Stability of 1-naphthalenediazonium ion in solution. Complexation and decomposition of 1-naphthalenediazonium tetrafluoroborate in the presence of crown ethers and acyclic polyethers in 1,2-dichloroethane and the gas phase under fast atom bombardment conditions

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ABSTRACT: The effects of solvent, temperature and pH on the rate of decomposition of uncomplexed 1-naphthalenediazonium tetrafluoroborate were studied by UV spectrometry. The complexation of the 1-naphthalenediazonium ion with crown ethers containing 4–10 oxygen atoms and some acyclic polyethers was detected and characterized in the gas phase by fast atom bombardment mass spectrometry (FAB-MS). In addition, the host–guest complexation and the kinetics of the thermal dediazoniation of 1-naphthalenediazonium ion in the presence of four crown ethers and two acyclic polyethers were studied in 1,2-dichloroethane (DCE) solution at 40 °C by UV spectrometry. All hosts, except 12-crown-4, formed 1:1 complexes under FAB conditions. The values of the thermodynamic stability K and the stabilizing ability of the complexation (k_2/k_1) in DCE were calculated from the kinetic data. The thermodynamic and kinetic stabilities were observed to be greater for the inclusion complex of the 1-naphthalenediazonium ion formed with crown ethers containing at least six oxygen atoms than for the non-spesific adduct formation formed with 15-crown-5. This was also true for tetraglyme, whose chain is too short to be capable of being fully wrapped around the diazonium group as in the complex of PEG 1000. Crown ethers with seven oxygen atoms are the strongest complexing agents for all the aromatic diazonium ions studied, for the 1-naphthalenediazonium ion investigated here and for arenediazonium ions examined earlier. The values of the activation enthalpy $\Delta H^{\neq}$ for the thermal dediazoniation of the uncomplexed salt in both the acidic aqueous solution and DCE were observed to be high, and the corresponding values of activation entropy $\Delta S^{\neq}$ were clearly positive. The results are consistent with a heterolytic S_N1-like mechanism involving the decomposition of the uncomplexed and complexed 1-naphthalenediazonium ion into a highly reactive naphthyl cation, followed by fast product-determining reactions with nucleophiles to give the products. Copyright © 2000 John Wiley & Sons, Ltd.

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

INTRODUCTION

Organic diazonium salts were first prepared as early as 1858[1] and their reactions were among the first to be studied systematically by organic chemists. Arenediazonium salts have been shown to be very important for synthetic chemistry[2,3] and the dyestuff industry.[4] The use of arenediazonium ions as chemical trapping reagents has also increased notably in recent years.[5] A great number of publications, many wide reviews and even several books concerned with arenediazonium compounds have been published.[2–8] The thermal dediazoniation of arenediazo-

nium ions has versatile applications in synthetic chemistry in the preparation of many widely different compounds.[2,3,6] It has been shown that thermal dediazoniations of aromatic diazonium salts involve a variety of mechanisms, heterolytic and homolytic, and small modifications to the reaction conditions (solvent, substituent, pH, atmosphere, addition of other solvents or substrates) may change the mechanism and products drastically.[2,3,5–8] Nevertheless, publications describing thermal dediazoniation of naphthalenediazonium salts are surprisingly very few.[6,9]

Host–guest complexation has been studied with great interest in recent decades owing to its many possible applications, e.g. synthetic chemistry, phase-transfer reactions, ion-selective electrodes, enhancement of the solubility and stability of compounds and studies of

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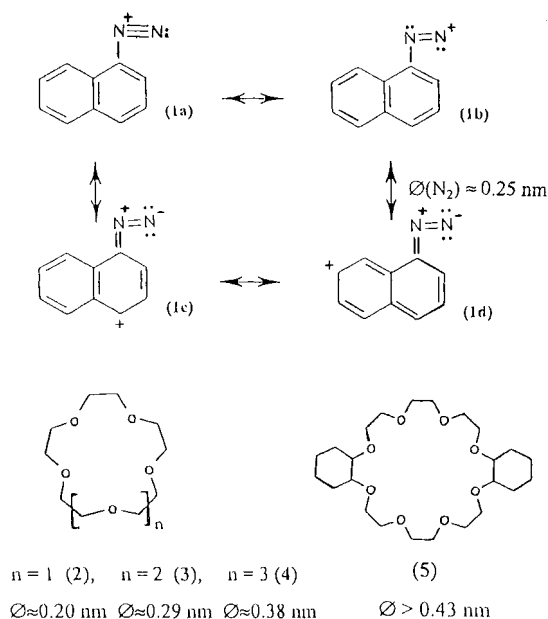
Scheme 1. Resonance formulae of the 1-naphthalenedia-zonium ion (**1a–d**) and structures of some crown ethers (**2–5**)

naturally occurring compounds.[10–12] Although acyclic polyethylene glycols (PEGs) are weaker complexing agents than crown ethers, they may have practical use in the future: it has been shown that inexpensive, commercially available PEGs can be used as effective phase transfer agents instead of expensive crown ethers for reactions of arenediazonium salts in solvents of low polarity.[13] The host–guest complexation in solution has usually been studied by spectroscopic, thermodynamic and kinetic methods.[10–15] Modern mass spectrometry with fast atom bombardment (FAB-MS), which is easily implemented with various mass spectrometric systems, and more recently electrospray ionization (ESI-MS), has emerged as a viable method for studying the host–guest complexation of large macro(poly)cycles with metal and organic ions in the gas phase.[16]

