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Stability of 2-naphthalenediazonium ion and its complexation with crown ethers and acyclic polyethers in solution

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ABSTRACT: The effects of solvent, temperature and pH (in aqueous solution) on the rate of decomposition of 2-naphthalenediazonium tetrafluoroborate were studied by UV spectrometry. The host–guest complexation and the kinetics of thermal dediazoniation of this model naphthalenediazonium ion, in the presence of four crown ethers and three acyclic polyethers, were studied in 1,2-dichloroethane (DCE) at 40 °C by UV spectrometry. Fast atom bombardment mass spectrometry (FAB-MS) was used for the gas phase complexation and characterization.

The values of the activation enthalpy $\Delta H^{\#}$ for the thermal dediazoniation of the uncomplexed salt were observed to be high, and the corresponding values of activation entropy $\Delta S^{\#}$ were clearly positive. All hosts, except short 12-crown-4, formed 1:1 complexes under FAB conditions. The complexation equilibrium constant K and the values of the stabilizing ability of the complexation (k_2/k_1) in DCE were calculated using a kinetic method. In accordance with earlier studies of arene- and 1-naphthalene diazonium ions, the thermodynamic and kinetic stabilities were observed to be greater for the inclusion complex—the largest for 21-crown-7 and its derivatives, formed with crown ethers containing at least six oxygen atoms—than for the non-specific adduct formation formed with 15-crown-5. The values of the thermodynamic and kinetic macrocyclic effect were discussed. The results are consistent with a heterolytic S_N1-like mechanism involving the decomposition of the uncomplexed and complexed naphthalenediazonium ion into a highly reactive naphthyl cation, followed by fast product-determining reactions with nucleophiles to give the products. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: naphthalenediazonium; crown ether; acyclic polyether; dediazoniation; host–guest complexation

INTRODUCTION

Arenediazonium salts were first prepared well over a century ago, and their reactions were among the first to be studied closely by organic chemists.[1] The considerable importance that these compounds possess in the chemical industry and applications today has also encouraged a great number of studies during recent years.[2–5] Nevertheless, papers describing the decomposition of naphthalenediazonium salts are relatively few.[6–8] Recently, we studied the effects of solvent, temperature and pH on the thermal stability of the 1-naphthalenediazonium ion.[8]

The unique chemical properties associated with the ability of crown ethers to form highly stable host–guest complexes with metal cations, such as alkali and alkaline earth ions and with other appropriately sized species, has led to extensive study of the utilization of host–guest complexes during the last 30 years. The focus has been on crown ether–metal ion systems, however.[9–11] Numerous books and reviews have also been published on their syntheses, binding phenomena, complex structures and applications.[9–11] Although acyclic polyethylene glycols (PEGs) are weaker complexing agents than crown ethers, they may have practical use in the future: it is shown that, instead of expensive crown ethers, inexpensive, commercially available PEGs can be used as effective phase transfer agents for reactions of arenediazonium salts in solvents of low polarity.[12]

Bartsch *et al.*[13] reported in 1976 that the complexation of 18-membered crown ethers with the *p-tert*-butylbenzenediazonium ion in 1,2-dichloroethane markedly stabilizes the arenediazonium salt against thermal dediazoniation. Subsequently, many papers have been published on the host–guest complexation between crown ethers and arenediazonium ions, but only a few have considered both the thermodynamic and the kinetic stability of these complexes.[14–18] Recently, we studied the complexation of the 1-naphthalenediazonium ion with crown ethers and acyclic polyethers in 1,2-dichloroethane solution, and characterized the complexes

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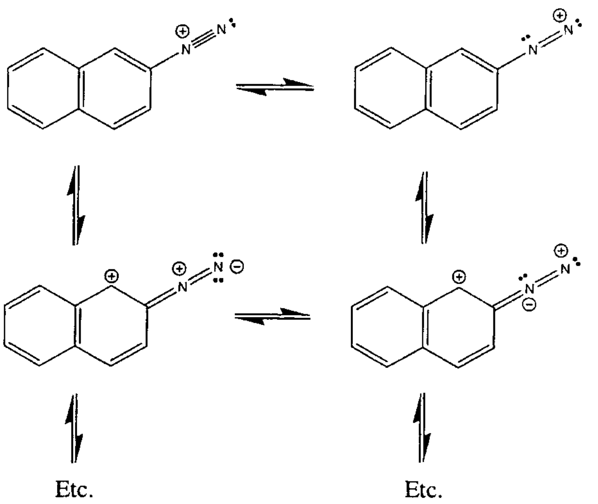

