Effect of an *ortho*-Substituent on the Decomposition of Crown Ether Complexed Arenediazonium Ions in 1,2-Dichloroethane

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The effect of an *o*-substituent (CH_3, C_2H_5 and $COCH_3$) on the complexation and the kinetics of thermal decomposition of arenediazonium tetrafluoroborates in the presence of crown ethers (15-crown-5, 18-crown-6 and 21-crown-7) and the effect of temperature on the decomposition of the complexed ions were studied by UV spectrophotometry in 1,2-dichloroethane. Solid 1:1 complexes were prepared and analyzed (by IR spectroscopy and by decomposition temperature).

In the solid state, none of the arenediazonium ions is stabilized by complexation with crown ethers. In solution they form at most very weak charge-transfer complexes with 15-crown-5 but stronger insertion-type complexes with the larger 18-crown-6 and 21-crown-7 molecules (except for the *o*-acetyl-substituted ion, which is destablized with increasing [18-crown-6] and [15-crown-5]). The values of the complexation equilibrium constant K and the stabilization ability of the complexation are largest for 21-crown-7, and are much smaller than the corresponding values for the complexation of *p*- or *m*-substituted arenediazonium ions with the same complexing agents: i.e. there are clear *ortho*-effects due to the steric hindrance for the complexation. The values of the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the thermal decomposition of the complexed ions are large and positive (largest for 21-crown-7) and suggest an isokinetic relationship for each ion. The complexation in solution causes a hypsochromic shift in the UV spectrum of the arenediazonium ion which is proportional to the strength of the complexation.

Starting with the pioneering work of Pedersen[1] the crown ethers have been enthusiastically investigated for over 20 years, and important applications have been found in many areas of science (synthetic chemistry, phase-transfer reactions, exploitation of their ability to enhance the solubility and stability of different compounds, studies of naturally occurring compounds, etc.).[2–4] Gokel and Cram[5] reported that crown ethers of appropriate dimensions markedly increase the solubility of arenediazonium ions in non-polar solvents, and Bartsch *et al.*[6] observed that 18-crown-6 and its derivatives strongly stabilize the *p*-t-butylbenzenediazonium ion against thermal decomposition in solution. Since then, the complexation of arenediazonium ions, substituted in the *p*- or *m*-position, with crown ethers has been widely investigated, especially by spectroscopic and kinetic methods.[3,7–12] We have observed, in accordance with other workers, that acyclic polyethers (PEGs, pentaglyme, etc.) also form stable complexes with arenediazonium ions.[13,14]

Complexes of arenediazonium ions and crown ethers are generally considered to form through insertion of the diazonium group, with a cylindrical diameter of about 0.24 nm,[8] into the hole of the macrocyclic polyether ring. Although it is usually assumed that the insertion complex is the only type of complexation between arenediazonium ions and crown ethers, we have recently[15] demonstrated, through several measurements, that arenediazonium ions form weak charge-transfer complexes with 15-crown-5, whose cavity diameter of 0.18–0.22 nm[9] is too small for insertion-type complexation. The crown ethers are flexible compounds, so that their ability to form complexes in a particular case cannot be concluded without experimental study. Using methyl-, ethyl- and acetyl-substituted arenediazonium tetrafluoroborates as model compounds, in this work we investigated by kinetic and spectroscopic methods the steric effect of *o*-substituents on the complexation and stabilization of arenediazonium ions in the presence of crown ethers (15-crown-5 and 18-crown-6, with cavity diameter[9] 0.26–0.32 nm, and 21-crown-7, with cavity diameter[9] 0.34–0.43 nm).

