Complexation of Substituted Benzenediazonium Ions with Polyethylene Glycols in 1,2-Dichloroethane

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The complexation and kinetics of thermal decomposition of various substituted benzenediazonium tetrafluoroborates in the presence of polyethylene glycols (PEG 300−PEG 2000) has been studied spectrometrically in 1,2-dichloroethane at 50 °C. Solid 1:1 complexes $ArN_2^+BF_4^-$/PEG 1000 were synthesized.

The complexation with PEG increases the stability of arenediazonium ions in solution but not in the solid state. The values of the complexation constant K for $ArN_2^+BF_4^-$/PEG 1000 obey well the Hammett equation with the value 1.12 for the reaction constant. The rates of the decomposition of the complex (k_2) are independent of the PEG's studied but the values of K increase linearly with the number of CH_2CH_2O units in the PEG chain. The values of k_2 are larger and those of K smaller than the corresponding values for $ArN_2^+BF_4^-$/crown ether systems. A linear correlation between the logarithms of k_2 for $ArN_2^+BF_4^-$/PEG 1000 and logarithms of the rate constants for the dediazoniation of uncomplexed diazonium ions indicates the similarity of these two dediazoniation mechanisms.

The thermal dediazoniation of arenediazonium salts in solution has been studied extensively during the last decades owing to the broad and versatile application of the reaction in synthetic chemistry.[1-5] The dediazoniation has been shown to occur by either homolytic or heterolytic mechanism. Slight changes in the reaction system (the substituent and its position, solvent, atmosphere, pH, other substrates, *etc.*) may affect the rate of the decomposition, mechanism or products drastically. The tendency to decompose homolytically increases with the nucleophilicity of the solvent and electrophilicity of the substituent of the benzenediazonium ion.[2,4-5]

Gokel and Cram[6] reported in 1973 that crown ethers of proper dimensions solubilize arenediazonium salts in nonpolar solvents and that this complexation, with insertion of the diazonium group into the hole of a macrocyclic polyether ring, changes the ^{1}H NMR spectra of crown ethers. Bartsch[7] reported in 1976 that the complexation with crown ethers strongly stabilizes *p-tert*-butylbenzenediazonium tetrafluoroborate against thermal decomposition in 1,2-dichloroethane. Since then, the complexation of arenediazonium salts with crown ethers has been studied widely by spectroscopic, kinetic and calorimetric methods.[8-11] Bartsch recently observed that glymes[12] and other acyclic polyethers[13] likewise stabilize *p-tert*-butylbenzenediazonium ion against thermal decomposition in solution, and that inexpensive, commercially-available polyethylene glycols (PEG) can be used as effective phase transfer agents[14] instead of expensive crown ethers (*e.g.* PEG 1000 instead of 18-crown-6)

for reactions of arenediazonium salts in solvents of low polarity. We have investigated earlier the complexation of variously substituted benzenediazonium ions with 18-crown-6,[10] as well as with the corresponding acyclic polyether pentaglyme,[15] in 1,2-dichloroethane. Now we report the results of kinetic and spectroscopic studies on the complexation and stabilization of arenediazonium ions in the presence of polyethylene glycols $HO(CH_2CH_2O)_nH$ (PEG 300, PEG 600, PEG 1000 and PEG 2000).

EXPERIMENTAL

Materials. Arenediazonium tetrafluoroborates, synthesized from the corresponding anilines by diazoniation with isopropyl nitrite or sodium nitrite in tetrafluoroboric acidic ethanol or ethanol-water mixtures, were available from our earlier studies.[10,16] Before use they were recrystallized.[10,17] Polyethylene glycols PEG 300, PEG 600, PEG 1000 and PEG 2000 were commercial products from Fluka AG, Buchs, Switzerland, and were used as received. 1,2-Dichloroethane (Fluka AG, Buchs, Switzerland) was purified, dried, distilled and preserved in nitrogen atmosphere.[18] Crystalline arenediazonium tetrafluoroborate/PEG 1000 complexes for H-, *p*-CH$_3$- and *m*-Cl-substituted benzenediazonium ions were synthesized in 1,2-dichloroethane and precipitated by addition of diethyl ether.[9]

