Decomposition of 15-Crown-5-Complexed Arenediazonium Ions in 1,2-Dichloroethane

Toivo Kuokkanen

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

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The complexation and kinetics of the thermal decomposition of substituted benzenediazonium tetrafluoroborates in the presence of 15-crown-5 have been studied spectrophotometrically in 1,2-dichloroethane. Effects of temperature and pressure on the decomposition of complexed ions were determined. Solid complexes were prepared.
Arenediazonium ions form only weak charge transfer complexes with 15-crown-5, and do not form stronger insertion-type complexes as with crown ethers possessing larger cavities (e.g. 18-crown-6). The complexation with 15-crown-5 increases the stability of arenediazonium ions in solution (though much less than insertion-type complexation) but not in the solid state, and causes a hypsochromic shift in their UV spectra. the values of the complexation equilibrium constant K are small and more or less independent of the substituent of the arenediazonium ion ($K = 100$–200 M^{-1}). Activation parameters ΔH^*, ΔS^* and ΔV^* for the decomposition of complexed ions are positive and larger than those for the corresponding uncomplexed ions.

The investigation of macrocyclic polyethers, or crown ethers as they are called after the appearance of their molecular structures, began in 1967 when Pedersen[1] published his pioneering work on their synthesis, and his observation that crown ethers form stable complexes with metal ions of an appropriate size (e.g. alkaline and alkaline earth metal cations). This discovery aroused a great deal of interest in many areas of chemistry and the interest continues to grow as new polycyclic compounds and applications are found (synthetic chemistry, phase-transfer reactions, exploitation of their ability to increase the stability and solubility of many compounds, investigations of naturally occurring compounds, etc.).[2-4] The investigation of complexation of crown ethers with arenediazonium ions began when Gokel and Cram[5] reported in 1973 that crown ethers of appropriate dimensions markedly increase the solubility of arenediazonium ions in non-polar solvents, and Bartsch[6] reported in 1976 that p-tert-butylbenzenediazonium tetrafluoroborate exhibits markedly enhanced thermal stability when complexed with 18-crown-6 or its derivatives in 1,2-dichloroethane. Since then, this complexation has been widely studied by kinetic, spectroscopic and calorimetric methods, and it is now generally concluded to occur through insertion of the diazonium group into the hole of the macrocyclic polyether ring.[3-9]

The insertion complex is possible only if the diazonium group, with a cylindrical diameter[4] of about 0.24 nm can fit into the cavity of the crown ether. Crown ethers with 18 or more members in the ring (the cavity diameter of 18-crown-6 is about 0.26–0.32 nm[3,4]) have been observed to form insertion complexes with arenediazonium ions.[3-9] But does the arenediazonium ion form a complex with crown

ethers, and if so, how strong a complex, if the diazonium group does not fit into the hole of the crown ether? Although this kind of situation has not been studied, it is often assumed that the insertion complex is the only type of complex between arenediazonium ions and crown ethers. Bartsch[4,7] has observed, nevertheless, that the rate constant k_{obsd} for the thermolysis of p-tert-butylbenzenediazonium tetrafluoroborate in 1,2-dichloroethane at 50 °C is decreased by 12 % (k_{obsd} 2.51×10^{-4} s^{-1} and 2.22×10^{-4} s^{-1}, respectively) in the presence of 1 equiv. of 15-crown-5 (cavity diameter[7] 0.17–0.22 nm). In addition, we have recently observed that arenediazonium ions form fairly strong charge transfer complexes with acyclic polyethers (e.g. pentaglyme and PEG 1000).[10] Using 15-crown-5 as the complexing agent we have now studied by kinetic and spectroscopic measurements, the complexation of arenediazonium ions with crown ethers in 1,2-dichloroethane under conditions where the diazonium group cannot fit into the cavity of the polyether ring.

