

166. Dediazoniations of Arenediazonium Ions. Part XXI. Dediazonation of Arenediazonium Ions Complexed with Crown Ethers¹⁾²⁾

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Summary

The evaluation of the dediazonation kinetics of various *m*- and *p*-substituted benzenediazonium tetrafluoroborates³⁾ in 1,2-dichloroethane at 50° in the presence of 18-crown-6, 21-crown-7 and dicyclohexano-24-crown-8 demonstrates that the rate constant for the dediazonation within the complex (k_2) is smallest, and the equilibrium constant for complex formation (K) is largest for the complexes with 21-crown-7 (cf. Scheme 1). The logarithms of the equilibrium constants (K) for complex formation with each of the crown ethers studied correlate well with Hammett's substituent constants, σ , to give reaction constants $\rho = 1.18$ -1.38.

A linear correlation between the logarithms of the rate constants for the dediazonation within the complex with those of the dediazonation rate constants of uncomplexed diazonium ions ($\log k_2$ vs. $\log k_1$), found for most substituted diazonium salts, indicates that the dediazonation mechanism of the complexed diazonium ions is not significantly different from that of the free ions. For very electrophilic diazonium ions (*p*-Cl, *m*-CN), k_2 was much larger than expected on the basis of the linear $\log k_2$ vs. $\log k_1$ relationship. Analysis of the dediazonation products showed that this was due to a change in mechanism from heterolytic to homolytic dediazonation.

The complexation rate of diazonium salts by crown ethers (k_c) is practically diffusion controlled and does not change much with the size of the crown ether. The decomplexation rate (k_d), however, is significantly lower for complexes with 21-crown-7, than for those with 18-crown-6 and dicyclohexano-24-crown-8, and is therefore the reason for the variations in the equilibrium constant (K) and thus for the fact that complexes of arenediazonium salts with 21-crown-7 are the most stable.

The amounts of the N_α - N_β rearrangement, as well as those of the exchange of the ¹⁵N-labelled diazonio group with external nitrogen during dediazonation of *p*-toluenediazonium salt were independent of the addition of crown ethers.

Part XX: see [1].

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A dediazonation mechanism involving a charge transfer, as well as an insertion-type diazonium ion-crown ether complex is proposed. In this mechanism, dediazonation of the insertion complex does not take place directly, but through the charge-transfer complex.

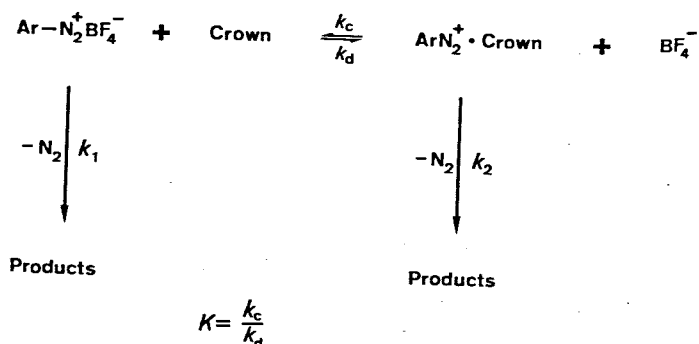
Introduction. - The complexation of arenediazonium ions by crown ethers is known [2]. Complexed diazonium salts exhibit enhanced thermal [3] and photochemical [4] stability as well as reduced shock sensitivity [5] relative to uncomplexed diazonium salts. 21-Crown-7 type macrocycles were found to be the best stabilizing agents for diazonium ions [3] [6].

In a preliminary communication [7] we demonstrated that, in the thermal dediazonation of benzene- and *p*-chlorobenzenediazonium tetrafluoroborate in 1,2-dichloroethane in the presence of 18-crown-6, 21-crown-7 and dicyclohexano-24-crown-8, the rate constant for the dediazonation within the complex (k_2) is smallest, and the equilibrium constant for complex formation (K) is largest for the complexes with 21-crown-7 (*Scheme 1*).

Having investigated the dediazonation mechanism of free diazonium ions [1], we wished to obtain further insight into the dediazonation mechanism of crown ether-complexed diazonium ions. In particular we wondered whether complexation by crown ethers would significantly change the dediazonation mechanism. By kinetic measurements of the secondary β -deuterium isotope effects on the dediazonation and the N_α - N_β rearrangement of benzenediazonium tetrafluoroborate [1] we have shown that the first intermediate along the heterolytic dediazonation pathway (*Scheme 2*) is a tight phenyl cation/nitrogen molecule pair. This intermediate certainly does not fit³⁾ into the cavity of standard crown ether macrocycles, and a change in mechanism of the dediazonation within the complex would be expected.

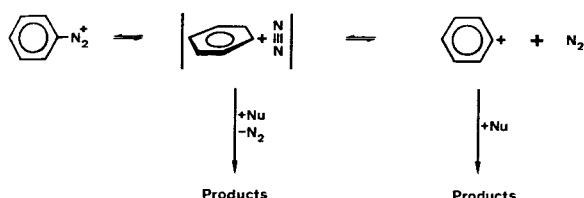
We therefore, decided to determine the equilibrium constants (K) and the rate constants (k_1 and k_2) for the dediazonation of a series of *p*- and *m*-substituted

Scheme 1



³⁾ This assumption is based on an insertion-type complex between diazonium salts and crown ethers. In fact, the only known crystal structure, that of the benzenediazonium salt (tetrafluoroborate or hexafluorophosphate)-18-crown-6 complex is indeed that of an insertion complex [8] [9].

