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Rates and Mechanism of Solvolysis of Arenediazonium Ions in Aqueous Trifluoroethanol*

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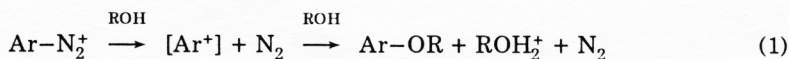
Rates of solvolysis of benzenediazonium tetrafluoroborate and six of its methyl-substituted analogues have been measured in water, trifluoroethanol, and mixtures of the two over a range of temperatures. The enthalpies of activation are uniformly high and show only a low dependence upon the solvent composition. The entropies of activation are all appreciably positive and also show only small variations with the composition of the solvent. Methyl substituents in *ortho* and *meta* positions are modestly rate enhancing; a *para*-methyl is rate retarding. The results are discussed in terms of a mechanism involving an initial fragmentation of the diazonium ion into a phenyl cation - nitrogen molecule complex which then undergoes rate-limiting dissociation followed by product-forming capture of the phenyl cation by solvent molecules.

INTRODUCTION

The reactions of arenediazonium ions are amongst the oldest known in organic chemistry and have their origin in the development of dyes during the nineteenth century. Besides the coupling reactions of these cations in which the bond from the nitrogen to the arene ring remains intact, dediazonation reactions have also been investigated for many years.¹ In these processes, a nitrogen molecule is liberated from the diazonium cation with cleavage of the carbon-nitrogen bond. Whether or not this process involves the formation of an aryl cation as a real reaction intermediate (whatever that term means) has been the subject of many investigations and even more speculation. The simplest heterolytic mechanism for dediazonation, in which the diazonium ion undergoes unimolecular fission to give an aryl cation and a nitrogen molecule, is shown in equation (1).^{2,3}

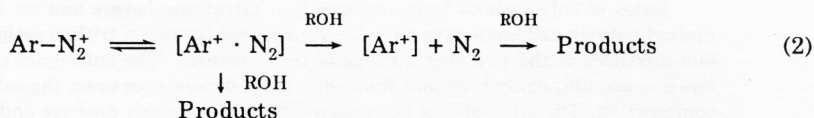
* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday

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In this mechanism, the aryl cation is generated irreversibly and is then intercepted by nucleophiles, for example the solvent in the case of water or simple alcohols. In principle, the lifetime of the aryl cation could be estimated by investigating the extent to which it reacts with dilute nucleophiles that may be expected to react under diffusion control with the electrophilic cation.⁴

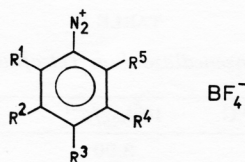
The mechanism of equation (1) had to be refined in the light of results of some classic physical organic chemistry reported by Zollinger and his colleagues in Zürich.⁵ In reactions using isotopically labelled nitrogen, they showed that the initial cleavage of the carbon-nitrogen bond is reversible. This work required the intervention of a cation-nitrogen pair as an intermediate, prior to the separately solvated aryl cation and liberated nitrogen molecule, which could be intercepted by nucleophiles as illustrated in equation (2). [They also showed that the dissociated aryl cation may recombine with nitrogen under high pressures so, under such conditions, the second step is also reversible. This is not likely to be the case under the more usual conditions that we employed, so the second step is shown as unidirectional in equation (2).]



The present paper describes part of a recent and ongoing investigation of the rates of dediazonation of the benzenediazonium cation and its methyl-substituted analogues (as their tetrafluoroborate salts) in aqueous trifluoroethanol. Trifluoroethanol (TFE) was chosen as cosolvent in order to maintain the ionizing power of the medium⁶ to facilitate heterolytic reactions at the expense of homolytic ones.^{1,7} By varying the proportions of the water and the trifluoroethanol, we are able to modify the nucleophilicity of the medium at high ionizing power. Aqueous trifluoroethanol also allows us to compare our results with what is now a substantial body of other work in the same medium.⁸

RESULTS

Benzenediazonium tetrafluoroborate (1) and its six methyl-substituted derivatives 2-7, see Figure 1, were all made from the corresponding arylamines using literature procedures. All were colourless or pale crystalline solids and were stored in the dark at about -5 °C. All reactions were cleanly first order and, in each case, rates were measured at several temperatures over about 30 °C. [Whilst this is not the subject of the present report, the corresponding reaction of *p*-nitrobenzenediazonium tetrafluoroborate did not, in our preliminary studies, react by a clean first-order solvolytic reaction; this does not appear to have been mentioned in earlier reports of the kinetics of solvolysis of this compound,^{3,9} although Lewis and Hinds detected a non-first order term which they ascribed to a second-order reaction with a nucleophilic solute.¹⁰] We demonstrated that, for the parent compound 1 in water, the uv spectrum at completion corresponds to that of phenol formed in 100% yield, so we are observing exclusively the heterolytic mechanism.⁷



