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THE INTERACTION OF HEXAFLUOROACETIC ANHYDRIDE WITH METHANE SULPHONIC ACID AND WITH SULPHURIC ACID

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Abstract - The reaction between methanesulphonic acid and hexafluoroacetic anhydride yields methanesulphonyltrifluoroacetic anhydride.

The reaction of an excess of sulphuric acid with hexafluoroacetic anhydride in a 1:1 mixture of nitromethane and dichloromethane results in the formation of trifluoroacetyl hydrogen sulphate. However, at higher concentrations of hexafluoroacetic anhydride, bis-trifluoroacetyl sulphate is formed. The rates of the reactions are dependent on the concentration of hexafluoroacetic anhydride and independent of the concentration of the acids when these are in excess. At low concentration of sulphuric acid a more complex relationship is observed.

Studies of interactions between acetic anhydride and sulphuric acid have been carried out as early as 1881[1-4]. It was suggested that the reaction resulted initially in a mixed anhydride which subsequently rearranged to sulphoacetic acid (eqn. 1 and 2).

$$(CH_3CO)_2O + H_2SO_4 \rightleftharpoons CH_3COOSO_2OH + CH_3CO_2H \qquad (1)$$

$$CH_3COOSO_2OH \rightleftharpoons HOSO_2CH_2CO_2H \qquad (2)$$

The most detailed study of this reaction was conducted by Jeffery and Satchell who investigated both acylation and formation of sulphoacetic acid in the presence of sulphuric acid[5]. They observed that the concentration of sulphuric acid had to be sufficiently small, so as not to give rise to a medium effect if sulphoacetic acid was to be formed. Secondly, the concentration dependency on acetic anhydride of both the rate of formation of sulphoacetic acid and acylation of phenol was identical. This therefore implied that both reactions follow a similar pathway. They then suggested a mechanism that takes into account the dibasic nature of sulphuric acid, the two observations above and (3):

$$2(CH_3CO)_2O + H_2SO_4 = (CH_3COO)_2SO_2 + 2CH_3CO_2H \qquad (3)$$

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The acylation of phenol would then involve a nucleophilic substitution reaction on both CH_3COOSO_2OH and $(CH_3CO_2)_2SO_2$. Similarly, any disproportionation of these into sulphur trioxide leads to the formation of sulphoacetic acid through the reaction with acetic acid. Conductivity studies[6] on a 2:1 mixture of acetic anhydride and sulphuric acid later confirmed the above results. ^{1}HNMR spectroscopy of this mixture was used to demonstrate the existence of acetylium ions. Although the reaction between hexafluoroacetic anhydride and sulphuric acid has not previously been studied its interaction with carboxylic acids has received a lot of attention. Cryoscopic measurements[7] of hexafluoroacetic anhydride dissolved in acetic acid ($R = CH_3$) showed a Van't Hoff factor of $i = 2$ instead of 3. These results are in agreement with the formation of the mixed anhydride as in eqn. (4) rather than acetic anhydride as in eqn. (5).

$$RCO_2H + (CF_3CO)_2O \rightleftharpoons RCOOCOCF_3 + CF_3CO_2H \qquad (4)$$

$$2RCO_2H + (CF_3CO)_2O \rightleftharpoons (RCO)_2O + 2CF_3CO_2H \qquad (5)$$

Changes observed in the infra-red absorption spectrum in the carbonyl region also supported these observations; new carbonyl peaks appeared at the expense of the carbonyl peaks of the components and these were attributed to the formation of the unsymmetrical anhydrides[8]. Conductivity studies[9] were also in agreement with eqn. (4). These showed an initial rise in conductivity to a maximum which was attributed to the dissociation of the mixed anhydride (eqn. (6)). The subsequent decrease in conductivity to a constant value may be ascribed to disproportionation to the two less conducting symmetrical anhydrides (eqn. (7)).

$$CF_3COOCOCH_3 \rightleftharpoons CH_3CO^+ + CF_3CO_2^- \qquad (6)$$

$$2CH_3COOCOCF_3 \rightleftharpoons (CH_3CO)_2O + (CF_3CO)_2O \qquad (7)$$

EXPERIMENTAL

Purification of reagents

(1) Nitromethane

Spectroscopic grade of nitromethane was extracted 3 times with a solution containing 2% sodium bicarbonate followed by washing with sodium sulphate, 5% sulphuric acid, again aqueous sodium bicarbonate and finally with water. It was dried with calcium sulphate (Drierite) overnight and then distilled. The distillate was kept in a brown bottle over molecular sieves type 4A for 1 week.