Scheme 2



benzenediazonium tetrafluoroborates in 1,2-dichloroethane in the presence of 18-crown-6, 21-crown-7 and dicyclohexano-24-crown-8. We also report the product analyses for the dediazonation of three diazonium salts (H, *p*-Cl, *m*-CN) with and without crown ether, as well as data on the N_α - N_β rearrangement and the exchange of the ^{15}N -labelled diazonio group with external nitrogen [1] for the dediazonation of *p*-toluenediazonium tetrafluoroborate.

Results and Discussion. - *Dediazoniation Kinetics.* The rates of the thermal decomposition of substituted benzenediazonium tetrafluoroborates in 1,2-dichloroethane at 50° in the absence and presence of crown ethers were determined spectrophotometrically at the longest wavelength maximum of diazonium ions. The absorption maxima of the diazonium ions were shifted to shorter wavelengths by complexation with crown ethers. The largest shift was observed for complexes with 18-crown-6 and the smallest for those with dicyclohexano-24-crown-8 (Table 1).

Table 1. UV Data for Substituted Benzenediazonium Tetrafluoroborates in 1,2-Dichloroethane

Substituent	Crown ether	$\lambda_{1\text{max}}^{\text{a)}}$ [nm]	$\lambda_{2\text{max}}^{\text{b)}}$ [nm]	$\Delta\lambda_{\text{max}}^{\text{c)}}$ [nm]
<i>p</i> -CH ₃ O	18-C-6	318	299	19
<i>p</i> -CH ₃	18-C-6	282	266	16
	21-C-7		271	11
	DCH-24-C-8		273	9
<i>m</i> -CH ₃	18-C-6	273	254	19
	21-C-7		260	13
	DCH-24-C-8		261	12
H	18-C-6	266	247	19
	21-C-7		252	14
	DCH-24-C-8		255	11
<i>m</i> -CH ₃ O	18-C-6	281	262	19
	21-C-7		268	13
	DCH-24-C-8		270	11
<i>p</i> -Cl	18-C-6	286	270	16
	21-C-7		274	12
	DCH-24-C-8		277	11
<i>m</i> -CH ₃ CO	18-C-6	264	- ^{d)}	-
<i>m</i> -CN	18-C-6	264	245	19

^{a)} In 1,2-dichloroethane. ^{b)} In 1,2-dichloroethane containing crown ether. ^{c)} $\Delta\lambda_{\text{max}} = \lambda_{1\text{max}} - \lambda_{2\text{max}}$.

^{d)} No clear maximum.

The reactions obeyed first-order kinetics both in the absence and in the presence of crown ether. For the evaluation of k_2 and K , the experimental technique first introduced by *Bartsch et al.* [10] and further developed by *Kuokkanen & Virtanen* [11] was used. The results are shown in *Table 2*. In accordance with previous observations for benzene- and *p*-chlorobenzenediazonium salts [7] we found that, among the crown ethers studied, 21-crown-7 produces maximum complexation of substituted benzenediazonium ions (largest K), as well as maximum stabilization towards thermal dediazonation in the complex (smallest k_2). 18-Crown-6 is the second best complexing agent, and dicyclohexano-24-crown-8 is the poorest.

Bartsch & Juri [3] have also reported that maximum complexation is achieved by a 21-membered polyether macrocycle. The estimated diameter of a diazonio group is about 2.4 Å [12]. Although the size of the 18-crown-6 cavity (2.6–3.2 Å) [13] would be expected to match the diazonio group best³), the observed thermolysis rate constant and equilibrium constant indicate that 21-crown-7 (cavity [13] 3.4–4.3 Å) is a better complexing agent. Steric crowding of the *o*-H-atoms in the benzenediazonium salts against the macrocycle ring, which would most interfere in an 18-crown-6 complex, could be the reason.

The k_2 -values in *Table 2* are generally 1–2% of k_1 for complexation with 18-crown-6, 0.1–0.5% of k_1 with 21-crown-7, and 2–10% of k_1 for that with dicyclohexano-24-crown-8. Diazonium salts with electron-withdrawing substituents (*p*-Cl, *m*-COCH₃ and *m*-CN) are exceptions, and the reasons for this will be discussed later.

Table 2. Rate Constants of Dediazonation of Substituted Benzenediazonium Tetrafluoroborates (k_1 and k_2) and Complex Formation Constants (K) in 1,2-Dichloroethane at 50°

Substituent	Crown ether	K [10 ⁴ l mol ⁻¹]	k_1 [10 ⁻³ s ⁻¹]	k_2 [10 ⁻⁵ s ⁻¹]	100 k_2/k_1 [%]
<i>p</i> -CH ₃	18-C-6	2.47	0.144	0.22	1.5
	21-C-7	30.8		0.032	0.22
	DCH-24-C-8	1.80		1.4	9.7
<i>m</i> -CH ₃	18-C-6	3.36	5.68	6.2	1.1
	21-C-7	36.0		3.0	0.53
	DCH-24-C-8	1.48		16	2.8
H	18-C-6	4.69	1.31	1.8	1.4
	21-C-7	50.6		0.16	0.12
	DCH-24-C-8	2.76		6.3	4.8
<i>m</i> -CH ₃ O	18-C-6	6.03	8.23	10	1.2
	21-C-7	70.2		0.63	0.08
	DCH-24-C-8	3.53		19	2.3
<i>p</i> -Cl ^{a)}	18-C-6	7.72	0.00235	0.023	9.8
	21-C-7	15.4		0.004	1.7
	DCH-24-C-8	2.05		0.039	17
<i>m</i> -COCH ₃	18-C-6	10.4	2.01	1.4	0.70
<i>m</i> -CN	18-C-6	18.6	0.00197	0.067	34

^{a)} From [7].

