Dediazoniation of Substituted Benzenediazonium Ions and Their Complexation with 18-Crown-6 in 1,2-Dichloroethane

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The kinetics of thermal decomposition of ten substituted benzenediazonium tetrafluoroborates in 1,2-dichloroethane at three temperatures have been studied by spectrophotometry and the reactions were concluded to proceed by heterolytic dediazoniation. Treatment of the substituent effects with Brown constants yielded two clusters of data. Treatment with the separate field and resonance constants of Swain and Lupton gave for p-substituted ions a linear dependence with a correlation coefficient of 0.994. The resonance effects are unusual.

The complexation of nine substituted benzenediazonium tetrafluoroborates with 18-crown-6 in 1,2-dichloroethane at 50 °C was studied and found to occur for p- and m-substituted and o-methyl-substituted but not for o-acetyl-substituted benzenediazonium ions. The data for the complexation constant obey satisfactorily the Hammett equation with a value of 1.19 for the reaction constant. The complexes, except that of the o-methylbenzenediazonium ion, exhibited enhanced stability against thermal dediazoniation.

The thermal decomposition of arenediazonium salts in homogeneous solution has been widely studied and found to occur via a complex variety of mechanisms yielding different products.[1] Heterolytic dediazoniation is predominant in solvents of low nucleophilicity and homolytic dediazoniation in solvents of high nucleophilicity.

Gokel and Cram[2] have reported that crown ethers increase the solubility of arenediazonium salts in non-polar, i.e. only weakly nucleophilic solvents. Recently, Bartsch and co-workers[3] reported on the basis of the decomposition of one diazonium salt, p-tert-butylbenzenediazonium tetrafluoroborate, that arenediazonium salts complexed with crown ethers exhibit

markedly enhanced thermal stability relative to the corresponding uncomplexed diazonium ions. As these observations could be of importance for the study of reactions involving arenediazonium ions in homogeneous non-polar media, we undertook a study of the decomposition of substituted benzenediazonium ions in 1,2-dichloroethane and their complex formation and stabilization by 18-crown-6, i.e. 1,4,7,10,-13,16-hexaoxacyclooctadecane.

EXPERIMENTAL

Substituted benzenediazonium tetrafluoroborates, synthesized from the corresponding substituted anilines by diazotization with isopentyl nitrite in tetrafluoroboric acidic ethanol or ethanol—water mixtures, were in part available from our earlier studies.[4] They were recrystallized before use from a mixture of three parts of 20 % aqueous tetrafluoroboric acid and five parts of glacial acetic acid, with ethyl ether added where necessary. 18-Crown-6 was purified by distillation in a Perkin-Elmer M—131T Microstill, m.p. 38.5—39.5 °C, lit.[5] 39—40 °C. 15-Crown-5, Parish Chemical Co., purified similarly, boiled at 120 °C/0.11 kPa, lit.[6] 78 °C/0.01 kPa. 1,2-Dichloroethane was purified, dried, distilled and preserved in nitrogen atmosphere.[7]

The spectra were scanned and the rate constants determined in nitrogen atmosphere by standard methods with a Beckman Acta MIV or Perkin-Elmer 139 spectrophotometer equipped with specially designed thermostated cell holders. A Perkin-Elmer Autobalance AD-2 was used for weighing small amounts.

RESULTS

The kinetics of the decomposition of substituted benzenediazonium ions in 1,2-dichloroethane were followed at the wavelength of the

Table 1. Dediazoniation of substituted benzenediazonium tetrafluoroborates in 1,2-dichloroethane.