Measurements. UV spectra were recorded with a Beckman Acta MIV spectrophotometer and kinetic measurements were carried out in nitrogen atmosphere by standard methods with a Perkin-Elmer 139 spectrophotometer equipped with a Hitachi Perkin-Elmer 139−0880 temperature-controlled cell attachment. The temperature was constant within ±0.03 °C. IR spectra of the synthesized complexes and the corresponding diazonium salts were scanned with a Perkin-Elmer 457 infrared spectrometer using nujol method and polystyrene as the calibration compound. The accuracy of the longest wavelength maximum λ_{max} was within ±1 nm and that of ν_{NN} within ±5 cm^{-1}. Dediazoniation products were determined on a Hewlett-Packard 5720A gas chromatograph equipped with a Hewlett-Packard 3373B integrator. The products of the dediazoniation of *p*-cyanobenzenediazonium tetrafluoroborate in the presence and absence of PEG 1000 were identified on a Kratos MS 80 RF Autoconsole mass spectrometer using a capillary gas chromatographic sample inlet system. A Perkin-Elmer Autobalance AD-2 was used for weighing small amounts of arenediazonium salts.

RESULTS

The complexation of arenediazonium tetrafluoroborates with polyethylene glycols (PEG) was studied by UV spectrometry by determining the values of the longest wavelength maximum (λ_{max}) and the rates of the thermal decomposition in 1,2-dichloroethane at 50 °C, (i) in the presence of PEG 300, PEG 600, PEG 1000 and PEG 2000 for *p*-C(CH$_3$)$_3$- and *m*-Cl-substituted ions (the effect of the number of CH$_2$CH$_2$O units in PEG), and (ii) in the presence of PEG 1000 for eight *o*-, *m*- or *p*-substituted benzenediazonium ions (the effect of substituent). The constants were measured for free diazonium ion and in the presence of five different concentrations of PEG with the concentration of the arenediazonium ion held constant. The reactions were followed for at least two half-lives and they all obeyed well first-order kinetics within the range studied: the correlation coefficient *r* for each rate constant k_{obs} was about 0.9998 and the standard deviation about ±1 %. The results for six reactions are presented in Table 1. Except for *p*-cyanobenzenediazonium tetrafluoroborate (change in the mechanism, discussed later), all arenediazonium ions studied were stabilized against thermal decomposition by complexation with PEG in solution. The complexation shifted their longest wavelength maxima toward shorter wavelengths, the amount of the hypsochromic shift being a measure of the degree of complexation.

Table 1. Data for the thermal decomposition of arenediazonium tetrafluoroborates in 1,2-dichloroethane at 50 °C in the presence of polyethylene glycols (PEG).

