Equilibria and Reactions of Acetylsulphuric Acid in Liquid Sulphur Dioxide

By **Enzo Montoneri, Mirco Fornaroli, Luigi Giuffré,* Ezio Tempesti,** and **Giancarlo Sioli,** Istituto di Chimica Industriale del Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133 Milano, Italy

Deprotonated acetylsulphuric and acetyldisulphuric acids form quantitatively when sulphur trioxide is added to acetic acid in liquid sulphur dioxide at −78°. With a SO_3 : AcOH mole ratio >1 formation and ionization of the free acids into acetylium and polysulphate ions occur. A plausible mechanism is given.

THE existence of acetylsulphuric acid, as an intermediate in the formation of suldhoacetic acid, has been long hypothesized.[1] Under appropriate conditions the sodium salt can be isolated,[2] but not the free acid, which is quite unstable at room temperature. As a sulphuric acid analogue, it may exhibit similar properties and its strong acidity has been noticed.[3] It may add sulphur trioxide and yield the correspondent polysulphuric species,[4] or be in equilibrium with diacetylsulphate, an intermediate which is the subject of controversy.[5,6] To comprehend more thoroughly its properties, it can however be catalogued as a mixed anhydride (as *e.g.* CH_3COX; $X = NO_3$,[7] HCO_2,[8] $CH_3{\cdot}SO_3$,[9] $CF_3{\cdot}SO_3$,[10]

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[1] M. Franchimont, *Compt. rend.*, 1881, **92**, 1054.

[2] A. J. Van Peski, *Rec. Trav. chim.*, 1921, **40**, 103.

[3] J. Russel and A. E. Cameron, *J. Amer. Chem. Soc.*, 1938, **60**, 1345.

[4] A. Casadevall, A. Commeyras, P. Paillous, and H. Collet, *Bull. Soc. chim. France*, 1970, 719.

[5] E. A. Jeffery and D. P. N. Satchell, *J. Chem. Soc.*, 1962, 1887; L. Laamen and H. Sihtola, *Paperi Ja Puu*, 1964, **46**, 159.

[6] L. G. Tanghe and R. J. Brewer, *Analyt. Chem.*, 1968, **40**, 350.

[7] J. Chedin, S. Feneant, and R. Vandoni, *Mem. Serv. Chim. Etat*, 1950, **35**, 53.

[8] W. Stevens and A. Vas Es, *Rec. Trav. chim.*, 1964, **89**, 863.

[9] M. H. Karger and Y. Mazur, *J. Org. Chem.*, 1971, **36**, 528; R. M. Laird and M. J. Spence, *J. Chem. Soc.* (*B*), 1971, 454.

[10] A. Germain, A. Commeyras, and A. Casadevall, *Bull. Soc. chim. France*, 1973, 2527.

ClO_4,[11] halogen), which may be isolated or characterized in solution. As such, it may behave both as an acetylating [5] and a sulphonating [12] agent.

With the advent of spectroscopic techniques, comprehension of the properties and equilibria of acetylsulphuric acid has improved. Quantitative data however are few. Although n.m.r. spectroscopy is useful in this kind of study, all work has been done in acetic acid and anhydride–sulphuric acid and oleum media, where acetyl sulphuric acid equilibria are supposed to take place, at $-10° \leqslant t \leqslant 35°$.[4,13,14] Unfortunately, because of fast exchange between the species present, results have mostly been interpreted on the basis of methyl proton band shift changes with changing medium composition. Furthermore, the acid proton band has only been considered qualitatively.[14]

In the attempt to obtain separate n.m.r. signals for different species and to study their behaviour with changing medium composition, we chose to examine the acetic acid–SO_3 system in liquid sulphur dioxide. This is an excellent solvent for the system even at *ca.* −80° and permits some equilibria to be frozen. Furthermore, quantitative interpretation of the acid proton band behaviour is facilitated by the lack of solvent background signals. Low temperature i.r. spectra have been correlated with the n.m.r. results. A Raman study was invalidated by strong background fluorescence.