Substituent	Temp./°C	k_1/s^{-1}	$\Delta H^{\ddagger a}/$ kJ mol^{-1}	$\Delta S^{\ddagger a}/$J K^{-1} mol^{-1}	k_1 in water^{a,b}/s^{-1}
p-COCH$_3$	50.0	1.98×10^{-4}	120	55.1	2.30×10^{-4}
	35.0	2.10×10^{-5}			
	25.0	4.30×10^{-6}			
m-COCH$_3$	50.0	3.83×10^{-3}	119	74.7	
	35.0	3.99×10^{-4}			
	25.9	1.02×10^{-4}			
o-COCH$_3$	60.0	1.44×10^{-4}			
	50.0	3.70×10^{-5}	121	43.5	
	40.0	8.34×10^{-6}			
p-CH$_3$	55.0	2.77×10^{-4}			
	50.0	1.45×10^{-4}	106	8.92	1.43×10^{-4}
	35.0	2.07×10^{-5}			
m-CH$_3$	35.0	7.13×10^{-4}	102	25.9	5.02×10^{-3}
	25.0	1.90×10^{-4}			
	15.0	4.18×10^{-5}			
o-CH$_3$	50.0	1.03×10^{-2}	103	34.3	$1.14 \times 10^{-3\,c}$
	35.0	1.63×10^{-3}			
	22.0	2.49×10^{-4}			
H	50.0	1.22×10^{-3}	108	34.1	1.41×10^{-3}
	35.0	1.72×10^{-4}			
	25.0	3.79×10^{-5}			
p-Cl	65.0	2.03×10^{-5}			
	50.0	2.38×10^{-6}	126	37.5	3.92×10^{-6}
	40.0	5.23×10^{-7}			
p-CN	60.0	5.35×10^{-5}			
	50.0	1.37×10^{-5}	120	31.4	
	35.0	1.49×10^{-6}			
p-OCH$_3$	75.0	8.93×10^{-6}			
	65.0	2.42×10^{-6}			
	55.0	6.29×10^{-7}	123	11.3	1.08×10^{-7}

^{a} At 50 °C. ^{b} From Ref. 8. ^{c} From Ref. 9, at 36.5 °C.

maximum absorbance of each benzenediazonium ion. The results are collected in Table 1. Under comparable conditions, Bartsch *et al.*[3] measured a rate constant value of 2.28×10^{-4} s^{-1} for the p-*tert*-butylbenzenediazonium ion at 50 °C. The values of the rate constants in 1,2-dichloroethane and in water are very similar to each other. This small solvent effect is apparently more general too, since Szele and Zollinger[1] have determined rates that differ by less than a factor of nine for the decomposition of benzenediazonium tetrafluoroborate in 19 solvents.

The rate constants in Table 1 do not obey the Hammett equation (the value of the correlation coefficient r is 0.100, $n = 8$ at 50 °C), nor does the treatment of Schulte-Frohlinde and Blume[8] yield satisfactory linearity ($r = 0.814$, $n = 8$). More information can be obtained by using Brown substituent constants,[10] evidently because the reaction consists of bond-breaking between the ring and the leaving group, so that partial positive charge should develop on the ring carbon in the transition state. The plot in Fig. 1 reveals a grouping of the data into one cluster containing the m-methyl-, p-*tert*-butyl- and p-methyl-substituted compounds and the unsubstituted one, and another group containing the rest. The last three compounds have substituents which can release electrons by resonance.

The substituent constants F and R calculated by Swain and Lupton,[11] which describe the different field (and/or inductive) and resonance effects of the substituents, give a good correlation for p-substituted benzenediazonium ions at 25 °C:

$$\log(k_1/k_{1\mathrm{H}}) = (-3.02 \pm 0.20)F + (4.56 \pm 0.32)R + (-0.26 \pm 0.11) \tag{1}$$

Table 2. The measured and calculated rate constants (eqns. 1 and 2) for the dediazoniation of *p*-substituted benzenediazonium ions in 1,2-dichloroethane at 25 and 50 °C.

Substituent	Substituent constant [a]		$\log(k_1/k_{1H})$ meas.	25 °C calc.	$\log(k_1/k_{1H})$ meas.	50 °C calc.
	F	R				
H	0.000	0.000	0.00	− 0.26	0.00	− 0.28
p-C(CH₃)₃	− 0.104	− 0.138	− 0.69 [b,c]	− 0.58	− 0.73 [b]	− 0.60
p-COCH₃	0.534	0.202	− 0.96	− 0.96	− 0.79	− 0.84
p-CH₃	− 0.052	− 0.141	− 0.89	− 0.75	− 0.92	− 0.76
p-CN	0.847	0.184	− 2.11	− 1.99	− 1.95	− 1.77
p-Cl	0.690	− 0.161	− 2.95	− 3.08	− 2.71	− 2.86
p-OCH₃	0.413	− 0.500	− 3.81	− 3.79	− 3.60	− 3.59

[a] From Ref. 11. [b] From Ref. 2. [c] Calculated using the value of the activation enthalpy for the *p*-methylbenzenediazonium ion.

with a correlation coefficient of 0.994 ($n = 7$). The correlation at 50 °C is slightly poorer,

$$\log(k_1/k_{1H}) = (-2.72 \pm 0.23)F + (4.38 \pm 0.37)R + (-0.28 \pm 0.12) \qquad (2)$$
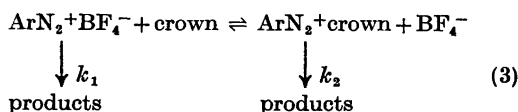
with a correlation coefficient of 0.991 ($n = 7$), perhaps because the values of F and R were calculated at 25 °C. The measured and calculated rate constant values, indicating a range of reactivities of more than 5000, are given in Table 2.

