Rates and mechanisms of the thermal solvolytic decomposition of arenediazonium ions

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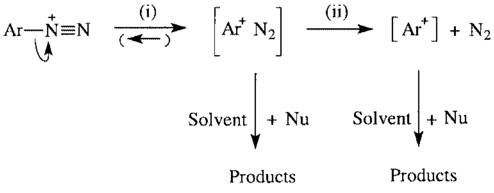
Arenediazonium tetrafluoroborates have been prepared and the kinetics of solvolysis have been investigated in water, trifluoroethanol, water–trifluoroethanol mixtures, hexafluoropropan-2-ol, trifluoroacetic acid, and ethanol by a UV method. A heterolytic mechanism involving short-lived aryl cations leads to products derived from nucleophilic capture of the aryl cations by solvent or a solute. Ionic solutes in aqueous trifluoroethanol and trifluoromethoxybenzene in trifluoroethanol have no kinetic effect and neither does replacement of the tetrafluoroborate counter-ion by chloride in trifluoroethanol. Rate constants for any one compound are not very solvent dependent, the reactions generally being characterised by high enthalpies of activation and appreciably positive entropies of activation. Compounds with 4-Cl, 4-F, 4-NO_2, and 4-MeO substituents proved too unreactive for kinetic studies, but for different reasons. In ethanol, a radical reaction with characteristically different activation parameters competes with the heterolytic path and leads to hydrodediazoniation (reduction) by hydrogen atom abstraction from the CH_2 group of ethanol.

Introduction

Reactions of arenediazonium ions, ArN_2^+, were amongst the first to be studied mechanistically,[1] and the diazonium group was reported to be replaceable by iodide as long ago as 1864.[2] In 1940, Hammett[3] postulated a slow unimolecular heterolytic dissociation of arenediazonium ions into aryl cations and N_2, and experimental support was provided;[4] Lewis[5–7], Swain[8–10] and DeTar[11,12] were amongst other early investigators of solvolytic dediazoniations. Zollinger[1a,13,14] has been pre-eminent amongst subsequent investigators[1b,15,16] who have continued to study the mechanisms of these important reactions by kinetics, isotope labelling studies, kinetic isotope effect measurements, and theoretical methods.

Arenediazonium ions undergo Nα–Nβ rearrangement (to a degree which depends upon the nature of the arene group and the reaction conditions) which indicated that the aryl cation formed in the initial heterolysis may undergo internal return with the nitrogen molecule.[7,8,13,17] Hydrogen and nitrogen kinetic isotope effect measurements[6,8,9,18,19] provided further support for the intermediacy of the aryl cation and, in particular, excluded the intermediacy of a benzenespirodiazirine cation. Zollinger proposed a second steady-state intermediate on the basis of further isotopic labelling studies as shown in the mechanism of Scheme 1 with an ion–molecule pair intervening between the diazonium ion and the fully dissociated aryl cation plus nitrogen molecule.[20]



Scheme 1 Heterolytic mechanism of dediazoniation.

Questions concerning the structure of the aryl cation intermediate formed in the decomposition of arenediazonium salts were first addressed by Taft who observed substantial enhancements in the rate due to electron donating substituents in the *meta* position of benzenediazonium salts.[21] He suggested that this effect implied a high degree of radical-cation character in the transition state of the dediazoniation reaction due to transfer of a π electron from the benzene ring into the vacant σ (sp^2) orbital of the cation. The triplet electronic state was claimed to be more stable than the corresponding singlet, but early semi-empirical and *ab initio* molecular orbital calculations were not supportive although results depended upon substituents.[22] More recent high level *ab initio* studies confirm a singlet ground state phenyl cation with an appreciably less stable, very short-lived triplet.[23] These theoretical studies have been complemented by experimental studies of the properties and reactions of aryl cations generated other than by thermolysis of diazonium ions.[24]