Experimental

Materials. Arenediazonium tetrafluoroborates, synthesized by a standard procedure from the corresponding anilines by diazotization with isopropyl nitrite or sodium nitrite in tetrafluoroboric acidic ethanol or ethanol–water mixtures at 0–4 °C, were in part available from our earlier studies and were recrystallized before use from suitable solvents.[8,10,11] 15-Crown-5, Parish Chemical Co., was purified by distillation in a Perkin-Elmer M-131T Microstill.[8] 1,2-dichloroethane (Fluka AG, Buchs, Switzerland) was purified, dried, distilled and preserved in a nitrogen atmo-
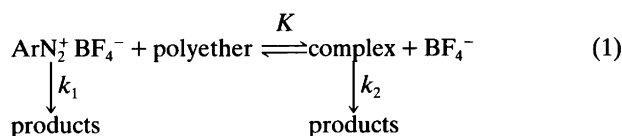
sphere.[12] Crystalline, white arenediazonium salt/15-crown-5 complexes for H- and p-CH$_3$-substituted benzenediazonium ions were synthesized and purified by a method similar to that described by Zollinger.[9]

Measurements. UV spectra were scanned with a Beckman Acta MIV 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 constant to within ±0.03 °C. The apparatus for high pressure measurements was that described earlier[13] and reactions were followed by taking samples (about 3 cm^3) at suitable intervals and measuring the absorbance immediately upon withdrawal (the temperature in the sample decreased markedly during the withdrawal) at the longest wavelength maximum of the complex. The bourdon gauge was calibrated by means of a piston loaded with weights and the pressures used were constant and accurate to within ±1.0 MPa. IR spectra were recorded with a Perkin 457 infrared spectrometer using the Nujol method and polystyrene as the calibration compound. The accuracy of the stretching frequency of the N−N bond (v_{NN}) was to within ±5 cm^{-1} and that of the longest wavelength maximum in UV (λ_{max}) to within ±1 nm. The decomposition products of benzenediazonium salt were identified with a Kratos MS 80 RF Autoconsole mass spectrometer using a capillary gas chromatographic sample inlet system, and determined quantitatively with a Hewlett-Packard 5720A gas chromatograph. Small amounts were weighed with a Perkin-Elmer Autobalance AD-2.

Results

The complexation of seven substituted benzenediazonium tetrafluoroborates with 15-crown-5 in 1,2-dichloroethane was studied by UV spectrophotometry by determining the values of the longest wavelength maximum (λ_{max}) and the rate constants of the thermal decomposition k_{obsd} (spectral and stabilization effects of complexation). Measurements were carried out for each free arenediazonium ion and in the presence of at least five suitable [15-crown-5], keeping the initial [ArN$_2^+$] constant. The reactions were followed about two half-lives and they all obeyed well first-order kinetics within the range studied: the correlation constant r for each rate constant k_{obsd} was about 0.9997 and the standard deviation usually ±(0.5–1.5)%. The results, presented in Table 1, show that, except for o-acetylbenzenediazonium ion, the increase in [15-crown-5] within suitable ranges causes a hypsochromic shift in λ_{max} of the arenediazonium ions and increases at the same time their thermal stability. these findings constitute strong evidence for a complexation of arenediazonium ions with 15-crown-5 in non-polar 1,2-dichloroethane.[4]

The reactions of arenediazonium salts in the presence of polyethers in solution can be described by eqn. (1) where

$$ArN_2^+ BF_4^- + polyether \overset{K}{\rightleftharpoons} complex + BF_4^- \qquad (1)$$
$$\downarrow k_1 \qquad\qquad\qquad\qquad \downarrow k_2$$
$$products \qquad\qquad\qquad products$$

k_1 and k_2 denote the rate constants for the thermal decomposition of the uncomplexed and complexed ions, respectively, and K is the complexation equilibrium constant.[6,8–10,13] The complexation and decomplexation reactions in the presence of crown ethers are very fast, the complexation reactions being practically diffusion-controlled.[9,14] In the conditions where $k_1 \gg k_2$ is not valid, the values of K and k_1-k_2 (and thus k_2) can be calculated by an iteration method from eqn. (2) by plotting $(k_1-k_{obsd})^{-1}$ vs. [polyether]$^{-1}$.[8,10] In eqn. (2), k_{obsd} denotes the observed rate

$$\frac{1}{k_1-k_{obsd}} = \frac{1}{(k_1-k_2)K} \frac{1}{[Polyether]} + \frac{1}{k_1-k_2} \qquad (2)$$