The decomposition of the benzenediazonium ion in 1,2-dichloroethane at 50 °C yielded 54 % fluorobenzene (Schiemann reaction) and 46 % chlorobenzene, as analyzed by gas chromatography. No other products were detected.

The complexation of substituted benzenediazonium ions with crown ethers was studied in 1,2-dichloroethane at 50 °C. The addition of 18-crown-6 to solutions of *o*-acetylbenzenediazonium tetrafluoroborate did not change the longest wavelength maximum nor the rate of

decomposition. For all other ions studied, however, the maximum shifted toward shorter wavelength by 15 − 19 nm and the rate decreased. An example is given in Table 3.

For the complexation and decomposition

$$ArN_2^+BF_4^- + crown \rightleftharpoons ArN_2^+crown + BF_4^-$$

$$\downarrow k_1 \qquad\qquad\qquad \downarrow k_2 \qquad (3)$$

products   products

the equilibrium constant

$$K = \frac{[ArN_2^+crown]}{[ArN_2^+]\,[crown]} \qquad (4)$$

The overall rate of the decomposition

$$v = k_1[ArN_2^+] + k_2[ArN_2^+crown] \qquad (5)$$

and if the concentration of the crown ether is constant

$$v = k_{obs}\,([ArN_2^+] + [ArN_2^+crown]) \qquad (6)$$

From equations (4), (5) and (6), one can easily derive the equation

$$\frac{1}{k_1 - k_{obs}} = \frac{1}{(k_1 - k_2)K} \times \frac{1}{[crown]} + \frac{1}{k_1 - k_2} \qquad (7)$$

which allows evaluation of k_2 and K. As the concentration of the free crown ether [crown] was not known, however, the iteration method based on the linearity of eqn. (7) was employed here for the evaluation of $k_1 - k_2$ and K. From the initial concentration of the crown ether to the final values required less than four steps. The final results are collected in Table 4.

Table 3. Sample data for the thermal dediazoniation of *p*-methylbenzenediazonium tetrafluoroborate in 1,2-dichloroethane at 50 °C.

[ArN₂⁺][a]/ mol dm⁻³	[18-Crown-6][a]/ mol dm⁻³	λ_{max}/ nm	k_{obs}/ s⁻¹
6.00 × 10⁻⁵	0	282	1.45 × 10⁻⁴
5.97 × 10⁻⁵	1.36 × 10⁻⁴	267	4.40 × 10⁻⁵
5.97 × 10⁻⁵	3.80 × 10⁻⁴	267	1.77 × 10⁻⁵
5.97 × 10⁻⁵	9.90 × 10⁻⁴	267	7.71 × 10⁻⁶

[a] Initial concentrations.

Table 4. Complexation of substituted benzenediazonium cations with 18-crown-6 in 1,2-dichloroethane at 50 °C.

Substituent	$\lambda_{max}{}^a$/nm	$\lambda_{max}{}^b$/nm	$\lambda_{max}{}^c$/nm	k_1/s^{-1}	(k_1-k_2)/s^{-1}	K/dm^3 mol^{-1}
p-COCH$_3$	270	277	260	1.98×10^{-4}	1.95×10^{-4}	1.12×10^5
m-COCH$_3$	259	265	247	3.83×10^{-3}	3.82×10^{-3}	1.15×10^5
o-COCH$_3$	273	273	272	3.70×10^{-5}	—	0
p-CH$_3$	278	282	267	1.45×10^{-4}	1.43×10^{-4}	2.54×10^4
m-CH$_3$	269	273	254	5.37×10^{-3}	5.31×10^{-3}	1.93×10^4
o-CH$_3$	266	270	254	1.03×10^{-2}	9.31×10^{-4}	2.18×10^3
H	262	266	247	1.22×10^{-3}	1.21×10^{-3}	2.77×10^4
p-Cl	281	287	269	2.38×10^{-4}	2.04×10^{-4}	5.48×10^4
p-C(CH$_3$)$_3$		285 ^{d}	276 ^{d}	2.28×10^{-4} ^{d}	2.25×10^{-4} ^{e}	1.92×10^4 ^{e}

^{a} In water. ^{b} In 1,2-dichloroethane. ^{c} In 1,2-dichloroethane containing 18-crown-6. ^{d} From Ref. 3. ^{e} Calculated from the values reported in Ref. 3.