The reduction of arenediazonium salts by ethanol to give arenes was a notable early preparative use of dediazoniations,[2,25] but yields are variable and substituent dependent; decomposition of benzenediazonium salts with ethanol, for example, yields phenyl ethyl ether and benzene in ratios which depend upon the precise experimental conditions. Electron-donating substituents favour the formation of aryl ethers whilst electron-withdrawing groups favour reduction to arenes. The thermal decomposition of arenediazonium tetrafluoroborates in the absence of solvent to give fluoroarenes reported by Balz and Schiemann is another useful dediazoniation reaction.[26,27] This reaction remains an important method for the production of fluoroarenes which continue to be increasingly important in the manufacture of pharmaceuticals and agrochemicals. There have been a number of subsequent developments and alternatives[28] which improve yields and safety including use of arenediazonium hexafluoroantimonates and hexafluorophosphates.[29]

We have decomposed arenediazonium tetrafluoroborates in ionising solvents of different nucleophilicities and sought to intercept the intermediate aryl cation by fluoride donating

Table 1 Rate constants at 25.0 °C and activation parameters for $XC_6H_4N_2^+BF_4^-$ in water

Compound, X	$10^6k_{25}/s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1a, H[a]	53.0	109	37
1b, 4-*tert*-Bu	6.77	109	23
1c, 3-MeO	240	99	16
1d, 3-CF_3	0.27	128	56
1e, 3-Cl	1.82	111	16
1f, 3-F	1.31	134	81
1g, 3-NO_2	9.69	99	−17
1h, 3-CN	11.3	79	−75

[a] Previously reported results,[35] $10^6k_{25}/s^{-1} = 35.1$, $\Delta H^{\ddagger}$/kJ mol^{-1} = 108, $\Delta S^{\ddagger}$/J K^{-1} mol^{-1} = 33; it was also established that EDTA had no effect upon the rate constant at 25 °C.

Table 2 Rate constants at 25.0 °C and activation parameters for $XC_6H_4N_2^+BF_4^-$ in TFE

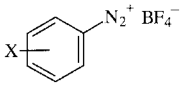
Compound, X	$10^6k_{25}/s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1a, H[a]	92.1	114	62
1b, 4-*tert*-Bu	12.2	113	40
1c, 3-MeO	873	103	42
1d, 3-CF_3	0.7	111	10
1e, 3-Cl	3.01	118	44
1f, 3-F	1.18	124	59
1g, 3-NO_2	0.60	124	54
1h, 3-CN	0.3	116	20

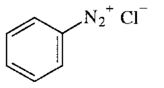
[a] Ref. 35; it was also established that EDTA had no effect upon the rate constant at 25 °C, and that replacement of the tetrafluoroborate (**1a**) by the chloride (**2**) gave identical results between 25 and 55 °C.

agents in order to improve the yields of fluoroarenes.[24,27,30,31] We report here preparations of our substrates, kinetics results, and mechanistic deductions regarding the rate-limiting step; further product analysis and mechanistic considerations will be reported separately.

Methods

Arenediazonium tetrafluoroborates (**1a**–**n**) were made by





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1a, X = H
b, X = 4-*t*-Bu
c, X = 3-MeO
d, X = 3-CF_3
e, X = 3-Cl
f, X = 3-F
g, X = 3-NO_2
h, X = 3-CN
i, X = 3-Me
j, X = 4-Mc
k, X = 4-MeO
l, X = 4-Cl
m, X = 4-F
n, X = 4-NO_2

Starkey's general method and yields were satisfactory;[32] all were stored below room temperature, protected from daylight, and usually purified before use. Benzenediazonium chloride (**2**) was made by a non-aqueous method and kept moist with diethyl ether until used, then destroyed; no samples of this compound were stored. Kinetics were investigated by our usual method of monitoring UV absorbance with time, all data collection being carried out automatically, and rate constants were computed by iterative non-linear regression methods. Rates of the more reactive compounds (**1a**,**c**,**i**) were investigated down to about 20 °C whereas the less reactive compounds (**1d**,**g**,**h**) were investigated at temperatures up to 85 °C in water. Mean values of first-order rate constants were obtained from at least two results at each temperature; the rate constant at 25.0 °C and the enthalpy and entropy of activation were then determined by a computer-based version of the Eyring equation.[33] The least reactive compounds, *i.e.* benzenediazonium tetrafluoroborate with 4-Cl, 4-F, and 4-NO_2 substituents (**1l**–**n**), proved too unreactive for us to investigate kinetically, and (for the same reason) we were able to make only very limited kinetic measurements with the 4-MeO compound (**1k**). Products were identified by comparison with authentic samples, and analysed by a combination of UV and NMR spectroscopy, and GLC.[34]