Experimental

Materials. *o*-Acetylbenzenediazonium tetrafluoroborate was available from our earlier investigations, and *o*-methyl- and *o*-ethyl-substituted benzenediazonium tetrafluoroborates were synthesized by standard[11,16] procedures from the corresponding substituted anilines by diazotization with sodium nitrite in a tetrafluoroboric acidic ethanol–water

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mixture at 0–4 °C. The salts were recrystallized before use from suitable solvents. UV spectral data in acidic aqueous solution (0.1 M HCl) were the following: for o-$CH_3C_6H_4N_2^+BF_4^-$ λ_{max} = 266 nm and log ε = 4.08, and for the o-C_2H_5-substituted salt λ_{max} = 266 nm and log ε = 4.02. 15-Crown-5 (Parish Chemical Co., Provo, Utah) and 18-crown-6 (Fluka AG, Buchs, Switzerland, *purum*), available from our earlier studies, and 21-crown-7 (Pfaltz & Bauer, Inc.) were used as received. Crystalline 1:1 complexes of o-$XC_6H_4N_2^+BF_4^-$ with the crown ether (18-crown-6 or 21-crown-7) were synthesized in 1,2-dichloroethane, and after filtration the white, solid complexes were precipitated and washed by addition of diethyl ether.[10] 1,2-Dichloroethane (Fluka AG, Buchs, Switzerland) was purified, dried, distilled and preserved in a nitrogen atmosphere.[17]

Measurements. UV spectra were recorded with a Beckman Acta MIV or 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 within ±0.03 °C. IR spectra were scanned with a Perkin–Elmer 457 infrared spectrometer using the Nujol method and polystyrene as the calibration compound. The accuracy of the longest wavelength maximum in the UV (λ_{max}) was within ±1 nm and that of the stretching frequency of the N–N bond (v_{NN}) was about ±5 cm^{-1}. The decomposition products of o-toluenediazonium tetrafluoroborate were identified with a Kratos MS 80 RF Autoconsole mass spectrometer using a capillary gas-chromatograhic sample inlet system (Scheme 1). The decomposition temperatures of the solid salts were determined using a Thermopan microscope (Reichert, Wien). Small amounts were weighed with a Perkin–Elmer AD-2 autobalance.

Results

The spectral and stabilization effects of the complexation of o-CH_3-, o-C_2H_5- and o-$COCH_3$-substituted benzenediazonium tetrafluoroborates with 15-crown-5, 18-crown-6 and 21-crown-7 in solution were investigated by UV spectrophotometry by determining the values of the longest wave-length maximum (λ_{max}) and the decomposition rate constant k_{obsd} in 1,2-dichloroethane. The measurements were carried out for free arenediazonium ions and in the presence of at least five suitable concentrations of crown ether, keeping the initial [ArN_2^+] constant for each arenediazonium ion. The decomposition reactions were followed for about two half-lives and they all obeyed well first-order kinetics within the interval studied: the correlation constant r for k_{obsd} was about 0.9998 and the standard deviation was usually ±(0.5–1.5) %. The results for the o-CH_3- and o-C_2H_5-substituted ions are presented in Table 1 and the kinetic results for the o-$COCH_3$-substituted compound in Fig. 1. The experiments show that, except for the o-acetyl-benzenediazonium ion in the presence of 15-crown-5 and 18-crown-6, the increase in [crown ether] within suitable ranges causes a hypsochromic shift in λ_{max} of the o-substituted benzenediazonium ions, and at the same time increases their thermal stability in solution.

The effect of temperature on the thermal decomposition of uncomplexed[11] and crown-ether-complexed o-substituted arenediazonium ions (or in the presence of a very large excess of crown ether if the ions do not form complexes) was studied in 1,2-dichloroethane at four temperatures (Table 2). All these reactions obeyed well the Arrhenius equation within the temperature interval studied ($r \approx$ 0.9999). The values of the activation enthalpy $\Delta H^{\neq}$ and activation entropy $\Delta S^{\neq}$ were calculated as earlier[11,15] according to transition-state theory, by ordinary procedures, from the constants E ($\Delta H^{\neq}$) and A ($\Delta S^{\neq}$) of the Arrhenius equation. The results are presented in Table 3.

The reactions of arenediazonium salts in the presence of polyethers (crown ether or acyclic polyether) in solution can be interpreted according to reaction (1), where k_1 and k_2 are the rate constants for the thermal decomposition of

$$ArN_2^+BF_4^- + \text{polyether} \overset{K}{\rightleftharpoons} \text{complex} + BF_4^-$$

$$\downarrow k_1 \qquad\qquad\qquad \downarrow k_2 \qquad\qquad (1)$$

products   products

Complex = insertion complex or charge transfer complex

Scheme 1.