RESULTS

Low temperature ($-20° \geqslant t \geqslant -78°$) n.m.r. and i.r. spectra were recorded in a wide sulphur trioxide : acetic acid mole ratio range ($0.00 \leqslant n_2 : n_1 \leqslant 2.8$). The sulphur trioxide concentration in the system (SO_2 included) never exceeded 15% (w/w). Under these conditions the system was stable for several hours in the experimental temperature range.

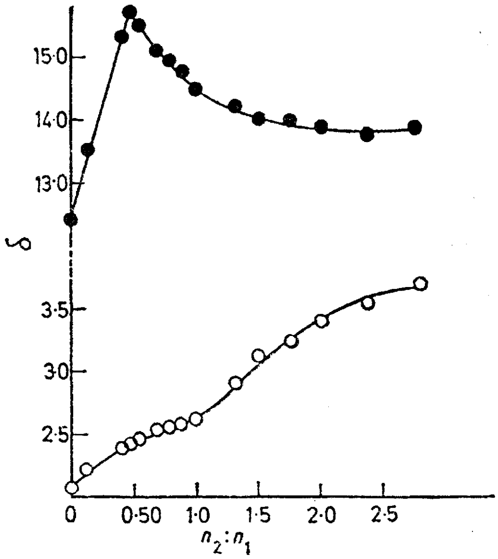
In the n.m.r spectra a single low field band was obtained for the acid proton in the experimental temperature range, whose chemical shift, at constant temperature (−78° in the Figure) depends on the mole ratio. The effect of SO_2 dilution was negligible down to *ca.* 1M-acetic acid. No attempt has however been made to obtain infinite dilution shifts.

The curve in the Figure may be divided into three plots, each for a different mole ratio interval (0.00—0.50, 0.50—1.00, and 1.00—2.80 respectively); the first two are linear. By increasing the temperature to −20°, neither the shape nor the slopes of the curve changed, but the whole curve shifts to higher field with a temperature coefficient independent of the mole ratio ($\Delta\delta/\Delta t = -0.008\ 6$ p.p.m. °C^{-1}).

The −20° spectra showed a single band in the high field resonance region ($\delta < 4.0$), whose chemical shift depends on the mole ratio (Figure). This curve may be graphically interpreted as that for the acid proton over the same mole ratio intervals; the first two plots are linear.

The −40° spectra showed two high field bands in the 0.40—0.50 mole ratio range only, and a wide band in the remaining ranges.

At −78°, however, we observed (Table 1) two high field bands over the greater part of the range, but at $0.00 \leqslant n_2 : n_1 \leqslant 0.14$ and $n_2 : n_1 \sim 1.00$ a single band resulted. When two bands were obtained, their weight average chemical shift always coincided with the −20° upfield band shift at the same mole ratio. When one band was obtained at −78°, its shift coincided with the −20° shift.



Plots of methyl and acid proton shifts against $n_2 : n_1$ (SO_3 : acetic acid mole ratio): open circles, methyl protons at −20°; filled circles, acid proton at −78°

TABLE 1

Methyl proton chemical shifts of acetic acid–sulphur trioxide in liquid sulphur dioxide at −78°

$n_2 . n_1$	δ		
0.00	2.07 (3.00 H)		
0.14	2.20 (2.95 H)		
0.41	2.25 (1.30 H)	2.49 (1.70 H)	
0.47	2.25 (1.40 H)	2.57 (1.60 H)	
0.54	2.25 (1.50 H)	2.68 (1.50 H)	
0.69	2.31 (1.50 H)	2.70 (1.55 H)	
0.78	2.36 (1.45 H)	2.69 (1.60 H)	
0.89	2.41 (1.45 H)	2.70 (1.55 H)	
1.00		2.61 (3.00 H)	
1.50		2.68 (0.97 H)	3.31 (2.03 H)
2.00		2.70 (0.75 H)	3.62 (2.30 H)
2.80		2.70 (0.40 H)	3.78 (2.65 H)

Integrated intensities (Table 1) are relative to that for the acid proton band, which was taken as unity. The −78° upfield band intensity sum and the −20° single upfield band intensity were always equivalent to *ca.* 3 H.