Gokel and Cram reported in 1973[17] that crown ethers of suitable dimensions solubilize arenediazonium ions through complexation in non-polar solvents in which they otherwise are insoluble. Bartsch *et al.*[18] reported 3 years later that the complexation of 18-membered crown ethers with the *p-tert*-butylbenzenediazonium ion in 1,2-dichloroethane markedly increases the stability of the diazonium salt against thermal decomposition. Since then, the host–guest complexation of crown ethers with arenediazonium ions has been investigated intensively.[3,10–12,14–22] Publications describing both the thermodynamic and the kinetic stability of these complexes are relatively few, however.[14,15,19,21,22] Polyether–arenediazonium ion systems (polyether = crown ether or acyclic polyether[22–24]) are the only host–guest systems for which the thermodynamic stabilities have been calculated from their kinetic data. As far as we know,

the host–guest complexation of polyethers with naphthalenediazonium ions has not been studied by any other groups (T. Kuokkanen and J. Palokangas, 2-naphthalene-diazonium ion under study).

Although it is generally assumed that the 1:1 inclusion complex is the only type of complexation between arenediazonium ions and crown ethers, we have demonstrated, through several spectroscopic, kinetic and gas–liquid chromatographic measurements, that organic diazonium ions form weak non-specific adducts (also called charge-transfer complexes[3]) with 15-crown-5, whose cavity diameter[12] is too small for inclusion-type complexation (see Scheme 1).[14,21] The peak of this complex has also been detected in the FAB mass spectrum.[14]

The strength of complexation is much more difficult to predict for flexible organic molecules than for rigid metal cations. We have used spectroscopic and kinetic methods to investigate, in solution, the effects of ring size and substituent of the crown ether, the length of the chain in acyclic polyethylene glycol, the character and position (*ortho*-effect) of the substituent of the benzenediazonium ion, the temperature, the solvent and the pressure on the host–guest complexation between crown ethers and arenediazonium ions.[13,18,20–23,25] Complexation in the gas phase under FAB conditions has been detected and characterized by mass spectrometry (FAB-MS).[14,24] Continuing our studies on the interactions of cyclic and acyclic polyethers with stable organic cations, we have now investigated, by spectroscopic and kinetic methods, the complexation of the 1-naphthalenediazonium ion with some crown ethers and PEGs. In addition, effects of solvent, temperature and pH on the thermal stability of the uncomplexed ion have been explained. The resonance formulae of the 1-naphthalenediazonium ion (**1a–d**) and the structure of some of the crown ethers used in this work (**2–5**) are shown in Scheme 1.

EXPERIMENTAL

Materials. 1-Naphthalenediazonium tetrafluoroborate was synthesized from 1-naphthalenamine (Merck) by diazotization with sodium nitrite at 2–5 °C in H_2O–EtOH (4:1) acidified with tetrafluoroboric acid, and was recrystallized twice from acetic acid–tetrafluoroboric acid (1:4). The melting temperature, 105–107 °C, and the UV spectral data for the 1-naphthalenediazonium salt in acidic aqueous solution (1×10^{-4} M HCl), $\lambda_{max} = 256$ nm, $\epsilon = 1.31 \times 10^4$ l mol^{-1} cm^{-1} and $\lambda_{max} = 365$ nm (broad), $\epsilon = 6.44 \times 10^3$ l mol^{-1} cm^{-1}, are in accordance with the corresponding values in the literature.[7] The diazonium salt was stored in the dark at a low temperature to minimize its thermal decomposition. The unsubstituted crown ethers, 12-crown-4, 15-crown-5 (**2**) and 18-crown-6 (**3**) from Fluka, and 21-crown-7 (**4**, Pfaltz & Bauer), the dicyclohexane-substituted crown
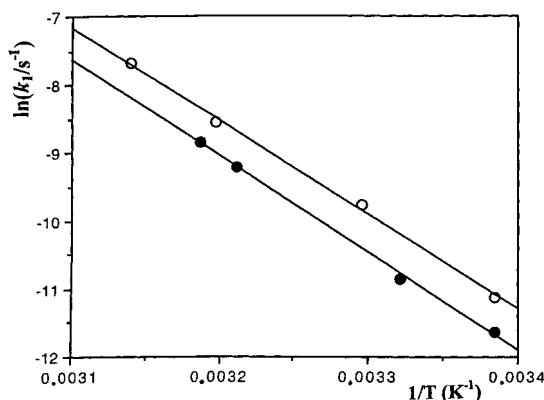
Figure 1. Effect of solvent and temperature on the thermal decomposition of uncomplexed 1-naphthalenediazonium tetrafluoroborate in (●) 1×10^{-4} M HCl and (○) 1,2-dichloroethane

ether dicyclohexano-24-crown-8 (**5**, Fluka), the benzene-substituted crown ethers dibenzo-21-crown-7 (Fluka) and dibenzo-30-crown-10 (Aldrich Chemie), and also acyclic polyethers tetraethylene glycol (TeEG) (Fluka), penta-glyme (pentaethylene glycol dimethylther, Riedel-de Haën) and PEG 1000 (polyethylene glycol 1000, Fluka), were commercial chemicals and were used without further purification. Dibenzo-24-crown-8 (Fluka) was purified as described previously.[13] 1,2-Dichloroethane (Fluka) was purified, dried and distilled by a common procedure.[26] 3-Nitrobenzyl alcohol (NBA) from Aldrich Chemie was used without further purification.