Table 1. Data for the complexation and thermal decomposition of *o*-methyl- and *o*-ethylbenzenediazonium tetrafluoroborates in 1,2-dichloroethane in the presence of crown ethers.

Crown ether	$T/°C$	$[ArN_2^+]/$ 10^{-4} M	[Crown ether]/ M	$\lambda_{max}/$ nm	k_{obsd}/s^{-1}
Substituent: *o*-methyl[a]					
18-crown-6	50.0	1.8	–	270	1.03×10^{-2}
			9.87×10^{-4}	260	4.15×10^{-3}
			1.39×10^{-3}	258	3.55×10^{-3}
			2.92×10^{-3}	256	2.41×10^{-3}
			5.37×10^{-3}	255	1.65×10^{-3}
			8.66×10^{-3}	254	1.31×10^{-3}
21-crown-7	40.0	1.2	–	271	2.16×10^{-3}
			2.4×10^{-4}	260	6.47×10^{-4}
			3.6×10^{-4}	258	4.81×10^{-4}
			6.0×10^{-4}	257	2.85×10^{-4}
			1.2×10^{-3}	256	1.38×10^{-4}
			3.6×10^{-3}	256	4.71×10^{-5}
Substituent: *o*-ethyl					
15-crown-5	30.0	1.4	–	271	1.76×10^{-3}
			1.40×10^{-3}	270	1.31×10^{-4}
			1.40×10^{-2}	268	9.96×10^{-4}
			2.79×10^{-2}	266	8.65×10^{-4}
			7.57×10^{-2}	260	6.35×10^{-4}
			9.95×10^{-2}	259	6.19×10^{-4}
			1.36×10^{-1}	258	5.93×10^{-4}
18-crown-6	30.0	1.4	5.18×10^{-4}	266	7.01×10^{-4}
			7.00×10^{-4}	264	6.51×10^{-4}
			1.04×10^{-3}	260	5.49×10^{-4}
			4.23×10^{-3}	255	2.17×10^{-4}
			6.99×10^{-3}	254	1.42×10^{-4}
21-crown-7	30.0	1.4	2.11×10^{-4}	259	2.72×10^{-4}
			2.81×10^{-4}	258	1.95×10^{-4}
			4.27×10^{-4}	257	1.19×10^{-4}
			7.00×10^{-4}	257	6.53×10^{-5}
			1.40×10^{-3}	256	3.02×10^{-5}
			6.98×10^{-3}	256	8.02×10^{-6}

[a] In the presence of 15-crown-5.[15]

the uncomplexed and complexed arenediazonium ions, K is the complexation equilibrium constant and complex denotes an insertion complex or charge-transfer complex.[6,11-15]

The rate at which the arenediazonium ions are complexed with crown ethers (k_c) was observed to be almost totally diffusion-controlled and to be nearly independent of the
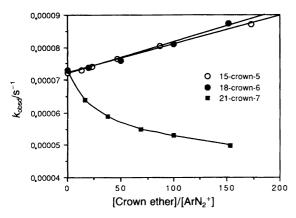

Fig. 1. Effect of crown ethers on the thermal decomposition of *o*-acetylbenzenediazonium tetrafluoroborate (1.5×10^{-4} M) at 55.0 °C in 1,2-dichloroethane (15-crown-5, Ref. 15).
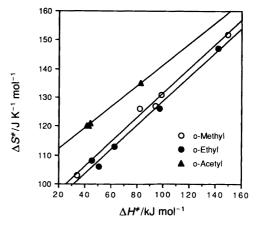
Fig. 2. Isokinetic relationships for the thermal decomposition of crown ether complexed *o*-substituted benzenediazonium tetrafluoroborates in 1,2-dichloroethane at 50.0 °C.

Table 2. Effect of temperature on the thermal decomposition of crown ether complexed *o*-substituted benzenediazonium tetrafluoroborates in 1,2-dichloroethane.