When the logarithms of the equilibrium constant for complex formation are plotted against the *Hammett* substituent constants, σ^+ , a good linear correlation is observed for each of the crown ethers studied (Fig. 1). The ρ -values were 1.38, 1.26 and 1.18 for 18-crown-6, 21-crown-7 and dicyclohexano-24-crown-8, respectively. This result is similar to values obtained previously for the complexation of arenediazonium ions with 18-crown-6 [8] [11] [14] [15]. As expected for a relatively weak electrostatic interaction, these ρ -values are much lower than those obtained for reactions of various nucleophiles with the β -N-atom of arenediazonium salts [16-18].

It would be interesting to know whether the variation in the complex stability constants (K), observed with the three crown ethers of different size, is due to changes in the complexation rate, the decomplexation rate, or both. This can be determined as follows. *Krane & Skjetne* [6] have studied the dynamic ^{13}C -NMR spectra of complexes of *p*-toluenediazonium ion with 18-crown-6, 21-crown-7 and 24-crown-8 in dichlorofluoromethane. They determined the decomplexation rate constants (k_d) and the free energy of activation for the decomplexation (ΔG_d^\ddagger), which also indicated that 21-crown-7 was the preferred host for arenediazonium salts. Extrapolating their results and using our value for the complex stability constant (K) the data shown in Fig. 2 are obtained⁵). It is obvious that the complexation rate of diazonium salts by crown ethers does not change much with the size of the macrocycle and is most likely diffusion-controlled. The decomplexation rate,

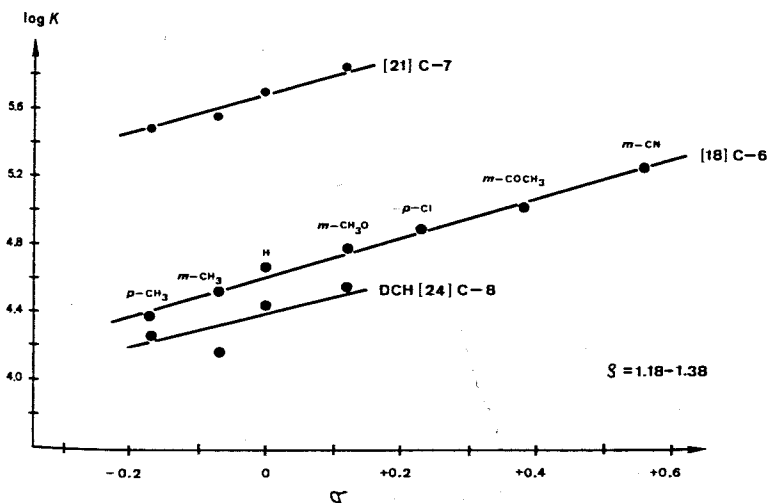


Fig. 1. Hammett plot for the equilibrium constants for complex formation of substituted benzenediazonium salts with crown ethers in 1,2-dichloroethane at 50°

⁵) A correlation with σ^+ -values was found to be much poorer than that with σ .

⁶) The calculation was made assuming that a) there is no large solvent effect in going from dichlorofluoromethane to 1,2-dichloroethane, b) the ΔG_d^\ddagger -values are constant over a wide temperature range, and c) the complexation with dicyclohexano-24-crown-8 does not differ much from that with 24-crown-8.

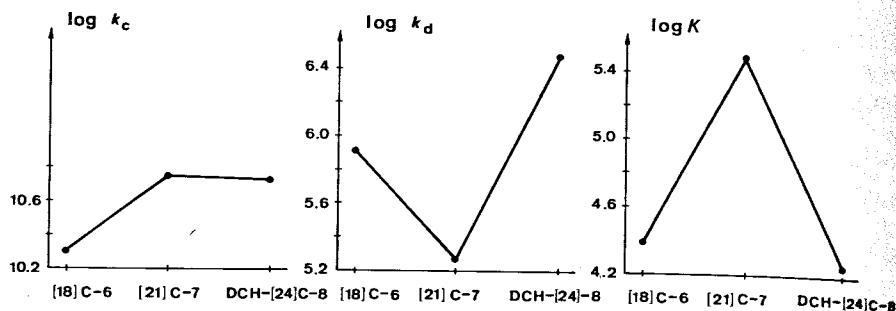


Fig. 2. Rate constants for the complexation (k_c) and decomplexation (k_d), and equilibrium constants for complex formation (K) of *p*-toluenediazonium ion with different crown ethers at 50°. Data from [6] and this work.

on the other hand, being much lower for complexes with 21-crown-7 than for those with 18-crown-6 and dicyclohexano-24-crown-8, is the reason for the variations in the equilibrium constant (K) and for the fact that the complexes of arenediazonium salts with 21-crown-7 are the most stable. This conclusion is analogous to that obtained earlier for the complexation of *tert*-butylammonium hexafluorophosphate with crown ethers of various size [19].

Since the detailed mechanism for the heterolytic dediazonation of uncomplexed benzenediazonium ions is known [1], a comparison of substituent effects on the dediazonation rate of free diazonium ions and within the complex should give information about the dediazonation mechanism of crown ether-complexed diazonium ions. The logarithms of the rate constants for the reaction within the complex ($\log k_2$) were plotted against those for the reaction of free diazonium ions ($\log k_1$) (Fig. 3). This dependence is linear for each of the crown ethers studied, with slopes of 0.92, 0.95 and 0.66 for reactions in the presence of 18-crown-6, 21-crown-7 and dicyclohexano-24-crown-8, respectively. The thermal dediazonation of complexed diazonium ions must therefore proceed by basically the same (or very similar) mechanism as that of free diazonium ions. This is surprising in view of the expectation advanced in the introduction and will be discussed later.