Half-height band widths at −78° increased from 2 to 10 Hz, as the mole ratio increased. At $n_2 : n_1 > 1.00$, the upper field band width (δ 2.70) was 5 Hz larger than that of the lower field band. Also the former was not symmetrical, but exhibited more broadening on the low field side.

The recorded i.r. frequencies at each mole ratio are listed in Table 2. SO_2 and $2\ 500 \leqslant \nu \leqslant 3\ 200$ broad absorption bands are omitted. The 1 785 cm^{-1} band, at $n_2 : n_1$ 0.47, shifts gradually to 1 812 cm^{-1}, as the mole ratio increases. The band shows maximum broadening at 1 805 cm^{-1} and

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[11] A. M. Avedikian and A. Commeyras, *Bull. Soc. chim. France*, 1970, 1258.

[12] A. Casadevall and A. Commeyras, *Bull. Soc. chim. France*, 1970, 1850.

[13] N. C. Deno, C. U. Pittman, jun., and M. J. Wisotsky, *J. Amer. Chem. Soc.*, 196, **86**, 4370.

[14] C. J. Clemett, *J. Chem. Soc.* (*B*), 1971, 2202.

TABLE 2

I.r. frequencies (cm^{-1}) of acetic acid–sulphur trioxide in liquid sulphur dioxide at −60°

$n_2 : n_1$													
0.00			1 745w	1 705s				1 015vw		925m			
0.41			1 785s	1 705s	1 590s	1 540s		1 025m	990m	930m	855m		
0.47			1 785s	1 705w	1 590s	1 540s		1 035m	992m	935m	855m		
0.54			1 790s		1 600s	1 545s		1 045m	992m	935m	860m	755s	
0.78		1 875w	1 795ms		1 610s	1 545s		1 045m	995m	940m	865s	755s	
1.00		1 875w	1 805ms		1 612s	1 545s		1 042m	995m	930m	850s	760s	
1.50	2 298s	1 875w	1 812s		1 615s	1 550s	1 212s	1 055m	1 000m	930m	850m	850s	705m
2.00	2 298s	1 875w	1 812m		1 615m	1 550m	1 212s	1 060m	1 005s	935s		795s	720m
2.80	2 298s	1 875vw	1 812mw		1 595mw	1 545mw	1 121s	1 060m	1 005s	935s		795s	720m

decreased intensity with respect to the 1 500—1 610 cm^{-1} bands. The 2 298 cm^{-1} band was very sharp and well defined.

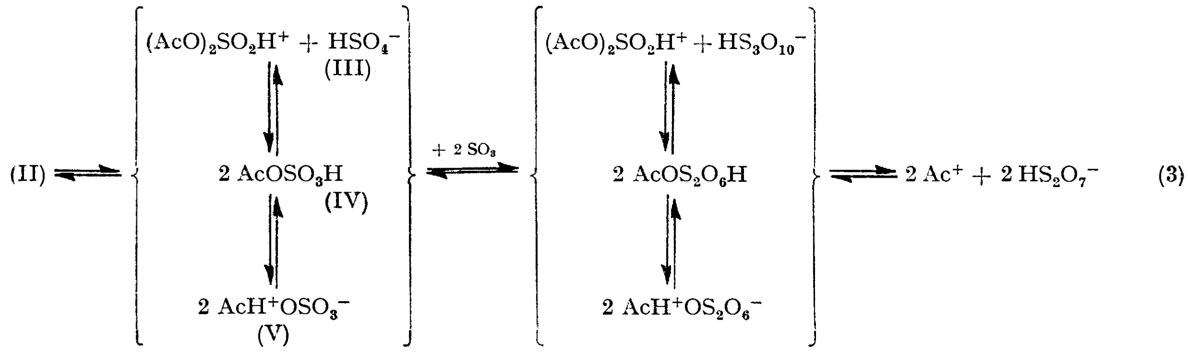
DISCUSSION

Equilibria (1)—(3) should be considered in discussion of the acetic acid–sulphur trioxide system in liquid SO_2 under our experimental conditions. They strongly depend on the SO_3 : AcOH mole ratio and lead respectively to the formation of the ion complexes $AcOSO_3^-,AcOH_2^+$