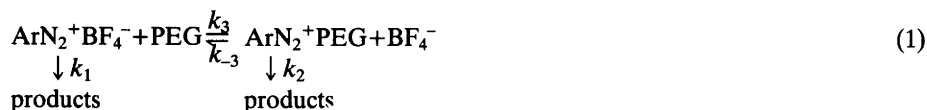| Substituent of ArN_2^+	Polyethylene glycol (PEG)	$[ArN_2^+]^a/$ M	$[PEG]^a/$ M	$\lambda_{max}/$ nm	$k_{obs}/$ s
p-C(CH$_3$)$_3$	–	6.0×10^{-5}	–	285	2.48×10^{-4}
	PEG 300	6.0×10^{-5}	6.0×10^{-4}	279	1.81×10^{-4}
	PEG 300	6.0×10^{-5}	9.0×10^{-4}	278	1.64×10^{-4}
	PEG 300	6.0×10^{-5}	1.2×10^{-3}	276	1.49×10^{-4}
	PEG 300	6.0×10^{-5}	2.4×10^{-3}	275	1.15×10^{-4}
	PEG 300	6.0×10^{-5}	6.0×10^{-3}	274	8.13×10^{-5}
	PEG 600	6.0×10^{-5}	3.0×10^{-4}	278	1.61×10^{-4}
	PEG 600	6.0×10^{-5}	4.5×10^{-4}	277	1.38×10^{-4}
	PEG 600	6.0×10^{-5}	6.0×10^{-4}	277	1.21×10^{-4}
	PEG 600	6.0×10^{-5}	1.2×10^{-3}	275	9.34×10^{-5}
	PEG 600	6.0×10^{-5}	3.0×10^{-3}	274	6.14×10^{-5}
	PEG 1000	6.0×10^{-5}	1.8×10^{-4}	279	1.64×10^{-4}
	PEG 1000	6.0×10^{-5}	3.6×10^{-4}	277	1.26×10^{-4}
	PEG 1000	6.0×10^{-5}	6.0×10^{-4}	276	1.03×10^{-4}
	PEG 1000	6.0×10^{-5}	1.2×10^{-3}	275	7.54×10^{-5}
	PEG 1000	6.0×10^{-5}	3.0×10^{-3}	274	5.12×10^{-5}
	PEG 2000	6.0×10^{-5}	1.2×10^{-4}	280	1.54×10^{-4}
	PEG 2000	6.0×10^{-5}	1.5×10^{-4}	278	1.40×10^{-4}
	PEG 2000	6.0×10^{-5}	3.0×10^{-4}	277	1.06×10^{-4}
	PEG 2000	6.0×10^{-5}	6.0×10^{-4}	276	8.34×10^{-5}
	PEG 2000	6.0×10^{-5}	1.2×10^{-3}	275	6.20×10^{-5}
m-Cl	PEG 1000	1.0×10^{-4}	–	270	5.20×10^{-5}
	PEG 1000	1.0×10^{-4}	2.0×10^{-4}	260	2.31×10^{-5}
	PEG 1000	1.0×10^{-4}	3.0×10^{-4}	259	1.93×10^{-5}
	PEG 1000	1.0×10^{-4}	6.0×10^{-4}	258	1.59×10^{-5}
	PEG 1000	1.0×10^{-4}	1.0×10^{-3}	258	1.41×10^{-5}
	PEG 1000	1.0×10^{-4}	3.0×10^{-3}	257	1.23×10^{-5}
H	PEG 1000	1.0×10^{-4}	–	266	1.20×10^{-3}
	PEG 1000	1.0×10^{-4}	3.0×10^{-4}	256	6.12×10^{-4}
	PEG 1000	1.0×10^{-4}	5.0×10^{-4}	255	4.95×10^{-4}
	PEG 1000	1.0×10^{-4}	1.0×10^{-3}	255	3.80×10^{-4}
	PEG 1000	1.0×10^{-4}	2.0×10^{-3}	254	3.01×10^{-4}
	PEG 1000	1.0×10^{-4}	4.0×10^{-3}	253	2.55×10^{-4}

^{a} The initial concentration.

The effect of complexation on the products of the dediazoniation was studied by analyzing by GLC the products from the dediazoniation of 4.0×10^{-3} M unsubstituted benzenediazonium tetrafluoroborate in 1,2-dichloroethane at 50 °C in the presence of 4.0×10^{-2} M PEG 1000. The major products in the dediazoniation of arenediazonium tetrafluoroborates in 1,2-dichloroethane are fluoroarenes and chloroarenes.[7,10,11,15] In the presence of PEG 1000, about 3 % benzene was found in addition to fluorobenzene and chlorobenzene. The addition of PEG 1000 was observed to decrease the amount of the Schiemann product[2] fluorobenzene to (30±2) %. A similar effect was earlier observed in the presence of pentaglyme.[15] Fluorobenzene and chlorobenzene are formed by a heterolytic mechanism and benzene *via* a homolytic pathway.[2,4,10,11]

Even small concentrations of polyethylene glycols increased the thermal stability of p-cyanobenzenediazonium tetrafluoroborate in 1,2-dichloroethane. After a minimum point an increase in the concentration of PEG increased the rate of the dediazoniation of this very

strongly electrophilic ion. The effect of the concentration of PEG 1000 on k_{obs} is presented in Fig. 1. The analysis of the products by GLC showed that the proportion of cyanobenzene was about 9 % in the absence of PEG 1000 ([ArN_2^+]=2.0×10^{-3} M) but increased to about 73 % in the presence of 6.0×10^{-2} M PEG 1000 ([PEG 1000]/[ArN_2^+]=30). Zollinger et al.[11] have observed a similar destabilization and an increase of arene products in the dediazoniation of p-chloro- and m-cyanobenzenediazonium tetrafluoroborates in the presence of crown ethers. Under comparable conditions homolytic dediazoniation reactions are known to be faster than the corresponding heterolytic reactions.[4,19] The results indicate that arenediazonium salts with strongly eletron-withdrawing substituents are destabilized by complexation with polyethers owing to the change from heterolytic to homolytic mechanism.[11]