Apparatus and measurements. The complexes of cyclic and acyclic polyethers with 1-naphthalenediazonium tetrafluoroborate and their fragments in the gas phase under FAB conditions were identified on a Kratos MS 80 autoconsole mass spectrometer operating with a DART data system. The atom gun was operated at 8 keV and argon was used as the bombarding gas with a pressure of about 1×10^{-6} Torr (1 Torr = 133.3 Pa) in the collision region. NBA was shown earlier to be the best solvent for our FAB experiments, owing to its electron-scavenging nature. NBA was also used as the liquid matrix in this study. The stainless-steel tip of the FAB probe was coated with a thin layer of a mixture of polyether, 1-naphthalenediazonium tetrafluoroborate, and the liquid NBA matrix ([polyether]$_{total}$ ≈ [1-NapN$_2^+$]$_{total}$ ≈ 2 × 10^{-2} M). The spectrum was recorded immediately after the sample had been inserted.

Spectra were scanned and kinetic measurements were carried out with a Shimadzu UV 160 A double-beam spectrometer with two cell holders. The quartz cells of 10 mm pathlength were held at the desired temperature by circulating water from an electrically thermostated water-bath into the self-constructed temperature attachment. The accuracy of the wavelength at the maximum λ_{max} was within ±1 nm. The temperature inside the cells

was monitored with a digital thermometer and was constant to within ±0.1 °C. Because benzo-substituted crown ethers are also UV absorbing, the same concentration of the host was used in both cells in the measurements of the complexation between dibenzo-21-crown-7 and 1-naphthalenediazonium ion in 1,2-dichloroethane. In the other studies, only the solvent was used in the reference cell. After thermostating, about 20 values of the absorbance A_t were recorded at suitable time intervals up to about 2–3 half-lives. The observed rate constant of the dediazoniation k_{obs} was calculated using the equation

$$-\ln(A_t - A_\infty) = a_1 \, t + a_0; \quad k_{obs} = a_1 \qquad (1)$$

The absorbance at infinite time A_∞, was determined by measuring the absorbance after about 10 half-lives. All decomposition reactions in this work were found to obey first-order kinetics within the intervals studied: the correlation constant r for the straight line (1) was about 0.9998 and the standard deviation usually 0.5–2%.

Two different buffer systems were used in studies of the effect of pH on thermal decomposition of the uncomplexed 1-naphthalenediazonium ion in aqueous solutions: HCl for pH 1.0 and 2.0 and citric acid–sodium biphosphate in the pH range 3.0–8.0. The pH values of the buffer solution were determined with a Radiometer PHM63 digital pH-meter. For measurements of complexation in solution, small amounts of the 1-naphthalenediazonium salt and polyether were accurately weighed with a Perkin-Elmer AD-2 autobalance. A solution of 1-naphthalenediazonium tetrafluoroborate was first prepared by weighing. An aliquot of this solution was transferred into a volumetric flask containing the desired amount of polyether. All other solutions, with constant [NapN$_2^+$]$_{total}$ but different concentrations of polyether, were prepared by mixing the desired aliquots of these two solutions. The melting point of the uncomplexed salt was determined with a Thermopan microscope (Reichert, Vienna, Austria).

RESULTS

Effects of temperature, solvent and pH on thermal stability of the uncomplexed 1-naphthalenediazonium ion

The effect of temperature on the thermal decomposition of 1-naphthalenediazonium tetrafluoroborate was studied by determining the first-order rate constant of dediazoniation k_1 in acidic aqueous solution (1×10^{-3} M HCl) and in 1,2-dichloroethane at four temperatures. The corresponding Arrhenius plots are presented in Fig. 1. The values of activation enthalpy $\Delta H^{\neq}$ and activation entropy $\Delta S^{\neq}$ were calculated using the usual procedure by comparing the constants E_a and A of the Arrhenius

Table 1. Activation enthalpy, $\Delta H^{\neq}$, activation entropy, $\Delta S^{\neq}$, and rate constant k_1 at 25 °C for decomposition of the 1-naphthalenediazonium ion in 1×10^{-4} M HCl and 1,2-dichloroethane

Solvent	Temperature range (°C)	E_a (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	k_1 (s^{-1}) (25 °C)
1,2-Dichloroethane	22–41	115.0	112 ± 4	43 ± 12	2.30 × 10^{-5}
Water[a]	22–46	118.6 (118[b])	116 ± 3	50 ± 10	1.28 × 10^{-5}

[a] 1.0×10^{-3} M HCl.
[b] Taken from Ref. 7.

equation

$$\ln k_1 = \ln A - (E_a/R)(1/T) \qquad (2)$$

with those in the equation

$$\ln(k_1/T) = \ln(k_B/h) + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/(RT) \qquad (3)$$

derived from the activated state theory, where k_B and h are the Boltzmann and Planck constants, respectively. Table 1 shows the values of the activation parameters, and, to reveal the solvent effect, we have included the calculated k_1 values at constant temperature, $T = 25$ °C.