$$2\,AcOH + SO_3 \rightleftharpoons \underset{(I)}{AcOSO_3^- + AcOH_2^+} \qquad (1)$$

$$(I) + SO_3 \rightleftharpoons \underset{(II)}{AcOS_2O_6^- + AcOH_2^+} \qquad (2)$$

(I) and $AcOS_2O_6^-,AcOH_2^+$ (II) and ultimately to acetylium ions. Compounds (III)—(V) and their polysulphuric homologues are tentatively assumed as probable intermediates as in equilibrium (3).



$$(II) \rightleftharpoons \left\{\begin{array}{c} (AcO)_2SO_2H^+ + HSO_4^- \;\text{(III)} \\ \updownarrow \\ 2\,AcOSO_3H \;\text{(IV)} \\ \updownarrow \\ 2\,AcH^+OSO_3^- \;\text{(V)} \end{array}\right\} \xrightleftharpoons{+\,2\,SO_3} \left\{\begin{array}{c} (AcO)_2SO_2H^+ + HS_3O_{10}^- \\ \updownarrow \\ 2\,AcOS_2O_6H \\ \updownarrow \\ 2\,AcH^+OS_2O_6^- \end{array}\right\} \rightleftharpoons 2\,Ac^+ + 2\,HS_2O_7^- \qquad (3)$$

Because of fast exchange between the species present, only one methyl proton band is observed in the −20° n.m.r. spectra. The lower temperature spectra show that the exchange rate depends both on temperature and probably on the SO_3 : AcOH mole ratio.*

The dependence of the methyl proton chemical shift on the SO_3 mole ratio at −20° (Figure) resembles the

$$AcOS_2O_6^- + nSO_3 \rightleftharpoons (AcOS_{n+2}O_{3n+6}^-) \rightleftharpoons Ac^+ + S_{n+2}O_{3n+7}^- \qquad (4)$$

$$AcOH_2^+ + nSO_3 \rightleftharpoons Ac^+ + H_2S_{11}O_{3n+1} \qquad (5)$$

$$\delta_{obs.} = (2\,\delta_1 - \delta_2) + 2\,(\delta_2 - \delta_1)\,n_1/n_1 \qquad (6)$$

data reported by other workers [4,13] whose conclusions, because of experimental conditions, were based on the behaviour of a single n.m.r. band. Deno *et al.* related the δ >2.8 p.p.m. plot to equilibrium (5). Casadevall *et al.* showed that the mechanism of Ac^+ formation is more complex than in (5). By complementary u.v. and i.r. measurements they concluded that, even at the curve maximum, where (5) should lie well to the right, free and/or deprotonated acetylsulphuric acid is present with the acetylium ion. Therefore the increase in chemical shift above δ 2.80 can be explained by increasing ionization of acetic–sulphuric mixed species rather than protonated acetic acid. The exact mechanism of acetylsulphuric acid formation, however, could not be established.

From the lower temperature n.m.r. and i.r. spectra quantitative data on equilibria (1) and (2) may be obtained. Also some evidence is given which justifies a tentative mechanism for the formation and behaviour of free acetylsulphuric acid as in (3). In the mole ratio range, $0.00 \leqslant n_2 : n_1 \leqslant 0.50$, equilibrium (1) is established and lies well to the right. A species with non-equivalent methyl groups such as (I) appears largely to account for the data. At −78° the δ 2.25 band (Table 1) can be assigned to acetylsulphate methyl protons.[9] The lower field band, with variable chemical shift (δ 2.49—2.68), should be assigned to both free and protonated acetic acid methyl protons, whose exchange rate cannot be slowed down sufficiently at this temperature in order to observe separate bands. From these bands relative intensities and on the basis of (1), the equilibrium concentrations of the species may be calculated. Acetylsulphate concentration always turns out equal to initial SO_3 concentration. Furthermore, by assigning the δ 2.68 value [13,14] to pure protonated acetic acid, we find that the low field band variable chemical shift is always the weight average of free (δ 2.07) and protonated acetic acid chemical shifts. At a mole ratio of 0.14 the species shift differences are not large enough to observe separate