Table 3 Rate constants at 25.0 °C and activation parameters for $XC_6H_4N_2^+BF_4^-$ in trifluoroacetic acid

Compound, X	$10^4k_{25}/s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1a, H	0.47	111	45
1i, 3-Me	2.25	110	54
1c, 3-MeO	5.15	108	55

Table 4 Rate constants at 25.0 °C and activation parameters for $XC_6H_4N_2^+BF_4^-$ in hexafluoropropan-2-ol

Compound, X	$10^6k_{25}/s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1a, H	97.2	116	66
1c, 3-MeO	1730	98	32
1d, 3-CF_3	1.7	73	−123
1h, 3-CN	0.01	172	178
1i, 3-Me	519	108	56

Table 5 Rate constants at 25.0 °C and activation parameters for $XC_6H_4N_2^+BF_4^-$ in ethanol

Compound, X	$10^4k_{25}/s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1a, H	2.32	75	−64
1c, 3-MeO	4.09	97	14
1d, 3-CF_3	8.44	85	−20
1f, 3-F	9.41	64	−87
1h, 3-CN	2.62	132	128
1i, 3-Me	3.63	100	26

Table 6 Rate constants at 25.0 °C and activation parameters for $XC_6H_4N_2^+BF_4^-$ in TFE–H_2O[a]

Compound, X	Molar ratio TFE : H_2O	10^5k_{25}/ s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1b, 4-*tert*-Bu	1 : 1	1.34	108	26
1c, 3-MeO	1 : 1	38.9	102	32
1f, 3-F	1 : 1	13.1	126	67
1f, 3-F	95 : 5	3.6	126	64

[a] Up to 0.25 mol dm^{-3} of $NaPF_6$, and $NaClO_4$ had no effect, or a slight rate-decreasing effect, upon the reaction of 4-$MeC_6H_4N_2^+BF_4^-$ (**1j**) in 1 : 1 aqueous TFE at 51 °C.

Results

First-order rate constants at 25.0 °C (k_{25}), $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for arenediazonium tetrafluoroborates in the five pure solvents are shown in Tables 1–5. Replacement of benzenediazonium tetrafluoroborate (**1a**) by the chloride (**2**) in TFE led to rate constants identical within experimental error at five temperatures between 25 and 55 °C. Our best estimate for the reactivity of the 4-methoxy compound (**1k**) is that it is 250 times less reactive than the 4-methyl compound at 84 °C in water. Table 6 contains results in aqueous trifluoroethanol (TFE); increasing concentrations of sodium or ammonium hexafluorophosphate and sodium perchlorate up to 0.25 mol dm^{-3} at 51 °C in 1 : 1 aqueous TFE led to either no effect or small decreases in the rate constant for 4-toluenediazonium tetrafluoroborate. Table 7 shows the effect of increasing concentrations of trifluoromethoxybenzene (TFMB) in pure TFE upon the rate constant

Table 7 Rate constants for 4-$MeC_6H_4N_2^+BF_4^-$ (**1j**) in TFE containing trifluoromethoxybenzene (TFMOB) at two temperatures

	$10^4k/s^{-1}$			
Temperature/ °C	100% TFE	TFE : TFMOB, 10 : 1	TFE : TFMOB, 5 : 1	TFE : TFMOB, 3 : 1
35.0	1.82	2.43	2.34	1.73
49.5	15.9	17.9	16.3	18.0

for decomposition of 4-toluenediazonium tetrafluoroborate (**1j**). In all cases, products have been identified and shown to be fluoroarenes, substitution products derived from the solvent, and (in the case of ethanol) reduction products; yields (relative and absolute) were measured by GLC.[34]