The effect of pH on the thermal stability of the 1-naphthalenediazonium ion in aqueous solution was studied by determining the first-order rate constant k_1 in aqueous solution, in HCl (pH 1.0 and 2.0) and in HOC(CH$_2$COOH)$_2$COOH–Na$_2$HPO$_4$ buffer solutions (pH 3.0–7.5). The results are presented in Fig. 2. For comparison, we have included the corresponding pH dependence in the case of benzenediazonium ion[27] in Fig. 2.
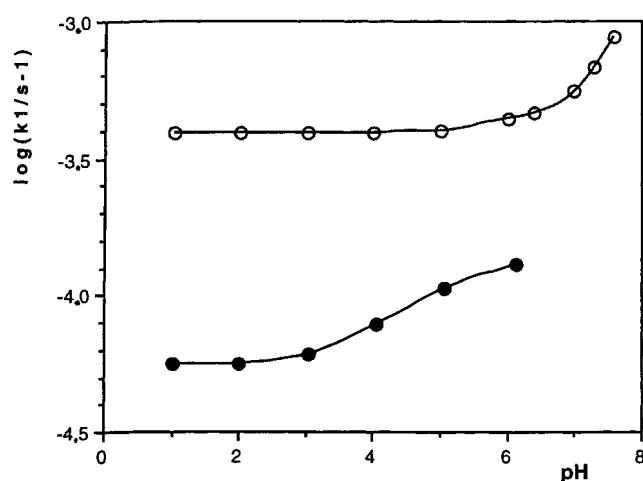
Figure 2. Effect of pH on the thermal stability of uncomplexed 1-naphthalenediazonium ion (●) and benzenediazonium ion (○) in acidic and neutral aqueous solution at 40 °C

Studies in the gas phase under FAB conditions

It has been shown repeatedly that FAB-MS is a viable and rapid method for studying the host–guest complexation of polyethers with stable organic cations such as arenediazonium, tropylium and pyridium in the gas phase.[14,16,20,24,28,29] In the FAB-MS method the complex is first formed in the liquid matrix and is then analysed in the gas phase by mass spectrometry. Hence the complex must exist both in solution and in the gas phase. In this work we studied TeEG and pentaglyme with the 1-naphthalenediazonium ion under FAB-MS conditions. The complexation between PEG 1000 and 1-NapN$_2^+$ was not studied in the gas phase because the molar mass of [PEG 1000-NapN$_2$]$^+$ is too large for our mass spectrometer. Fig. 3 shows the positive ion FAB mass spectrum of 1-NapN$_2^+$BF$_4^-$ in the presence of 18-crown-6 in the NBA matrix. The ions at m/z 155 (100%) and 265 (28.4%) indicate the presence of the abundant NapN$_2^+$ ion and [18C6 + H]$^+$ cation. The peak of the complex [18C6−Na]$^+$ at m/z 287 shows that the Na$^+$ ion competes effectively in complex formation with 1-naphthalenediazonium ion. The peak of the two cation–one anion cluster (PhN$_2^+$)$_2$BF$_4^-$ has always been observed in our FAB spectra but never its Na adduct at m/z 297 + 22. Hence we believe that the signal at m/z 397 belongs to the two cation–one anion cluster (NaphN$_2^+$)$_2$BF$_4^-$ and the peak at m/z 419 (3.6%) only to the complex [18C6−NapN$_2$]$^+$. Furthermore, the fragmentation of 1-naphthalenediazonium ion gives naphthyl ion (Nap$^+$) at m/z 127, phenyl cation (C$_6$H$_5^+$) at m/z 77, etc. Partial positive ion FAB mass spectra for the investigated systems are presented in Table 2. In agreement with earlier studies, the fragmentation pattern of the crown ether and PEG consists of a series of losses of protonated C$_2$H$_4$O structural units, and the mass spectra therefore consistently include m/z 45, 89, 133, 177, etc., depending on the size of the crown ether or PEG, and in addition m/z 103, 147, etc. for glymes. The ion [PhOC$_2$H$_4$O]$^+$ at m/z 136 is typical in the mass spectra of benzene-substituted crown ethers, while the peaks at m/z 154, 136 and 107 are due to the fragmentation of the NBA matrix. Possible adducts of NBA with crown ethers have not been observed in our FAB spectra of the studied polyether–PhN$_2^+$ systems.

It is interesting to observe that 15-crown-5 and the 1-naphthalenediazonium ion also form a 1:1 complex under
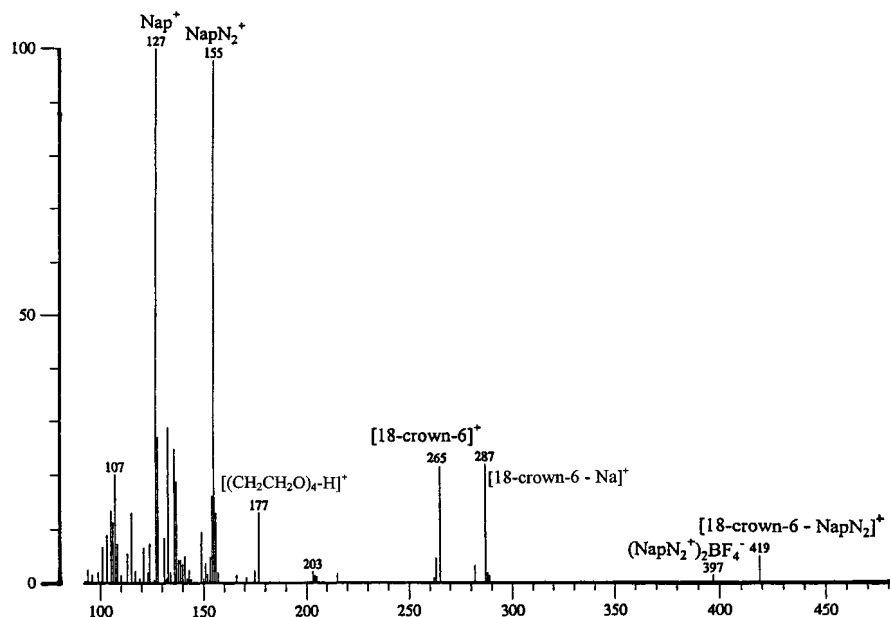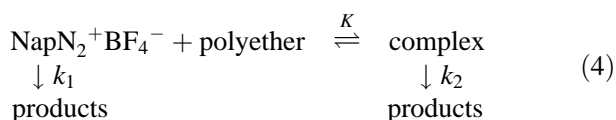
Figure 3. Mass spectrum of 1-naphthalenediazonium tetrafluoroborate in the presence of 18-crown-6 ([crown ether]$_{tot}$ ≈ [NapN$_2^+$]$_{tot}$) recorded by the FAB technique in NBA as the matrix