The decomposition temperatures of H-, p-CH$_3$- and m-Cl-substituted benzenediazonium tetrafluoroborates are 108−110, 109−111 and 147−149 °C, respectively, and m.p. of PEG 1000 is 37−40 °C. The melting points of all three corresponding white complexes ArN_2^+ BF_4^-/PEG 1000 were similar to that of PEG 1000. Our results now and earlier[15] show that the complexation of arenediazonium salts with acyclic polyethers does not increase their thermal stability in the solid state; and the same was observed by Zollinger et al.[11] in the presence of cyclic crown ethers. The longest wavelength maxima λ_{max} of the complexes $ArN_2^+BF_4^-$/PEG 1000 for H-, p-CH$_3$- and m-Cl-substituted diazonium salts in 1,2-dichloroethane were 3, 4 and 9 nm, respectively – smaller than those of the corresponding uncomplexed salts in 1,2-dichloroethane. The values of ν_{NN} were 2300, 2275 and 2305 cm^{-1}, respectively, for H-, p-CH$_3$- and m-Cl-substituted benzenediazonium tetrafluoroborates. The complexation of these salts with PEG 1000, as earlier[15] observed in the presence of pentaglyme, did not cause a measurable shift in the stretching frequency of the N−N bond in IR. By contrast, the complexation of arenediazonium salts with crown ethers, which are stronger complexation agents than PEG or glymes,[12,13] causes an unusual increase in their ν_{NN}.[8,9,11]

The reactions of arenediazonium tetrafluoroborates in the presence of polyethylene glycols in solution can be described by the equation

$$ArN_2^+BF_4^- + PEG \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} ArN_2^+PEG + BF_4^-$$
$$\downarrow k_1 \qquad\qquad\qquad \downarrow k_2$$
$$\text{products} \qquad\qquad\quad \text{products} \tag{1}$$

where k_1 and k_2 are the rate constants for the decomposition of the uncomplexed and complexed ions, respectively, and k_3 and k_{-3} are the rate constants for the complexation and decomplexation.[10–13,15] The complexation and decomplexation reactions can be assumed to be very fast, as recently has been observed for these reactions in the presence of crown ethers.[20] The complexation equilibrium constant K of eqn. (1) is

$$K=[ArN_2^+PEG]/([ArN_2^+][PEG])=k_3/k_{-3} \tag{2}$$

and the overall rate of the decomposition

$$v=k_1[ArN_2^+]+k_2[ArN_2^+PEG]=k_{obs}([ArN_2^+]+[ArN_2^+PEG]) \tag{3}$$

where k_{obs} is the observed rate constant of the decomposition. If we assume that the complex

Table 2. Complexation of substituted benzenediazonium ions with polyethylene glycols (PEG) in 1,2-dichloroethane at 50 °C.