Six of the eight k_{25} results in Table 1 represent a relatively narrow range of reactivity in water (a factor of 40 between highest and lowest) but there are two out-liers; the 3-MeO analogue (**1c**) is appreciably more reactive and the 3-CF_3 compound (**1d**) appreciably less so. However, the substantially negative $\Delta S^‡$ values for the 3-NO_2 and 3-CN compounds (**1g**) and (**1h**), compensated in part by somewhat lower $\Delta H^‡$ values, appear qualitatively different from the other results. For TFE and trifluoroacetic acid (TFA) shown in Tables 2 and 3, the 3-MeO compound (**1c**) is again the most reactive, but now the activation parameters for all compounds are qualitatively the same—large $\Delta H^‡$ values and distinctly positive $\Delta S^‡$ values. Results for the 3-CF_3 and 3-CN compounds (**1d**) and (**1h**) in hexafluoropropan-2-ol (HFIP) shown in Table 4 appear anomalous but for different reasons. The former has a low $\Delta H^‡$ value and a very negative $\Delta S^‡$ value, whereas the latter has a strongly positive (favourable) $\Delta S^‡$ value and a massively unfavourable $\Delta H^‡$ value. In Table 6 we see that the proportion of water in TFE has little effect upon the kinetics of four compounds; the counter-ion has no detectable effect upon the rate constant for reaction of the parent benzenediazonium ion in TFE. Molecular and ionic solutes (Table 7 and the footnote to Table 6) have no significant effect upon rate constants for 4-toluenediazonium tetrafluoroborate (**1j**) in TFE and aqueous TFE, respectively. In ethanol, Table 5, the range of reactivity at 25 °C is very narrow, but differences in the activation parameters and product analyses indicate mechanistic differences (see below).

Discussion

Solvolytic dediazoniation reactions of arenediazonium salts are typically characterised by entropies of activation appreciably more positive than those for S_N1 reactions of aliphatic substrates, and have considerably larger enthalpies of activation.[10,12,35] These activation parameters have been interpreted as evidence for the rate-limiting step being either the initial heterolysis of the C–N bond of the arenediazonium ion, or the subsequent separation of the initially formed ion–molecule pair, *i.e.* steps (i) or (ii) in Scheme 1. The increase in entropy due to the impending departure of the nitrogen molecule in the formation of the rate-limiting transition structure is not cancelled out by increased solvation, hence the positive $\Delta S^‡$ values. The absence of significantly enhanced solvation as substrate becomes transition structure also means there is little assistance to the enthalpic cost of the heterolysis, hence the large $\Delta H^‡$ values. We have no explanation at the moment, however, for the very few reactions in polar media which have activation parameters significantly different, *i.e.* of **1g** in water, **1d** in HFIP, and **1h** in water and HFIP but note that the two reactions in HFIP are very slow and results from them may be less reliable. Earlier isotopic labelling studies showed that the initial ionization is reversible[7,8,17] in which case the separation of the ion–molecule pair, step (ii) in Scheme 1, is the rate-limiting step. [Our reactions were all carried out under normal atmospheric conditions, consequently step (ii) is not expected to be reversible as was observed under very high pressures of nitrogen.[17]] The mechanism of Scheme 1 allows capture of the initial ion–molecule pair by high concentrations of strong nucleophiles such as thiocyanate, which would reduce internal return and hence lead to a rate enhancement, as has been reported.[6] The reaction conditions we used would not be expected to affect internal return and we observed no second-order rate effects with any solutes. In the absence of strongly nucleophilic solutes, and for the more reactive compounds even in the presence of such solutes, the products of reactions in solvents other than ethanol are exclusively by solvent derived nucleophilic substitution and fluoroarenes; in ethanol, reduction products are also observed.[30,34,35] Ratios of trifluoroethyl ethers to phenols from reactions in aqueous TFE and appreciable yields of fluoroarenes from reactions in TFE implicate a highly reactive, short-lived, and non-discriminating aryl cation intermediate.[30,36] We conclude that simple arenediazonium ions in the polar solvents of our investigation decompose by the mechanism of Scheme 1 proposed previously.