Scheme 1. The resonance formulae of the 2-naphthalenediazonium ion

using fast atom bombardment spectrometry (FAB-MS).[8] As far as we know, the complexation of polyethers with naphthalenediazonium ions has not been previously reported. Furthermore, polyether–organic diazonium ion systems are the only host–guest systems for which the thermodynamic stabilities have been calculated from kinetic data.

Ring size and steric factors have important effects on the strength of host–guest complexes, but the strength is more difficult to predict for flexible organic molecules than for rigid metal ions. Continuing our studies on the interactions of polyethers with stable organic cations, we have now investigated the host–guest complexation of 2-naphthalenediazonium ions with crown ethers and acyclic polyethers using kinetic and spectroscopic methods. The 2-naphthalenediazonium ion (Scheme 1) is, for steric reasons, the model naphthalenediazonium ion, and the 1-naphthalenediazonium ion, studied recently,[8] can be considered as one kind of *ortho*-substituted benzenediazonium ion with *ortho* effects on complexation. Furthermore, effects of solvent, temperature and pH on the thermal stability of the uncomplexed model compound have been determined in this work.

EXPERIMENTAL

Materials. 2-Naphthalenediazonium tetrafluoroborate was synthesized from 2-naphthalene amine (Aldrich) by dediazoniation with sodium nitrite at 2–4 °C in tetrafluoroboric acid aqueous solution and was recrystallized twice from methanol–tetrafluoroboric acid (1:4) mixture.[6] The elemental analyses were calc. for $C_{10}H_7BF_4$: C, 49.61; H, 2.92; N, 11.58; found: C, 49.74; H, 2.96; N, 11.58%. These data, as well as the melting temperature, 111–113 °C, and the UV spectral data for 2-naphthalenediazonium tetrafluoroborate in acidic aqueous solution (1×10^{-3} M HCl), $\lambda_{max} = 207$ nm, $\varepsilon = 2.11 \times 10^4$ M^{-1} cm^{-1}, $\lambda_{max} = 259$ nm, $\varepsilon = 2.48 \times 10^4$ M^{-1} cm^{-1} and $\lambda_{max} = 317$ nm, $\varepsilon = 1.15 \times 10^4$ M^{-1} cm^{-1}, are in accordance with the values in the literature.[6] The diazonium salt was stored in the dark at low temperature to minimize its decomposition. The unsubstituted crown ethers, 12-crown-4 (Fluka), 15-crown-5 (Fluka), 18-crown-6 (Fluka), and 21-crown-7 (Pfaltz & Bauer), and the dicyclohexane-substituted crown ether, dicyclohexano-24-crown-8 (Fluka), were commercial chemicals and were used without further purification. 3-Nitrobenzyl alcohol (NBA; Aldrich-Chemie) was used without further purification. 1,2-Dichloroethane (Fluka) was purified, dried, and distilled by a common procedure.[19]

Apparatus and measurements. The complexation of crown ethers with 2-naphthalenediazonium tetrafluoroborate was detected and characterized by FAB-MS on a Kratos MS 80 autoconsole operating with a DART data system. Argon was used as bombarding gas with a pressure of about 1×10^{-6} Torr (1 Torr = 133.3 Pa) in the collision region, and the atom gun was operated at 8 keV. NBA was used as the liquid matrix in this work. The stainless steel tip of the FAB probe was coated with a thin layer of a mixture of crown ether, diazonium salt ($[\text{polyether}]_{tot} \approx [\text{NaphN}_2^+]_{tot} \approx 2 \times 10^{-2}$ M), and the liquid NBA matrix. The FAB spectrum was recorded immediately after the sample had been inserted.