The evaluated value of k_1-k_2 for the o-methylbenzenediazonium ion is less than one tenth of the value of k_1. Thus the crown complex of this diazonium ion is almost as reactive as the uncomplexed diazonium ion and must be structurally different from the other crown complexes. The complex formed by the p-chlorobenzenediazonium ion also has a measurable rate of decomposition. But for all other diazonium ions studied the evaluated values of k_1-k_2 are close to the values of k_1 and show that for these complexes $k_1 \gg k_2$.

Our values for k_1-k_2 and K of the p-tert-butylbenzenediazonium ion differ from those reported by Bartsch et al.,[3] possibly because we used the iteration method rather than assuming [crown] $\gg$ [ArN$_2^+$].

The values of the complexation constant K obey satisfactorily the Hammett equation. Using the *sigma* values reported by Ritchie and Sager [10] we found the equation

$$\log(K_X/K_H) = (1.19 \pm 0.14)\sigma + (0.05 \pm 0.04) \quad (8)$$

with a correlation coefficient of 0.965 ($n=7$).

The decomposition of 7×10^{-3} M benzenediazonium tetrafluoroborate in 1,2-dichloroethane containing 1.3×10^{-2} M 18-crown-6 yielded 45 % fluorobenzene, 51 % chlorobenzene and 4 % benzene, as analyzed by gas chromatography.

When benzenediazonium or the p-methylbenzenediazonium ion was dissolved in 1,2-dichloroethane containing about twice as much of 15-crown-5 as diazonium ion, the longest wavelength maximum was the same as in the solution without crown ether. Moreover, the values of k_{obs}, 1.12×10^{-3} s^{-1} for benzenediazonium ion and 1.32×10^{-4} s^{-1} for the p-methylbenzenediazonium ion, were only slightly lower than the corresponding values of k_1 (Table 4), indicating that complex formation and therefore also stabilization are not significant. Owing to solubility problems we did not undertake more studies.

DISCUSSION

On the basis of the thorough examinations of Swain et al.[12] and Zollinger et al.,[1] the decomposition of arenediazonium ions in solution in the absence of nucleophiles, strong bases, reducing agents or light, can be said to proceed by a rate-determining cleavage to a singlet aryl cation intermediate. The conditions of this work, tetrafluoroborate salts in 1,2-dichloroethane solutions and nitrogen atmosphere, the values of the activation parameters listed in Table 1, and the large positive volume changes during the activation measured under the same conditions [13] are all in accord with a unimolecular, heterolytic dediazoniation mechanism. The absence of benzene from the reaction products when benzenediazonium tetrafluoroborate is decomposed is expected for this mechanism.

The use of the equation

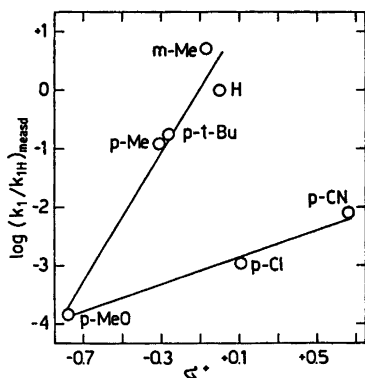$$\log(k_1/k_{1H}) = fF + rR + i \quad (9)$$

Fig. 1. The logarithm of the relative rate constant for the dediazoniation of substituted benzenediazonium ions as a function of the Brown σ value in 1,2-dichloroethane at 25 °C.