Effect of substituents

We have already reported[35] that 2- and 3-alkyl substituents are rate-enhancing in polar solvents and conclude that the stabilising (electron-releasing) inductive effect of these groups is greater for the aryl cation (and hence, by the Hammond Postulate,[33] for the transition structure leading to its formation) than for the arenediazonium ion precursor. This is not surprising as only little of the positive charge of the arenediazonium ion will be delocalised into the arene ring. Correspondingly, electron-withdrawing groups without opposing electron-supplying resonance effects (3-nitro, 3-cyano, and 3-trifluoromethyl) destabilise the aryl cation more than they destabilise the arenediazonium ion and hence are rate retarding. Groups at position 3 which are inductively electron-withdrawing but able to supply electron density into the aromatic ring by resonance (halogen and methoxy) are particularly interesting; 3-Cl and 3-F are rate retarding (comparable with 3-NO_2, 3-CN, and 3-CF_3) whereas 3-MeO is strongly rate-enhancing—more so than 3-alkyl. On the grounds that the 3-MeO is further from the electron-deficient centre in the diazonium ion than in the aryl cation, we can dismiss any notion that this substituent is more destabilising for the reactant than for the transition structure. Clearly, the 3-methoxy substituent stabilises the aryl cation (and hence the preceding transition structure) more than the arenediazonium ion which indicates that, as in electrophilic aromatic substitution,[37] the electron supply through resonance dominates electron withdrawal by induction. There must, therefore, be delocalisation of the positive charge of the aryl cation to carbons able to access the stabilising electron density of the 3-methoxy substituent. Any electron supply by resonance from 3-halo substituents, however, is more than cancelled by electron withdrawal through induction, and such substituents remain rate retarding (again, as in electrophilic aromatic substitution).

As reported previously,[35] 4-alkyl groups are rate-retarding; consequently, their cation-stabilising effect upon the diazonium ion must be greater than upon the aryl cation. In view of their greater distance from the cationic site of the diazonium ion of 4-alkyl than 3-alkyl, the mechanism of the stabilising effect of 4-alkyl is not principally induction. We also see by comparison of our present and earlier studies[35] that the 4-*tert*-butyl group is consistently less rate-retarding than the 4-methyl group. The 4-*tert*-butyl group is more polarisable than methyl which confirms that induction is not the principal diazonium ion-stabilising mechanism of 4-alkyl groups and implicates hyperconjugation, the C–C effect being less than the C–H effect. There is earlier evidence supporting hyperconjugative stabilization of the aryl cation formed in dediazoniation[9] and otherwise.[38] Groups

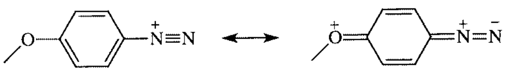

Fig. 1 Resonance stabilisation of the 4-methoxybenzenediazonium ion.

which are better able conjugatively to stabilise the arenediazonium ion, *e.g.* N- or O-bonded substituents or cyclopropyl and vinyl, are predicted to be more strongly rate retarding. This is observed in the present results for the 4-methoxy group and wholly consistent with resonance stabilisation of the arenediazonium ion illustrated in Fig. 1 and proposed earlier by Hughes[39] and Swain.[10]

Nitro, cyano, and trifluoromethyl substituents at position 4 are rate retarding so (as at position 3) they destabilise the aryl cation by induction more than they destabilise the arenediazonium ion. Halogens, like methoxy, are inductively electron-withdrawing but electron-donating by resonance. We have observed the former effect to be greater upon the aryl cation than upon the arenediazonium cation so, by this mechanism, 4-halo substituents are expected to be rate retarding. The electron-donating resonance effect of 4-halo groups will also be rate retarding because (as with 4-methoxy, Fig. 1) it selectively stabilises the arenediazonium ion; these compounds were, in fact, too unreactive for us to be able to investigate kinetically.