The fact that the slopes of the straight lines in Fig. 3 are less than one is to be expected, since the substituent effects on the dediazonation of free diazonium ions in a nonpolar, relatively poorly solvating solvent like 1,2-dichloroethane, should be somewhat larger than those on the reaction of complexed diazonium salts, where the positive charge is 'solvated' by the crown ether. For the same reason the substituent effects on dediazonation in 1,2-dichloroethane reported here are larger than those observed by Swain *et al.* in aqueous HCl [20].

In Fig. 3 points for two of the diazonium salts studied (*p*-Cl, *m*-CN) deviate markedly from the straight lines obtained for the other compounds. With these strongly electronegative diazonium salts the dediazonation rate of the complexed diazonium ion is much faster than expected, indicating a change in mechanism caused by addition of crown ethers. Diazonium salts with electron-withdrawing substituents may decompose by homolytic dediazonation in the presence of nucleophiles (here crown ethers), and under comparable conditions homolytic

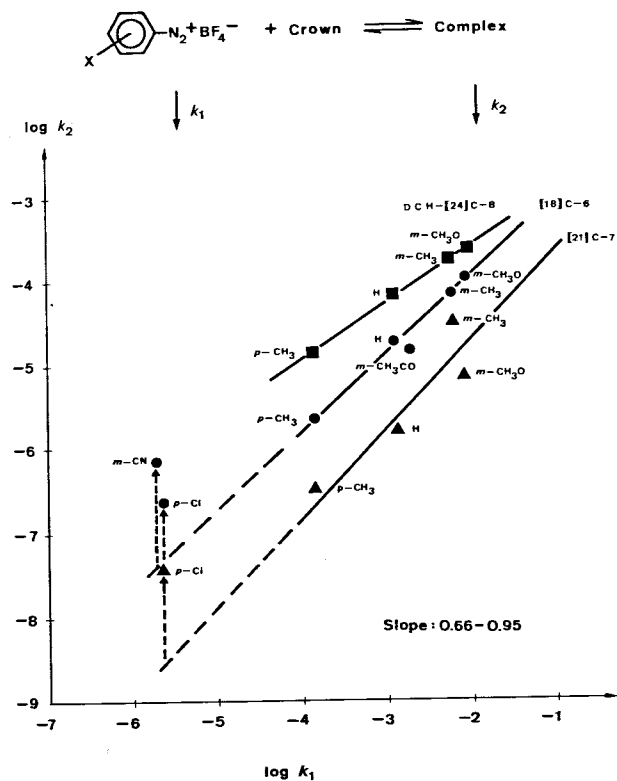


Fig. 3. Rate constants for the dediazonation of complexed diazonium ions (k_2) vs. those for free diazonium ions (k_1) in 1,2-dichloroethane at 50°

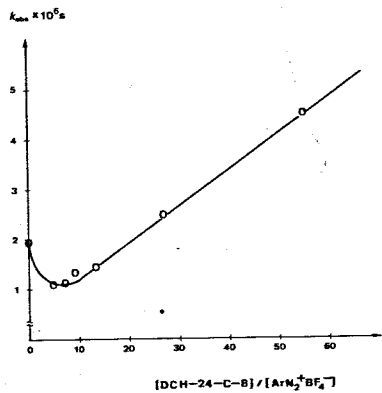


Fig. 4. Observed rate constant for the dediazonation of *m*-cyanobenzediazonium tetrafluoroborate vs. the concentration ratio of dicyclohexano-24-crown-8 and the diazonium salt in 1,2-dichloroethane at 50°

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rates are faster than the corresponding rates of heterolysis [21]. This explanation is clearly supported by the analysis of dediazonation products described below.

The observed rate constant for the dediazonation of *m*-cyanobenzenediazonium tetrafluoroborate in the presence of increasing amounts of dicyclohexano-24-crown-8, first decreases, and after reaching a minimum at [crown ether]/[ArN₂⁺] = 4.5, starts increasing linearly (Fig. 4). Similar behaviour is observed with *p*-chlorobenzenediazonium ion.

Reaction Products. Arenediazonium tetrafluoroborates thermally decomposing in a given solvent yield different dediazonation products depending on the mechanism. While heterolytic dediazonation results in fluoroarenes (reaction with the BF₄⁻ counter-ion) and products derived from the reaction of the intermediate aryl cation with any nucleophile present, the major products in homolytic dediazonations, derived from aryl radicals, are the corresponding arenes and often also biphenyls. Accordingly, the thermal dediazonation of substituted benzenediazonium tetrafluoroborates in 1,2-dichloroethane with and without added crown ethers afforded the products shown in Scheme 3 and Table 3.

The major products in the dediazonation of benzenediazonium salt are fluoro- and chlorobenzene, as expected for a heterolytic reaction, independent of whether crown ether is present in the solution or not. With *p*-chloro- and *m*-cyanobenzenediazonium salt, on the other hand, complexation by crown ether drastically changes the dediazonation products from predominantly heterolytic (fluoro- and chloroarene) to predominantly homolytic (arene). This result proves that the deviations in Fig. 3 observed for these two diazonium salts are indeed, as presumed, due to a change in the dediazonation mechanism induced by the complexation with crown ethers. To the best of our knowledge, this is the first example of complete change in the dediazonation products and reaction mechanism due to the addition of crown ethers. A similar change in the reaction products was observed by Moss *et al.* [22] in micellar dediazonation, compared with nonmicellar reaction. In aqueous bromide solutions micellar dediazonation gave more than 95% of the corresponding aryl bromide, whereas nonmicellar reaction gave only the corresponding phenol. This is, however, probably not due to a change in mechanism, but to the local concentration of bromide ions around the cationic micelle.

