	$5.66 \times 10^{-4}$	
40.0		18-crown-6	$6.46 \times 10^{-3}$	251	$4.83 \times 10^{-4}$	
40.0		18-crown-6	$1.38 \times 10^{-2}$	249	$3.35 \times 10^{-4}$	
40.0		18-crown-6	$2.69 \times 10^{-2}$	248	$2.36 \times 10^{-4}$	
40.0		15-crown-5	$6.50 \times 10^{-3}$	260	$7.71 \times 10^{-4}$	
40.0		15-crown-5	$1.31 \times 10^{-2}$	260	$7.59 \times 10^{-4}$	
40.0		15-crown-5	$2.60 \times 10^{-2}$	259	$7.53 \times 10^{-4}$	
40.0		15-crown-5	$5.19 \times 10^{-2}$	259	$7.63 \times 10^{-4}$	
Trifluoroethanol [ArN <sub>2</sub> <sup>+</sup> ] <sub>initial</sub> = $1.3 \times 10^{-4}$ M		40.0	21-crown-7	0	262	$8.06 \times 10^{-4}$
	40.0	21-crown-7	$6.51 \times 10^{-4}$	260	$6.25 \times 10^{-4}$	
	40.0	21-crown-7	$8.98 \times 10^{-4}$	259	$5.78 \times 10^{-4}$	
	40.0	21-crown-7	$1.35 \times 10^{-3}$	258	$5.03 \times 10^{-4}$	
	40.0	21-crown-7	$3.25 \times 10^{-3}$	255	$3.33 \times 10^{-4}$	
	40.0	21-crown-7	$6.50 \times 10^{-3}$	253	$2.07 \times 10^{-4}$	
	40.0	18-crown-6	$6.54 \times 10^{-3}$	260	$6.60 \times 10^{-4}$	
	40.0	18-crown-6	$1.31 \times 10^{-2}$	259	$5.67 \times 10^{-4}$	
	40.0	18-crown-6	$2.60 \times 10^{-2}$	255	$4.36 \times 10^{-4}$	
	40.0	18-crown-6	$5.20 \times 10^{-2}$	251	$2.91 \times 10^{-4}$	
	40.0	18-crown-6	$8.17 \times 10^{-2}$	249	$2.27 \times 10^{-4}$	
	40.0	18-crown-6	$1.56 \times 10^{-1}$	247	$1.25 \times 10^{-4}$	
	40.0	15-crown-5	$1.30 \times 10^{-2}$	262	$7.69 \times 10^{-4}$	
	40.0	15-crown-5	$2.60 \times 10^{-2}$	262	$7.55 \times 10^{-4}$	
	40.0	15-crown-5	$5.20 \times 10^{-2}$	262	$7.41 \times 10^{-4}$	
	40.0	15-crown-5	$1.04 \times 10^{-1}$	262	$7.39 \times 10^{-4}$	
	DMSO [ArN <sub>2</sub> <sup>+</sup> ] <sub>initial</sub> = $1.5 \times 10^{-4}$ M	40.0	21-crown-7	0	262	$4.22 \times 10^{-4}$
		40.0	21-crown-7	$7.67 \times 10^{-3}$	260	$4.01 \times 10^{-4}$
40.0		21-crown-7	$8.86 \times 10^{-3}$	260	$3.94 \times 10^{-4}$	
40.0		21-crown-7	$3.17 \times 10^{-2}$	260	$3.31 \times 10^{-4}$	
40.0		18-crown-6	$3.13 \times 10^{-2}$	260	$4.22 \times 10^{-4}$	

**Experimental**

**Materials.** Benzenediazonium tetrafluoroborate was available from our earlier investigation<sup>7</sup> and was crystallized before use from about 25 wt% aqueous tetrafluoroboric acid. 15-Crown-5 (Fluka AG, Buchs, Switzerland, *purum*), 18-crown-6 (Fluka AG, Buchs, Switzerland, *purum*) and 21-crown-7 (Pfaltz & Bauer, Waterbury, USA, *p.a.*) were used as received. Dichloromethane (Merck, BRD, *p.a.*) was purified by being shaken with sulfuric acid, washed with sodium hydroxide solution and water, dried with calcium chloride, refluxed with phosphorus pentoxide and distilled. This solvent was kept under a nitrogen atmosphere.<sup>11</sup> Methanol (Merck, BRD, *p.a.*) was dried with molecular sieves 4 A, treated with magnesium activated with iodine and distilled.<sup>10</sup> Dimethyl sulfoxide (Fluka AG, Buchs, Switzerland, *purum*) was dried and distilled from calcium hydride at reduced pressure. 2,2,2-Trifluoroethanol (Fluka AG, Buchs, Switzerland, *puriss.*) was used as received.