As discussed above, we have observed appreciable effects of substituents upon rates of dediazoniation, and qualitative inductive, resonance, and hyperconjugative effects have been invoked to account for them. Attempts to fit the results to a two-parameter Hammett type correlation failed. More sophisticated approaches using multiparameter equations would doubtless allow improved correlations, and might allow better resolution of effects between resonance, inductive, and (for 2-substituents) steric effects.[9,40,41] This was not a primary objective of the present investigation, however, and a course we have not taken.

Effect of solutes

Increasing concentrations of sodium and ammonium hexafluorophosphate and sodium perchlorate have no appreciable effect upon the rate constant for decomposition of 4-toluenediazonium tetrafluoroborate in aqueous trifluoroethanol. The former, a potential fluoride donor, modestly increases the yield of fluoroarene.[34] Trifluoromethoxybenzene is also a potential fluoride donor but, as Table 7 shows, even high proportions in TFE have no measurable effect upon the rate of decomposition of 4-toluenediazonium tetrafluoroborate. These results support the mechanistic proposal that the decomposition of the arenediazonium ion in polar media is unimolecular; the effects of solutes upon the product distributions are due to involvement in product-forming steps subsequent to the rate-limiting step, Scheme 1.

Effect of solvent

Only a modest solvent effect upon rate constants is anticipated for the mechanism of Scheme 1 since the rate-limiting step, regardless of whether it is (i) or (ii), involves conversion of one cation into another, *i.e.* there is no change in the charge type, only a charge redistribution. This is generally observed; rate constants for the parent compound at 25 °C in H_2O, TFE, HFIP, and TFA are all within a factor of 2. Thus, with the exception of ethanol, the solvent effects are wholly accommodated by the mechanism in Scheme 1 and warrant little further discussion. The first kinetic indication that reactions in EtOH were different is the effect of substituents upon k_{25}; 3-Me and 3-MeO were found to be rate enhancing as expected, but so were 3-F, 3-CN, and 3-NO_2 which are strongly rate retarding in other solvents. In EtOH, therefore, the parent diazonium salt was the least reactive of the set. We also note that the activation parameters in EtOH do not follow the normal pattern.

Product analytical evidence confirmed that reactions in EtOH are qualitatively different from the reactions in the more ionising media;[30,34] products of hydrodediazoniation, *i.e.* reduction products, are formed in appreciable yields in ethanol. Our observation of faster rates and higher yields for hydrodediazoniation with electron-withdrawing substituents is compatible with intrusion of a radical mechanism for reactions in ethanol. This is in agreement with an earlier report that thermal homolytic dediazoniation is favoured over heterolytic by increasing the electrophilicity of the β nitrogen atom of the diazonium ion, *e.g.* by suitable electron-withdrawing substituents in the aromatic ring.[18] Previously, both heterolytic and radical mechanisms have been provided for the reduction reaction in methanol, the former by DeTar[42] with hydride transfer as the crucial step but this has not been widely upheld. A radical mechanism proposed by DeTar[42,43] and others,[44,45] following much earlier suggestions by Hey and by Waters,[46] is generally accepted. We have now shown that when 3-nitro- and 3-fluorobenzenediazonium tetrafluoroborate are decomposed in 1,1-dideuterioethanol, deuterium is incorporated to give 3-deuterionitrobenzene and 3-deuteriofluorobenzene[34] as required by Scheme 2. Zollinger also reported that addition of pyridine to TFE for the dediazoniation of benzenediazonium tetrafluoroborate increased the overall rate and yields of the products of homolytic decomposition, concluding that increasing the nucleophilicity of the solvent itself, as well as introducing nucleophilic solutes, promotes homolysis of diazonium ions.[47] On this basis, the electron donor in Scheme 2 is probably the solvent, ethanol. It remains now to quantify by further product analysis the relative extents of the the parallel heterolytic and homolytic paths for individual arenediazonium salts in ethanol, and to investigate systematically which other solvents allow the homolytic reductive reaction path.