PEG	Sub-stituent of ArN_2^+	$\lambda_{2max}^a/$ nm	$\Delta\lambda_{max}^b/$ nm	$k_1/$ s^{-1}	$(k_1-k_2)^c/$ s^{-1}	$K^c/$ M^{-1}
PEG 300	p-C(CH$_3$)$_3$	274	11	2.48×10^{-4}	$(1.966\pm0.05)\times10^{-4}$	$(8.84\pm0.40)\times10^2$
PEG 600	p-C(CH$_3$)$_3$	273	12	2.48×10^{-4}	$(2.10\pm0.05))\times10^{-4}$	$(2.59\pm0.12)\times10^3$
PEG 1000	p-C(CH$_3$)$_3$	274	11	2.48×10^{-4}	$(2.08\pm0.033)\times10^{-4}$	$(4.32\pm0.12)\times10^3$
PEG 2000	p-C(CH$_3$)$_3$	274	11	2.48×10^{-4}	$(1.99\pm0.044)\times10^{-4}$	$(9.92\pm0.41)\times10^3$
PEG 300	m-Cl	257	13	5.20×10^{-5}	$(4.23\pm0.04)\times10^{-5}$	$(2.94\pm0.07)\times10^3$
PEG 600	m-Cl	257	13	5.20×10^{-5}	$(4.20\pm0.04)\times10^{-5}$	$(1.11\pm0.05)\times10^4$
PEG 1000	m-Cl	257	13	5.20×10^{-5}	$(4.00\pm0.03)\times10^{-5}$	$(2.03\pm0.07)\times10^4$
PEG 2000	m-Cl	257	13	5.20×10^{-5}	$(3.79\pm0.06)\times10^{-5}$	$(3.83\pm0.24)\times10^4$
PEG 1000	H	253	13	1.20×10^{-3}	$(9.72\pm0.08)\times10^{-4}$	$(6.32\pm0.20)\times10^3$
PEG 1000	p-CH$_3$	271	11	1.41×10^{-4}	$(1.11\pm0.02)\times10^{-4}$	$(6.07\pm0.16)\times10^3$
PEG 1000	o-CH$_3^d$	257	11	2.25×10^{-3}	$(1.79\pm0.04)\times10^{-3}$	$(1.29\pm0.07)\times10^3$
PEG 1000	p-COCH$_3$	261	14	1.92×10^{-4}	$(1.53\pm0.02)\times10^{-4}$	$(2.92\pm0.13)\times10^4$
PEG 1000	m-Br	257	15	1.05×10^{-4}	$(8.65\pm0.05)\times10^{-5}$	$(2.04\pm0.07)\times10^4$

[a] In 1,2-dichloroethane containing PEG in excess; [b] $\Delta\lambda_{max}=\lambda_{1max}-\lambda_{2max}$, where λ_{1max} is the longest wavelength maximum of diazonium ion in 1,2-dichloroethane in the absence of PEG; [c] Calculated by equation (5); [d] At 40 °C.

ArN_2^+PEG is unreactive or $k_2<<k_1$, the complexation constant K can be calculated by the equation

$$K=(k_1-k_{obs})/(k_{obs}[PEG]) \tag{4}$$

where [PEG] is the initial concentration of polyethylene glycol.[12,13] Our results show, however, that all values of K decrease with increasing concentration of PEG (*e.g.* in the presence of PEG 1000 from 2846 to 1281 M^{-1} for p-C(CH$_3$)$_3$-substituted and from 6255 to 1076 M^{-1} for m-Cl-substituted benzenediazonium ion). This decrease in the constant K indicates that the assumption $k_2<<k_1$ is not correct, a finding that we also made in the presence of pentaglyme.[15] Therefore, the values of the constants K and k_1-k_2 (or k_2) were instead calculated by iteration method from Eq. (5), derived from equations (2) and (3).

$$\frac{1}{k_1-k_{obs}}=\frac{1}{(k_1-k_2)K}\frac{1}{[PEG]}+\frac{1}{k_1-k_2} \tag{5}$$

The results are presented in Table 2.

DISCUSSION

The thermal dediazoniation of arenediazonium salts in 1,2-dichloroethane, a nonpolar and weakly nucleophilic solvent, occurs predominantly by an S$_N$1-like reaction mechanism with formation of the highly reactive aryl cation in the slow rate-determining step, followed by fast product-determining reactions of the cation with nucleophiles (Scheme 1).[2-4,10,11,16] We have observed the values of activation enthalpy for these reactions to be large ($\Delta H^{\neq}\geq100$ kJ mol^{-1}),[10,16] those of activation entropy $\Delta S^{\neq}$ clearly positive,[10,16] and the values of activation
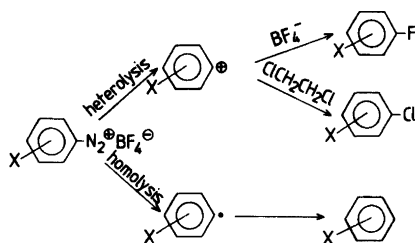
Scheme 1.

volume $\Delta V^{\neq}=+8.5\pm0.3$ cm^3 mol^{-1} independent of the substituent of the arenediazonium ion;[20] the substituent effects on the rate of the dediazoniation can be described by dual substituent constants[3] (F and R) separately for p- and m-substituted ions.[10,16]