**Measurements.** UV spectra were obtained with a Philips PU 8740 spectrophotometer. The accuracy of the longest wavelength maximum in UV ( $\lambda_{\max}$ ) was to within  $\pm 1$  nm. Kinetic measurements were carried out with a Perkin-Elmer 139 spectrophotometer (UV and VIS), equipped with a Hitachi Perkin-Elmer 139-0880 temperature-controlled cell attachment, keeping the temperature constant to within  $\pm 0.03^\circ\text{C}$ . Small amounts of the

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

**Results**

The spectral and stabilization effects of the host-guest complexation of benzenediazonium tetrafluoroborate with 15-crown-5, 18-crown-6 and 21-crown-7 in dichloromethane, methanol, 2,2,2-trifluoroethanol and dimethyl sulfoxide were studied UV spectrophotometrically by determining the values of the longest wavelength maximum ( $\lambda_{\max}$ ) and the decomposition rate constant ( $k_{\text{obsd}}$ ). The measurements were carried out for the uncomplexed benzenediazonium salt and in the presence of at least five suitable concentrations of the crown ether, keeping the total initial concentration of the benzenediazonium salt constant in each solvent. The decomposition reactions were followed for about two half-lives and were found to obey first-order kinetics within the intervals investigated. The standard deviation of  $k_{\text{obsd}}$  was usually  $\pm(0.5\text{--}2.0)\%$  with a correlation coefficient  $r$  of about 0.9997. The experimental results, presented in Table 1, show that in all solvents, except DMSO, an increase in the concentration of 18-crown-6 and 21-crown-7 within suitable ranges, caused an increase in the thermal stability of the benzenediazonium salt. Simultaneously, a hypsochromic shift in the UV spectrum was observed. Except

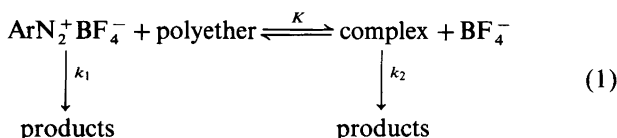
**Table 2.** Solvent effect on the complexation and stabilization of benzenediazonium tetrafluoroborate in the presence of a crown ether in solution.

System	$\lambda_{\max}/\text{nm}^a$	$\Delta\lambda_{\max}/\text{nm}$	$K/\text{dm}^3 \text{mol}^{-1b}$	$(k_1 - k_2)/\text{s}^{-1b}$	$k_2/k_1$ (%)
Solvent: $\text{CH}_2\text{Cl}_2^c$					
21-crown-7	253	14	$(9.90 \pm 0.30) \times 10^{4b}$	$(9.36 \pm 0.02) \times 10^{-4d}$	0.2
18-crown-6	246	20	$(1.02 \pm 0.05) \times 10^4$	$(2.12 \pm 0.08) \times 10^{-4}$	5.8
15-crown-5	255	11	—	—	100
Solvent: $\text{CH}_3\text{OH}^c$					
21-crown-7	254	6	$(1.22 \pm 0.03) \times 10^3$	$(7.98 \pm 0.02) \times 10^{-4}$	0.2
18-crown-6	248	12	$(1.43 \pm 0.18) \times 10^2$	$(6.84 \pm 0.55) \times 10^{-4}$	14
15-crown-5	259	1	—	—	95
Solvent: $\text{CF}_3\text{CH}_2\text{OH}^c$					
21-crown-7	253	9	$(4.77 \pm 0.10) \times 10^2$	$(7.89 \pm 0.11) \times 10^{-4}$	2.1
18-crown-6	247	15	$(3.5 \pm 0.2) \times 10^1$	$(7.85 \pm 0.20) \times 10^{-4}$	2.6
15-crown-5	262	0	—	—	92
Solvent: $\text{ClCH}_2\text{CH}_2\text{Cl}^e$					
21-crown-7 <sup>d,f</sup>	252	14	$5.06 \times 10^5$	$1.22 \times 10^{-3}$	0.12
18-crown-6 <sup>d,g</sup>	247	19	$(2.77 \pm 0.04) \times 10^4$	$(1.21 \pm 0.02) \times 10^{-3}$	1.0
15-crown-5 <sup>h</sup>	249	17	$(1.36 \pm 0.15) \times 10^2$	$(2.33 \pm 0.19) \times 10^{-4}$	26