Crown ether	[Crown ether]/ M	$T/°C$	k_{obsd}/s^{-1}
Substituent: *o*-CH$_3$ [a]			
15-crown-5	1.0×10^{-1}	20.0	3.90×10^{-5}
		30.0	2.03×10^{-4}
		40.0	9.75×10^{-4}
		45.0	2.07×10^{-3}
18-crown-6	2.0×10^{-2}	25.0	1.12×10^{-5}
		30.0	2.72×10^{-5}
		40.0	1.49×10^{-4}
		50.0	7.20×10^{-4}
21-crown-7	1.0×10^{-2}	30.0	2.98×10^{-6}
		40.0	2.04×10^{-5}
		50.0	1.30×10^{-4}
		60.0	7.34×10^{-4}
Substituent: *o*-C$_2$H$_5$ [a]			
–	–	15.0	1.83×10^{-4}
		20.0	4.14×10^{-4}
		30.0	1.63×10^{-3}
		35.0	3.49×10^{-3}
15-crown-5	1.35×10^{-1}	25.0	2.60×10^{-4}
		30.0	5.93×10^{-4}
		35.0	1.24×10^{-3}
		40.0	2.45×10^{-3}
18-crown-6	7.0×10^{-3}	20.0	2.72×10^{-5}
		30.0	1.42×10^{-4}
		40.0	8.25×10^{-4}
		50.0	3.48×10^{-3}
21-crown-7	7.0×10^{-3}	30.0	8.02×10^{-6}
		40.0	4.88×10^{-5}
		50.0	3.20×10^{-4}
		60.0	1.64×10^{-3}
Substituent: *o*-COCH$_3$ [a]			
15-crown-5	3.0×10^{-2}	40.0	1.19×10^{-5}
		50.0	5.14×10^{-5}
		60.0	1.96×10^{-4}
		65.0	3.94×10^{-4}
18-crown-6	2.28×10^{-2}	40.0	9.74×10^{-6}
		50.0	4.31×10^{-5}
		55.0	8.73×10^{-5}
		65.0	3.13×10^{-4}
21-crown-7	2.3×10^{-2}	45.0	1.03×10^{-5}
		55.0	4.99×10^{-5}
		65.0	2.24×10^{-4}
		70.0	4.53×10^{-4}

[a]The initial concentrations were [*o*-CH$_3$C$_6$H$_4$N$_2$$^+$] = 1.0×10^{-4} M, [*o*-EtC$_6$H$_4$N$_2$$^+$] = 1.4×10^{-4} M and [*o*-COCH$_3$C$_6$H$_4$N$_2$$^+$] = 1.5×10^{-4} M.

size of the crown ether.[12,18] The decomposition reaction (k_d) was also fast, but k_d is much less than k_c ($K = k_c/k_d$) and is dependent on the crown ether, being the least for 21-crown-7.[12] In the conditions of this study, where $k_1 \gg k_2$ is not valid, the constants K, $k_1 - k_2$ and k_2 (Table 3) can be calculated as described earlier[12,13,15] by an iteration

method from the linear eqn. (2) by plotting $1/(k_1 - k_{obsd})$ vs. $1/$[polyether], where k_{obsd} denotes the observed rate constant for thermal decomposition in the presence of the polyether at a particular concentration [polyether]. The correlation coefficient r for the final plot of eqn. (2) in this work was about 0.993.

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

The UV and IR spectroscopic data and the decomposition temperatures for the synthesized, uncomplexed and complexed, white crystalline salts are collected in Table 3. The data show that the complexation of *o*-substituted benzenediazonium salts with crown ethers, as reported earlier for solid complexes of *p*- and *m*-substituted arenenediazonium ions with crown ethers[12,15,19] (insertion or charge-transfer complexes) and acyclic polyethers[13,19] (charge-transfer complexes), does not stabilize them in the solid state; on the contrary, they are usually destabilized. In agreement with findings for the *p*- and *m*-substituted ions,[12,13,15,19] only strong complexation of *o*-substituted benzenediazonium salts with crown ethers causes a measurable shift in the stretching frequency of the N–N bond (v_{NN}) in IR spectroscopy (Table 3). Haymore *et al.*[20] reported that v_{NN} for the benzenediazonium salt increases by 32 cm^{-1} upon complexation with dicyclohexano-18-crown-6, the first observation of the effect for a diazonium complex in which v_{NN} increases upon complexation.[12] The complexation of arenediazonium salts with acyclic polyethers (e.g. pentaglyme and PEG 1000) and 15-crown-5[15] (charge-transfer complexes) is not observed to cause this kind of unusual increase in the v_{NN} values.[13,19]