Scheme 3

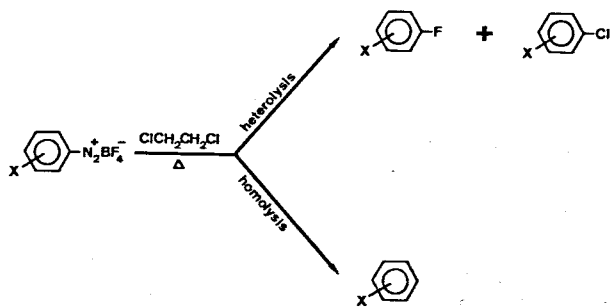


Table 3. Thermal Dediazonation Products^{a)} of Substituted Benzenediazonium Tetrafluoroborates in 1,2-Dichloroethane at 50° with and without Added Crown Ether

Substituent (X)	Crown ether	F-C ₆ H ₄ -X [%]	Cl-C ₆ H ₄ -X [%]	C ₆ H ₅ -X [%]	Total [%]
H ^{b)}	-	45.9	48.6	-	94.5
	18-C-6	21.2	45.2	3.2	69.5
	21-C-7	11.2	19.7	4.3	35.2
	DCH-24-C-8	12.9	26.8	2.3	42.0
<i>p</i> -Cl ^{c)}	-	33.5	37.3	5.1	75.9
	18-C-6	1.5	3.1	66.8	71.4
	21-C-7	1.0	1.3	61.2	63.5
	DCH-24-C-8	0.5	1.8	64.5	66.8
<i>m</i> -CN ^{d)}	-	38.2	43.4	12.9	94.5
	18-C-6	1.4	6.4	87.6	95.4

^{a)} In mol-% (obtained from the relative peak areas, corrected by the response factors determined from mixtures of authentic samples of known composition).

^{b)} Products analyzed after 10 reaction half-lives.

^{c)} Products analyzed after 3 reaction half-lives.

^{d)} Products analyzed after 5 reaction half-lives. Owing to the extremely low solubility of the salt without added crown ether, the product run was done in a two phase system and 61.3% unreacted diazonium salt was isolated after 5 $t_{1/2}$. The product composition shown in the Table was obtained by extrapolation to 100% reaction.

The yields of fluoro- and chlorobenzene (Table 3) in the dediazonation of benzenediazonium salt without crown ether agree well with previous results [10] [11] [23] [24]. The low total product yields in the reactions of this salt complexed with crown ethers are due to reactions of the intermediate phenyl cation with the macrocycles⁶⁾.

IR Spectra of Complexed Benzenediazonium Tetrafluoroborates. Kinetic investigations show that 21-crown-7 type macrocycles are the best complexing agents for arenediazonium ions. On the other hand, when the size of the macrocycle cavity and the diameter of the diazonio group are considered, the best complexation would be expected from 18-crown-6. We thought that the variation of the N,N-stretching frequency of the complexes would provide some additional information. It was reported [25] that $\nu_{N,N}$ for benzenediazonium salt increases by 32 cm⁻¹ upon complexation with dicyclohexano-18-crown-6. This is the first example of a diazo complex in which $\nu_{N,N}$ increases upon coordination [25]. We prepared crystalline complexes of benzenediazonium and *p*-chlorobenzenediazonium tetrafluoroborate with 18-crown-6 and 21-crown-7⁷⁾. The corresponding N,N-stretching frequencies

⁶⁾ In addition to the products shown in Table 3, 1,4-dioxane was found by GC/MS in all mixtures resulting from complexed benzenediazonium salt. Cyclohexanone and cyclopentanecarboxaldehyde were found after complexation with dicyclohexano-24-crown-8, and 1-ethoxy-2-phenoxyethane was detected after complexation with 21-crown-7. In the mixtures resulting from *p*-chlorobenzenediazonium salt chloroethane, 1,1,2-trichloroethane and 1,4-dichloro-1(or 2)-butene were detected by GC/MS in addition to the products in Table 3.

⁷⁾ Attempts to prepare the corresponding complex with dicyclohexano-24-crown-8 were unsuccessful, probably owing to the lower stability of this complex.

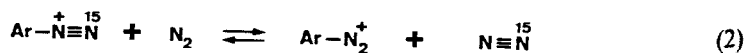
Table 4. *N,N*-Stretching Frequencies of Complexed Arenediazonium Salts

Complex	$\nu_{N,N}^a$ [cm ⁻¹]	
	Nujol	Acetone
C ₆ H ₅ N ₂ ⁺ BF ₄ ⁻	2300	2300
C ₆ H ₅ N ₂ ⁺ BF ₄ ⁻ · 18-C-6	2320	2320
C ₆ H ₅ N ₂ ⁺ BF ₄ ⁻ · 21-C-7	2300	2310
<i>p</i> -ClC ₆ H ₄ N ₂ ⁺ BF ₄ ⁻	2297	2300
<i>p</i> -ClC ₆ H ₄ N ₂ ⁺ BF ₄ ⁻ · 18-C-6	2319	2325
<i>p</i> -ClC ₆ H ₄ N ₂ ⁺ BF ₄ ⁻ · 21-C-7	2302	2315

^a) Accuracy ca. ± 5 cm⁻¹.

are shown in *Table 4*. The data for *p*-chlorobenzenediazonium salt and its 18-crown-6 complex compare well with previous values [26], and those for the benzenediazonium ion complexes with unpublished results of *Haymore* [9]. The data in *Table 4* show that the frequency shift upon complexation with 18-crown-6 (20–25 cm⁻¹) is larger than that upon complexation with 21-crown-7 (0–15 cm⁻¹). This parallels the observed UV-spectral changes (*Table 1*). Obviously in this case no conclusions regarding the kinetic or thermodynamic stability of the complexes can be made from their spectroscopic behaviour. An answer to this problem might be possible if, in addition to the crystal structure of the benzenediazonium ion-18-crown-6 complex [9], that of the 21-crown-7 complex were known.