<sup>a</sup>For the complex. <sup>b</sup>At  $40.0^\circ\text{C}$ , calculated by eqn. (2). <sup>c</sup> $\lambda_{\max}$  and  $k_1$  for the non-complexed ion, see Table 1. <sup>d</sup>At  $50.0^\circ\text{C}$ . <sup>e</sup> $\lambda_{\max} = 266$  nm and  $k_1$  ( $40^\circ\text{C}$ ) =  $3.15 \times 10^{-4} \text{s}^{-1}$  and  $k_1$  ( $50^\circ\text{C}$ ) =  $1.22 \times 10^{-3} \text{s}^{-1}$  for the non-complexed ion. <sup>f</sup>From Ref. 5. <sup>g</sup>Recalculated from data in Ref. 12. <sup>h</sup>From Ref. 7.

for the hypsochromic shift in dichloromethane the corresponding effects of 15-crown-5 were negligible.

The reactions of an arenediazonium salt in the presence of a polyether in solution can be described by eqn. (1) where  $K$  is the complexation equilibrium constant and  $k_1$  and  $k_2$  are the rate constants for the thermal decomposition of the uncomplexed and complexed ions, respectively. 'Complex' denotes an insertion and/or a



charge-transfer complex.<sup>5,7,8,12</sup> As earlier reported, 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  $k_{\text{obsd}}$  is the observed rate constant in the presence

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

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

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

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

of the free polyether concentration  $[\text{polyether}]$  and  $[\text{ArN}_2^+]$  is the free arenediazonium concentration.<sup>5,7,8,12</sup> The decomposition reactions, for which the host-guest complexation had a stabilizing effect, obeyed eqn. (2), with a correlation coefficient  $r$  for the final plot being about 0.997. The calculated values of the equilibrium constant  $K$  and the stabilization ability of the complexation  $k_2/k_1$ , together with the values of the maximum hypsochromic shift in UV  $\Delta\lambda_{\text{max}}$ , are presented in Table 2. The degree of hypsochromic shift (Table 1) is a measure of the degree of complexation.

We also determined the effect of 21-crown-7 and 18-crown-6 (Table 1) on the decomposition rate and  $\lambda_{\text{max}}$  for benzenediazonium tetrafluoroborate in DMSO. The experiments showed that in this polar and nucleophilic solvent the crown ethers cause only a negligible hypsochromic shift ( $\Delta\lambda_{\text{max}} = 2$  nm) in the UV spectrum of the benzenediazonium salt. 18-Crown-6 has no measurable effect while 21-crown-7 exerts only a slight effect on the stability of benzenediazonium tetrafluoroborate ( $[21\text{-crown-7}]/[\text{ArN}_2^+] = 206$ ;  $k_{\text{obsd}}/k_1 = 78\%$ ).

## Discussion

The complexation equilibrium constant  $K$  for host-guest complexation between arenediazonium ions and crown ethers in solution can be determined by three methods: spectrophotometrically by UV<sup>9</sup> from differences in the absorbance values, by calorimetric titration techniques<sup>13</sup> and by kinetic studies of decomposition reactions.<sup>5,7,8,12</sup> The complexation of the benzenediazonium ion with 18-crown-6 in methanol has been investigated by all

these methods. Using the value  $\Delta H = -35.2$  kJ mol<sup>-1</sup>, determined by Izatt *et al.*,<sup>13</sup> the calculated value of  $K$  at 40°C, using the van 't Hoff equation, is the following: spectrophotometrically  $K \approx 90$  dm<sup>3</sup> mol<sup>-1</sup> (Hashida and Matsui<sup>9</sup>); calorimetrically  $K \approx 160$  dm<sup>3</sup> mol<sup>-1</sup> (Izatt *et al.*); kinetically  $K \approx 143$  dm<sup>3</sup> mol<sup>-1</sup> (this work). The value of the equilibrium constant  $K$  is thus fairly independent of the method used.

