Proton Transfer to the Fluorine Atom in Fluorobenzene: a Dramatic Temperature Dependence in the Gas Phase

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Collisionally induced decomposition mass spectrometry has shown that during the gas phase reaction of CH_5^+ with fluorobenzene at temperatures <300 K, a proton transfers preferentially to the F atom even though its proton affinity is *ca.* 180 kJ mol^{-1} less than the ring.

Protonated species postulated as transients in solution can often be prepared and studied by mass spectrometry (m.s.) in the gas phase.[1] Usually, however, structures can be assigned only by indirect means.[2] The best method for determining the thermodynamically most favourable protonation site is to match molecular orbital (M.O.) calculations on postulated structures against relative proton affinity (P.A.) measurements (provided the molecule is not too large).[3] P.A. correlation methods have also been used.[4] None of these methods takes into account kinetic effects[2] during proton transfer.

Cooks *et al.*[2] have investigated the use of collisionally induced decomposition (c.i.d.) m.s. to determine protonation sites more directly. Of special interest for substituted aromatic compounds is the competition for the proton between the ring and a substituent X. It is thought that a peak in the c.i.d. spectrum corresponding to the loss of HX from the protonated molecule ought to be a measure of the degree of protonation on the substrate itself. Unfortunately, conclusions based on this premise are usually ambiguous[2] because the possibility always remains that, under the influence of collisional activation, proton migraton occurs prior to decomposition. Even deuterium labelling c.i.d. experiments can be ambivalent because of possible isotope exchange, in parallel with proton transfer, in the ion source.

We report here interesting observations from a c.i.d. study of proton transfer reactions involving fluorobenzene. The spectra are unusual because they exhibit a strong temperature dependence when CH_5^+ is the proton donor. Because of this it is possible to identify directly from the spectra species which are protonated on the fluorine atom, the lowest proton affinity site on the molecule PhF.

The protonated species were generated in a variable temperature chemical ionisation source, and c.i.d. spectra were recorded in the usual way after collision of the mass selected ion beam in a reverse geometry mass spectrometer.[5] The only experimental parameters significantly affecting the spectra were the conditions in the ion source.

Table 1. Comparison of calculated and experimental proton affinities (kJ mol^{-1}) over the ring and and substituent of fluorobenzene.

Site of protonation: w.r.t. F	*F Atom*	*Ipso*	*Ortho*	*Meta*	*Para*
MNDO:	679	670	732	704	736
ab initio (4–31G):	580	711	771	746	780
Experiment:	552–601[a]			760[7,8]	

[a] This work.

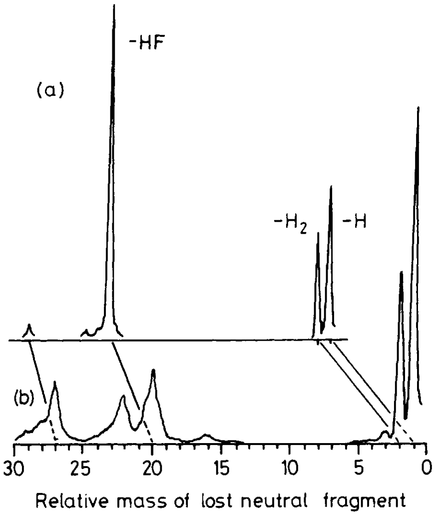

Figure 1. C.i.d. mass analysed ion kinetic energy spectra of $(PhF)H^+$ formed by proton transfer from CH_5^+ to (a) the F atom, source temperature $T = 30\,°C$, sample pressure low; (b) the benzene ring, $T = 350\,°C$. Collision gas (analyser ion gauge) pressure = 2×10^{-6} Torr (N_2).

