Photogeneration of HF from Fluoromethoxybenzenes in Aqueous Solution

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Photolysis of fluoromethoxybenzenes in aqueous solution results in a clean substitution of fluoride by water, resulting in the generation of HF, the mechanism of which is believed proceed *via* aryl cations from loss of fluoride ion in the primary photochemical step.

The efficient photogeneration of acids is of interest in industry as photoinitiators in polymerization and in photoimaging.[1] Most notable of these are the triarylsulfonium salts,[1,2] which typically photogenerate HBF_4 or HPF_6. Photosystems that generate bases have also been explored for possible use in related applications.[3,4] We report here the clean photohydrolysis of several fluoromethoxybenzenes which release HF in aqueous solution.

Interest in the photochemistry of methoxy-substituted benzenes[5,6] in aqueous solution prompted us to study several fluoro-substituted derivatives **1–3**. The chloroderivative **4** was also studied for comparison purposes. Photolysis of all of **1–3** in 2 : 1 H_2O–MeCN (50–100 mg; 50–200 ml solvent; Rayonet RPR 100 photochemical reactor; 16 × 254 nm lamps; 0.5–2 h) gave clean conversion (>50%) to the corresponding methoxy-substituted phenols [eqn. (1)]. Photolysis in 100% MeCN gave no observable reaction, even on prolonged irradiation (>5 h) and the substrates could be recovered unchanged. **3** Was the most reactive, as measured by the quantum yield of product formation ($\Phi \approx 0.02$) in 2 : 1 H_2O–MeCN, to give 2,3-dimethoxyphenol (**5**). Substrates **2** and **1** were several times less reactive.

Formation of HF in all reactions was confirmed by detection of fluoride ion using a fluoride ion-selective electrode and by the decrease in pH observed on photolysis. The measured yields of F^- and H^+ corresponded roughly to the conversion of the photochemical reaction, as measured by ^1H NMR.

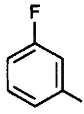
Photolysis of **2** in acid solution (5–30% H_2SO_4; MeCN cosolvent) gave higher yields of **7** (up to three-fold enhancement), compared to runs in the pH region 2–12, indicating acid catalysis of photosubstitution. Photolysis in aqueous D_2SO_4 gave **7** (after H_2O wash) with no detectable deuterium incorporation into the benzene ring. In addition, no deuterium was incorporated into recovered substrate **2** after the photolysis. Control experiments also indicated that **2** was not reactive in acid solutions without photolysis.

Photolysis of **3** in 1 : 1 (v/v) MeOH–H_2O gave an equimolar amount of phenol **5** and methyl ether **6** [eqn. (2)], after normalizing for the concentrations of H_2O and MeOH in the solution. This suggests that the critical intermediate of the reaction displays no selectivity with respect to H_2O and MeOH, indicating that it is probably highly reactive. Control experiments showed that **5** is completely photostable and does not give **6** on photolysis in 1 : 1 H_2O–MeOH.

Additional insight into the reaction mechanism was available by studying the photochemistry of **4**. Photolysis of **4** in 1 : 1 H_2O–CH_3CN gave the photosubstitution product **7** (40%) as well as 1,3-dimethoxybenzene **8** (8%) [eqn. (3)]. Photolysis of **4** in 1 : 1 H_2O–Pr^iOH resulted in enchancement of the yield of **8** to >40%. These results are consistent with reaction *via* initial aryl–Cl bond homolysis of **4**. Escape from the solvent cage and subsequent hydrogen abstraction from solvent gives **8**. Electron transfer within the geminate cage gives rise an ion pair which is responsible for **7**.

Photosubstitution of the fluoro group in aromatic systems is not common.[7] Those that have been reported involve the use of the highly activating nitro group in the presence of powerful nucleophiles (*e.g.* ^-OH or ^-OMe). The mechanisms of such reactions involve initial nucleophilic attack of the benzene ring by nucleophile, forming a σ-adduct, followed by release of the fluoride ion. There is compelling evidence to indicate that the primary photochemical step of reaction of **1–3** is aryl–F heterolysis *via* S_1† which is assisted by general acid, *viz*. H_2O in neutral solution or hydronium ion in aqueous H_2SO_4 (Scheme 1). The first formed intermediate is an aryl cation, which may be stabilized by the methoxy groups *via* a carbenoid-type resonance structure. Nucleophilic attack by solvent (H_2O or MeOH) leads to the observed product.