The results of the present work show that in 1,2-dichloroethane the complexation with polyethylene glycols increases the thermal stability of arenediazonium salts that do not have very strongly electron-withdrawing substituents (Tables 1 and 2); but the thermal stability is not increased for diazonium salts in the solid state. Arenediazonium ions with very strongly electron-withdrawing substituents, *e.g.* cyano (Fig. 1.), are not stabilized in solution against thermal dediazoniation owing to a change from heterolytic to homolytic mechanism (Scheme 1). The complexation of arenediazonium ions with PEG causes a hypsochromic shift in their UV spectra but, in contrast to their complexation with cyclic crown ethers,[8,9,11] no measurable shift in the IR stretching frequency of the N−N bond. The hypsochromic shift (Table 2) was independent of the PEG studied but increased slightly (11−15 nm) with increasing complexation constant K, and indicates a more localized π-electron system in the complexed arenediazonium ion than in the free ion. The complexation effects, that is, the hypsochromic shift and stabilization, can be assumed to be due to the electrostatic interactions in the complex between the diazonium group carrying a positive charge and the oxygen atoms of polyether.[11,21]

The results in Table 2 and the comparison of these results with those observed in the presence of pentaglyme[15] suggest that the rate of dediazoniation of complexed arenediazonium ion k_2 is independent of the polyethylene glycol used or its methyl derivative. The slight increase of k_2 (from 9.7×10^{-6} s^{-1} to 1.4×10^{-5} s^{-1}) observed for m-Cl-substituted benzenediazonium ion, a relatively strong electrophilic ion, with increasing chain length of polyethylene glycol and with increase in the complexation constant K, can be explained by a small increase in the contribution of the homolytic dediazoniation mechanism (Scheme 1). The values of the complexation constant K increase linearly with the number of CH$_2$CH$_2$O units of PEG within the range studied (Fig. 2). The values of K calculated for the ArN$_2^+$/pentaglyme system[15] (*i.e.* pentaethylene glycol dimethyl ether) correlate well with the corresponding data for the complexation in the presence of pure polyethylene glycols. This suggests that the complexation efficiency is determined almost completely by the number of CH$_2$CH$_2$O units in the polyoxygen compound.

The values of the complexation equilibrium constant K for the complexation of m- and p-substituted benzenediazonium ions with PEG 1000 obey well the Hammett $\rho\sigma$ equation[22]

$$\log (K/\text{M}^{-1})=(1.12\pm0.03)\sigma+(3.89\pm0.10) \tag{6}$$

with a correlation coefficient of 0.987 ($n=6$) (Fig. 3). The results indicate that electron-donating substituents of the benzenediazonium ring weaken the complexation,
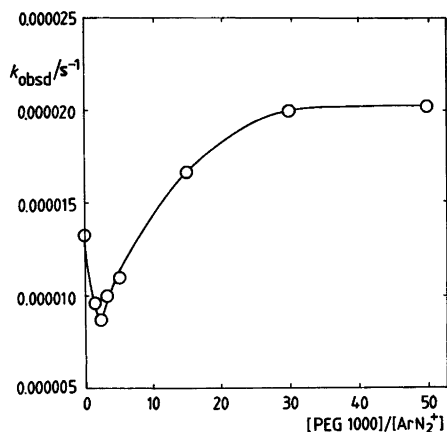
Fig. 1. The observed rate constant k_{obsd} for the dediazoniation of p-cyanobenzenediazonium tetrafluoroborate as a function of the concentration ratio of PEG 1000 and the diazonium salt $(7.0 \times 10^{-5}$ M) in 1,2-dichloroethane at 50 °C.
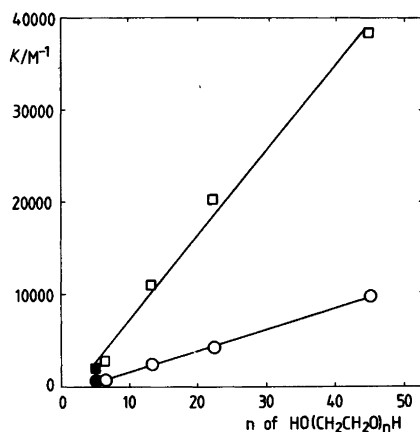
Fig. 2. The complexation constant K for the complexation of p-tert-butylbenzenediazonium tetrafluoroborate ($\square$) and m-chlorobenzenediazonium tetrafluoroborate ($\bigcirc$) with polyethylene glycols as a function of the number of CH_2CH_2O units of PEG, in 1,2-dichloroethane at 50 °C; ($\blacksquare$) and ($\bullet$) in the presence of pentaglyme.