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* No detailed study of line widths has however been attempted.

bands.[15] The protonated acetic acid band chemical shift should in fact be δ 2.18 which is too close to the acetylsulphate shift.

The linear dependence of the acid proton shift on the mole ratio (Figure) is well accounted for, if we assume that the observed shift represents the weight average shift of fast exchanging acid protons of free acetic acid (I). The value at $n_2 : n_1$ 0.50 is the shift of the acid protons of pure (I) ($\delta_{(I)}$ 15.69).[*]

The i.r. spectra (Table 2) agree well with the n.m.r. results. Band assignments are 1 785, 990 (acetylsulphate [9,14]), 1 705 (free acetic acid), and 1 590, 1 540 (protonated acetic acid [14]) cm^{-1}. It is evident that as (I) forms, the free acetic acid concentration decreases and beyond $n_2 : n_1$ 0.50 cannot be detected.

In the range, $0.50 < n_2 : n_1 \leqslant 0.89$, the acetylsulphate n.m.r. band (Table 1) shifts to low fields, whereas that of the protonated acetic acid remains constant. Band intensity ratios are still *ca.* 1. This behaviour may be largely consistent with the formation of (II) as in (2), although the fact that the low field band intensity seems slightly higher than that of the high field band may suggest minor contributions ($<5\%$) from other structures, as in (3).

The upfield band shift change to lower fields shows that acetylsulphate is exchanging with the more deshielded acetyldisulphate. If (2) lies well to the right, the upfield band observed shift ($\delta_{\text{obs.}}$) should depend linearly on the SO_3 : AcOH mole ratio as in (6), where δ_1 and δ_2 are the pure sulphate and disulphate mixed species shifts respectively. This is in fact the case. From the extrapolation of (6) to $n_2 : n_1$ 1.00, we obtain δ_2 2.46. Addition of a further equivalent of SO_3 to acetylsulphate will therefore deshield the methyl protons by *ca.* 0.21 p.p.m.; a similar effect, *ca.* 0.31 p.p.m., was noted by Robinson and Silberberg [18] upon formation of methanedisulphonic acid from methanesulphonic acid. Although no band separation is observed at a mole ratio of 1.00, the band position for this value corresponds approximately to the weight average shift of acetyldisulphate and protonated acetic acid.

A drastic slope inversion is observed in the acid proton shift plot in this mole ratio range (Figure). The acid protons of (I) and (II) now exchange and the shift of pure complex (II) ($\delta_{(II)}$ 14.47) is found at $n_2 : n_1$ 1.00.[†] The acid protons of (II) appear significantly more shielded than those of (I) by *ca.* 1.20 p.p.m. Hydrogen bonding in the former should be less than in the latter; in fact acetylsulphate should be a stronger proton acceptor than acetyldisulphate, just as HSO_4^- is stronger than $HS_2O_7^-$.[19]

The i.r. spectra (Table 2) over the same mole ratio range may well be interpreted according to the n.m.r. conclusions. $AcOS_2O_6^-$ formation causes the 1 785 cm^{-1} ($AcOSO_3^-$) band to shift gradually to 1 805 cm^{-1}. Significantly no free SO_3 band [20] is observed; in a spectrum of SO_3 in SO_2 this last band was observed at 1 060 cm^{-1}. The presence of other species (III) and (IV), suggested above, may be responsible for the 1 875 cm^{-1} band and for the increased broadening of the 1 805 cm^{-1} band respectively.