As far as we are aware, the only other system which reacts *via* direct photochemical aryl–F heterolysis was that reported by Yang *et al.*[9] for 4-fluoroindoles. It is well known that the 4-position of indoles is electron-rich in S_1.[10–13] This fact was utilized to explain the facility of Ar–F bond heterolysis from such systems.[9] We have shown in this work that such a mechanism appears to be general when the benzene ring is substituted with electron-donating methoxy groups. Studies aimed at enhancing the quantum yield of the reaction and delineating the mechanistic details are in progress.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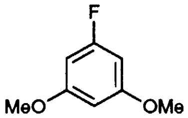
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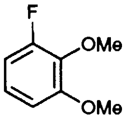
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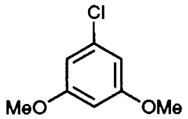
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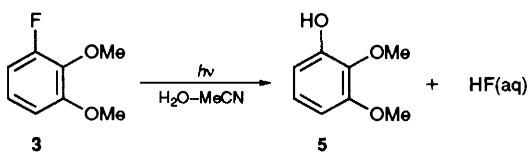
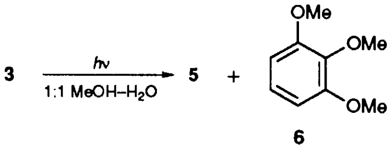
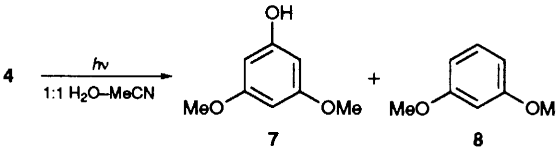


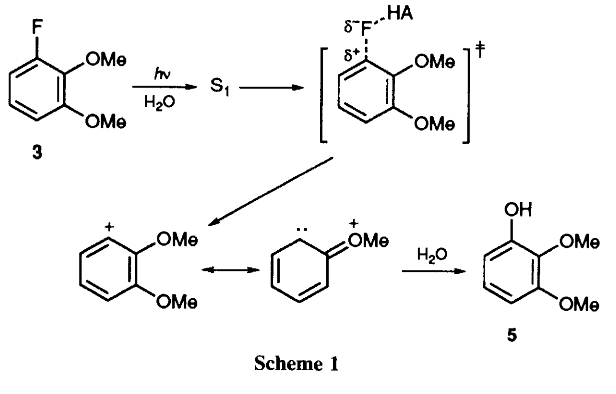
3 **5** (1)



6 (2)



7 **8** (3)



Scheme 1

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References

1 J. L. Dektar and N. P Hacker, *J. Am. Chem. Soc.*, 1990, **112**, 6004 and references therein.
2 F. D. Saeva, *Top. Curr. Chem.*,1990, **156**, 59.
3 J. F. Cameron and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1991, **113**, 4303.
4 J. F. Cameron and J. M. J. Fréchet, *J. Org. Chem.*, 1990, **55**, 5919.
5 P. Wan and D. Shukla, *Chem. Rev.*, 1993, **93**, 571.
6 R. Pollard, S. Wu, G. Zhang and P. Wan, *J. Org. Chem.*, 1993, **58**, 2605.
7 J. Cornelisse and E. Havinga, *Chem. Rev.*, 1975, **75**, 353.
8 S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973.
9 N. C. Yang, A. Huang and D. H. Yang, *J. Am. Chem. Soc.*, 1989, **11**, 8060.
10 I. Saito, H. Sugiyama, A. Yamamoto, S. Muramatsu and T. Matsuura, *J. Am. Chem. Soc.*, 1984, **106**, 4286.
11 I. Saito, S. Muramatsu, H. Sugiyama, A. Yamamoto and T. Matsuura, *Tetrahedron Lett.*, 1985, 5891.
12 H. Shizuka, M. Serizawa, H. Kobayashi, K. Kameta, H. Sugiyama, T. Matsuura and I. Saito, *J. Am. Chem. Soc.*, 1988, **110**, 1726.
13 H. Shizuka, M. Serizawa, T. Shimo, I. Saito and T. Matsuura, *J. Am. Chem. Soc.*, 1988, **110**, 1930.

Footnote

† Homolysis of Ar–F bonds is prohibitive since this is a very strong bond [*ca.* 125 kcal mol^{-1},[8] noting that the singlet-state energy of dimethoxybenzenes is estimated to be *ca.* 100 kcal mol^{-1} (onset of emission at 280 nm)]. Heterolytic cleavage is facilitated by the solvation energy available in the released fluoride ion in aqueous solution. The singlet state appears to be reactive since these compounds are very weakly fluorescent, unlike the simple (non-fluoro-substituted) methoxybenzenes.