N_α-N_β Rearrangement and Exchange of the Diazonio Group with External N₂. We have demonstrated [1] that two reactions, the N_α-N_β rearrangement (1) and the exchange of the diazonio group with external N₂ (2) proceed parallel to the decomposition of the diazonium salt. We have also shown that they proceed *via* the first and the second reaction intermediate, respectively (*cf. Scheme 2*).



As mentioned in the introduction, the first intermediate in *Scheme 2* does not fit into the cavity of the crown ethers under study (with the possible exception of dicyclohexano-24-crown-8). It was therefore interesting to check whether complexation by crown ethers influences reactions (1) and (2). The results obtained with *p*-toluenediazonium tetrafluoroborate are shown in *Table 5*. Addition of any of the crown ethers does not influence the amount of the rearranged product observed. The rearrangement in 1,2-dichloroethane is much smaller than that in the more polar non-nucleophilic fluoroalcohols studied earlier [1]. The exchange reaction (2) cannot be demonstrated at all, since the values obtained are close to zero within experimental error.

Table 5. Extent of N_α - N_β Rearrangement at 70% Dediazoniation for *p*-Toluenediazonium- β - N^{15} Ion (1,2-dichloroethane, 50°, 300 atm N_2)

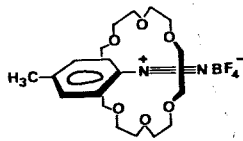
Added crown ether	%Rearrangement ^{a)}
-	4.0
18-C-6	3.4 (3.9)
21-C-7	4.2 (2.9)
DCH-24-C-8	3.9

^{a)} Accuracy ca. ± 1 . For runs with crown ethers the necessary amount of macrocycle was added so that 99% (99.9% for the values in brackets) of the diazonium ion present was complexed.

The mechanistic consequences of these experiments are the same as those obtained by the kinetic investigation, *i.e.* that the dediazoniation mechanism of complexed diazonium salts does not significantly differ from that of the free diazonium salts.

Conclusion. - Two opposing facts must be reconciled. All the available data indicate that, with the exception of very electronegative diazonium salts, the dediazoniation mechanism of diazonium ions complexed with crown ethers is basically the same as the mechanism of free, uncomplexed diazonium ions. On the other hand, assuming an insertion type diazonium ion/crown ether complex **1** in accordance with the only crystal structure known [8] [9], it is not possible for the first intermediate along the dediazoniation pathway (*Scheme 2*) to fit in the crown ether cavity in such a complex. We propose the following mechanism.

In the dediazoniation of arenediazonium salts in the presence of macrocyclic polyethers two different diazonium ion/crown ether complexes are involved, one of an insertion type **1** and another in which the electrostatic interaction between the two species has not led to insertion of the diazonio group into the crown ether cavity. For convenience we shall call the latter a charge transfer complex as it is known that arenediazonium ions form such complexes with electron-donor compounds [27]. There is a fast equilibrium between the two complexes. The insertion complex **1** is unreactive in dediazoniations, and all the reactions of the complexed diazonium ion proceed *via* the charge transfer complex.

**1**

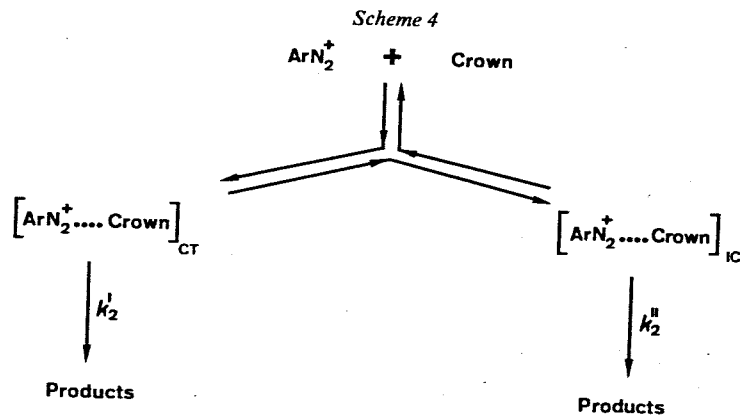
As mentioned before, the crystal structure shows an insertion-type complex [8] [9]. This structure was also supported by an ESCA study [28]. For relatively weak complexes, as in this case, with equilibrium constants for complex formation of the order of 10^4 - 10^5 , it is not surprising that in solution another complex form, for example a charge-transfer complex, may also exist. There are already several precedents for similar charge-transfer complexes. *Kuokkanen & Virtanen* [11] have

observed some stabilization towards dediazonation of *o*-toluenediazonium ion by 18-crown-6, although, for steric reasons, an insertion-type complex is not possible in this case. Probably a charge-transfer complex is involved. Charge-transfer bands were also observed in the complexation of diazonium salts with dibenzo- [29] and dinaphtho- [2] [30] 18- or 20-crown-6-type macrocycles, and there are indications for the existence of charge-transfer complexes of crown ethers and glymes with ammonium tetrahedral intermediates formed in ester aminolysis [31]. Finally, charge-transfer complexes of diazonium ions with naphthalene and its derivatives are known [27] and the resulting stabilization of diazonium salts with arenesulfonic acids has been used on large scale for many decades [32].