The higher concentration range ($n_2 : n_1 > 1.0$) pertains to the interaction of excess of SO_3 with (II). There is an excellent direct intensity correlation between the acetylium ion (see Experimental section) i.r. bands (ν 2 298 and 1 005 cm^{-1}) and the variable chemical shift (δ 3.31—3.78 p.p.m.) of the methyl protons. The change in this low field shift [‡] with increasing Ac^+ concentration suggests that these ions exchange with some other species, which is not protonated acetic acid (always observed separately at δ 2.70).

If only one of the ions in (II) is the immediate precursor of Ac^+, this is probably $AcOS_2O_6^-$. Reaction (4) is more plausible than (5). However the relative intensities of methyl proton bands are not accounted for by Ac^+–$AcOS_{n+2}O_{3n+6}^-$ exchange only; since $AcOH_2^+$ does not appear in (4) and does not exchange with Ac^+, the low field band intensity should never be greater than that of the high field band. The data (Table 1) suggest that both ions in (II) convert into Ac^+ and call for a more complex mechanism than (4) or (5) separately.

Equilibrium (3) is a tentative model which accounts better for the Ac^+ concentration dependence on the SO_3 : AcOH mole ratio. It is evident that this concentration dependence cannot be accounted for quantitatively as for equilibria (1) and (2) since the specific absorption frequency of free SO_3 (ν 1 060 cm^{-1}, Table 2) can be detected. This may contribute to the non-linearity of the −20° methyl protons and to the flattening out of the acid proton shift plots (Figure). This last behaviour is typical of oleum [21] and may be consistent with formation of higher inorganic polysulphate anions as in (3).

The i.r. spectra (Table 2) may be interpreted according to (3). $HS_2O_7^-$ Bands [22] (ν 805 and 705 cm^{-1}) are

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[*] Both the magnitude of this shift and negligible dependence on SO_2 concentration may suggest an ion pair cyclic structure for this complex. However no definite assessment can be made since if the behaviour of pure acetic acid in liquid sulphur dioxide [16] seems to support this argument, the differences found for the same acid in other solvents [17] necessarily require further studies.

[†] Although at $n_2 : n_1 > 0.78$ an internal standard could not be used, the linear relationships found up to $n_2 : n_1$ 1.00, if not completely accidental, suggest that the assumption made in obtaining true δ values (see Experimental section) may be close enough to reality within this mole ratio range.

[‡] Although there may be some uncertainty in the true δ values within this concentration range (see Experimental section), the increasing difference between the low and high field band shifts suggest that the chemical shift change of the low field band is largely real. No chemical shift quantification was however attempted in this range.

[15] N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 1948, **73**, 679.

[16] S. Brownstein and A. E. Stillman, *J. Phys. Chem.*, 1959, **63**, 2061.

[17] G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' Freeman, San Fancisco and London, 1960, p. 150.

[18] E. A. Robinson and V. Silberberg, *Canad. J. Chem.*, 1966, **44**, 1437.

[19] R. J. Gillespie and K. C. Malhotra, *J. Chem. Soc.* (*A*), 1968, 1933.

[20] G. E. Walrafen, *J. Chem. Phys.*, 1964, **40**, 2326.

[21] R. J. Gillespie and R. F. M. White, *Canad. J. Chem.*, 1960, **38**, 1371; H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 1953, **21**, 1688.

[22] G. E. Walrafen, D. E. Irish, and T. F. Young, *J. Chem. Phys.*, 1962, **37**, 662.