(2) Dichloromethane

Dichloromethane was shaken with portions of sulphuric acid until the acid layer remained colourless. It was washed with water then with aqueous sodium carbonate and again with water. Thereafter, it was pre-dried with calcium chloride and then distilled from calcium sulphate (Drierite). The resulting distillate was stored in a brown bottle over molecular sieves of the type 4A.

(3) Methanesulphonic acid

The water was removed by an azeotropic distillation with sodium-dried benzene, the acid then carefully distilled under reduced pressure (b.p. 106°C at 0.1 mmHg) and the distillate kept in a brown bottle in the dark.

(4) Sulphuric Acid

Sulphur trioxide was distilled from oleum into 98% sulphuric acid (Analar) in an all glass apparatus until a strong 'Analar' was obtained. This colourless sulphuric acid was distilled into a known weight of sulphuric acid to make a weak oleum (approx. 102%). This oleum was standardised by titrating with standard NaOH using methyl orange as indicator. The value obtained was used as a guide to convert the oleum to 100% sulphuric acid by adding successive amounts of water until a maximum freezing point was obtained (10.3°C).

(5) Hexafluoroacetic anhydride

Hexafluoroacetic anhydride was distilled over P_2O_5 and the distillate collected over P_2O_5. The distillate was then redistilled (b.p. 38° - 39°C) and again collected over P_2O_5. To remove dissolved gases the anhydride was frozen in liquid nitrogen and then evacuated to about 0.1 mmHg, the anhydride allowed to return to room temperature and the vacuum released. Solutions of this anhydride were used to determine the extinction coefficient at 1910 cm^{-1} for concentrations ranging from 0.01 to 0.04 $mol.dm^{-3}$ (ext. coeff. = 25.64 $mol^{-1}dm^3mm^{-1}$).

Method of analysis

All the reagents were kept in a dry box containing a large dish of P_2O_5. The dry box was saturated with nitrogen predried by passing through a series of drying towers containing, respectively H_2SO_4, $CaCl_2$ (anhydrous) and indicating silica gel. The preparation of all solutions was carried out in the dry box.

Infra-red spectra were recorded using a grating spectrophotometer (Perkin-Elmer Model 127). The infra-red cells were fitted with silver chloride windows, a 1 mm teflon spacer and surrounded by a water jacket through which water was circulated at 24°C ± 0.5°C. This temperature was the same as that of the dry box. Before the analysis, all pipettes, volumetric flasks, syringes and the reaction cells were oven-dried and then allowed to equilibriate for 30 minutes in the dry box. All mixings of solutions were carried out inside the dry box.

RESULTS AND DISCUSSION

Although the interaction between methane sulphonic acid and acetic anhydride has been examined[10] as part of the C-acylation mechanism, its interaction with hexafluoroacetic anhydride has so far not been studied. The present studies were carried out in order to facilitate an understanding of the mechanism of sulphonylation reactions of aromatic hydrocarbons in the presence of hexafluoroacetic anhydride and a sulphonic acid[11,12].

If the reaction of methanesulphonic acid was identical to those of carboxylic acids, it was expected that a mixed anhydride would be formed as in eqn. (8). However, attempts to isolate the unsymmetrical anhydride were unsuccessful even at low temperature and reduced pressure because of disproportionation to the symmetrical anhydrides (eqn. (9)).

$$(CF_3CO)_2O + CH_3SO_3H \rightleftharpoons CH_3SO_2OCOCF_3 + CF_3CO_2H \qquad (8)$$

$$2CH_3SO_2OCOCF_3 \rightleftharpoons (CH_3SO_2)_2O + (CF_3CO)_2O \qquad (9)$$

Kinetic studies were then carried out on mixtures of hexafluoroacetic anhydride and methanesulphonic acid in dichloromethane. Infra-red spectroscopy was used to monitor the C=O stretching vibration of hexafluoroacetic anhydride at 1910 cm^{-1}. All reactions were carried out under anhydrous conditions in balanced thermostated cells fitted with silver chloride windows.