constant for the thermal decomposition in the presence of the polyether at a particular concentration [polyether]. The calculated results are presented in Table 2. The measurements (Table 1) showed the values of k_{obsd} for o-toluenediazonium ion to decrease with increased [15-crown-5] at low complexing agent concentration, but not beyond the last value shown in Table 1, and the values for o-acetyl-substituted benzenediazonium ion actually increased slightly with increased [15-crown-5]. Therefore, eqn. (2) was not used to calculate the values of the constant K or the stabilization ability k_2/k_1 for the $ortho$-substituted ions (the value $k_2 = 4.30 \times 10^{-4}$ s^{-1} at 30 °C was estimated for o-toluenediazonium ion). The kinetic results show, in accordance with the UV spectroscopic data (Table 1), that $ortho$-substituted benzenediazonium ions form, at most, very weak complexes with 15-crown-5, apparently due to steric reasons.

The effects of temperature and pressure on the thermal decomposition of complexes in 1,2-dichloroethane were investigated at four temperatures and five pressures from 0.1 to 202.5 MPa. The results are presented in Tables 3 and 4. All reactions studies obeyed very well the Arrhenius equation within the ranges investigated (correlation constant r at least 0.9999). The values of the activation parameters were calculated according to the transition state theory, as earlier:[8,13] the values of the activation enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ by the ordinary procedure from the constants of the Arrhenius equation and the values of the activation volume $\Delta V^{\neq}$ by eqn. (3) where B is the constant

$$\Delta V^{\neq} = -RT(B \pm \delta B) \qquad (3)$$

of the parabolic eqn. (4) and δB is the standard deviation

$$\ln (k_{obsd}/s^{-1}) = A + Bp + Cp^2 \qquad (4)$$

Table 1. Data for the thermal decomposition of arenediazonium tetrafluoroborates in 1,2-dichloethane in the presence of 15-crown-5.

Substituent	$T/°C$	$[ArN_2^+]/M$	$[15\text{-crown-}5]/M$	λ_{max}/nm	k_{obsd}/s^{-1}
H	40.0	1.0×10^{-4}	0	266	3.15×10^{-4}
			1.71×10^{-3}	264	2.71×10^{-4}
			2.39×10^{-3}	263	2.58×10^{-4}
			3.57×10^{-3}	262	2.42×10^{-4}
			5.00×10^{-3}	259	2.24×10^{-4}
			8.08×10^{-3}	253	1.95×10^{-4}
			1.61×10^{-2}	249	1.39×10^{-4}
p-CH$_3$	50.0	9.0×10^{-5}	0	282	1.45×10^{-4}
			1.81×10^{-3}	280	1.26×10^{-4}
			2.73×10^{-3}	278	1.19×10^{-4}
			4.52×10^{-3}	276	1.10×10^{-4}
			9.59×10^{-3}	270	9.56×10^{-5}
			1.96×10^{-2}	268	8.18×10^{-5}
m-Cl	50.0	1.1×10^{-4}	0	270	6.40×10^{-5}
			1.89×10^{-3}	266	5.25×10^{-5}
			2.70×10^{-3}	265	4.88×10^{-5}
			4.62×10^{-3}	260	4.13×10^{-5}
			9.02×10^{-3}	254	3.19×10^{-5}
			1.72×10^{-2}	252	2.39×10^{-5}
m-Br	50.0	1.2×10^{-4}	0	273	1.06×10^{-4}
			1.98×10^{-3}	270	8.82×10^{-5}
			2.74×10^{-3}	269	8.21×10^{-5}
			4.26×10^{-3}	267	7.52×10^{-5}
			8.96×10^{-3}	260	5.53×10^{-5}
			2.00×10^{-2}	255	3.85×10^{-5}
p-COCH$_3$	50.0	8.0×10^{-5}	0	276	1.90×10^{-4}
			1.80×10^{-3}	268	1.60×10^{-4}
			2.40×10^{-3}	265	1.52×10^{-4}
			4.11×10^{-3}	262	1.34×10^{-4}
			7.38×10^{-3}	258	1.07×10^{-4}
			1.54×10^{-2}	257	8.86×10^{-5}
o-CH$_3$	30.0	1.2×10^{-4}	0	270	6.25×10^{-4}
			1.93×10^{-3}	268	5.04×10^{-4}
			2.85×10^{-3}	267	4.81×10^{-4}
			4.54×10^{-3}	266	4.58×10^{-4}
			8.80×10^{-3}	265	4.40×10^{-4}
			2.62×10^{-2}	264	4.30×10^{-4}
o-COCH$_3$	55.0	1.5×10^{-4}	0	276	7.22×10^{-5}
			2.00×10^{-3}	275	7.30×10^{-5}
			3.50×10^{-3}	275	7.40×10^{-5}
			7.00×10^{-3}	275	7.65×10^{-5}
			1.31×10^{-2}	274	8.04×10^{-5}
			2.60×10^{-2}	273	8.70×10^{-5}

