# Mechanism of Acetylium Ion Formation from the Ambident Base Acetic Trifluoromethanesulphonic Anhydride

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*Summary* Acetic trifluoromethanesulphonic anhydride is an ambident base which is protonated on either the carbonyl group or on the sulphonyl oxygen atom; it dissociates in very strong acid media to form the acetylium ion.

Recently it was reported[1] that *p*-methylanisole is protonated either on oxygen or the ring depending upon solvent acicity. We report here a similar observation with the mixed anhydride $MeCO-O-SO_2-CF_3$.

The room temperature i.r. spectra of mixtures of acetic anhydride and trifluoromethanesulphonic acid show three $\nu(C{=}O)$ bands at 1815, 1680, and 1875 cm$^{-1}$, attributed respectively to the mixed anhydride, the mixed anhydride with the carbonyl group protonated, and the mixed anhydride with a sulphonyl group protonated. The variation of the intensities of these bands as a function of the molar fraction of trifluoromethanesulphonic acid is given in the Figure. As the composition of the mixture is varied from one in which acetic anhydride predominates to one in which trifluoromethanesulphonic acid predominates,

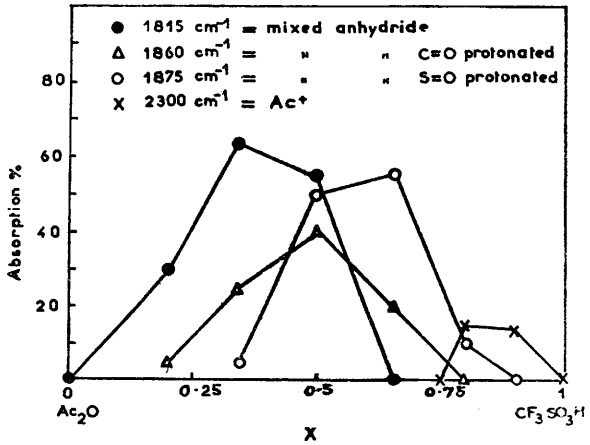

Figure. *Intensity of* $\nu(C{=}O)$ *as a function of the molar fraction* X *of trifluoromethanesulphonic acid in solventless mixtures of acetic anhydride and trifluoromethanesulphonic acid* (AgCl cell, 7 $\mu$m).

protonation first takes place on the carbonyl group of the mixed anhydride, then on the sulphonyl group, and finally the acetylium ion [ν(C = O) 2300 cm$^{-1}$] is formed.[2]

Kinetic constants for the formation of the acetylium ion can be obtained from the temperature dependence (−30 to +20°C) of the n.m.r. spectra of solutions containing this ion. The values obtained for trifluoromethanesulphonic acid and also fluorosulphonic acid are given in the Table. The positive $\Delta S^‡$ values indicate that the rate-determining step is not heterolysis of a neutral molecule to give two oppositely charged ions, but rather heterolysis of the protonated mixed anhydride (the leaving group being a neutral solvent molecule). The higher rate constant for fluorosulphonic acid, a stronger acid than trifluoromethanesulphonic acid,[3] and also the rate decrease in the presence of salts are mainly a result of the change in $\Delta S^‡$. It seems that the solvent intervenes in the transition state, and since the reaction rate increases with solvent acidity, electrophilic assistance of the single C–O bond rupture is suggested, by a mechanism similar to that envisaged for amide hydrolysis in strong acid media[4] for which it was postulated that the step involving fission of the protonated amide is generally catalysed by strong acids.

TABLE. *Rate constants and thermodynamic activation parameters for the formation of the acetylium ion at* 0 °C.

| | | $k_1 \times 10^{-3}$/s$^{-1}$ | $\Delta H^‡$/kcal mol$^{-1}$ | $\Delta S^‡$/cal K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|
| A | $CF_3SO_3H$–$Ac_2O$[a] | 0·80 ± 0·05 | 16·3 ± 0·3 | 14·3 ± 1·0 |
| B | $CF_3SO_3H$–$Ac_2O$–$CF_3SO_3Na$[b] | 0·105 ± 0·005 | 15·1 ± 0·4 | 6·2 ± 1·4 |
| C | $FSO_3H$–$Ac_2O$[c] | 2·4 ± 0·1 | 16·5 ± 0·4 | 16·9 ± 1·2 |

[a] 1:0·147. [b] 1:0·147:0·144. [c] 1:0·134.

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