UV spectra were recorded and kinetic measurements were carried out with a Shimadzu UV 160 A double-beam spectrometer. Kinetic experiments were detailed recently in the case of the 1-naphthalenediazonium ion.[8] All decomposition reactions studied were found to obey first-order kinetics within the intervals investigated (three half-lives; the correlation constant r about 0.9998). The melting point of the uncomplexed salt was determined with a Thermopan microscope (Reichert, Vienna). Elemental analysis was carried out with Perkin–Elmer 2400 instrument. The preparation of solutions for host–guest measurements has been described previously.[8]

RESULTS

Effect of temperature, solvent and pH on thermal stability of the uncomplexed ion

The effect of temperature on the thermal stability of 2-naphthalenediazonium salt was studied by determining the rate constant of decomposition k_1 in aqueous acid solution (1×10^{-3} M HCl) and in 1,2-dichloroethane at four temperatures. Figure 1 shows the corresponding Arrhenius plots. Table 1 shows the calculated values of the activation parameters, E_a, $\Delta H^{\#}$ and $\Delta S^{\#}$, and, for comparison, we have included the calculated k_1 values at one fixed temperature, $T = 25$ °C.

The effect of pH on the thermal stability of the 2-

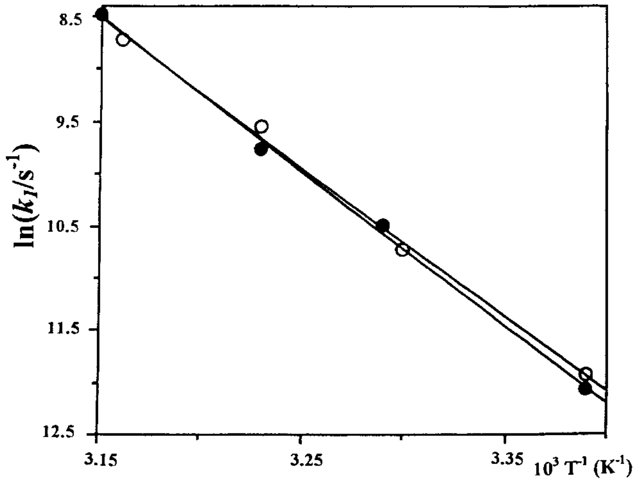

Figure 1. The effect of solvent and temperature on the thermal decomposition of the uncomplexed 2-naphthalenediazonium tetrafluoroborate in 1×10^{-3} M HCl (○) and 1,2-dichloroethane (●)

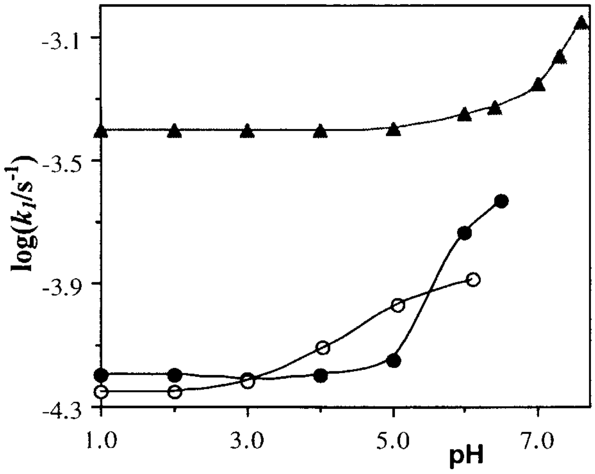

Figure 2. The effect of pH on the thermal stability of the uncomplexed 2-naphthalenediazonium (●) and 1-naphthalenediazonium (○) ions at 35 °C and the uncomplexed benzenediazonium ion (▲) at 40 °C in acidic and neutral aqueous solution

naphthalenediazonium ion in aqueous solution at 35 °C was studied by determining the first-order rate constant k_{obs} in aqueous solution, in HCl (pH 1.0 and 2.0) and in $HOC(CH_2COOH)_2COOH/Na_2HPO_4$ buffer solutions (pH from 3 to 7). The results for the corresponding pH dependency in the cases of benzene- and 1-naphthalenediazonium ions are presented in Fig. 2.

