Dediazoniation reactions of arenediazonium ions under solvolytic conditions: fluoride anion abstraction from trifluoroethanol and α-hydrogen atom abstraction from ethanol

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Arenediazonium salts decompose thermally and photochemically in trifluoroethanol to yield trifluoroethyl ethers and (in part by fluoride abstraction from the solvent) fluoroarenes; the less reactive compounds in trifluoroethanol decompose readily in ethanol to give arenes in a radical reaction involving abstraction of the α-hydrogen from the ethanol.

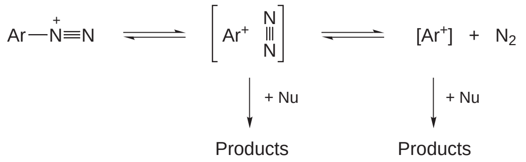
Dediazoniation reactions are amongst the oldest known industrial organic chemical reactions, and their mechanisms are also amongst the earliest to have been investigated.[1] For some years, thermal decomposition of arenediazonium tetrafluoroborates has been used as a route for making fluoroarenes—compounds of increasing importance for the production of pharmaceuticals and agrochemicals. The Balz–Schiemann reaction is one method which involves isolation of the salt and its subsequent thermal decomposition,[2] a potentially hazardous process. Other methods involve decomposition of diazonium salts in liquid hydrogen fluoride,[3] but these also have obvious potential for danger. We have been investigating alternative procedures for decomposing diazonium salts with a view to (i) understanding better the mechanisms involved, and (ii) developing a method more environmentally acceptable and less hazardous than ones currently available. In the course of these investigations, we have discovered that aryl cations (generated by loss of dinitrogen from the arenediazonium ions) are able to abstract fluoride from fluoro alcohols in competition with being captured by the hydroxylic residue of the alcohol. We have also shown that the intermediates involved in the decomposition in ethanol of arenediazonium cations with electron-withdrawing substituents abstract an α-hydrogen from the ethanol. Additionally, we have demonstrated that, under photolysis in trifluoroethanol (TFE), otherwise very unreactive arenediazonium ions react very readily. This product analytical evidence, and the attendant kinetics studies, contribute further to ongoing investigations world-wide of the chemistry of exceedingly short-lived reactive intermediates.

Table 1 Kinetics results[a] for the solvolysis of arenediazonium tetrafluoroborates $XC_6H_4N_2^+\ BF_4^-$

Solvent	X	$k_{25}/10^{-6}s^{-1}$	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
TFE	*m*-NO_2	0.60	124	54
TFE	*m*-F	1.18	124	59
TFE[b]	H	92.1	114	62
TFE	*m*-OMe	873	103	42
EtOH	*m*-OMe	409	97	14
EtOH	*m*-F	941	64	−87
EtOH	H	232	75	−64

[a] Rate constants at 25 °C were extrapolated using the Eyring equation from average values obtained at other temperatures. Standard deviations on individual rate constants were generally about 1% and reproducibility was better than about 5%. The estimated uncertainty on $\Delta H^‡$ is *ca.* 6 kJ mol^{-1} and 12 J K^{-1} mol^{-1} on $\Delta S^‡$. [b] Previously reported values (ref. 5): k_{25} = 68.3×10^{-6} s^{-1}, $\Delta H^‡$ = 114 kJ mol^{-1} and $\Delta S^‡$ = 58 J K^{-1} mol^{-1}.

Table 1 gives kinetics results for arenediazonium tetrafluoroborates investigated by our normal UV method.[4,5] In TFE, a solvent which generally promotes heterolytic reactions, we observe high enthalpies of activation and appreciably positive entropies of activation in agreement with previous results.[5,6] Such findings are accommodated by the Zollinger heterolytic mechanism[7] [Scheme 1, where Nu = nucleophile (*e.g.* solvent)] except that under our reaction conditions, the first two steps will be essentially irreversible. In accord with earlier workers, we also observe that electron-withdrawing substituents decrease reactivity,[5,6,8] an effect brought about principally through increases in the enthalpy of activation (Table 1). For the *m*-methoxy compound, the most reactive of these compounds in TFE, we note comparable reactivity in ethanol. However, for the much less reactive *m*-fluoro analogue in TFE, we note unexpectedly high reactivity in ethanol, and quite different activation parameters; $\Delta H^‡$ is now much lower and $\Delta S^‡$ strongly negative, signalling a different mechanism.



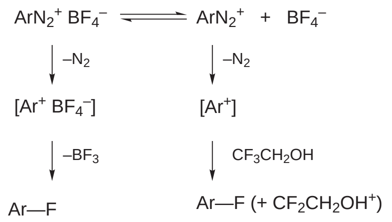
Scheme 1

In TFE, the products of the thermally induced solvolyses are principally the aryl trifluoroethyl ethers, but between 10 and 35% of aryl fluorides are observed (Table 2). These compounds

Table 2 Product analyses[a] from solvolytic decompositions of arenediazonium salts $XC_6H_4N_2^+\ Z^-$ Products (%)

Solvent/ROH	X	Z^-	Mode	ArOR	ArF	ArH
TFE	H	BF_4^-	thermal	72	28	< 0.1
TFE	H	Cl^-	thermal	90	10	—
TFE[b]	H	BF_4^-	thermal	66	34	—
TFE	H	BF_4^-	*hν*	57	43	—
TFE	*m*-F	BF_4^-	thermal	65	35	< 0.1
TFE	*m*-F	BF_4^-	*hν*	67	33	< 0.1
TFE	*m*-NO_2	BF_4^-	*hν*[c]	57	43	—
EtOH	H	BF_4^-	thermal	96	4	< 1
EtOH	*m*-F	BF_4^-	thermal	20	< 0.1	80
EtOH	*m*-F	BF_4^-	*hν*	15	< 0.1	85
EtOH	*m*-NO_2	BF_4^-	thermal	8	< 1	92[d]