$$\begin{aligned}
\mathrm{ArN_2^+} &\xrightarrow{e^-} \mathrm{ArN_2^{\bullet}}\\
\mathrm{ArN_2^{\bullet}} &\longrightarrow \mathrm{Ar^{\bullet} + N_2}\\
\mathrm{Ar^{\bullet} + CH_3CL_2OH} &\longrightarrow \mathrm{ArL + CH_3\dot{C}LOH}\\
\mathrm{CH_3\dot{C}LOH + ArN_2^+} &\longrightarrow \mathrm{ArN_2^{\bullet} + CH_3CLO^+H}\\
\mathrm{CH_3CLO^+H} &\rightleftharpoons \mathrm{CH_3CLO + H^+}
\end{aligned}$$

Scheme 2 Radical mechanism for reduction of arenediazonium ions by ethanol.

Experimental

All starting materials were purchased from either Aldrich or Fluorochem and were of reagent grade purity. Trifluoroethanol (TFE) purchased from Fluorochem was distilled and stored over 4 Å molecular sieves, and water was distilled using all-glass equipment. Other solvents were laboratory grade and purified by standard methods. ^1H NMR spectra were recorded on a Bruker WP200 (200 MHz) spectrometer, the solvent being $CDCl_3$ unless otherwise stated.

Preparations

Arenediazonium salts were all prepared by the same general method (see below for benzenediazonium tetrafluoroborate) and stored in the dark at −5 °C; they all decomposed upon melting.

Benzenediazonium tetrafluoroborate (1a). Aniline (7.2 g, 76 mmol) was added to a stirred solution of tetrafluoroboric acid (20 cm^3, 48% wt) and water (20 cm^3). The solution was placed in an ice bath and stirred as a cold aqueous solution of sodium nitrite (5.34 g, 76 mmol) in water (5 cm^3) was added dropwise. The reaction mixture was stirred as the temperature rose to room temperature, then filtered under reduced pressure to separate the precipitate which was washed with dilute aqueous tetrafluoroboric acid, ethanol, and diethyl ether, then dried under vacuum. The product was purified by dissolution in acetone followed by precipitation with diethyl ether. This was carried out three times to remove colouration (5.95 g, 41%, mp = 105–110 °C, lit.,[45] 108–110 °C).

4-*tert*-Butylbenzenediazonium tetrafluoroborate (1b). The crude product was recrystallised from ethanol to give white crystals (55%, mp = 100–102 °C, lit.,[27] 99–102 °C).

3-Methoxybenzenediazonium tetrafluoroborate (1c). The crude precipitate was a dark red solid which was purified by recrystallisation from acetonitrile–ether three times to give a pale yellow powder (83%, mp = 85–87 °C, lit.,[45] 87–88 °C).

3-(Trifluoromethyl)benzenediazonium tetrafluoroborate (1d). The product was a white powder which was purified by dissolution in acetonitrile followed by precipitation using diethyl ether (58.2%, mp = 146–147 °C, lit.,[48] 148 °C).

3-Chlorobenzenediazonium tetrafluoroborate (1e). The pale pink product was purified by dissolution in acetonitrile and precipitation with diethyl ether (95%, mp = 144–146 °C, lit.,[45] 146–148 °C).

3-Fluorobenzenediazonium tetrafluoroborate (1f). Colourless crystals of the pure compound were obtained either by recrystallisation from aqueous methanol or by dissolution in acetonitrile and precipation by diethyl ether (52%, mp = 154–156 °C, lit.,[49] 154.5–156 °C).

3-Nitrobenzenediazonium tetrafluoroborate (1g). The crude product was a light brown solid which was purified by recrystallisation from acetone–ether (89%, mp = 168–170 °C, lit.,[50] 165 °C).

3-Cyanobenzenediazonium tetrafluoroborate (1h). The crude slightly off-white product was recrystallised twice from acetonitrile–ether to give a white powder (82%, mp = 152–157 °C, lit.,[51] 155–156 °C).

3-Methylbenzenediazonium tetrafluoroborate (1i). The crude red solid product was purified by recrystallisation from acetonitrile–ether three times to give a white powder (78%, mp = 101–102 °C, lit.,[45] 97–101 °C).