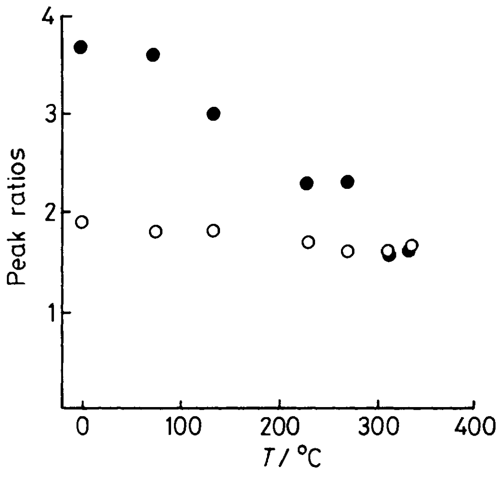

Figure 2. Variation of peak (neutral fragment loss) height ratios with temperature, all other conditions kept constant: $[CH_4]/[PhF]$ *ca.* 1000 : 1; source pressure adjusted so that the ion intensity ratio, $97^+/96^+$, in the source *ca.* 1 : 1; collision gas ion gauge pressure *ca.* 2×10^{-6} Torr. ● HF/H_2; ○ H/H_2.

Figure 1 shows the spectra of fluorobenzene protonated by CH_5^+ at two different temperatures. They consist principally of three peaks assigned to the c.i.d. losses of H, H_2, and HF from the parent ion. There is in addition a low intensity 'baseline' spectrum containing peaks assigned to sequential multiple decomposition processes, such as those at the lost masses of 22 and 27, corresponding to much higher energy processes. At high source temperatures the spectrum [Figure 1(b)] is fully consistent with ring protonation because there is very little HF loss. This was expected because of the indirect evidence[4] that the ring carbon atoms are the most favoured site of protonation. It was surprising therefore to see that when the source is cooled the loss of HF becomes the most dominant peak in the spectrum [(Figure 1(a)]. Since the proton must surmount an energy barrier of >180 kJ mol^{-1} (see below) in order to pass from the ring to the substituent, collision induced migration prior to decomposition must be less probable in ions of lower internal energy. If the HF loss peak reflected a migration process it would decrease in abundance at lower temperatures, opposite to the observed behaviour. These spectra therefore clearly demonstrate that the proton transfer from CH_5^+ occurs directly to the F atom at lower temperatures, despite being the least favoured site on the molecule.

A P.A. map of PhF was constructed using both semi-empirical (MNDO) and *ab-initio* (4-31G basis set) calculations[6] (see Table 1). There is relatively good agreement between the calculations and the experimental value[7] for the ring carbon atoms, but there is a large discrepancy at the F atom, although both show the F site to be considerably lower in P.A. than the ring. In experiments using convenient reagents (C_2H_6, H_2O, and MeOH with P.A.'s of 601, 697, and 761 kJ mol^{-1} respectively[7]), all of higher P.A. than CH_4 (552 kJ mol^{-1})[7] the ring, but not the F atom, was readily protonated in each case. This is consistent with the actual P.A. of the F atom site being in the region 552—601 kJ mol^{-1} in agreement with the *ab initio* result.

The fact that the highest energy species is favoured at the lowest temperatures is clearly a kinetic effect. It can only happen if the incoming proton is channelled, by the shape of the reaction potential energy surface, over the F atom. This allows it to become trapped in the local P.A. well, before penetrating the much deeper and broader[8] well of the benzene ring. Qualitatively this is readily understood in terms of classical ion–dipole interaction theory[9] because the F atom forms the negative end of the fluorobenzene dipole, and the interaction is at a maximum when the ion and dipole are aligned. Furthermore the degree of alignment is higher at lower temperatures. The theory predicts the total capture collision rate constant to be only weakly temperature dependent, whilst it is clear from Figure 2 that the proton transfer channel leading to the F atom is strongly temperature dependent. Other proton transfer reactions with a strong negative temperature dependence have been reported.[10] It is possible here that an intermediate stage is the formation of a weakly bound proton adduct (an ion corresponding to $CH_4{\cdot}PhF{\cdot}H^+$ is seen as a minor peak in the conventional methane chemical ionisation spectrum), because the rate constants for association reactions often exhibit a strong negative temperature dependence.[11]