FAB conditions, m/z 375 (0.8% 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[12] of 15-crown-5 is only 0.17–0.22 nm.[14–16] 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 1-naphthalene-diazonium ion is, at most, very weak even in the gas phase, where there are no complicating effects of counterion and solvation.

Calculation of kinetic and thermodynamic stability in solution

The reactions of 1-naphthalenediazonium salt in the presence of polyether in solution can be represented by the equation

$$
\begin{array}{ccc}
NapN_2^+BF_4^- + polyether & \overset{K}{\rightleftharpoons} & complex \\
\downarrow k_1 & & \downarrow k_2 \\
products & & products
\end{array} \quad (4)
$$

in which 'complex' denotes a 1:1 complex (inclusion complex or non-specific adduct formation), 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.[3,13–15,19,21–24]

Complexation and decomplexation reactions in the presence of crown ethers have been observed to be very

fast compared with dediazoniation, the complexation process being in effect diffusion-controlled.[10,15] When the decomposition of the complex cannot be ignored, the values of K and $k_1 - k_2$ can be calculated from the kinetic data by an iteration method using the linear Eqn. (5) and Eqns. (6)–(9);

$$
\frac{1}{k_1 - k_{obs}} = \frac{1}{(k_1 - k_2)K} \times \frac{1}{[polyether]} + \frac{1}{k_1 - k_2} \quad (5)
$$

$$
K = [complex]/([NapN_2^+] \times [polyether]) \quad (6)
$$

$$
[polyether] = [polyether]_{total} - [complex] \quad (7)
$$

$$
[NapN_2^+] = [NapN_2^+]_{total} - [complex] \quad (8)
$$

$$
[complex] =
$$
$$
\{sum - \sqrt{(sum^2 - 4[NapN_2^+][polyether])}\}/2 \quad (9)
$$

where sum = $[NapN_2^+]_{total} + [polyether]_{total} + 1/K$; k_{obs} is the dediazoniation constant measured in the presence of the free polyether, [polyether]. If the complex is unreactive, or $k_2 \ll k_1$, the value of K can be calculated more easily for every data pair (k_{obs}, [polyether]) by the equation

$$
K = (k_1 - k_{obs})/k_{obs} \times (1/[polyether]) \quad (10)
$$

We studied the host–guest complexation in solution using as model crown compounds 15-crown-5, 18-crown-6, dibenzo-21-crown-7 and dicyclohexano-24-crown-8, and as model acyclic hosts we used tetraglyme

Table 2. Partial positive ion FAB mass spectra of 1-naphthalenediazonium tetrafluoroborate in the presence of crown ethers and acyclic polyethers,[a] $[\text{host}]_{\text{tot}} \approx [\text{NapN}_2{}^+]_{\text{tot}}$

Crown ether	Ion (m/z) with relative abundance (%) in parentheses
12-C-4	155 (10) $[\text{1-NapN}_2]^+$; 177 (100) $[\text{12C4}]^+$; 331 (0.0) $[\text{1-NapN}_2{:}\text{12C4}]^+$
15-C-5	155 (42) $[\text{1-NapN}_2]^+$; 221 (100) $[\text{15C5}]^+$; 375 (0.8) $[\text{1-NapN}_2{:}\text{15C5}]^+$
18-C-6	155 (100) $[\text{1-NapN}_2]^+$; 265 (16) $[\text{18C6}]^+$; 419 (3.6) $[\text{1-NapN}_2{:}\text{18C6}]^+$
21-C-7	155 (100) $[\text{1-NapN}_2]^+$; 309 (1.1) $[\text{21C7}]^+$; 464 (2.2) $[\text{1-NapN}_2{:}\text{21C7}]^{+\text{c}}$
DB-21-C-7[b]	155 (100) $[\text{1-NapN}_2]^+$; 404 (5.1) $[\text{DB21C7}]^+$; 559 (1.5) $[\text{1-NapN}_2{:}\text{DB21C7}]^+$
DC-24-C-8[b]	155 (100) $[\text{1-NapN}_2]^+$; 461 (3.0) $[\text{DC24C8}]^+$; 615 (1.1) $[\text{1-NapN}_2{:}\text{DC24C8}]^+$
DB-24-C-8	155 (100) $[\text{1-NapN}_2]^+$; 448 (3.9) $[\text{DB24C8}]^+$; 603 (1.4) $[\text{1-NapN}_2{:}\text{DB24C8}]^+$
DB-30-C-10	155 (100) $[\text{1-NapN}_2]^+$; 536 (5.8) $[\text{DB30C10}]^+$; 691 (1.9) $[\text{1-NapN}_2{:}\text{DB30C10}]^+$
TeEG	155 (10) $[\text{1-NapN}_2]^+$; 195 (100) $[\text{TeEG}]^+$; 349 (0.1) $[\text{1-NapN}_2{:}\text{TeEG}]^+$
Tetraglyme	155 (31) $[\text{1-NapN}_2]^+$; 223 (100) $[\text{Tetraglyme}]^+$; 349 (2.8) $[\text{1-NapN}_2{:}\text{Tetraglyme}]^+$
Pentaglyme	155 (44) $[\text{1-NapN}_2]^+$; 267 (100) $[\text{pentaglyme}]^+$; 421 (2.2) $[\text{1-NapN}_2{:}\text{pentaglyme}]^+$