- 1** R¹ - R⁵ = H
2 R¹ = Me; R² - R⁵ = H
3 R² = Me; R¹, R³ - R⁵ = H
4 R³ = Me; R¹, R², R⁴, R⁵ = H
5 R², R⁴ = Me; R¹, R³, R⁵ = H
6 R¹, R⁵ = Me; R² - R⁴ = H
7 R¹, R³, R⁵ = Me; R², R⁴ = H

Figure 1.

Extrapolated (or interpolated) rate constants at 25 °C, the temperatures over which the rates were investigated, and the derived activation parameters are shown in Tables I–VII for compounds 1–7. Tables VIII and IX are comparisons of the results for the different compounds in water and trifluoroethanol, respectively.

Several features are immediately obvious from these results. First, the enthalpies of activation are high as is common for many unimolecular (S_N1) reactions of aliphatic and alicyclic compounds. The reason that the reactions take place at appreciable rates

TABLE I
Benzenediazonium Tetrafluoroborate (1)

Solvent ^a	Temp. Range/°C	10 ⁵ k ₂₅ /s ⁻¹	ΔH [‡] /kJ mol ⁻¹	ΔS [‡] /J K ⁻¹ mol ⁻¹
100 H ₂ O	26–62	3.51	108	33
80 H ₂ O	26–59	5.95	111	45
50 H ₂ O	26–61	6.96	110	46
100 TFE	26–61	6.83	114	58

^a In this and the other Tables, the solvent composition is expressed as mole fraction percentage, e.g. 80 H₂O is H₂O:TFE in the molar ratio 4:1

TABLE II
2-Methylbenzenediazonium Tetrafluoroborate (2)

Solvent	Temp. Range/°C	10 ⁴ k ₂₅ /s ⁻¹	ΔH [‡] /kJ mol ⁻¹	ΔS [‡] /J K ⁻¹ mol ⁻¹
100 H ₂ O	26–61	1.76	100	18
50 H ₂ O	26–50	4.25	99	23
100 TFE	26–60	4.55	105	43

TABLE III
3-Methylbenzenediazonium Tetrafluoroborate (3)

Solvent	Temp. Range/°C	10 ⁴ k ₂₅ /s ⁻¹	ΔH [‡] /kJ mol ⁻¹	ΔS [‡] /J K ⁻¹ mol ⁻¹
100 H ₂ O	25–50	1.56	103	28
50 H ₂ O	26–59	2.85	109	51
100 TFE	26–53	3.35	105	39

TABLE IV

4-Methylbenzenediazonium Tetrafluoroborate (4)

Solvent	Temp. Range/°C	$10^6 k_{25}/s^{-1}$	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$
100 H ₂ O	40-69	3.90	113	30
80 H ₂ O	37-68	5.18	116	43
50 H ₂ O	42-69	7.78	113	36
100 TFE	37-75	6.51	116	44

TABLE V

3,5-Dimethylbenzenediazonium Tetrafluoroborate (5)

Solvent	Temp. Range/°C	$10^4 k_{25}/s^{-1}$	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$
100 H ₂ O	19-51	4.40	103	36
50 H ₂ O	26-51	10.4	102	41
100 TFE	25-61	12.0	97	25

TABLE VI

2,6-Dimethylbenzenediazonium Tetrafluoroborate (6)

Solvent	Temp. Range/°C	$10^3 k_{25}/s^{-1}$	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$
100 H ₂ O	26-50	0.596	101	32
50 H ₂ O	19-52	1.53	106	57
100 TFE	19-39	1.79	102	44

TABLE VII

2,4,6-Trimethylbenzenediazonium Tetrafluoroborate (7)

Solvent	Temp. Range/°C	$10^5 k_{25}/s^{-1}$	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$
100 H ₂ O	31-64	4.90	107	32
50 H ₂ O	26-61	11.3	108	43
100 TFE	28-61	13.7	105	33

is that the entropies of activation (unlike those for most unimolecular (S_N1) reactions of aliphatic and alicyclic compounds) are substantially positive and, therefore, compensate for the adverse enthalpy term. Secondly, the rate constants are not particularly sensitive to the composition of the aqueous trifluoroethanol, and this is not due to compensating changes in the enthalpies and entropies of activation: neither ΔH^\ddagger nor ΔS^\ddagger change very much as the solvent is changed from pure water to pure TFE. Thirdly, the rate constants in both solvents are distinctly sensitive to the position of the methyl substituent. In the *ortho* and *meta* positions, a single methyl is rate enhancing to similar extents but, in the *para* position, it is rate retarding as had been observed earlier.¹¹ Interestingly, a second *ortho* methyl substituent (compounds **2** and **6** enhances the rate even further; the effect of the second *meta* methyl (compounds **3** and **5**) is much the same as that of the second *ortho* methyl. The results for compound **7** indicate that the rate-enhancing effects of the two *ortho* methyl substituents are almost wiped out by the rate-retarding effect of the single *para* methyl group.