It has been suggested previously[12] that CH_5^+ in particular attacks fluorobenzene directly at the substituent. This is now confirmed. Experiments on the fluorotoluenes showed similar behaviour, but the spectra of the corresponding chloro compounds were inconclusive because their c.i.d. spectra are dominated by the loss of HCl under all conditions. Clearly, in this case ring to substituent proton migration occurs much more readily. Other reports of c.i.d. spectra affected dramatically by the ion source conditions have appeared recently. For example, Cooks *et al.*[13] report a dramatic temperature effect, but it is in the electron impact–c.i.d. spectrum of pentan-2-one, reflecting the changing equilibrium concentrations of keto–enol forms in the sample. Harrison *et al.*[14] found that the chemical ionisation–c.i.d. spectrum of protonated heroin is dependent on the protonating agent, reflecting a kinetic influence over the protonation site. The present spectra provide direct and clear evidence of kinetic control over the site of protonation on an ambident molecule in the gas phase, even when there is a very large difference in the proton affinities of the competing sites.

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References

1 W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, 1972, **94**, 6901; G. A. Olah, J. S. Staral, G. Ascencio, G. Liang, D. A. Forsyth, and G. D. Mateesscu, *ibid.*, 1978, **100**, 6299; R. W. Taft, in 'Kinetics of Ion-Molecule Reactions,' ed. P. Ausloos, Plenum Press, New York, 1979, p. 271.

2 K. V. Wood, D. J. Burinsky, D. Cameron, and R. G. Cooks, *J. Org. Chem.*, 1983, **48**, 5236; and references therein.

3 W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, '*Ab Initio* Molecular Orbital Theory,' Wiley, New York, 1986, ch. 6, pp. 310—323; M. J. S. Dewar and K. M. Dieter, *J. Am. Chem. Soc.*, 1986, **108**, 8075.

4 Y. K. Lau, K. Nishizawa, A. Tse, R. S. Brown, and P. Kebarle, *J. Am. Chem. Soc.*, 1981, **103**, 6291; M. T. Fernandez, K. R. Jennings, and R. S. Mason, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 159.

5 R. P. Morgan, J. H. Beynon, R. H. Bateman, and B. N. Green, *Int. J. Mass Spectrom. Ion Phys.*, 1978, **28**, 171.

6 All calculations were performed using Quantum Chemistry Program Exchange packages, either Gaussian 76 (*ab initio*) or MNDO (semi-empirical).

7 S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695.

8 R. S. Mason, M. T. Fernandez, and K. R. Jennings, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 89.

9 D. P. Ridge, in 'Structure/Reactivity and Thermochemistry of Ions,' eds. P. Ausloos and S. G. Lias, Reidel, Dordrecht, 1987, p. 1.

10 A. A. Vigianno, J. F. Paulson, and F. Dale, in reference 9, p. 19; T. F. Magnera and P. Kebarle, in 'Ionic Processes in the Gas Phase,' ed. M. A. Almoster Ferreira, Reidel, Dordrecht, 1984, p. 135.

11 J. I. Brauman, in 'Kinetics of Ion-Molecule Reactions,' ed. P. Ausloos, Plenum Press, New York, 1979, p. 153; M. Meot-Ner, in 'Gas Phase Ion Chemistry,' ed. M. T. Bowers, Academic Press, New York, 1979, vol. 1, ch. 6, 197—221.

12 F. Cacace and M. Speranza, *J. Am. Chem. Soc.*, 1976, **98**, 7299; H. Leung and A. G. Harrison, *J. Am. Chem. Soc.*, 1979, **102**, 1623.

13 K. V. Wood, S. A. McLuckey, and R. G. Cooks, *Org. Mass Spectrom.*, 1986, **21**, 11.

14 S. Nacson, A. G. Harrison, and W. R. Davison, *Org. Mass Spectrom.*, 1986, **21**, 317.