The diazonium ion and the crown ether are in a fast equilibrium with *two* complexes (Scheme 4), a) the charge-transfer complex (CT) whose stability is based on the interaction of the acceptor (ArN_2^+) and donor component (Crown). The acceptor centre of the diazonium ion is either the β -N-atom and/or the combined π -electron system of the aryl part and the diazonio group. Donor centres are one or more of the ether-O-atoms; b) the insertion complex (IC) as shown in structure 1. The CT complex is weaker than the IC complex [11].

Scheme 4 is intended to leave the question open as to whether CT and IC complexes are competitively or consecutively formed from the components⁸⁾.

All our data (linear correlation of k_1 and k_2 , same values for N_α - N_β rearrangement for complexed and free diazonium ions) indicate that the dediazonation of the complexed diazonium ions proceeds only through the CT complex, as the ion-molecule pair for which we have given strong evidence [1] [33] cannot be formed in the cavity of the IC complex. The calculated rate constants for dediazoniations of complexed diazonium ions (k_2 in Scheme 1) are, however, not identical with k_2' in Scheme 4, as part of the complexed particles are present as CT complexes and part as IC complexes. We see, at least at the present time, no possibility of determining the ratio $[\text{ArN}_2^+ \dots \text{Crown}]_{\text{CT}} / [\text{ArN}_2^+ \dots \text{Crown}]_{\text{IC}}$ a prerequisite for calculating



⁸⁾ This open question is symbolised by the unusual type of equilibrium arrows which we use in Scheme 4.

k_2^* and for checking whether k_2^* is really zero. However, k_2^* is definitely much smaller than k_1^* and k_2^* can hardly show a linear relationship to k_1^* .

Another open question is the problem of whether the homolytic dediazonation observed for *m*-cyano- and *p*-chlorobenzenediazonium ions in the presence of crown ethers is possible in the IC-complex cavity.

Note Added in Proof. - Gokel *et al.* [43] have very recently discussed the discrepancy between the UV- and IR-spectral shifts for diazonium salts complexed by 18-crown-6 and 21-crown-7, respectively, and the amount of stabilization achieved by the complexation.

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Experimental Part

Materials. - 1,2-Dichloroethane (Merck AG., for spectroscopy) was used directly. The crown ethers (Fluka AG. and Parish Chemical Co.) were purified by distillation. Substituted benzenediazonium tetrafluoroborates were prepared by diazotization of the corresponding anilines [34] and purified several times by dissolving them in the minimum amount of acetonitrile, followed by reprecipitation with the addition of diethyl ether.

Benzenediazonium Tetrafluoroborate: m.p. 108-110° (dec.) ([35]: 114-116° (dec.)).

p-Methylbenzenediazonium Tetrafluoroborate: m.p. 111-113° (dec.) ([36]: 110° (dec.)).

m-Methylbenzenediazonium Tetrafluoroborate: m.p. 107.5-109° (dec.) ([37]: 108° (dec.)).

p-Methoxybenzenediazonium Tetrafluoroborate: m.p. 142-143° (dec.) ([38]: 139° (dec.)).

m-Methoxybenzenediazonium Tetrafluoroborate: m.p. 95-96.5° (dec.).

$C_7H_7BF_4NO_2$ Calc. C 37.88 H 3.18 N 12.62% Found C 37.96 H 3.15 N 12.60%

m-Acetylbenzenediazonium Tetrafluoroborate: m.p. 113-114° (dec.).

$C_8H_7BF_4NO_2$ Calc. C 41.07 H 3.02 N 11.97% Found C 41.30 H 3.13 N 11.17%

m-Cyanobenzenediazonium Tetrafluoroborate: m.p. 155-156° (dec.).

$C_7H_4BF_4N_3$ Calc. C 38.73 H 1.86 N 19.37% Found C 38.75 H 2.03 N 19.24%

m-Fluorobenzonitrile (b.p. 74.8°/15 Torr) was synthesized from *m*-fluoroaniline by a Sandmeyer reaction [39], and used as an authentic sample for the analysis of the decomposition products.

Crystalline diazonium salt/crown ether complexes were prepared by a method similar to that reported by Bohman *et al.* [28]. A solution of 0.096 g (0.5 mmol) of benzenediazonium salt and 0.1323 g of 18-crown-6 (0.5 mmol) in 1,2-dichloroethane was filtered to remove insoluble benzenediazonium salt, then the solvent was removed (rotary evaporator) at r.t. To the crystals or oily material obtained, Et_2O was added. The white, microcrystalline complex was filtered and washed with Et_2O . The product was dried in a vacuum desiccator; yield 76%, m.p. 83.5-86°. Other complexes were similarly prepared in yields of 79-88%.

The m.p.'s and elemental analyses of these complexes are shown in Table 6.

Kinetic Measurements. - A solution containing $ca. 7.50 \times 10^{-5}$ mol/l of diazonium salt and different mole ratios (2-20 times) of crown ether in 1,2-dichloroethane was prepared in a 25 ml volumetric flask, 4 ml of the solution were removed with a pipette and transferred to a UV cell. After bubbling N_2 through the solution in the cell for 10-30 min, the cell was put in cell holders thermostated at 50° during the measurement. Plots of $\ln(A_t - A_\infty)$ vs. time were linear with slope k_{obs} . The rate was measured for $ca. 1.0$ half-life. From k_{obs} , the rate constants k_2 and the equilibrium constants K were determined graphically using equation (3) [10] [11]. Representative data for the dediazonation of benzenediazonium tetrafluoroborate are shown in Table 7.