Discussion

The spectroscopic and kinetic data of this study indicate that benzenediazonium ions substituted in the *o*-position also form complexes with crown ethers of appropriate dimensions. Of the ions studied, *o*-methyl- and *o*-ethyl-benzenediazonium ions can be assumed to form insertion-type complexes with both 18-crown-6 and 21-crown-7, but the *o*-acetyl-substituted ion forms complexes only with 21-crown-7. The complexation of the *p*-, *m*- or *o*-substituted arenediazonium salt with crown ethers (insertion or charge-transfer complex) or acyclic polyethers (charge-transfer complex only) increases its thermal stability in solution but not in the solid state, and causes a hypsochromic shift in its UV spectrum (e.g. 13–15 nm for *o*-substituted ions with 21-crown-7). The degree of hypsochromic shift is a measure of the degree of complexation (Table 1) and the strength of the complex (Table 3). It is interesting to note that, in contrast to the dependence of the complexation equilibrium constant K and the stabilizing ability of the complexation k_1/k_2 (or decrease in the value of k_2/k_1 in Table 3) on the size of crown ether, the hypsochromic shift, $\Delta\lambda_{max}$, in the UV

Table 3. Effect of crown ether on the thermal decomposition, stabilization and complexation of *o*-substituted tetrafluoroborates in 1,2-dichlororoethane.

Physical constant	No complex	15-Crown-5	18-Crown-6	21-Crown-7
Substituent: *o*-CH$_3$				
λ_{max}/nm [a]	270	264	254	255
$\Delta\lambda_{max}$/ nm	–	7	16	15
K/mol^{-1} dm^3 [b]	–	c	$(2.14\pm0.13)\times10^3$	$(1.52\pm0.09)\times10^4$
k_2/k_1/% [b]	–	69	9.1	1.1
$\Delta H^{\#}$/kJ mol^{-1} [d]	103±2	126±1	131±1	152±1
$\Delta S^{\#}$/J K^{-1} mol^{-1} [d]	34±4	82±2	99±1	149±3
T_{decomp}/°C [e]	81–84	c	83–84	83–85
ν_{NN}/cm^{-1} [f]	2255	c	2255	2270
Substituent: *o*-C$_2$H$_5$				
λ_{max}/nm [a]	270	258	254	256
$\Delta\lambda_{max}$/ nm	–	12	16	14
K/mol^{-1} dm^3 [b]	–	c	$(4.09\pm0.73)\times10^3$	$(5.54\pm0.33)\times10^4$
k_2/k_1/% [b]	–	43.5	8.5	1.1
$\Delta H^{\#}$/kJ mol^{-1} [d]	106±2	113±3	126±3	147±3
$\Delta S^{\#}$/J K^{-1} mol^{-1} [d]	51±4	63±8	97±8	142±8
T_{decomp}/°C [e]	64–65	c	68–70	72–74
ν_{NN}/cm^{-1} [g]	2250	c	2265	2265
Substituent: *o*-COCH$_3$				
λ_{max}/nm [a]	273	271	268	260
$\Delta\lambda_{max}$/ nm	–	2	5	13
K/mol^{-1} dm^3 [b]	–	c	c	205±12
k_2/k_1/% [b]	–	g	g	63.5
$\Delta H^{\#}$/kJ mol^{-1} [d]	121±2	120±1	120±2	135±1
$\Delta S^{\#}$/J K^{-1} mol^{-1} [d]	44±4	43±3	41±5	83±1

[a] [Crown] in large excess. [b] The temperature, see Table 1 or Fig. 1. [c] Cannot be determined. [d] At 50 °C. [e] For the solid 1:1 complex. [f] Determined by the nujol method. [g] Destabilized.

caused by insertion-type complexation is largest for the *o*-substituted benzenediazonium/18-crown-6 systems. Zollinger[12] has observed that 18-crown-6 also causes the largest $\Delta\lambda_{max}$ for *p*- and *m*-substituted benzenediazonium ions. Only a strong complexation of *o*-substituted benzenediazonium salts with crown ethers (Table 3) causes a measurable, unusual increase in their ν_{NN} value in IR spectroscopy.