Studies in the gas phase under FAB conditions

In the FAB-MS method, the complex is first formed in the liquid matrix (NBA in our studies) and then analysed in the gas phase by MS. Thus, the complex must exist both in solution and in the gas phase. It has been repeatedly observed that FAB-MS is a rapid and viable method for detecting and characterizing the complexation of polyethers with stable organic cations, such as arenediazonium, tropylium, and pyridinium cations, in the gas phase.[18,20–24] We now studied the complexation of crown ethers, containing four to eight oxygen atoms, and acyclic polyethers TeEG and pentaglyme (six oxygen atoms) with the 2-naphthalenediazonium ion under FAB-MS conditions. The molar mass of $[PEG\ 1000{-}NapN_2]^+$ is too large for our mass spectrometer. The fragmentations of the host, guest and complex ions were explained recently in the case of polyether–1-naphthalenediazonium systems.[8] Our results in this work are similar. Only 1:1 complexes were observed. Partial positive ion FAB mass spectra for the systems studied are presented in Table 2.

The complex peak at *m/z* 331 was not detected in the presence of 12-crown-4, which means that complexation of this small and rigid host with the 2-naphthalenediazonium ion is, at most, very weak even in the gas phase, although in the gas phase there are no complicating effects of solvation and counterion. Yet it is interesting to observe that 15-crown-5 and the 2-naphthalenediazonium ion also form a 1:1 complex under FAB conditions, *m/z* = 375 (0.4% in Table 2), although they cannot form an inclusion complex, since the diazonium group has a cylindrical diameter[2] of about 0.25 nm and the cavity diameter[11] of 15-crown-5 is only 0.17–0.22 nm.

Calculation of kinetic and thermodynamic stability in solution

As presented earlier for other diazonium ions, the reactions of the 2-naphthalenediazonium salt in the presence of polyether in solution can simply be

Table 1. Activation parameters E_a, $\Delta H^{\#}$ and $\Delta S^{\#}$, and the rate constant k_1 at 25 °C for the decomposition of 2-naphthalenediazonium tetrafluoroborate in 1×10^{-3} M HCl and 1,2-dichloroethane

Solvent	T range (°C)	E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	k_1 (s^{-1} at 25 °C)
Water[a]	22.0–43.6	118.5 (118.8[b])	116 ± 5	48 ± 14	1.09×10^{-5}
1,2-Dichloroethane	22.0–43.6	123.4	121 ± 4	64 ± 12	9.92×10^{-6}

[a] 1.0×10^3 M HCl.
[b] Taken from Ref. 6.

Table 2. Partial positive ion FAB mass spectra of 2-naphthalenediazonium tetrafluoroborate in the presence of polyethers,[a] $[\text{polyether}]_{\text{total}} \approx [\text{NaphN}_2^+]_{\text{total}} \approx 2 \times 10^{-2}$ M

Polyether	Ion (m/z) with relative abundance (%) in parentheses
12-C-4	155 (53.6) $[\text{2-NafN}_2]^+$; 177 (100) $[\text{12C4}]^+$; 331 (0.0) $[\text{2-NafN}_2\text{:12C4}]^+$
15-C-5	155 (28.3) $[\text{2-NafN}_2]^+$; 221 (100) $[\text{15C5}]^+$; 375 (0.4) $[\text{2-NafN}_2\text{:15C5}]^+$
18-C-6	155 (100) $[\text{2-NafN}_2]^+$; 265 (28.4) $[\text{18C6}]^+$; 419 (3.2) $[\text{2-NafN}_2\text{:18C6}]^+$
21-C-7	155 (100) $[\text{2-NafN}_2]^+$; 309 (3.1) $[\text{21C7}]^+$; 463 (5.9) $[\text{2-NafN}_2\text{:21C7}]^+$
DC-24-C-8[b]	155 (100) $[\text{2-NafN}_2]^+$; 461 (3.0) $[\text{DC24C8}]^+$; 615 (1.1) $[\text{2-NafN}_2\text{:DC24C8}]^+$
Tetraglyme	155 (30) $[\text{2-NafN}_2]^+$; 223 (100) $[\text{tetraglyme}]^+$; 377 (2.5) $[\text{2-NafN}_2\text{:tetraglyme}]^+$
Pentaglyme	155 (100) $[\text{2-NafN}_2]^+$; 267 (19.2) $[\text{pentaglyme}]^+$; 421 (2.7) $[\text{2-NafN}_2\text{:pentaglyme}]^+$