TABLE VIII
Comparison of Results for Compounds 1–7 in Water

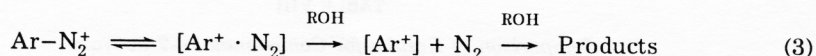
Compound	$10^5 k_{25}/s^{-1}$	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}mol^{-1}$
1	3.51	108	33
2	17.6	100	18
3	15.6	103	28
4	0.39	113	30
5	44.0	103	36
6	59.6	101	32
7	4.90	107	32

TABLE IX
Comparison of Results for Compounds 1–7 in Trifluoroethanol

Compound	$10^5 k_{25}/s^{-1}$	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}mol^{-1}$
1	6.83	114	58
2	45.5	105	43
3	33.5	105	39
4	0.65	116	44
5	120	97	25
6	179	102	44
7	13.7	105	33

DISCUSSION

The Zollinger mechanism⁵ for solvolytic dediazonation (equation (2)) serves as an initial model for the interpretation of our results. This involves a reversible cleavage of the carbon–nitrogen bond to give a cation/molecule complex within a single solvation shell which then undergoes either of alternative parallel processes: (i) product formation by direct nucleophilic capture, and (ii) dissociation to give the separately solvated nitrogen molecule and aryl cation which then also suffers nucleophilic capture in further product-forming steps. According to this mechanism, the rate is determined by the flux through these two parallel channels from the first-formed intermediate. In the first, the activated complex will resemble an aryl cation weakly bonded to a solvent molecule with a closely attendant nitrogen molecule; the aryl moiety will carry a reduced positive charge according to the extent of formation of the developing bond to the solvent molecule. Whilst we cannot completely rule out a small extent of reaction through this channel, it clearly is not a major route in the present investigation. Such a reaction involving rate-limiting nucleophilic attack by solvent would lead to a strong dependence of the rate constant upon the composition of the aqueous trifluoroethanol, and a substantially negative entropy of activation. Neither is observed. Furthermore, a second *ortho* methyl group would inhibit approach of the nucleophile and, consequently, be rate retarding; in fact, the second *ortho* methyl is almost as rate enhancing as the first. In the second potentially rate-limiting process from the first-formed intermediate, the activated complex still includes a fully developed phenyl cation. Our results are more readily interpreted on this basis [a truncated version of equation (2)], the mechanism embodied in equation (3).



In a range of other unimolecular solvolyses, the entropies of activation are close to zero. In such reactions, a neutral substrate molecule dissociates to give an ion-pair, and the developing dipolarity at the transition state polarises the solvent molecules. This solvation of the activated complex leads to an appreciable loss of entropy due to restricted motion of solvating solvent molecules which approximately cancels out the gain in entropy due to the loosening of the molecular vibrations of the substrate molecule as it is on the verge of becoming two species. Overall, therefore, the entropy of activation does not contribute appreciably to the free energy of activation. However, the solvation process, whilst tying down solvent molecules, contributes very significantly towards lowering the enthalpy of activation since the high enthalpy cost of the bond heterolysis is partially offset by the enthalpy-favourable solvation. But the enthalpy term still dominates the free energy of activation, and such reactions are particularly dependent upon the nature of the solvent.

Dediazoniation, as described by equation (3), is characteristically different in that both substrate and the activated complex are cationic, consequently, the formation of the one from the other does not involve the separation of charge, merely its redistribution. This will lead to an appreciably smaller difference in solvation between substrate and activated complex, and the gain in entropy due to the impending departure of the nitrogen molecule is not wholly cancelled out by a loss of entropy due to increased solvation. Correspondingly, there is less enthalpic assistance to the dissociation, so we see rather high ΔH^\ddagger values and reactions which are not particularly sensitive to the composition of the aqueous trifluoroethanol.

The effects of the methyl substituents are intriguing though modest. In the *ortho* and *meta* positions, methyl is rate enhancing; in the *para* position it is rate retarding. Methyl is electron releasing in its interaction with an electron-deficient site and this so-called inductive effect is due to the electron-deficient site being able to attract electron density from the polarisable alkyl group through the sigma bonded system; the effect is attenuated by distance.