[a] Fragmentations of polyethers and 1-naphthalenediazonium ions are omitted; see Results.
[b] B = benzo; DB = dibenzo; DC = dicyclo.
[c] In addition, 463 (0.5%) $[\text{1-NapN}_2{:}\text{21C7}]^+$.

and PEG 1000 (Table 3). We used the iteration procedure, or Eqns. (4)–(9), for all systems studied. The systems studied obeyed Eqn. (5) with a correlation coefficient $r \approx 0.996$. The calculated values of K (the thermodynamic stability) and k_2/k_1, a measure of the effect of complexation on the kinetic stability of the 1-naphthalenediazonium ion in solution, are presented in Table 4.

Table 3. Effect of complexation on the thermal decomposition of 1-naphthalenediazonium tetrafluoroborate in the presence of crown ethers and acyclic polyethers in 1,2-dichloroethane at 40 °C

Crown ether	[Crown] (M)	k_{obs} (s^{-1})	λ_{max} (nm)
15-Crown-5	0	2.71×10^{-4}	262
	1.55×10^{-4}	2.49×10^{-4}	261
	2.03×10^{-4}	2.45×10^{-4}	260
	2.64×10^{-4}	2.38×10^{-4}	260
	3.75×10^{-4}	2.30×10^{-4}	260
	4.51×10^{-4}	2.28×10^{-4}	260
18-Crown-6	1.30×10^{-4}	1.30×10^{-4}	258
	1.76×10^{-4}	1.09×10^{-4}	258
	2.36×10^{-4}	9.82×10^{-5}	257
	3.47×10^{-4}	6.60×10^{-5}	257
	4.24×10^{-4}	5.06×10^{-5}	256
Dibenzo-21-crown-7	1.00×10^{-4}	4.76×10^{-5}	—[a]
	1.47×10^{-4}	3.48×10^{-6}	—[a]
	2.10×10^{-4}	2.11×10^{-6}	—[a]
	3.27×10^{-4}	1.36×10^{-5}	—[a]
	4.05×10^{-4}	8.40×10^{-6}	—[a]
Dicyclohexano-24-crown-8	1.40×10^{-4}	1.54×10^{-4}	258
	1.87×10^{-4}	1.32×10^{-4}	258
	2.46×10^{-4}	1.08×10^{-4}	257
	3.57×10^{-4}	8.80×10^{-5}	256
	4.33×10^{-4}	7.10×10^{-5}	254
Tetraglyme[b]	0	2.38×10^{-4}	262
	7.03×10^{-4}	1.89×10^{-4}	262
	1.02×10^{-3}	1.78×10^{-4}	261
	2.00×10^{-3}	1.53×10^{-4}	261
	2.80×10^{-3}	1.46×10^{-4}	261
	3.71×10^{-3}	1.41×10^{-4}	259
PEG 1000[b]	1.50×10^{-4}	1.44×10^{-4}	261
	3.00×10^{-4}	1.16×10^{-4}	259
	4.98×10^{-4}	1.04×10^{-4}	258
	9.96×10^{-4}	7.94×10^{-3}	258
	2.00×10^{-3}	7.68×10^{-3}	258

[a] Not determined owing to the absorption of the host.
[b] At 39.8 °C.

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

Crown ether	K (l mol^{-1})[a]	k_2/k_1 (%)[a,b]	$\Delta\lambda_{max}$ (nm)[c]
15-Crown-5	$(2.15 \pm 0.32) \times 10^3$	67	6
18-Crown-6	$(7.62 \pm 0.83) \times 10^3$	4.0	6
Dibenzo-21-crown-7	$(4.05 \pm 0.22) \times 10^4$	2.5	—[d]
Dicyclohexano-24-crown-8	$(4.64 \pm 0.31) \times 10^3$	10	8
Tetraglyme	$(9.40 \pm 0.61) \times 10^2$	46	4
PEG1000	$(1.37 \pm 0.14) \times 10^4$	31	6

[a] Calculated by Eqn. (5).
[b] $k_1 = 2.71 \times 10^{-4}$ s^{-1}.
[c] The maximum hypsochromic shift due to the complexation.
[d] Not determined owing to the absorption of the host.