Spectroscopic, kinetic and calorimetric data combined with product analyses show that arenediazonium ions form insertion-type complexes with the large crown ethers 18-crown-6 and 21-crown-7.<sup>2-10,12</sup> With 15-crown-5 only very weak charge-transfer complexes<sup>5</sup> are formed.<sup>7,8</sup> Our results, Tables 1 and 2, indicate clearly that 15-crown-5 stabilizes the benzenediazonium salt in 1,2-dichloroethane but not in the other solvents; only in 1,2-dichloroethane and in dichloromethane may a hypsochromic shift in the UV spectrum be observed. The host-guest complexation with insertion-type orientation between the benzenediazonium ion and the crown ethers 18-crown-6 or 21-crown-7 strongly stabilizes the benzenediazonium salt in all solvents except in the most nucleophilic one, DMSO. In these solvents a clear hypsochromic shift in the UV spectrum was detected.

Since arenediazonium ions are strongly electrophilic (the substituent constant  $\sigma_p$  for diazonium group is 1.8<sup>10</sup>), polar, electrophilic and nucleophilic properties of the solvents can be assumed to affect their reactions. It has been observed that their tendency to react through homolytic dediazonation increases with the nucleophilicity of the solvent; that is with an increase in their  $B$  (Table 3),  $N_{\text{BS}}$  or  $DN$  values.<sup>10,14,15</sup> Correspondingly, an increase in the electron-withdrawing properties of the substituent in the benzenediazonium ion will favor the homolysis in borderline solvents. It is known that the dediazonation of 4-CN- and 4-NO<sub>2</sub>-substituted benzenediazonium ions in DMSO occurs homolytically, while that of H- and 4-CH<sub>3</sub>-substituted ions is a heterolytic process.<sup>16</sup> Conversely, the heterolysis is favored with increasing acceptor character of the solvent, e.g. the  $E$  (Table 3) or  $AN$  value.<sup>10,15</sup> The acceptor character of the solvent, however, has a much smaller effect on heterolysis than does the donor property on homolysis.<sup>10,14</sup> Under comparable conditions homolytic dediazonation reactions are faster than the corresponding heterolytic reactions.

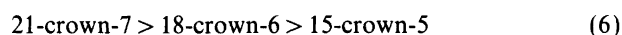
Table 3. Physical constants and parameters of the solvents.<sup>10,14,15</sup>

Solvent	$\epsilon^a$	$E_T(30)^b$	$B^c$	$E^d$
CH <sub>2</sub> Cl <sub>2</sub>	8.9	41.1	23	2.7
CH <sub>3</sub> OH	32.7	55.5	218	14.9
CF <sub>3</sub> CH <sub>2</sub> OH	26.7	59.5		
ClCH <sub>2</sub> CH <sub>2</sub> Cl	10.4	41.9	40	3.0
(CH <sub>3</sub> ) <sub>2</sub> SO	48.9	45.0	362	3.2

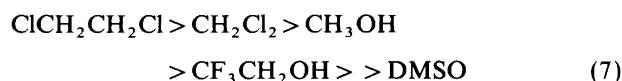
<sup>a</sup>Permittivity at 25°C. <sup>b</sup>Solvent polarity parameter in kcal mol<sup>-1</sup>. <sup>c</sup>Koppel and Paju's nucleophilicity parameter. <sup>d</sup>Koppel and Paju's electrophilicity parameter.