which makes use of the dual substituent constants evaluated by Swain and Lupton [11] about ten years ago, was shown by Swain et al.[12] in 1975 to be suitable for quantitative correlation of rates in 0.1 M aqueous hydrochloric acid. For comparison, this same treatment was also used now for interpretation of our results in non-polar media. The Brown plot in Fig. 1 reveals grouping of the data, whereas the data for p-substituted compounds plotted in Fig. 2 against values calculated with the aid of the separate field (and/or inductive) and resonance substit-
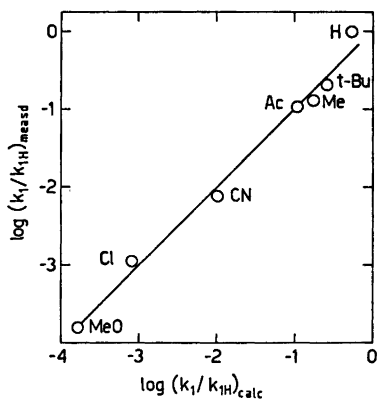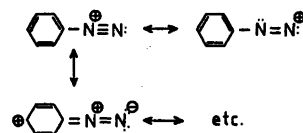

Fig. 2. The logarithm of the relative rate constant for the dediazoniation of p-substituted benzenediazonium ions as a function of the logarithm of the value calculated using dual substituent constants, in 1,2-dichloroethane at 25 °C.

Scheme 1.

uent constants, F and R, respectively, give a good correlation, equation (1). The failure of the single substituent constants to interpret the substituent effects is obviously due to the unusual relative sensitivity of the studied reaction to substituent influences. It is noteworthy that none of the forty-three reaction sets considered by Swain and Lupton in evaluating F and R values had an f/r ratio even of the same magnitude as the present reaction.

Resonance formulae for the benzenediazonium cation are represented in Scheme 1. Obviously the formation of a transition state presupposes a partial electron transfer from a single $C-N$ bond to the nitrogen atom. The value -3.02 of the field sensitivity parameter f is thus of the expected sign.

Eight of the nine substituents studied by Swain et al.[12] have a negative R value.[14] These by resonance electron-donating substituents increase the double-bond character of the $C-N$ bond, however, and thereby strongly stabilize the initial state. We have now investigated also aceto- and cyano-substituents, which have a positive R value. Since their calculated and measured values correlate well too, the resonance electron-accepting effect must facilitate the reaction. This is understandable because the aceto- and cyano-substituents tend to produce a $C^+ - N^+$ system which can be considered weakly stable and susceptible to heterolytic breaking. Thus, both resonance effects work in an unusual way, and even strongly, as seen from the high value $+4.56$ of the resonance sensitivity parameter r at 25 °C.

The sensitivity parameters are slightly lower in their values in 1,2-dichloroethane than in water where f is -2.60 and r $+5.08$,[12] implying a lower electron density on nitrogen in the transition state in 1,2-dichloroethane. The sensitivity of the Hammett reaction constant to solvent effects apparently may depend more on the hydrogen bonding than on the dielectric constant.[15]

No special *ortho*-effects are noticeable. Also the rate of the *m*-methylbenzenediazonium ion (Table 4) is of the expected magnitude as the parameter *r* is now negative. The rate of the *m*-acetylbenzenediazonium ion (Table 1) is clearly too high.[16] Again, the only explanation we can offer at this time is the unusual resonance effect. The positive charge on the *o*-carbon atom near the positive charge on the nitrogen atom has to be considered an unstable arrangement.

The cylindrical diameter of a diazonium cation group is about 240 pm. As benzenediazonium ions form complexes with crown ethers having an estimated diameter of 260 pm (18-crown-6) or larger but not with crowns having a hole size of 220 pm (binafto-17-crown-5) or less, the complexes have been assumed to form through insertion of a diazonium group into the hole of a macrocyclic polyether.[2,3,17] Further, sterically hindered *o,o'*-dimethylbenzenediazonium ions do not form complexes in chloroform.[3] By titration calorimetry, *o*-methylbenzenediazonium ion was found not to bind to 18-crown-6 in methanol.[17] As seen in Table 4, we found a spectral shift of 16 nm and measured a formation constant of 2.18×10^3 dm^3 mol^{-1} when this ion was dissolved in 1,2-dichloroethane containing 18-crown-6. However, this complexation did not markedly stabilize the ion and must therefore differ from the others.

A reduced rate was measured for the complex of *p*-chlorobenzenediazonium ion, but in all other cases the rate was as low as 1 – 2 % of the rate of the uncomplexed ion. Besides this thermal stabilization, the complexes have recently been reported to exhibit photochemical stability.[18]

The value 1.19 for the reaction constant of the Hammett equation for the complexation is, as expected, relatively small. For the ionization of benzoic acids in the same solvent it can be assumed to be much higher.[15] For hydrogen bonding of phenols with 18-crown-6 in carbon tetrachloride the reaction constant has a value 1.30[19]

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