Table 6. Melting Points and Elemental Analyses for Diazonium Salt/Crown Ether Complexes

Complex	Elemental Analysis [%], Found (Calc.)			M.p. [°C]
	C	H	N	
$C_6H_5N_2^+ BF_4^- \cdot 18\text{-crown-6}$	46.65 (47.39)	6.22 (6.41)	6.04 (6.14)	83.5–86
$C_6H_5N_2^+ BF_4^- \cdot 21\text{-crown-7}$	47.52 (48.02)	6.51 (6.65)	5.84 (5.60)	83.5–85
$p\text{-Cl}C_6H_4N_2^+ BF_4^- \cdot 18\text{-crown-6}$	43.06 (44.06)	5.30 (5.75)	6.07 (5.71)	109–111 ^a
$p\text{-Cl}C_6H_4N_2^+ BF_4^- \cdot 21\text{-crown-7}$	44.36 (44.92)	5.81 (6.03)	5.41 (5.24)	124–126

^a) [40]: 115–116.5°.

Table 7. Data for the Dediazonation of $C_6H_5N_2^+ BF_4^-$

$[ArN_2^+ BF_4^-]$ [mol/l]	[Crown] [mol/l]	[Crown]/ $[ArN_2^+]$	k_{obs} [s ⁻¹]
7.58×10^{-5}	0	0	$k_1 = (1.31 \pm 0.002) \times 10^{-3}$
<i>18-Crown-6</i>			
7.60×10^{-5}	1.86×10^{-4}	2.43	$(2.09 \pm 0.03) \times 10^{-4}$
7.58×10^{-5}	3.71×10^{-4}	4.91	$(1.09 \pm 0.02) \times 10^{-4}$
7.59×10^{-5}	1.29×10^{-3}	17.0	$(3.53 \pm 0.04) \times 10^{-5}$
$k_1 - k_2 = 1.292 \times 10^{-3} \text{ sec}^{-1}$, $k_2 = 0.018 \times 10^{-3} = 1.8 \times 10^{-5} \text{ s}^{-1}$, $K = 4.69 \times 10^4 \text{ l} \cdot \text{mol}^{-1}$			
<i>21-Crown-7</i>			
7.53×10^{-5}	1.80×10^{-4}	2.39	$(2.56 \pm 0.006) \times 10^{-5}$
7.62×10^{-5}	3.50×10^{-4}	4.59	$(1.04 \pm 0.013) \times 10^{-5}$
7.58×10^{-5}	1.28×10^{-3}	16.9	$(4.07 \pm 0.015) \times 10^{-6}$
$k_1 - k_2 = 1.3084 \times 10^{-3} \text{ s}^{-1}$, $k_2 = 0.0016 \times 10^{-3} = 1.6 \times 10^{-6} \text{ s}^{-1}$, $K = 5.06 \times 10^5 \text{ l} \cdot \text{mol}^{-1}$			
<i>DCH-24-Crown-8</i>			
7.43×10^{-5}	2.11×10^{-4}	2.84	$(3.04 \pm 0.07) \times 10^{-4}$
7.54×10^{-5}	4.45×10^{-4}	5.90	$(1.74 \pm 0.08) \times 10^{-4}$
7.62×10^{-5}	1.34×10^{-3}	17.6	$(9.65 \pm 0.03) \times 10^{-5}$
$k_1 - k_2 = 1.247 \times 10^{-3} \text{ s}^{-1}$, $k_2 = 0.063 \times 10^{-3} = 6.3 \times 10^{-5} \text{ s}^{-1}$, $K = 2.76 \times 10^4 \text{ l} \cdot \text{mol}^{-1}$			

$$\frac{1}{k_1 - k_{obs}} = \frac{1}{(k_1 - k_2)K} \cdot \frac{1}{[Crown]} + \frac{1}{k_1 - k_2} \quad (3)$$

The straight lines in the Hammett plot (Fig. 1) are described by Equations 4–6.

$$\log K = (1.38 \pm 0.15)\sigma + 4.63 \quad \text{for 18-C-6} \quad (4)$$

$$r = 0.988$$

$$\log K = (1.26 \pm 0.15)\sigma + 5.69 \quad \text{for 21-C-7} \quad (5)$$

$$r = 0.986$$

$$\log K = (1.17 \pm 0.55)\sigma + 4.39 \quad \text{for DCH-24-C-8} \quad (6)$$

$$r = 0.835$$

Product Analyses. - The analysis of products in the thermolysis of arenediazonium salts was performed on a *Hewlett Packard 5880A* gas chromatograph using a capillary column (50 × 0.31 mm) of methylsilicone (*HP-PN 19091-61050* or *OV-101, 19091-60010*). The following temp. programmes were used for the substituted benzenediazonium salt product mixtures: H (7 min at 35°, 20°/min, 45 min at 180°), *p*-Cl (3 min at 70°, 20°/min, 20 min at 200°), *m*-CN (4 min at 55°, 30°/min, 2 min at 150°). Anisole was used as internal standard for mixtures from the first two diazonium salts, and nitrobenzene for those from the last. The concentrations used were H (0.003 mol/l or 0.01 mol/l + 0.05 mol/l crown ether), *p*-Cl and *m*-CN (0.003 mol/l or 0.01 mol/l + 0.03 mol/l crown ether).

The by-products were identified by GC/MS (*Carlo Erba Fractovap 2150/Varian Mat 112* with *Finnigan INCOS Data System*).

N_{α} - N_{β} Rearrangement and Exchange of the Diazonio Group with External N_2 . - The dediazonation of β - ^{15}N -labelled *p*-toluenediazonium tetrafluoroborate in an autoclave and the determination of the extent of rearrangement and exchange were carried out as before [41] [42].

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