4-Methylbenzenediazonium tetrafluoroborate (1j). Recrystallisation of the product was from aqueous methanol to give a white solid (28%, mp = 109–111 °C, lit.,[45] 109–111 °C).

4-Methoxybenzenediazonium tetrafluoroborate (1k). White crystals of the pure compound were prepared by dissolution of the brown crude product in acetonitrile and precipitation with diethyl ether (78%, mp = 140–141 °C, lit.,[45] 142 °C).

4-Chlorobenzenediazonium tetrafluoroborate (1l). White crystals were obtained directly (91%, mp = 131–133 °C, lit.,[52] 134 °C).

4-Fluorobenzenediazonium tetrafluoroborate (1m). White crystals of the pure compound were prepared by dissolution of the colourless crude product in acetonitrile and precipitation with diethyl ether (49%, mp = 152–154 °C, lit.,[26] 154.5 °C).

4-Nitrobenzenediazonium tetrafluoroborate (1n). The pale yellow solid was obtained by dissolution of the crude product in acetonitrile and precipitation with diethyl ether (96%, mp = 156–157 °C, lit.,[45] 157–158 °C).

Isopentyl nitrite. A solution of sodium nitrite (8.3 g) in water (34 cm^3) was added to a solution of water (2.5 cm^3), concentrated sulfuric acid (3.1 cm^3), and isopentyl alcohol (10.0 g) cooled in ice. The reaction mixture was allowed to stand for 1.5 h as the temperature rose to room temperature, then crystalline sodium sulfate was removed by filtration. The upper yellow isopentyl nitrite was separated, washed with a solution of sodium hydrogen carbonate (0.1 g) and sodium chloride (1.3 g) in water (5 cm^3), dried ($MgSO_4$), and filtered (10.6 g, 80%, δ_H: 1.0 (d, 6H), 1.6 (m, 1H), 1.7 (m, 2H), 4.6 (t, 2H)).

Benzenediazonium chloride (2).[4] A saturated solution of hydrogen chloride in ethanol (0.375 cm^3) was added to aniline hydrochloride (2.63 g, 20.3 mmol) in ethanol (20 cm^3). This solution was cooled in ice and isopentyl nitrite (3.00 g, 25.6 mmol) was added. The mixture was allowed to stand for 5–10 min at room temperature then the product was precipitated by the gradual addition of diethyl ether. The crystals were filtered under reduced pressure and washed with a 1 : 1 mixture of ethanol–ether followed by ether (10 cm^3). Care was taken to ensure that the crystals were kept moist with ether; δ_H (d_6-DMSO): 3.3 (m, 2H), 4.2 (m, 2H), 5.2 (d, 1H); λ_m (ethanol): 267 nm.

Solvolytic media

Densities of solvents were used to calculate the volumes of each solvent that were required to produce the correct mixtures. Small volumes were delivered using a Gilson Pipetman.

Kinetics

UV spectral analysis was carried out either on a Pye Unicam SP8-300 or a Cecil 5000 series (5502 model) UV–VIS spectrophotometer and 1 cm path-length quartz cells were used. Spectrophotometer cell compartments were thermostatted by circulating water. The absorbance at or close to λ_{max} was recorded automatically at fixed time intervals for at least 3 half lives. The absorbance–time data were fitted to a single exponential decay equation by an iterative method to give the rate constant. Depending on the rate of reaction, up to four cells could be studied at one time and average rate constants from at least two determinations at each of several measured temperatures over a 25–30 ° range between about 20 and 85 °C were obtained. Standard deviations on individual rate constants were generally about 1% and reproducibility about 5%. Rate constants at 25.0 °C, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ were calculated using the Eyring equation, correlation coefficients on the Eyring plots being never less than 0.997 and usually greater than 0.999. The estimated uncertainties are *ca.* 20% on k_{25}, *ca.* 6 kJ mol^{-1} on $\Delta H^\ddagger$, and *ca.* 12 J K^{-1} mol^{-1} on $\Delta S^\ddagger$.

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