[a] Fragmentations of polyether and 2-naphthalenediazonium ions are omitted.
[b] DC = dicyclo.

interpreted by Eqn. (1) where 'complex' denotes a 1:1 complex, k_1 and k_2 are the rate constants for the thermal decomposition of the uncomplexed and complexed benzenediazonium ion respectively, and K is the complexation equilibrium constant.[3,12–18,22,25–26]

$$\begin{array}{ccc} \mathrm{NaphN_2{}^+BF_4{}^-} + \text{polyether} & \overset{K}{\rightleftharpoons} & \text{complex} \\ \downarrow k_1 & & \downarrow k_2 \\ \text{products} & & \text{products} \end{array} \qquad (1)$$

complex = inclusion complex or
non-specific adduct formation

The equilibrium can be assumed to be fast compared with dediazoniation, the complexation process being in effect diffusion controlled.[9,15] When the decomposition of the complex (k_2) cannot be ignored and $[\text{polyether}] \gg [\text{NaphN}_2^+]$ is not valid, the values of K and $k_1 - k_2$, as previously presented in detail for the 1-naphthalenediazonium salt,[8] can be calculated from the kinetic data by an iteration method using the linear Eqn. (2):

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

Here k_{obs} is the dediazoniation rate constant measured in the presence of the free polyether [polyether]. If the complex is unreactive, or $k_1 \gg k_2$, the value of K can be calculated more easily by Eqn. (3):

$$K = \frac{k_1 - k_{\text{obs}}}{k_{\text{obs}}[\text{polyether}]} \qquad (3)$$

In this work we studied the host–guest complexation of the 2-naphthalenediazonium ion with crown ethers 15-crown-5, 18-crown-6, 21-crown-7, and dicyclohexano-24-crown-8 and with acyclic polyethers tetraglyme, pentaglyme and PEG 1000. The iteration method, i.e. Eqn. (2), was used in the calculation of the equilibrium constant K for all systems investigated. Kinetic data are presented in Table 3. The systems studied obeyed Eqn. (2) with a correlation coefficient r of about 0.993. Table 4 presents the calculated values of the thermodynamic

Table 3. The effect of complexation on the thermal decomposition of 2-naphthalenediazonium tetrafluoroborate (1.0×10^{-4} M) and on the wavelength at its maximum $\lambda_{\max}$ in the presence of polyethers in 1,2-dichloroethane at 40 °C

Crown ether	[crown] (M)	k_{obs} (s^{-1})	$\lambda_{\max}$ (nm)
15-Crown-5	0	1.23×10^{-4}	264
	1.80×10^{-4}	1.20×10^{-4}	264
	2.33×10^{-4}	1.19×10^{-4}	264
	3.00×10^{-4}	1.18×10^{-4}	263
	4.20×10^{-4}	1.16×10^{-4}	263
	5.00×10^{-4}	1.15×10^{-4}	263
18-Crown-6[a]	1.07×10^{-4}	3.13×10^{-5}	256
	1.52×10^{-4}	2.40×10^{-5}	256
	2.15×10^{-4}	1.68×10^{-5}	256
	3.30×10^{-4}	1.18×10^{-5}	255
	4.08×10^{-4}	9.16×10^{-6}	255
21-Crown-7[a]	1.20×10^{-4}	9.68×10^{-6}	259
	1.36×10^{-4}	5.60×10^{-6}	258
	1.61×10^{-4}	4.74×10^{-6}	258
	2.01×10^{-4}	2.54×10^{-6}	257
	3.09×10^{-4}	2.25×10^{-6}	257
	4.02×10^{-4}	5.52×10^{-7}	256
Dicyclohexano-24-crown-8[a]	1.38×10^{-4}	5.77×10^{-5}	259
	1.84×10^{-4}	4.67×10^{-5}	258
	3.05×10^{-4}	2.79×10^{-5}	258
	4.31×10^{-4}	1.80×10^{-5}	258
	1.00×10^{-3}	1.58×10^{-5}	258
Tetraglyme[a]	4.96×10^{-4}	9.60×10^{-5}	262
	9.97×10^{-4}	8.28×10^{-5}	261
	1.99×10^{-3}	7.69×10^{-5}	260
	2.99×10^{-3}	7.12×10^{-5}	261
	4.18×10^{-3}	6.88×10^{-5}	260
Pentaglyme[b]	0	1.28×10^{-4}	264
	1.96×10^{-4}	8.52×10^{-5}	262
	3.00×10^{-4}	7.57×10^{-5}	261
	5.00×10^{-4}	6.86×10^{-5}	261
	9.66×10^{-4}	5.65×10^{-5}	260
	2.02×10^{-3}	4.93×10^{-5}	258
PEG 1000[b]	1.51×10^{-4}	5.80×10^{-5}	262
	3.00×10^{-4}	3.99×10^{-5}	259
	5.00×10^{-4}	3.25×10^{-5}	258
	1.00×10^{-3}	2.29×10^{-5}	258
	2.01×10^{-3}	1.47×10^{-5}	258