Table 2. Complexation and stabilization of arenediazonium ions in the presence of 15-crown-5 in 1,2-dichloroethane.

Substituent	$\Delta\lambda_{max}{}^a/nm$	$T/°C$	$k_1-k_2{}^b/s^{-1}$	K^b/M^{-1}	k_2/k_1 (%)
H	17	40.0	$(2.33\pm0.19)\times10^{-4}$	136 ± 15	26
p-CH$_3$	14	50.0	$(8.06\pm0.20)\times10^{-5}$	173 ± 7	44
m-Cl	18	50.0	$(6.04\pm0.24)\times10^{-5}$	126 ± 7	6
m-Br	18	50.0	$(9.80\pm0.89)\times10^{-5}$	115 ± 13	8
p-COCH$_3$	19	50.0	$(1.64\pm0.13)\times10^{-4}$	126 ± 13	16
o-CH$_3$	7	30.0	$(1.95\pm0.04)\times10^{-4}$ c	c	69^c

$^a \Delta\lambda_{max} = \lambda_{1max} - \lambda_{2max}$, where λ_{1max} and λ_{2max} are the longest wavelength maxima in, respectively, the absence and presence (in excess) of 15-crown-5. ^{b}Calculated by eqn. (2); k_1, see Table 1. ^{c}See the text.

Table 3. Effect of temperature on the thermal decomposition of arenediazonium tetrafluoroborates complexed with 15-crown-5 in 1,2-dichloroethane.

Substituent	[15-crown-5]/M^{-1} [a]	T/°C	k_{obsd}/s^{-1}	$\Delta H^{\neq}$ [b]/kJ mol^{-1}	$\Delta S^{\neq}$ [b]/J K^{-1} mol^{-1}
H	9.0×10^{-2}	50.0	4.86×10^{-4}	121±2	66±5
		40.0	1.04×10^{-4}		
		30.0	2.22×10^{-5}		
		20.0	4.30×10^{-6}		
m-Cl	1.0×10^{-1}	65.0	1.33×10^{-4}	137±1	84±2
		55.0	2.85×10^{-5}		
		50.0	1.33×10^{-5}		
		40.0	2.53×10^{-6}		
p-CH$_3$	8.0×10^{-2}	60.0	3.37×10^{-4}	136±1	95±1
		50.0	7.10×10^{-5}		
		40.0	1.37×10^{-5}		
		35.0	5.80×10^{-6}		

[a][ArN$_2^+$] see Table 1. [b]At 50 °C.

Table 4. Effect of pressure on the thermal decomposition of benzenediazonium tetrafluoroborate complexes with 15-crown-5 in 1,2-dichloroethane at 40.0 °C.

Pressure/MPa	k_{obsd}/s^{-1}	k_{calc} [a]/s^{-1}	The constants of equation (4), the activation volume $\Delta V^{\neq}$ [b]
0.1	1.04×10^{-4}	1.03×10^{-4}	$A = -9.178$
50.5	7.90×10^{-5}	8.02×10^{-5}	$B = -5.236\times10^{-3}$ MPa
101.5	6.37×10^{-5}	6.35×10^{-5}	$C = +4.340\times10^{-6}$ MPa^2
152.0	5.21×10^{-5}	5.15×10^{-5}	$\delta\ln (k/s^{-1}) = 0.011$
202.5	4.25×10^{-5}	4.28×10^{-5}	$\Delta V^{\neq} = +13.6 \pm 0.9$ cm^3 mol^{-1}

[a]Calculated from the parabolic eqn. (4), [b]Calculated from eqn. (3).