DISCUSSION

It has been shown earlier that three different stability regions for every arenediazonium ion in aqueous solution can be identified: (i) the arenediazonium ion is more or less stable in clearly acidic solutions with the formation of a corresponding substituted phenol via an S_N1-like heterolytic reaction mechanism; (ii) above a certain specific pH the stability decreases abruptly {d[log(k_1/s^{-1})]/d(pH) <1}, 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 in two steps, followed by slower isomerization to the stable *anti*-diazotate ion.[2,3,27,30] Figure 2 shows that the pH dependence of the stability of the 1-naphtalenediazonium ion in acidic and neutral aqueous solution is similar to that of the benzenediazonium ion, but its region of decreasing stability, region ii, begins already above pH ≈ 3, whereas the same region for benzenediazonium ion does not begin until the pH is above ca 6. In region ii, the value of log(k_1/s^{-1}) increases linearly with pH for both 1-naphtalenediazonium ion (pH range 3.0–6.1 in Fig. 2) and the arenediazonium ions. The dependence of stability on pH is less for the 1-naphtalenediazonium ion, however, than it is for the benzenediazonium ion: the values of d[log(k_1/s^{-1})]/d(pH) are 0.11 ($n = 4$) and 0.40[27] (pH range 7–8, $n = 4$), respectively. Above a certain pH, all dediazoniation reactions lost the behaviour of first-order kinetics [Eqn. (1)]. The main reaction in the lower part of region ii can be assumed to be the coupling reaction of the formed phenol or naphthol with an unreacted diazonium ion.[3,27,30]

Our measurements in 1,2-dichloroethane and acidic aqueous solution (Fig. 1 and Table 1) show that the rate of the heterolytic dediazoniation of the 1-naphthalenediazonium ion is more or less independent of the polarity of the solvent. This coincides with earlier observations[31] that the rate constants k_1 for the heterolytic dediazoniation of benzenediazonium ion, measured in 19 solvents, differ only by a factor of about 9. The k_1 values measured here for the dediazoniation of benzenediazonium salt in 1,2-dichloroethane and in 1×10^{-3} M HCl at 25 °C are 3.8×10^{-5} and 4.6×10^{-5} s^{-1}, respectively, and also show similarity to each other. The insensitivities of the k_1 values to the solvent observed for the 1-naphthalenediazonium and benzenediazonium ions indicate, according to the Hughes–Ingold rules,[32,33] that heterolytic dediazoniation reactions involve only small changes in the charge density during the activation step, which agrees well with the proposed S_N1-like reaction mechanism.

The effect of temperature on the rate of dediazoniation of the 1-naphthalenediazonium ion is relatively large, but similar in 1,2-dichloroethane and acidic aqueous solutions (Fig. 1 and Table 1). The values of activation enthalpy $\Delta H^{\neq}$ are high, as high as those for the dediazoniation of uncomplexed and complexed arenediazonium ions,[5,7,19,21] and for many unimolecular reactions of acyclic and aliphatic compounds.[33] The high $\Delta H^{\neq}$ values can be explained with a transition state that has undergone bond breaking with little compensating bond making. Our $\Delta S^{\neq}$ values in Table 1 are clearly positive, like those calculated earlier for the dediazoniation of uncomplexed and complexed arenediazonium salts[5,7,19,21] and for some other unimolecular reactions with an S_N1 mechanism, but contrast with the negative $\Delta S^{\neq}$ values for bimolecular reactions with an S_N2 mechanism.[34]

Although it is generally assumed and reported[10] that the inclusion 1:1 complex (called the insertion-type complex by Zollinger and co-workers[3,15]) is the only type of complexation between crown ether and arenediazonium ions, we have demonstrated by kinetic and spectroscopic measurements and product analyses that the benzenediazonium ion, whose diazonium group has a cylindrical diameter[3] of about 0.25 nm, can form a non-specific adduct with 15-crown-5[14,21] whose cavity diameter[12] is only 0.17–0.22 nm, both in the gas phase and in solution. The results of earlier work and this study suggest that in the presence of a crown ether containing at least an 18-membered ring, the complex between crown ether and naphthalenediazonium or arenediazonium ion
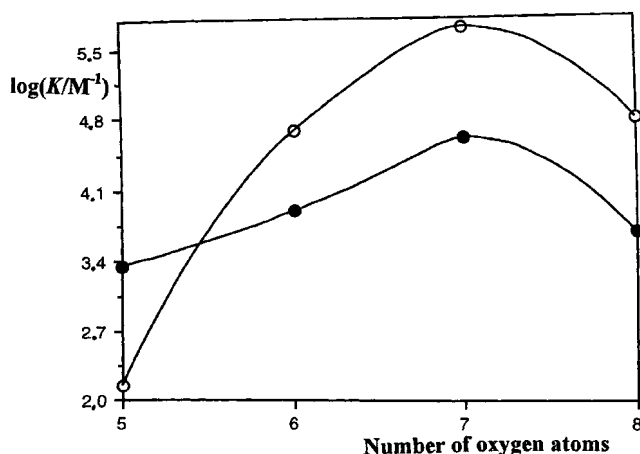
Figure 4. Effect of the number of oxygen atoms in the host molecules on the thermodynamic stability of the crown ether–1-naphthalenediazonium ion (●) and crown ether–benzenediazonium ion (○) systems in 1,2-dichloroethane at 40 °C

is of the inclusion type, whereas with 15-crown-5 it is a weaker non-specific adduct (see hole diameters in Scheme 1). Rigid and small polyether 12-crown-4 is such a weak complexing agent for organic diazonium ions, that no complexation has been detected either in solution or in the gas phase. Acyclic polyethers form pseudo-cyclic complexes with organic diazonium ions when the chain of a acyclic polyether, PEG or glyme, is long enough to wrap fully around the diazonium group.[14,23,24] The complexation caused a slight hypsochromic shift in the UV spectrum, which indicates a more localized π-electron system in the complexed 1-naphthalenediazonium ion than in the uncomplexed ion. This has been explained by the electrostatic interactions in the complexes between the oxygen atoms of the polyether and the diazonium group carrying a positive charge. Zollinger and co-workers[15] have argued that, in the charge-transfer complex, the acceptor centre of the arenediazonium ion is either the β-N atom and/or the combined π-electron system of the aryl part and the diazonio group, while the donor centre is one or several of the oxygen atoms in the crown ether.