The results (Fig. 1 and Table 3) suggest that *o*-acetylbenzenediazonium tetrafluoroborate does not form a complex, at least not an insertion or charge-transfer complex, with

15-crown-5 or 18-crown-6. Presumably this is due to the steric hindrance of the *o*-substituent for complexation. Under comparable conditions homolytic dediazonation reactions are known to be faster than the corresponding heterolytic reactions, and thus the slight destabilization with increasing [crown ether] in these cases can be assumed to be due to the increase of homolytic decomposition reactions. A destabilization with an increase in [polyether] has earlier been observed for the thermal decomposition of *p*-cyanobenzenediazonium ion in the presence of PEG 1000[13] and

Table 4. Effect of substituent on the complexation and stabilization of arenediazonium tetrafluoroborates complexed with polyethers in 1,2-dichloroethane.

Polyether	K/M^{-1}			k_2/k_1/%		
	o-CH$_3$	H	*p*-CH$_3$	*o*-CH$_3$	H	*p*-CH$_3$
15-crown-5 [a]	–	1.36×10^2	1.73×10^2	69	26	44
18-crown-6 [b]	2.14×10^3	4.69×10^4	2.47×10^4	9.1	1.4	1.5
21-crown-7 [b]	1.51×10^4	5.06×10^5	3.08×10^5	1.1	0.12	0.22
pentaglyme [c]	9.59×10^1	1.17×10^3	8.46×10^2	20	17	22
PEG 1000 [c]	1.29×10^3	6.32×10^3	6.07×10^3	20	19	21

[a] From Ref. 15. [b] This work (*o*-CH$_3$) or from Ref. 12. [c] From Ref. 13.

for m-cyano- and p-chlorobenzenediazonium salts in the presence of dicyclohexano-24-crown-8[12] (also for all these reactions in 1,2-dichloroethane). The values of the activation enthalpy $\Delta H^{\neq}$ and activation entropy $\Delta S^{\neq}$ for the thermal decomposition reactions of o-substituted benzenediazonium ions complexed with crown ethers are large, and clearly larger than the corresponding values for the uncomplexed ions (Table 3). The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are largest for $ArN_2^+BF_4^-$/21-crown-7 systems. Thus the size of the increase in both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is a measure of the strength of complexation (cf. non-complex systems in Table 3). Taking into consideration the structure of the ArN_2^+/crown ether complex (insertion or charge-transfer complex) and the increase in entropy with disorder, the values of $\Delta S^{\neq}$ are in good accord with the proposed reaction mechanism (see below). A comparison of the corresponding values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in Table 3 suggests an isokinetic relationship (Fig. 2) for all o-substituted ions investigated, with values of the correlation coefficient r of 0.996 ($n = 5$), 0.994 ($n = 5$) and 0.999 ($n = 4$) for o-CH$_3$-, o-C$_2$H$_5$- and o-COCH$_3$-substituted ions, respectively. It is interesting to observe that these isokinetic relationships also include the corresponding values of the uncomplexed ions, and the values $\Delta H^{\neq} = 127 \pm 2$ kJ mol^{-1} and $\Delta S^{\neq} = 94 \pm 4$ J K^{-1} mol^{-1} calculated in this work for the o-CH$_3$C$_6$H$_4$N$_2^+$BF$_4^-$/pentaglyme system (acyclic polyether, only charge-transfer complexation possible) in 1,2-dichloroethane, and $\Delta H^{\neq} = 108 \pm 2$ kJ mol^{-1} and $\Delta S^{\neq} = 45 \pm 6$ J K^{-1} mol^{-1} calculated here for the o-C$_2$H$_5$N$_2^+$BF$_4^-$/pentaglyme system.