Table 5. Effect of complexation on the products of the thermal decomposition of benzenediazonium tetrafluoroborate (2×10^{-3} M) at atmospheric pressure at 50 °C in 1,2-dichloroethane.

Polyether	Ratio [a]	Complexation (%) [b]	C_6H_5F (%)	C_6H_5Cl (%)	C_6H_6 (%)	C_6H_5OMe (%)	Total (%)
	0	0	47	49	0	0	96
15-crown-5	20	83.9	18	50	1–2	4	74
15-crown-5	200	98.2	8	34	6	4	52
18-crown-6 [c]	20	99.9	22	49	3	<1	74
Pentaglyme [c]	200	99.8	14	26	9	9	58

[a]The ratio of the initial concentrations [polyether] and [ArN$_2^+$]. [b]Calculated from the value of the constant K. [c]From Ref. 13.

of the constant B. Comparison of the values of the activation parameters presented in Tables 3 and 4 with the corresponding values for the uncomplexed ions[8] shows in accordance with our earlier results[13] that the complexation of arenediazonium salts with cyclic and acyclic polyethers (the insertion and charge transfer complexes) increases the values of the activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta V^{\neq}$ of their thermal decomposition reactions in solution.

Products of the thermal decomposition of benzenediazonium tetrafluoroborate in the presence of 15-crown-5 in

1,2-dichloroethane were identified by GLC/MS and the proportions of products were identified by GLC method. The results, together with comparable data from earlier work[13] with cyclic polyether 18-crown-6 (insertion-type complexation) and acyclic pentaglyme (charge transfer complexation), are presented in Table 5. In addition to the known products of the heterolytic dediazoniation mechanism[8–10] – fluorobenzene (the Schiemann product[15]) and chlorobenzene – small amounts of benzene (a product of the homolytic dediazoniation) and anisole were found in

Table 6. Data for solid arenediazonium tetrafluoroborate: polyether complexes.

Compound	$T/°C$	$\lambda_{max}/\text{nm}^a$	$\Delta\lambda_{max}/\text{nm}^b$	$v_{NN}{}^c/\text{cm}^{-1}$
$C_6H_5N_2{}^+BF_4{}^-$	108–110	266	–	2300
$C_6H_5N_2{}^+BF_4{}^-$–15-crown-5	96– 98	265	1	2300
$C_6H_5N_2{}^+BF_4{}^-$–18-crown-6	89– 91	253	13	2320
$C_6H_5N_2{}^+BF_4{}^-$–pentaglyme^d	104–106	264	2	2300
$p\text{-}CH_3C_6H_4N_2{}^+BF_4{}^-$	109–111	282	–	2275
$p\text{-}CH_3C_6H_4N_2{}^+BF_4{}^-$–15-crown-5	103–105	281	1	2275
$p\text{-}CH_3C_6H_4N_2{}^+BF_4{}^-$–18-crown-6	106–108	273	9	2295
$p\text{-}CH_3C_6H_4N_2{}^+BF_4{}^-$–pentaglyme^d	107–109	280	2	2275

^{a}In 1,2-dichloroethane. ^{b}The hypsochromic shift due to the complexation. ^{c}By the Nujol method. ^{d}From Ref. 10.

the presence of 15-crown-5. Anisole can be assumed to be formed by the heterolytic dediazoniation mechanism in the reaction of the phenyl cation with polyether.[9] The amount of fluorobenzene and the total amount of the known products in Table 5 are observed to decrease with increased [15-crown-5] (increase of the complexation). A similar decrease in the amount of the known products has been found in the presence of all polyethers studied[9,13] evidently due to the reactions of the intermediate phenyl cations with polyethers.