[a] $k_1 = 1.23 \times 10^{-4}$ s^{-1}.
[b] $k_1 = 1.28 \times 10^{-4}$ s^{-1}.

Table 4. Thermodynamic and kinetic stability of the 2-naphthalenediazonium ion in the presence of polyethers and the maximum hypsochromic shift due to the complexation in 1,2-dichloroethane at 40 °C

Crown ether	K (M^{-1})[a]	k_2/k_1 (%)[a]	$\Delta\lambda_{\max}$ (nm)[b]
15-Crown-5	$(4.70 \pm 1.55) \times 10^2$	64[c]	3
18-Crown-6	$(6.82 \pm 0.45) \times 10^4$	4[c]	9
21-Crown-7	$(4.53 \pm 0.46) \times 10^5$	0.2[c]	8
Dicyclohexano-24-crown-8	$(1.37 \pm 0.16) \times 10^4$	0.7[c]	7
Tetraglyme	$(1.74 \pm 0.16) \times 10^3$	50[c]	4
Pentaglyme	$(7.54 \pm 0.67) \times 10^3$	36[d]	6
PEG 1000	$(1.81 \pm 0.54) \times 10^4$	13[d]	6

[a] Calculated by Eqn. (2).

[b] The maximum hypsochromic shift due to the complexation.

[c] $k_1 = 1.23 \times 10^{-4}\ \mathrm{s}^{-1}$.

[d] $k_1 = 1.28 \times 10^{-4}\ \mathrm{s}^{-1}$.

stability K and k_2/k_1, which are measures of the effect of complexation on the kinetic stability.

DISCUSSION

The results for the 2-naphthalenediazonium ion in 1,2-dichloroethane and acidic aqueous solution show (in Fig. 1 and Table 1), in accordance with those observed earlier for the benzenediazonium (19 solvents[27]) and 1-naphthalenediazonium[8] ions, that the rate of the heterolytic dediazoniation of the aromatic diazonium ion is more or less independent of the polarity of the solvent. The insensitivities of the k_1 values to solvent polarity indicate, according to the Hughes–Ingold rules[28,29] and in accordance with new *ab initio* calculations,[30] that heterolytic dediazoniation reactions involve only small changes in the charge density during the activation step.

As seen in Fig. 1 and Table 1, the effect of temperature on the rate of dediazoniation of the 2-naphthalenediazonium ion is relatively large, but similar in both 1,2-dichloroethane and the acidic aqueous solution. Our values of activation enthalpy $\Delta H^{\#}$ are high, as high as those calculated earlier for the dediazoniation of all uncomplexed and complexed organic diazonium ions studied,[5,6,8,14,16,26] and for many other unimolecular reactions.[29] The high $\Delta H^{\#}$ values can be explained with a transition state that has undergone bond breaking with little compensating bond making. The $\Delta S^{\#}$ values in Table 1 are clearly positive, like those calculated earlier for the dediazoniation of the other uncomplexed or complexed organic diazonium ions.[5,6,8,14,16,26]