The rates of reaction were found to be independent of the concentration of methanesulphonic acid and showed a first-order dependence on hexafluoroacetic anhydride (HFAA) concentration, viz. (eqn. (10)).

$$-\frac{d[HFAA]}{dt} = k_{obs}[HFAA] \qquad (10)$$

The results showing the observed rate coefficients for three different concentrations of methanesulphonic acid at constant concentration of hexafluoroacetic anhydride (0.03 mol. dm^{-3}) and constant temperature (24°C ± 0.5°C) are tabulated below (Table 1). (The rate coefficients, k_{obs}, are the mean of three separate determinations at each concentration of methanesulphonic acid).

Table 1

Concentration of methanesulphonic acid/(mol.dm^{-3})	$k_{obs}/10^{-4}s^{-1}$
0.03	2.80
0.05	2.74
0.10	2.81

Mean $k_{obs} = 2.79 \times 10^{-4}s^{-1}$

These results are consistent with the mechanism in which the rate-determining step is the slow heterolysis of the protonated anhydride, formed as in eqn. (11) to the trifluoroacetylium ion and trifluoroacetic acid (eqn. (12)). This is followed by the reaction of the trifluoroacetylium ion with methanesulphonic acid to form the protonated unsymmetrical anhydride (eqn. 13)).

$$(CF_3CO)_2O + CH_3SO_3H \overset{K_1}{\rightleftharpoons} (CF_3CO)_2OH^+ + CH_3SO_3^- \qquad (11)$$

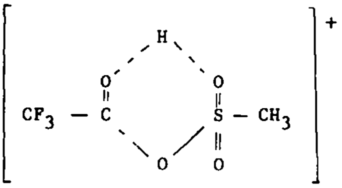
$$(CF_3CO)_2OH^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CF_3CO^+ + CF_3CO_2H \qquad (12)$$

$$CF_3CO^+ + CH_3SO_3H \overset{k_3}{\rightleftharpoons} CH_3SO_2O^+H(COCF_3) \qquad (13)$$

$$CH_3SO_2O^+H(COCF_3) \overset{K_4}{\rightleftharpoons} CH_3SO_2OCOCF_3 + H^+ \qquad (14)$$

$$CH_3SO_2O^+H(COCF_3) \rightleftharpoons CH_3SO_2^+ + CF_3CO_2H \qquad (15)$$

In the presence of a suitable substrate, e.g. an aromatic hydrocarbon, deprotonation may not occur (eqn. (14)) but rather heterolysis giving the methyl sulphonium ion (eqn.(15)). Alternatively the aromatic hydrocarbon may react directly with the protonated mixed anhydride (eqn. (16)) particularly if it has a structure analogous to that which has been suggested for the product of the interaction of acetic anhydride with trifluoromethylsulphonic acid[13] in which proton transfer can occur readily between the carbonyl and sulphonyl oxygens.



$$\xrightarrow[-H^+]{ArH} ArSO_2CH_3 + CF_3CO_2H \qquad (16)$$

Application of the steady state hypothesis to the trifluoroacetylium ion gives:

$$k_{obs} = \frac{K_1\ k_2\ k_3\ [CH_3SO_3H]^2}{(1 + K_1\ [CH_3SO_3H])(k_3[CH_3SO_3H] + k_{-2}[CF_3CO_2H])} \qquad (17)$$

If the equilibrium in eqn. (11) favours the protonation of the hexafluoroacetic anhydride so that $K_1[CH_3SO_3H] > 1$ and $k_3 >> k_{-2}$ then $k_{obs} \sim k_2$. (A value of $K_1 = 200$ gives only a ±5% variation in $K_1[CH_3SO_3H]/(1 + K_1[CH_3SO_3H])$ for a change in $[CH_3SO_3H]$ from 0.05 to 0.03 or to 0.10 mol. dm^{-3}).