The decomposition temperatures and the UV and IR spectroscopic data for the synthesized, white crystalline arenediazonium tetrafluoroborate/polyether complexes are presented in Table 6. The decomposition temperatures show that the complexation of arenediazonium ions with 15-crown-5, as earlier observed for other crown ethers[9] (insertion complexes) and acyclic polyethers[10] (charge transfer complexes), does not increase their thermal stability in the solid state; on the contrary, they all are somewhat destabilized. In the UV results, the values of λ_{max} of crystalline $ArN_2^+\, BF_4^-$/15-crown-5 complexes in 1,2-dichloroethane are only slightly less ($\Delta\lambda_{max}$ ca. 1 nm) than those of the corresponding uncomplexed ions, whereas the corresponding hypsochromic shifts of complexes $ArN_2^+\, BF_4^-$/18-crown-6 ($\Delta\lambda_{max}$ ca. 9–13 nm), $ArN_2^+\, BF_4^-$/pentaglyme[10] ($\Delta\lambda_{max}$ ca. 2–3 nm) and $ArN_2^+\, BF_4^-$/PEG 1000[10] ($\Delta\lambda_{max}$ ca. 3–9 nm) are unmistakable. The amount of the hypsochromic shift is a measure of the strength of the complex. In agreement with the UV spectroscopic results, the complexation of arenediazonium tetrafluoroborate with 15-crown-5 does not cause a measurable shift in the stretching frequency of the N–N bond in IR spectroscopy, whereas the insertion complexation of arenediazonium salts with 18-crown-6 and 21-crown-7[7,9] causes an unusual increase in their v_{NN} values.

Discussion

The kinetic and spectroscopic measurements and product analyses of this investigation all indicate that arenediazonium salts form complexes with 15-crown-5 in solution. These are nevertheless very weak compared with the insertion complexes formed with 18-crown-6 and other larger

crown ethers, and cannot be observed at low concentrations of the complexing agent. The complexation of arenediazonium ions with 15-crown-5 increases their thermal stability in solution (Tables 1 and 2) but not in the solid state (Table 6) and causes a hypsochromic shift in their UV spectra (Tables 1 and 2), but in contrast with the insertion complexes, causes no measurable shift in the IR stretching frequency of the N–N bond.[4–9] Keeping in the mind that fluoroarene, the product of the Schiemann reaction, is formed from the Ar^+/BF_4^- ion pair,[15] the observed decreases in the proportion of this product and in the total amount of the known products with increasing [15-crown-5] (Table 5) support the conclusion that complexation does occur. For steric reasons, *ortho*-substituted arenediazonium ions form, at most, very weak complexes with 15-crown-5.

Comparison of the values of the complexation equilibrium constant K of this investigation (Table 2) with those of earlier work[8–10] shows the charge transfer complexes of arenediazonium ions with 15-crown-5 to be much weaker than the insertion-type complexes with larger crown ethers (e.g. 18-crown-6 and especially 21-crown-7[9]) but also much weaker than their charge transfer complexes with acyclic polyethers, pentaglyme and PEGs. It has often been observed that the strength of the complexation of polyethers with cations does not solely depend on the relative sizes of the species of the host–guest complex but also on the flexibility of the host molecules.[3] The present results suggest that the acyclic polyethers pentaglyme and PEGs are more flexible than cyclic 15-crown-5. In contrast with all previous studies where stronger complexation was involved, the complexation equilibrium constant K in this work was more or less independent of the substituent in the case of the *m*- and *p*-substituted benzenediazonium ions. As expected for a relatively weak electrostatic interaction, the value of K in all systems studied[9,10] is however not sensitive to the character of the substituent in the benzene ring: the reaction constant ϱ of the Hammett equation[16] $\log K = \varrho\sigma$ varies from 0.68 for the ArN_2^+/pentaglyme system[10] to about 1.3 for the ArN_2^+/18-crown-6[9,10] and ArN_2^+/21-crown-7[9] systems. By contrast, the value of the equilibrium constant of the nucleophilic cation–anion combination reactions of arenediazonium ions (with anions OH^-, CN^-, etc.) has been

Table 7. Activation parameters of the thermal decomposition of arenediazonium tetrafluoroborates complexes with polyethers in 1,2-dichloroethane at 50°C.