As for the pH dependency of the thermal stability of all arenediazonium ions studied in aqueous solution, three different regions have been observed: (i) the arenediazonium ion is stable in clearly acidic solutions with the formation of a corresponding phenol via an $\mathrm{S_N}1$-like heterolytic dediazoniation; (ii) above a certain specific pH, the stability decreases abruptly and reactions become increasingly complex; (iii) in clearly basic solutions, the arenediazonium ion is very unstable, as evidenced by a rapid change to *syn*-diazotate, followed by slower isomerization to the more stable *anti*-diazotate ion.[2,4,31,32] Figure 2 shows that the pH dependencies of the stabilities of the 2- and 1-naphthalenediazonium ions and the benzenediazonium ion are similar, but the region of decreasing stability, i.e. region (ii), in the case of the 1-naphthalenediazonium ion[8] has already begun above pH ≈ 3, whereas the same regions for the 2-naphthalenediazonium and benzenediazonium ions do not begin until above pH ≈ 5 and pH ≈ 6, respectively. Above a certain pH, all dediazoniation reactions lost the behaviour of first-order kinetics. The main reaction in the lower part of region (ii) can be assumed to be the coupling reaction between the phenol or naphthol formed and an unreacted diazonium ion. In region (ii), the value of $\log(k_1/\mathrm{s}^{-1})$ is observed to increase linearly with pH.[31,32] The value of $\mathrm{d}(\log(k_1/\mathrm{s}^{-1}))/\mathrm{d(pH)}$ depends on the diazonium ion; it is 0.11[8] (pH region 3–6, $n = 4$) for the 1-naphthalenediazonium ion, 0.40[31] (pH region 7–8, $n = 4$) for the benzenediazonium ion and 0.35 (pH region 5–7, $n = 3$) for the 2-naphthalenediazonium ion.

It was generally assumed earlier that the inclusion-type complex is the only type of complex formed between the arenediazonium ion and crown ether.[9] In accordance with earlier work concerning benzene- and 1-naphthalenediazonium ions,[8,16,18] the present results show, however, that both in the gas phase and solution the organic diazonium ions, whose diazonium group has a cylindrical diameter[2] of about 0.25 nm, can form a non-specific 1:1 adduct with 15-crown-5, whose cavity diameter[11] is only 0.17–0.22 nm. In the presence of crown ether containing at least an 18-membered ring, the complex is of the inclusion type. The rigid and small 12-crown-4 is such a weak complexing agent for organic diazonium ions that complexation is not detected in solution or in the gas phase. PEGs and glymes form pseudocyclic complexes with organic diazonium ions when their chains are long enough—at least six oxygen atoms—to wrap fully around the diazonium group.[8,18,22,25] The complexation with polyethers causes a slight hypsochromic shift in the UV spectrum of the naphthalenediazonium ion that is clearly smaller than the corresponding shift caused by polyether–arenediazonium complexation.

The K values of this study in Table 4 and Fig. 3 parallel the earlier observations that the thermodynamic stability of the complex polyether–organic diazonium ion in solution varies markedly with the ring size of the crown ether and the chain length of the acyclic polyether. The very large stability of the complex of every diazonium ion studied with 21-crown-7 and its derivatives has been explained as being due to the structure of the modified insertion-type complex. That is, one of the $\mathrm{CH_2—O—CH_2}$ units in 21-crown-7 will either turn upwards and away from the mean plane of the other oxygen atoms (18-

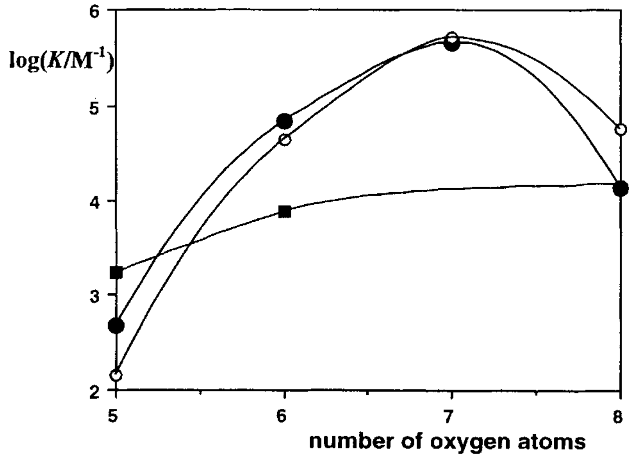

Figure 3. The effect of the number of oxygen atoms in the host molecule on the thermodynamic stability of the crown ether–2-naphthalenediazonium ion (●), the acyclic polyether–2-naphthalenediazonium ion (■, PEG 1000 taken into consideration) and the crown ether–benzenediazonium ion (○) systems in 1,2-dichloroethane at 40 °C