In accordance with earlier observations for crown ether–arenenediazonium ion[14,16,20] and acyclic polyether–arenenediazonium ion[24] systems, but in contrast to crown ether–metal systems,[10–12] the peaks of sandwich complexes $[(polyether)_2NapN_2]^+$ were not detected in the FAB spectra in this study. Omitting the results for short tetraethylene glycol, the values of the relative abundance of the 1:1 complex peak in Table 2 are 0.8–3.6%.

The calculated K values in Table 4 and Fig. 4 show that in solution the thermodynamic stability of the 1-naphthalenediazonium ion complexed with four crown ethers and two acyclic polyethers studied varies markedly with the ring size of the crown ether and the chain length

of the acyclic host molecule. The results of this study parallel the earlier conclusions[3,14,15,21–24] that the K values of the inclusion complexes of organic arenediazonium ions with polyethers containing six or more oxygen atoms are clearly larger than those of non-specific adduct formation in the presence of 15-crown-5. Correspondingly, the small K value for the tetraglyme-1-naphthalenediazonium ion in Table 4 shows that the chain of tetraglyme with five oxygen atoms is too short to be fully wrapped around the diazonium group, thus forming a pseudocyclic complex. It has been observed recently[14] that a cyclohexano or benzo substituent(s) in the host molecule has only a small effect on the equilibrium constant K for the crown ether–benzenediazonium ion complex. The greater ring flexibility of 21-crown-7 and its derivatives ($\phi \approx 0.34$–0.43nm) compared with 18-crown-6 ($\phi \approx 0.26$–0.32nm) may allow for the relief of steric interaction between the macrocyclic ring and 2-substituents of naphthalene- and benzenediazonium ions. 18-Crown-6 is planar (D_{3d} configuration) in its complexes,[10,35] but it seems reasonable to assume that one of the CH_2—O—CH_2 units in 21-crown-7 or its derivatives will turn upwards and away from the mean plane of the other oxygen atoms, or else inwards over the naphthalene or benzene ring of organic diazonium ion in the modified inclusion-type complex structure with σ-base–π-acid interactions.[14,20,35] The modified structure would present a cavity of similar size to that found in 18-crown-6 to the diazonium group, but the extra oxygen atom of 21-crown-7 and its derivative can now interact with other electrophilic centres to provide additional stabilization to the overall complex. Correspondingly, in solution the larger crown ethers, e.g. dicyclohexano-24-crown-8, can also be assumed to be capable of wrapping around the cation in order to form a stabilizing three-dimensional cavity[11,14] with all oxygen atoms coordinated to the guest.

Figure 4 shows that the effect of the ring size on the thermodynamic stability of the 1-naphthalenediazonium ion complexed with crown ethers is less than it is on the crown ether–benzenediazonium ion system. The K value for the non-specific adduct formation in the presence of 15-crown-5 is slightly larger for the 1-naphthalenediazonium ion than for the benzenediazonium ion, whereas all K values of inclusion complexes of the 1-naphthalenediazonium ion are lower than those for the corresponding crown ether–benzenediazonium ion system. Owing to the flexibility of acyclic polyethers, the equilibrium constant K for tetraglyme (five oxygen atoms) in Table 4 is only slightly less than it is in the presence of 15-crown-5. For the same reason the thermodynamic macrocyclic effect $K(15\text{-crown-5/PhN}_2^+)/K(\text{tetraglyme/PhN}_2^+)$ in DCE was earlier[24] observed to be even less than 1.

Of the studied polyethers (Table 4), only 18-crown-6 and dibenzo-21-crown-7 are relatively strong stabilizing agents for the 1-naphthalenediazonium ion in solution.
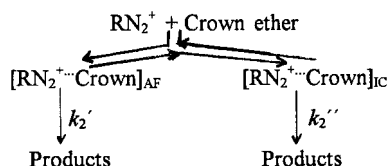
Scheme 2. Complexation and decomposition of organic diazonium ion in the presence of crown ether in solution.[3,15]

The stabilizing ability of 15-crown-5 is much weaker. Also, the value of k_2/k_1 for PEG1000, which can form pseudocyclic complexes with diazonium compounds (the number of oxygen atoms is 22.3), is large. The effect of benzo and cyclohexane groups on the kinetic stability can be assumed to be weak.[14] It seems that 21-crown-7 and its derivatives are the strongest complexing and stabilizing agents for the 1-naphthalenediazonium ion in solution.

CONCLUSIONS

In accordance with earlier work concerning crown ether–arenediazonium ion systems,[2–16] the present kinetic and spectroscopic study suggests that, in solution, the thermal decomposition of 1-naphthalenediazonium salt in the absence or presence of polyethers occurs by an S_N1-like[23] reaction mechanism, with the formation of a highly reactive 1-naphthyl cation in the slow rate-determining step of the heterolytic decomposition 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 co-workers' assumption[3,15] and suggest that decomposition reactions of arenediazonium or 1-naphtalenediazonium ions complexed with crown ether occur via non-specific adduct formation, called a charge-transfer complex by Zollinger and co-workers (k_2'), not directly from the unreactive inclusion complex (k_2''), or $k_2' \gg k_2''$, and that there is a fast equilibrium between these two types of complexes and the uncomplexed arenediazonium ion, as presented in Scheme 2, where R = arene or 1-naphtalene and, AF and IC = non-specific adduct formation and inclusion complex, respectively.

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