If the methyl group is conjugated to the electron-deficient site, *e.g.* through an aromatic system, then it has an extra effect indicated by its appreciably negative σ^+ value.¹² This hyperconjugative effect is usually ascribed to the supply of electron density from the appropriately oriented carbon-hydrogen bonds of the methyl group through the π -system to the electron-deficient site. The rate retardation by the *para*-methyl in the present case indicates that the stabilization of the substrate by hyperconjugative electron supply must be greater than that of the activated complex. In other words, the benzenediazonium ion is stabilized more by the *para*-methyl than is the phenyl cation. On this basis, we would expect that a substituent with a greater electron-releasing tendency than methyl, *e.g.* *para*-methoxy, would be even more rate retarding. This has already been observed,^{3,13} and is in agreement with our own preliminary results.

The rate enhancement due to a *para*-methyl upon the solvolysis of compound 8, Figure 2, in aqueous TFE is about a factor of 10 and the ρ value of -3.3 in a very well behaved Hammett correlation indicates that, in the transition state, the positive charge is about three-quarters developed at the benzylic carbon.¹⁴ The substrate in the

dediazonation bears a full positive charge on the nitrogen at the position corresponding to the benzylic carbon in **8**, so we may assume that the effect of the *para*-methyl group in this diazonium ion is similar to that in the intermediate benzylic cation generated from **8**. The rate effect of the *para*-methyl in both reactions (in one an acceleration, in the other a retardation) is a factor of about 10. So, assuming that the *para*-methyl has no major unanticipated stabilising effect upon substrate **8**, it appears that the *para*-methyl has, at the most, only a small stabilizing effect upon the phenyl cation in the dediazonation.

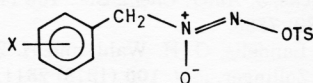


Figure 2.

The effects of single *ortho* and *meta* methyl groups are very similar and modestly rate enhancing. Clearly, they selectively stabilise the activated complex rather than the substrate, but the effect is only small.¹⁵ A second *ortho* or *meta*-methyl is further rate enhancing to a comparable degree.

EXPERIMENTAL

All seven substrates were known compounds and were prepared by literature methods¹⁶ from unpurified commercially available amines, 48% aqueous tetrafluoroboric acid, and sodium nitrite as illustrated below.

Benzenediazonium Tetrafluoroborate (1). An ice-cold solution of sodium nitrite (2.67 g) in water (3 cm³) was slowly added drop-wise to a stirred ice-cold solution of aniline (3.64 g, 39.0 mmol) in aqueous tetrafluoroboric acid (20 cm³) and water (10 cm³). Crystallization of the product from the reaction mixture appeared complete after only a few minutes whereupon it was filtered at the pump, washed with dilute aqueous HBF₄, then with ethanol and diethyl ether, and dried under vacuum (5.39 g, 28.0 mmol, 74%), and stored at -5 °C in a glass vessel wrapped in aluminium foil.

Compounds **2-6** were prepared in the same way from the appropriate amines. 2,4,6-Tri-methylbenzenediazonium tetrafluoroborate (**7**) was prepared in the same way but purified by dissolution in acetonitrile and precipitation by the addition of diethyl ether.

Determination of Yield of Phenol. Compound **1** (2.50 mg) was dissolved in water (100 cm³) and heated under reflux. The concentration of phenol in the cooled solution was calculated by comparison of its absorbance at 270 nm with that of a standard solution of phenol in water; the yield was 99%.

Kinetics

Water that was used for making up solvolytic media was distilled from glass equipment; the trifluoroethanol was dried over molecular sieves (type 4A) then fractionally distilled, bp 78–80 °C.

Rates were investigated by monitoring the uv absorbance at a suitable wavelength in the thermostatted cell compartment of a Pye Unicam SP8-300 spectrophotometer under the control of an Apple-II Europlus microcomputer as described previously,¹⁷ and rate constants were calculated automatically by a non-linear least squares routine. The temperature of the cell block was monitored continuously using a calibrated platinum resistance thermometer. The standard deviations on individual rate constants were generally less than 1%, and the correlation coefficients on the Eyring plots leading to the activation parameters were invariably greater than 0.997 and usually better than 0.999.

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SAŽETAK

Brzina i mehanizam solvolize arendiazonijevih iona u vodenom trifluoroetanolu

H. Maskill i Katharine McCrudden

Izmjerene su konstante brzine solvolize benzendiazonium tetrafluoroborata i njegovih metiliranih analogona u vodi, trifluoroetanolu i smjesi navedenih otapala. Podrobno je prodiskutiran mehanizam reakcije.