strong at $n_2 : n_1$ 1.50. A shift to 795 and 720 cm^{-1} at higher mole ratios suggests the presence of the higher inorganic polysulphate anions. The $AcOS_2O_6^-$ band frequency shift to 1 812 cm^{-1} at $n_2 : n_1$ 1.50 may be consistent with formation of $AcOSO_3H$ (or more generally with a mixture of acetylpolysulphuric acids). These acids should absorb at higher frequencies than their conjugate bases.[23] Special attention should be given to the 1 612 and 1 550 cm^{-1} bands which in the lower mole ratio range have been assigned to protonated acetic acid. At $n_2 : n_1$ 1.50 these band intensities seem unchanged, whereas the relative intensities in the n.m.r. suggest that $AcOH_2^+$ concentration should be greater either than 30% (if the δ 3.31 band accounts for Ac^+ and all SO_3-containing species) or 15% (if the δ 2.70 band accounts for all $AcOH_2^+$ and $AcOS_2O_6^-$ ions). Most likely acetylsulphuric acid (or whichever of the undissociated acetylpolysulphuric acids is present) have both free and protonated carbonyl groups as in $AcOSO_3H$ (IV) and $AcH^+OSO_3^-$ (V), with the latter responsible for the behaviour of the 1 612 and 1 550 cm^{-1} bands. Because of band broadness these structures may be appreciated in the i.r. spectra only when (3) is sufficiently displaced to the right ($n_2 : n_1$ 1.50) and the band contribution of (II) is diminished. The concentration of (IV) and (V) significantly decreases at higher mole ratios when the prevailing species in the system is Ac^+.

$(AcO)_2SO_2H^+,HSO_4^-$ (III) is a very controversial intermediate.[5,6] Spectroscopic evidence (ν 1 875 cm^{-1}, δ 2.80) for a similar species, $AcOSO_2H^+Me,X^-$, whose cation is sulphur–oxygen protonated acetic methanesulphonic anhydride, has been reported.[10] Its n.m.r. low temperature band could not be separated from that of protonated acetic acid. These spectral features may be recognized in the i.r. spectra (Table 2) at $n_2 : n_1 \geqslant 0.78$ and in the δ 2.70 band at $n_2 : n_1 \geqslant 1.50$, whose half height width (15 Hz, greater than that of the low field signal, 10 Hz) and contour suggest that a species is present with a chemical shift close to that of protonated acetic acid. Also the possible presence of the HSO_4^- band [24] (ν 1 045 cm^{-1} at $n_2 : n_1 \leqslant 1.0$) seems to support (III). * The 1 875 cm^{-1} band intensity is however weak in the greatest part of the $n_2 : n_1 \geqslant 0.78$ range and even weaker at $n_2 : n_1$ 2.80. It seems therefore that $(AcO)_2SO_2H^+$, if present, is always a minor constituent of the system.

Equilibria (1)—(3) suggest that acetylsulphuric acid may react both as acetylating and sulphonating agent. In fact two powerful electrophiles are present, free acetylium cation and loosely bound SO_3. It has been shown that acetylsulphate is not an aromatic carbon acetylating, but only a sulphonating agent.[12] This suggested an S_N1 type acetylation mechanism. We carried out experiments with anisole in the acetic acid–sulphur trioxide system in liquid SO_2, at SO_3 : AcOH mole ratios up to 3.0, where the free acetylium ion concentration is significant and therefore S_N1 acetylation should be favoured. Only sulphonated anisole was however obtained. The fact that, even when anisole was added in excess over sulphur trioxide and acetic acid, no acetylated anisole product was found, confirms indirectly that equilibria (1)—(3) are reversible. As SO_3 adds to anisole irreversibly, the concentration of acetylium cation decreases because the free SO_3 : acetic acid mole ratio decreases. Therefore no acetylium ions are available to react when excess of anisole over SO_3 is used.

Conclusions.—The behaviour of the acetic acid–sulphur trioxide system strongly depends on the SO_3 : AcOH mole ratio. The system leads to the formation of acetyl-sulphuric and -disulphuric acid. These acids are quite stable in the presence of a proton acceptor (in this case excess of acetic acid) and form salt complexes (I) and (II) as in (1) and (2). The free acids (IV) and (V) which may be obtained from the complexes in excess of SO_3, as in (3), are not stable and may be considered the immediate precursors of acetylium ions.

For a complete interpretation of the spectral data obtained, the existence of diacetylsulphate in the system has been considered. It appears that this species, if present, is always a minor constituent and should be regarded as a low concentration intermediate which favours the formation of the free acetylpolysulphuric acids from the $AcOS_2O_6^-,AcOH_2^+$ complex.