whereas electron-withdrawing substituents strengthen it, and (Fig. 2) that the dependence of the complexation constant K on the chain length of polyethylene glycol increases with increasing electrophilicity of the arenediazonium ion. These observations agree well with the proposal that the interaction between the diazonium group and oxygen atoms of polyether is
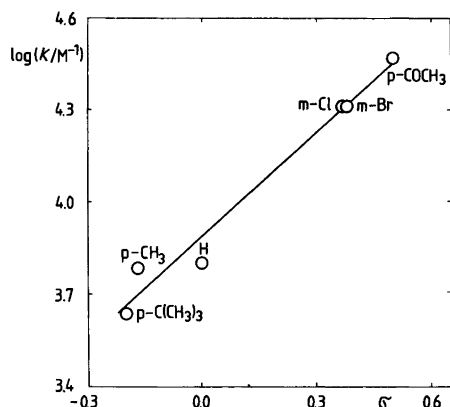
Fig. 3. The logarithm of the complexation constant K for the complexation of substituted benzenediazonium ion with PEG 1000 as a function of the Hammett substituent constant σ in 1,2-dichloroethane at 50 °C.
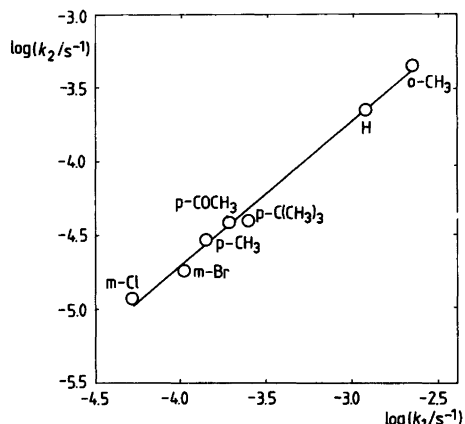
Fig. 4. The logarithm of the rate constant k_2 for the dediazoniation of substituted benzenediazonium ion complexed with PEG 1000 as a function of the logarithm of the rate constant k_1 for the uncomplexed ion in 1,2-dichloroethane at 50 °C, and that for the o-CH$_3$-substituted ion at 40 °C.

electrostatic.[10,11,21] Also the signs and sizes of the reaction constants ρ of 0.68,[15] 1.12 (here) and 1.2$-$1.4[10,11] calculated for ArN_2^+/pentaglyme, ArN_2^+/PEG 1000 and ArN_2^+/crown ether systems, respectively, support this assumption.

The calculated values of k_2/k_1 (the stabilization ability) for ArN_2^+/PEG and ArN_2^+/pentaglyme [15] systems (m-Cl-substituted ion is omitted owing to the homolytic contribution and o-$COCH_3$-substituted ion owing to the steric hindrance for complexation[15]) are 15$-$22 %, whereas the corresponding values in the presence of 18-crown-6[10,11] are 1$-$2 %. The values of the complexation constant K for the complexation of arenediazonium ions with 18-crown-6[10] are about four-fold the corresponding values for the ArN_2^+/PEG 1000 system, which is a clear macrocyclic effect.[15] The magnitude of the macrocyclic effect is observed to depend strongly on the nature of the cationic species being complexed.[12]

The values of log (k_2/s^{-1}) for the ArN_2^+/PEG 1000 system correlate linearly with the corresponding values of log (k_1/s^{-1}) (Fig. 4), giving a slope of 0.98$\pm$0.04 with a correlation coefficient r=0.996 (n=7). Similar relations have been observed earlier for dediazoniation reactions in the presence of crown ethers [11] and pentaglyme.[15] The linearity indicates that the mechanism of the dediazoniation of complexed arenediazonium ion is similar to that of uncomplexed diazonium ion.[2-5,11]

CONCLUSION

Polyethylene glycols are effective complexing agents for arenediazonium ions. Therefore, it should be possible to substitute inexpensive PEG's for expensive crown ethers as solubilizing agents and phase transfer catalysts in the reactions of arendediazonium salts in solvents of low polarity.[13]

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