This fact has to be taken into consideration when, for example, the proportion of homolysis increases with increasing concentration of the crown ether.<sup>5,8</sup>

The complexation equilibrium constant  $K$ , Table 2, shows that in each solvent studied the complexation ability of crown ethers with the benzenediazonium ion decreases in the same order:



It might be assumed that the cavity of 21-crown-7 with a cavity diameter of 0.34–0.43 nm is somewhat too large for a diazonium group with a cylindrical diameter of about 0.24 nm. However, its higher ring flexibility as compared with that of 18-crown-6 with a cavity diameter of 0.26–0.32 nm, may allow for a relief of steric interactions between the 2-hydrogens or other 2-substituents in the arenediazonium cation and the macrocyclic ring.<sup>3,8</sup> This order accords with previous observations that 21-crown-7 produces the highest degree of arenediazonium ion complexation.<sup>3,5,6,8</sup> The results indicate that the value of  $K$  for the benzenediazonium tetrafluoroborate–crown ether complex, when the crown ether is 18-crown-6 or 21-crown-7, depends strongly on the solvent and decreases in the order



In DMSO, a strongly nucleophilic solvent, the complexation is negligible. The results suggest ( $r < 0.8$ ), in agreement with Hashida and Matsui,<sup>9</sup> that there is no observable correlation between the measured  $K$ -values and the common physical constants or parameters of the solvents (see Table 3). When using the values of  $\log K$  instead of the  $K$ -values one arrives at the following correlations for  $\text{C}_6\text{H}_5\text{N}_2^+\text{BF}_4^-$ –18-crown-6:

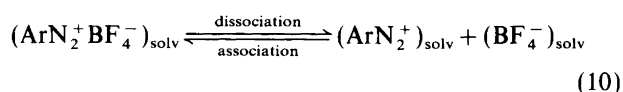
$$\begin{aligned} \log K &= -0.15E_T(30) + 10.35, r \approx 0.99, n = 4 \\ \log K &= -0.011B + 4.55, r \approx 0.97, n = 3 \end{aligned} \quad (8)$$

and for  $\text{C}_6\text{H}_5\text{N}_2^+\text{BF}_4^-$ –21-crown-7:

$$\begin{aligned} \log K &= -0.15E_T(30) + 11.61, r \approx 0.97, n = 4 \\ \log K &= -0.012B + 5.70, r \approx 0.94, n = 3 \end{aligned} \quad (9)$$

$E_T(30)$  and  $B$  are the polarity parameter and Koppel and Paju's nucleophilicity parameter of the solvent, respectively.<sup>10,14,15</sup> The values are too few for an exact mathematical treatment, but indicate that the complexation of the arenediazonium ion with the crown ethers decreases strongly with polar and/or nucleophilic/donor<sup>10,15</sup> properties of the solvent. In solvents of low permittivity ( $\epsilon$  ( $\epsilon < 10$ – $15$ )), salts are known to exist as solvated ion pairs, whereas in solvents of high  $\epsilon$  ( $\epsilon > 40$ ) they are dissociated into solvated cations and anions.<sup>15</sup> The effect of the solvent on the complexation as experienced in this work may therefore be explained by the

ability of the arenediazonium ion to be more strongly stabilized by solvation,  $(\text{ArN}_2^+)_{\text{solv}}$ , in a solvent of higher polarity and/or nucleophilicity/donicity:



The values of  $k_2/k_1$  in Table 2 indicate that the stabilization induced by the complexation of the benzenediazonium ion with crown ethers is insensitive to the solvent. In each solvent the stabilizing effect due to complexation depends strongly on the complexing agent and decreases in the same order as the complexation equilibrium constant  $K$ , eqn. (6). Thus, 21-crown-7 produces both maximal complexation and maximal stabilization for the arenediazonium ion.

The values of  $\Delta\lambda_{\text{max}}$  in Table 2 show that the hypsochromic shift, caused by complexation of the arenediazonium ion with a crown ether, is also not sensitive to the solvent. In agreement with Zollinger's<sup>5</sup> and our earlier results<sup>8</sup> in 1,2-dichloroethane, but in contrast with the complexation and the stabilization effects ( $K$ - and  $k_2/k_1$ -values), 18-crown-6 produced, in all solvents, the maximal hypsochromic shift in UV: 18-crown-6 > 21-crown-7 > 15-crown-5. Likewise, the stretching frequency shift  $\Delta\nu_{\text{NN}}$  in the IR spectra obeys this order.<sup>5,6,8</sup>

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