Polyether	H-substituted ion		p-CH$_3$-substituted ion	
	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}
	108	34	108	16
15-crown-5	121	66	136	95
Pentaglyme	138[a]	110[a]	137[b]	90[b]
PEG 1000	129[a]	85[a]		
PEG 2000	126[a]	76[a]		
18-crown-6	157[a]	153[a]	153[b]	125[b]

[a]From Ref. 13; [b]From our poster (Finnish Chemical Congress, 1988).

shown to be very sensitive to the substituent of the benzenediazonium ion.[17]

The calculated values of the stabilization ability k_2/k_1 in Table 2 show, as expected from the small values of the complexation constant K, that 15-crown-5 stabilizes arenediazonium ions against thermal decomposition in solution much less than 18-crown-6 and 21-crown-7 during insertion complexation, for which the calculated values of k_2/k_1 are about 1–2 %[8,9] and 0.1–0.5 %,[9] respectively. The stabilization ability of the acyclic polyethers pentaglyme and PEGs[10] in charge transfer complexation is similar (k_2/k_1 generally 15–22 %) to that observed in this work.

The values of the activation enthalpy $\Delta H^{\neq}$ and the activation entropy $\Delta S^{\neq}$ for the thermal decomposition of arenediazonium tetrafluoroborates complexed with 15-crown-5 are large, and clearly larger than the corresponding values for the uncomplexed ions, but smaller than those for the decomposition of stronger complexes, such as those formed with 18-crown-6 (Table 7). A comparison of the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in Table 7 suggests an isokinetic equation for both benzenediazonium tetrafluoroborate ($r = 0.9993$, $n = 6$) and p-toluenediazonium salt ($r = 0.994$, $n = 4$), including the thermal decompositions of the uncomplexed ions. Likewise, the value of the activation volume $\Delta V^{\neq}$ (Table 4) for the thermal decomposition of the complex C$_6$H$_5$N$_2^+$/15-crown-5 in 1,2-dichloroethane is large and positive, and clearly larger (evidence of the complexation) than the value $\Delta V^{\neq} = +8.4 \pm 0.2$ cm^3 mol^{-1} calculated[13] for the corresponding reaction of the uncomplexed ion. The activation volume in this work, $\Delta V^{\neq} =$

$+13.6 \pm 0.9$ cm^3 mol^{-1}, is slightly smaller, however, than the value $\Delta V^{\neq} = +15.7 \pm 0.7$ cm^3 mol^{-1} determined for the stronger complexes of benzenediazonium ion with pentaglyme, PEG 1000, PEG 2000 and 18-crown-6.[13] Zollinger et al.[9] have recently suggested that all decomposition reactions of arenediazonium salts complexed with crown ethers occur via a charge transfer complex, not via the unreactive insertion complex, and that there is a very fast equilibrium between these two complexes and the uncomplexed ion. This suggestion could explain the similarity of the activation volumes observed in our investigation[13] in the presence of cyclic and acyclic polyethers under conditions where the strength of the complexation and the stabilization ability varied strongly.

Our present results suggest that the thermal decomposition of arenediazonium tetrafluoroborate in the presence of 15-crown-5 occurs by an S$_N$1-like reaction mechanism (Scheme 1) via two competing, independent pathways, with the formation of a highly reactive aryl cation (heterolysis) and an aryl radical (homolysis) in the slow rate-determining decomposition step of the uncomplexed ion or the charge transfer complex. Subsequent fast product-determining reactions with nucleophiles (counter ion, solvent, polyether, etc.) give the products ArF, ArCl and ArOCH$_3$ in the heterolysis and ArH in the homolytic pathway.[8–10,13]

Complex = charge transfer complex
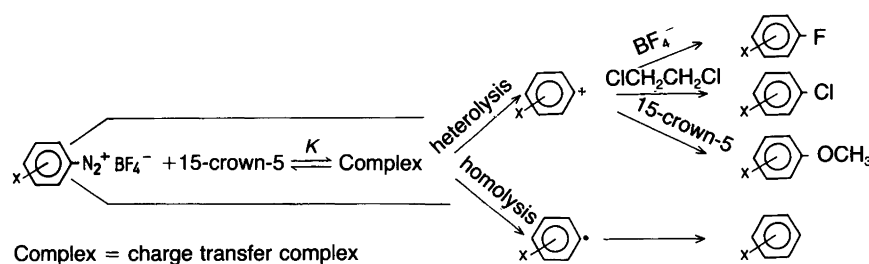
Scheme 1.

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