Table 2

% nitromethane in dichloromethane	$k_{obs}/10^{-3}s^{-1}$
0	0.279
10	0.981
25	2.56
37	8.91
50	22.8

In Table 2 a relationship between the observed rate coefficients and the polarity of the solvents obtained by an increase in the percentage of nitromethane in dichloromethane, is shown. The results further support the proposed mechanism, i.e. the more polar the solvent the faster the reaction proceeds and the easier the dissociation of the protonated anhydride (eqn. (12)) occurs.

A similar dependence of the reaction rate on hexafluoroacetic anhydride was found in the reaction of mesitylenesulphonic acid with hexafluoroacetic anhydride. The rate coefficient in 20% nitromethane (mesitylenesulphonic acid is insoluble in dichloromethane) of the reaction of mesitylenesulphonic acid (0.03, 0.05 and 0.10 mol.dm^{-3}) and hexafluoroacetic anhydride (0.03 mol.dm^{-3}) was calculated to be 4.10 x $10^{-4}s^{-1}$. This value is lower than that extrapolated from a plot of the results in Table 2 (1.72 x $10^{-3}s^{-1}$), although according to eqn. (12) the rates should be the same. The reason for the slower rate is not yet easily interpreted. However, as methanesulphonic acid is a stronger acid than mesitylenesulphonic acid, it is possible that the protonation, (eqn. (11)), will be even more complete with methanesulphonic acid.

Before examining the kinetics of the reaction of hexafluoroacetic anhydride with sulphuric acid an application of the Job's method[14] showed that 2 molecules of hexafluoroacetic anhydride react with 1 molecule of sulphuric acid.

The initial kinetic studies involved measuring the rate of the reaction of 0.03 mol.dm^{-3} of hexafluoroacetic anhydride with varied but excess amounts of sulphuric acid in a 1:1 mixture of nitromethane and dichloromethane. Table 3 shows values of the rate coefficients (k_{obs}) obtained with different concentrations of sulphuric acid. The behaviour of these solutions resembled those of sulphonic acids being independent of the concentration of sulphuric acid and only dependent on the concentration of hexafluoroacetic anhydride. As with sulphonic acids the rate determining step was found to be the heterolysis of the protonated hexafluoroacetic anhydride(eqn. (12)), followed by the rapid formation of mixed monoanhydride (eqn. (19) and (20)):

$$(CF_3CO)_2O + H_2SO_4 \overset{K_5}{\rightleftharpoons} (CF_3CO)_2O^+H + HSO_4^- \quad (18)$$

The formation of the trifluoroacetylium ion then occurs as before (eqn.(12)).

$$CF_3CO^+ + H_2SO_4 \xrightarrow{k_6} HOSO_2O^+H(COCF_3) \quad (19)$$

$$HOSO_2O^+H(COCF_3) + HSO_4^- \overset{K_7}{\rightleftharpoons} HOSO_2OCOCF_3 + H_2SO_4 \quad (20)$$

Table 3

Concentration of sulphuric acid/(mol.dm.$^{-3}$)	$k_{obs}/10^{-4}s^{-1}$
0.15	4.60 ± 0.05
0.25	5.10 ± 0.05
0.40	4.96 ± 0.05

Mean k_{obs} = (4.89 ± 0.32) x $10^{-4}s^{-1}$

However, when the concentration of sulphuric acid was reduced to 0.06 mol.dm^{-3}, the rate suddenly decreased to 2.47 x $10^{-4}s^{-1}$, i.e. almost half the average observed in large excess of H_2SO_4. Further decrease in sulphuric acid concentration to 0.03 and 0.015 mol.dm^{-3} showed a deviation from first order kinetics. Application of the steady state hypothesis to the trifluoroacetylium ion gives:

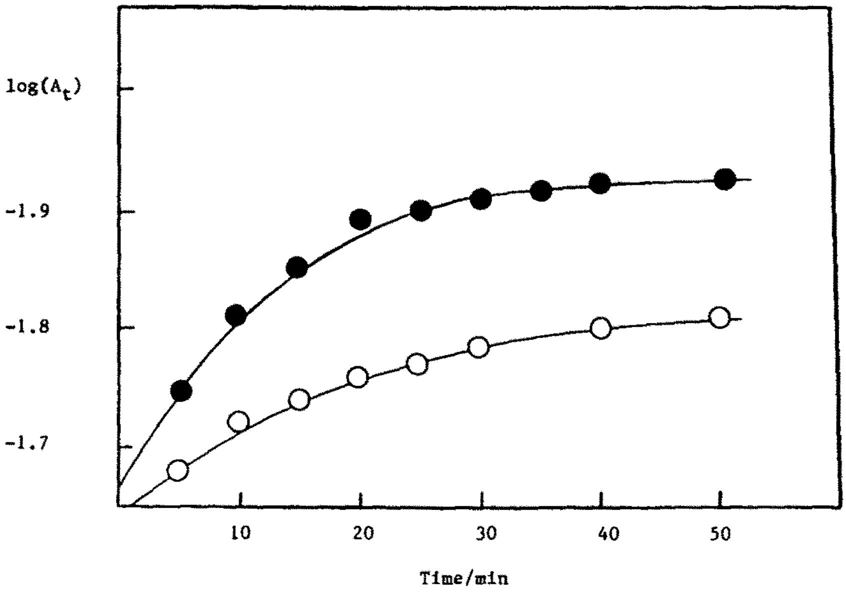
$$\text{rate} = \frac{K_5\ k_2\ k_6\ [H_2SO_4]^2[(CF_3CO)_2O]}{(1 + K_5\ [H_2SO_4])(k_6[H_2SO_4] + k_{-2}\ [CF_3CO_2H])} \quad (21)$$

With a large excess of sulphuric acid, $k_6[H_2SO_4] > k_{-2}\ [CF_3CO_2H]$ and $K_5[H_2SO_4] > 1$. Therefore the rate $\sim k_2[(CF_3CO)_2O]$ i.e. $k_{obs} \sim k_2$. With lower concentrations of sulphuric acid, the rate of formation of the protonated mixed anhydride (eqn. (19)), is reduced thus:

$$\text{rate} = \frac{k_2\ k_6\ [H_2SO_4]\ [(CF_3CO)_2O]}{k_{-2}\ [CF_3CO_2H]} \qquad (22)$$

This is consistent with the behaviour shown in Fig. 1.

Fig. 1



$[H_2SO_4]$: ● 0.03 mol.dm^{-3}, ○ 0.015 mol.dm^{-3}

$(A_t) = [(CF_3CO)_2O]$ at time = t min.

When the reaction was carried out in a 1:9 mixture of CH_3NO_2 and CH_2Cl_2, the reaction rate was considerably slower. With the concentration of hexafluoroacetic anhydride at 0.03 mol.dm^{-3} and that of sulphuric acid at 0.015 mol.dm^{-3}, the reaction showed an initial observance of the first order rate law and a deviation from it when 30% of the reaction had occurred. When equimolar quantities were used (0.03 mol.dm^{-3}) the deviation occurred only when 50% of the hexafluoroacetic anhydride had been consumed. These results have to be interpreted taking into account the conversion of the mixed monoanhydride into the dianhydride (eqn. (23) and (24)):

$$CF_3CO^+ + HOSO_2OCOCF_3 \xrightarrow{k_8} CF_3COOSO_2O^+H(COCF_3) \qquad (23)$$

$$HSO_4^- + CF_3COOSO_2O^+H(COCF_3) \overset{K_9}{\rightleftharpoons} (CF_3COO)_2SO_2 + H_2SO_4 \qquad (24)$$

Deriving the rate law for the disappearance of the hexafluoroacetic anhydride and application of the steady state approximation to the concentration of trifluoroacetylium ion gives:

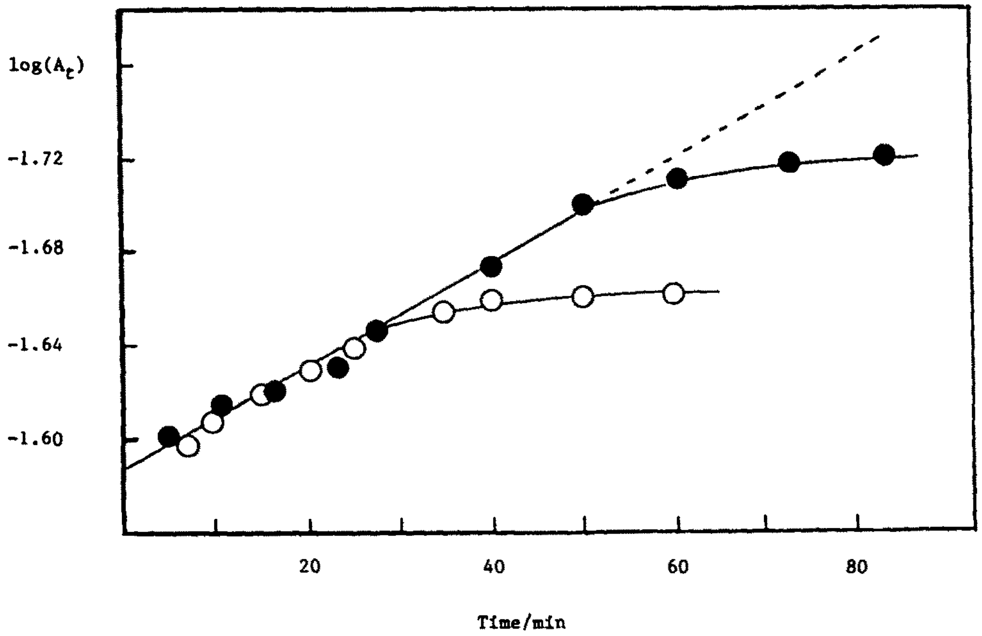
$$\text{rate} = \frac{K_5k_2[(CF_3CO)_2O][H_2SO_4](k_6[H_2SO_4] + k_8[HOSO_2OCOCF_3])}{(1+K_5[H_2SO_4])(k_{-2}[CF_3CO_2H]+k_6[H_2SO_4]+k_8[HOSO_2OCOCF_3])} \qquad (25)$$

In the less polar medium both K_5 and k_2 would be expected to be smaller. In the early stages of the reaction $k_8[HOSO_2OCOCF_3] << k_6 [H_2SO_4]$ so if $k_6[H_2SO_4]$ is now greater than $k_{-2}[CF_3CO_2H]$ then $k_{obs} \sim k_2$. However, as the concentration of sulphuric acid reduces through conversion to the mixed monoanhydride,the reaction in eqn. (23) becomes more significant and there is a reduction in the reaction rate given by:

$$\text{rate} = \frac{k_2k_8 \; [(CF_3CO)_2O] \; [HOSO_2OCOCF_3]}{k_{-2} \; [CF_3CO_2H]} \qquad (26)$$

The deviation from first-order kinetics thus predicted is illustrated in figure 2.

Fig. 2



$[H_2SO_4]$: ● 0.03 mol.dm^{-3}, ○ 0.015 mol.dm^{-3}
(A_t) = $[(CF_3CO)_2O]$ at time = t min.

From these results one can conclude, that sulphonic acids resemble carboxylic acids in their interactions with hexafluoroacetic anhydride. The products of these reactions are alkyl- or arylsulphonyltrifluoroacetic anhydrides. These are formed very fast in polar solvents like nitromethane and can therefore be expected to play an intermediate role in the reactions of the hexafluoroacetic anhydride - sulphonic acid reagent with aromatic hydrocarbons.

The formation of diaryl sulphones by the addition of aromatic hydrocarbons to mixtures of sulphuric acid and hexafluoroacetic anhydride may involve protonated bis-trifluoroacetyl sulphate. This has been shown to form readily under conditions where there is an excess of hexafluoroacetic anhydride particularly in the 1:1 nitromethane - dichloromethane system.

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