crown-6 is planar), or else inwards over the benzene ring, forming a complex that also includes σ-base–π-acid interactions.[8,18,21,33] The K value for the non-specific adduct formation in the presence of 15-crown-5 is slightly larger for the 2-naphthalenediazonium ion than for the benzenediazonium ion, whereas the K values of inclusion complexes of the benzenediazonium ion with 18-crown-6 and 21-crown-7 are similar to those of the corresponding crown ether–2-naphthalenediazonium ion systems. Owing to the larger flexibility of acyclic polyethers, the thermodynamic macrocyclic effect K(15-crown-5/2-NaphN$_2^+$)/K(tetraglyme/2-NaphN$_2^+$) is significantly less than unity (0.27). For larger crown ethers, with the structure of the inclusion complex, the thermodynamic macrocyclic effect is much larger than unity, e.g. K(18-crown-6/2-NaphN$_2^+$)/K(pentaglyme/2-NaphN$_2^+$) ≈ 9 and its estimated value (see Fig. 3) in the case of seven oxygen atoms in the host molecule is about 60.

The values of k_2/k_1 in Table 4 show, in accordance with previous results for 1-naphthalenediazonium ion,[8] that of the polyethers studied, only crown ethers 21-crown-7 and 18-crown-6, in this order, are strong stabilizing agents for the 2-naphthalenediazonium ion. The stabilizing ability of 15-crown-5, which undergoes only a non-specific adduct formation, is much weaker. For the same reason as presented above in the case of the thermodynamic macrocyclic effect, the value of the kinetic macrocyclic effect for small hosts is less than unity, e.g. k_2/k_1(tetraglyme/2-NaphN$_2^+$)/k_2/k_1(15-crown-5/2-NaphN$_2^+$) ≈ 0.78, but for the inclusion complex its value is much larger, e.g. k_2/k_1(pentaglyme/2-NaphN$_2^+$)/k_2/k_1(18-crown-6/2-NaphN$_2^+$) ≈ 9. The effect of benzo and cyclohexano groups on the kinetic and thermodynamic stability can be assumed to be small.[18] The results[8] show that 21-crown-7 and its derivatives are both the strongest complexing and stabilizing agents for naphthalenediazonium ions.

CONCLUSIONS

The thermal decomposition of a naphthalenediazonium salt in the solutions studied, in the absence or presence of polyether, occurs through an S$_N$1-like[23] reaction mechanism. A highly reactive naphthyl cation forms in the rate-determining heterolysis of the uncomplexed ion or the complex. Subsequent, fast product-determining reactions with nucleophiles (counterion, solvent, crown ether, etc.) give the products. The results support Zollinger and coworkers' assumption[4,15] that the decomposition of organic diazonium ions occurs via non-specific adduct formation, not directly from the unreactive inclusion complex, and that there is a fast equilibrium between these two types of complex and the uncomplexed ion. The strength of the complexation is shown to be dependent on electrostatic and steric factors, and macrocyclic thermodynamic and kinetic effects on complexation can be observed. Glaser *et al.*[30] using *ab initio* methods, have recently studied the energetic, structural, and electronic relaxations along the dediazoniation path of benzenediazonium ions to form phenyl cations. Their results support the electron-density-based model, which describes CN bonding by σ-dative N $\rightarrow$ C and C $\rightarrow$ N π-backdative bonding, and suggest that diazonium ions are best thought of as a carbenium ion closely associated with an N$_2$ group that is internally polarized in the fashion $N_\alpha^{\delta-}$—$N_\beta^{\delta+}$. Hence, we have begun to study with *ab initio* methods the structures of the naphthalenediazonium ions and their host–guest complexes.

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