[a] Analyses were carried out by GLC, usually with undecane as internal standard. Each reaction was carried out at least twice, and up to *ca.* six chromatograms were obtained for each reaction. Yields quoted are normalised (total = 100%), absolute recoveries being variable between *ca.* 80–100%. [b] Reaction contained 0.63 mol dm^{-3} $NaBF_4$. [c] This reaction was too slow thermally for a reliable product analysis to be obtained. [d] When the reaction was carried out in CH_3CD_2OH, *m*-$DC_6H_4NO_2$ was isolated by preparative GLC, and characterised by mass spectrometry and ^1H NMR spectroscopy.

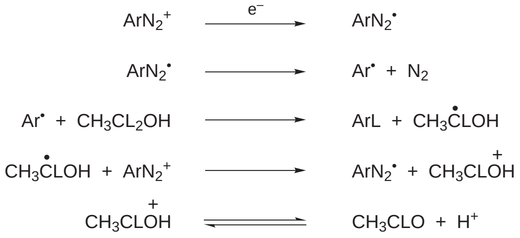


Scheme 2

were identified by comparison with authentic samples, and in some cases were isolated by preparative GLC and characterised. If aryl radical intermediates are the source of this fluorine transfer, the same intermediates would also be expected to give some degree of hydrogen transfer. No appreciable yields of reduction product were detected in reactions in TFE, so aryl cations are implicated as the source of fluorine abstraction. Aryl fluorides had previously been detected from reactions of very dilute arenediazonium tetrafluoroborates in aqueous TFE in which the reactants will have been fully dissociated. Since aryl cations are exceedingly short lived,[9] they cannot diffuse through the medium and select very dilute tetrafluoroborate as a reaction partner. Consequently, the TFE component of the solvent was implicated as the source of the fluorine in the product aryl fluorides. This was confirmed by solvolysing benzenediazonium chloride in TFE and obtaining 10% fluorobenzene (compared with 28% from the tetrafluoroborate). We conclude that the fluoroarenes generated from arenediazonium tetrafluoroborates in TFE arise from fluoride abstraction by the aryl cation in part from the solvent and in part from the tetrafluoroborate anion within undissociated ion-pairs (Scheme 2) (where possible involvement of ion-molecule pair intermediates, as in Scheme 1, has been omitted for clarity). In agreement with this proposal, addition of sodium tetrafluoroborate (which will increase the degree of ion-pair association) led to a modest increase in the yield of fluoroarene in TFE. We have no evidence yet regarding the identity of the species remaining after fluoride abstraction from the trifluoroethanol, $(CF_2CH_2OH)^+$, or about whether the fluoride abstractions are concerted or stepwise.

Strongly electron-withdrawing substituents decrease the reactivity of benzenediazonium tetrafluoroborate in TFE, and high temperatures or long times are required for their reactions (Table 1). However, we observed that photolysis using a low wattage UV source at room temperature of a dilute solution in TFE effected complete reaction within minutes; similar observations in liquid hydrogen fluoride have already been reported.[3] Analysis by GLC confirmed that the products (aryl fluoride and aryl trifluoroethyl ether) are the same as in the very slow thermal reaction, and that the yields are rather similar (Table 2). It appears, therefore, that photolysis in TFE involves the same aryl cation intermediates as the much slower thermal reaction.

Analytical results using ethanol as solvent confirmed the kinetics results—the reaction is qualitatively different from that in TFE for compounds with electron-withdrawing substituents. It was already known that ethanol can act as a reducing agent for some arenediazonium ions,[10] and that analogous reactions in methanol involve radical intermediates.[11] Additionally, there is a report that the reaction in methanol involves abstraction of the α-hydrogen.[12] Ethanolysis of *m*-fluoro- and *m*-nitro-benzenediazonium tetrafluoroborates gives high yields of the reduction product, and the former gives a very similar product analysis under photolysis at room temperature. The parent compound (X = H) gives very little reduction and (not surprisingly) very little fluorobenzene under these reaction conditions. The product analysis of the parent compound, therefore, does not provide evidence of a change in mechanism upon transfer from TFE to ethanol intimated by the changed kinetics parameters; at the present we have no ready explanation of this. When *m*-nitrobenzenediazonium tetrafluoroborate was solvolysed in [1,1-$^2H_2$]ethanol (CH_3CD_2OH), [3-^{2}H]nitrobenzene was isolated by preparative GLC and identified by ^{1}H NMR spectroscopy and mass spectrometry. Given the characteristically different kinetics parameters for these arenediazonium salts deactivated in the heterolytic pathway by electron-withdrawing substituents and the different product analytical profiles in ethanol, a different mechanism must be involved. Taking into account the previous evidence for reactions in methanol,[11] and proof that the intermediate abstracts an α-hydrogen from the ethanol, we propose the radical chain mechanism in Scheme 3 based upon earlier proposals by DeTar[13] and Bunnett.[11] The reductant in the initiating step has not yet been identified, but is almost certainly ethanol itself.



Scheme 3

We thank the EPSRC for studentships to P. S. J. C., K. M. and B. S., and Zeneca (formerly ICI) for financial support; we also thank Drs J. H. Atherton and D. J. Moody of Zeneca for helpful and stimulating discussions.

Notes and References

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Received in Cambridge, UK, 22nd June 1998; 8/04686G