A comparison (Tables 3 and 4 and Refs. 11–15) of the corresponding values of the complexation ability (K values) and the stabilization ability (increase in k_1/k_2 values or decrease in k_2/k_1 values) indicates a clear $ortho$-effect on the host–guest complexation of arenediazonium ions with both cyclic crown ethers and acyclic polyethers in solution: the complexation is much weaker and the stabilizing effect of complexation is much less for o-substituted benzenediazonium ions than for p- or m-substituted ions in the presence of the same complexing agent. This can be explained by the steric hindrace of the o-substituent for complexation, and this effect depends on the size of the substituent and the size and flexibility of the polyether. In this study we measured $K = 663$ M^{-1} and $k_2/k_1 = 37\%$ for the o-EtC$_6$H$_4$N$_2^+$BF$_4^-$/pentaglyme system. These values, together with those in Table 4, show that the complexation ability and stabilizing effect (decrease in k_2/k_1) of the complexing agents, at least for unsubstituted and o-CH$_3$-, p-CH$_3$- and o-C$_2$H$_5$-substituted arenediazonium salts, increase in the same order: 15-crown-5 < pentaglyme < (or $\approx$) PEG 1000 < 18-crown-6 < 21-crown-7. Assuming that the insertion complex is not sterically hindered due to a large substituent in the o-position of the diazonium group, this order can be assumed to be rather general.[11–15,19] The present work shows, in accordance with the literature,[8,10,12] that 21-crown-7 is the strongest complexing and stabilizing agent for all arenediazonium salts studied, independent of

the position of the substituent. Although it might appear that the cavity of 21-crown-7 is somewhat too large for the diazonium group (see above), the greater ring flexibility compared with 18-crown-6 may allow for relief of steric interactions between the o-hydrogens or other o-substituents of the arenediazonium cation and the macrocyclic ring.[8]

As expected for relatively weak electrostatic interactions, the value of K for ArN_2^+/polyether systems in the case of p- and m-substituted ions is found[11–13,15] to be rather insensitive to the character of the substituent in the benzene ring: the reaction constant ϱ of the Hammett equation, log $(K/M) = \varrho\sigma$, varies from about 0 (observed for ArN_2^+/15-crown-5) to about 1.3 (calculated for the ArN_2^+/18-crown-6 and ArN_2^+/21-crown-7 systems). The values indicate, however, that electron-donating substituents in the benzene ring weaken the complexation, whereas electron-withdrawing groups favour it. It can be assumed that the character of the substituent in o-substitued benzenediazonium ions has a similar effect on the complexation of the ion with the polyether, but that the steric factors are strongly dominating in these cases. Izatt et al.[21] have studied the thermodynamics of formation of 18-crown-6 complexes with arenediazonium and anilinium salts in methanol, and observed (for o-methyl- and o,o'-dimethyl-substituted ions) that the complexation of anilinium salts (a charge-transfer complex where $ArNH_3^+$ binds to the oxygen atoms of the crown ether via hydrogen bonds and sits on top of the macrocycle) is much less sensitive to steric factors than is binding to the corresponding arenediazonium cations.

The results of this investigation, in accordance with earlier work,[6–8,11–15,19] suggest that the thermal decomposition of o-, m- or p-substituted arenediazonium ions complexed with polyethers (crown ether, pentaglyme, PEG, etc.) in solution occurs by an S_N1-like reaction mechanism (Scheme 1) via two competing, independent pathways, with the formation of the highly reactive aryl cation (heterolysis) and aryl radical (homolysis) in the slow rate-determining decomposition step of the uncomplexed ion or the complex (insertion or charge-transfer complex). Subsequent fast product-determining reactions with nucleophiles (counterion, solvent, polyether, etc.) give the products ArF, ArCl and ArOCH$_3$ in the heterolytic pathway in 1,2-dichloroethane and ArH and ArAr' in the homolysis.

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