Neither the acetic–sulphuric mixed species nor free acetylium ions may be used as aromatic carbon acetylating agents under the reported experimental conditions, because sulphonation of the substrate prevails.

The effect of solvent concentration on the establishment of new tautomeric equilibria is currently being studied.

EXPERIMENTAL

Acetic acid, sulphur dioxide and trioxide (in that order) were mixed at *ca.* −70° in a jacketted cylindrical reactor, which terminated in an appropriate device for sampling in an evacuated n.m.r. tube (Wilmad). The tube was sealed and the spectra recorded with a Varian HA 100 spectrometer. An outer tube (Wilmad) was used for the external reference solution (15% benzene in CS_2). Two sets of runs were made, with and without tetramethylsilane (TMS) in the inner tube. TMS was suitable as an internal reference, when the SO_3 mole ratio in the system was not greater than 0.78. Above this value TMS reacted. It was found that the correction, to be applied to the chemical shifts relative to the external reference to obtain shifts relative to internal TMS, depends on the SO_3 mole ratio in the system. It amounted to +0.6 p.p.m. at 0.00 mole ratio, and 0.15 p.p.m. at 0.78 mole ratio. The latter correction was applied over the remaining mole ratio range, since a band was found in the −78° spectra at constant resonance position (δ 2.70).

I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer, with a RIIC VLT 2 variable temperature cell between AgCl windows.

Materials.—Acetic acid (C. Erba) and SO_3 from 60% (w/w) oleum (Snia Viscosa) were distilled before use. SO_2 (SIO)

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* Although HSO_4^- may be differently accounted for, no evidence of Ac^+ is found when the 1 045 cm^{-1} band is present. This however may depend on the relative molar absorption coefficients.

[23] R. M. Silverstein and G. C. Bassler, ' Spectrometric Identification of Organic Compounds,' Wiley, New York, 1968.

[24] P. A. Giguere and R. Savoie, *Canad. J. Chem.*, 1960, **38**, 2467.

was purified by known methods.[25] C. Erba benzene and anisole were used.

Acetylium Ion Identification.—A procedure similar to that of Olah *et al.*[21] for the preparation of solid acetylium salts, Ac^+X^- (X^- MF_4 or MF_6) has been adopted in an attempt to obtain by fractional crystallization one or more acetylium polysulphate salts ($X^- = HS_{n+1}\,O^-_{3n+4}$) in the present system.

A solution of acetic acid and SO_3 in SO_2, prepared as above with a *ca.* 2.0 SO_3 mole ratio, was evaporated at −50° under vacuum until a precipitate was obtained. After filtering at −70°, a limpid solution was recovered.

The i.r. spectrum of the filtered solution was similar to the starting solution (Table 2) in the 700—1 500 cm^{-1} region, but contained only a band at 2 298 cm^{-1} in the remaining region. Its n.m.r. spectrum at −78° contained only a δ 4.00 band and the downfield acid proton band. The spectral features (ν 2 298 and 1 005 cm^{-1}, δ 4.00) are common to free acetylium ions,[26,27] regardless of the nature of X^-. The i.r. bands [19,21] at 1 060, 790, and 720 cm^{-1} suggest that X^- is most likely a mixture of inorganic polysulphate anions, in equilibrium with free SO_3.

The spectral features of the solid, which was taken up in liquid SO_2, showed a marked decrease in Ac^+ concentration, with respect to the original solution. New species, which were not in the original solution, appear too.

It thus appears that pure acetylium polysulphate salts may be obtained only in solution at low temperature, but not as solids. It has been found more generally that as SO_3 concentration exceeds 15% (w/w, SO_2 weight included), the stability of the system decreases. This is because of the establishment of slow tautomeric equilibria, which are currently being studied and will be reported later.

Reaction with Anisole.—Anisole was added to SO_2 solutions, containing SO_3 and acetic acid at 0.5, 1.0, and 2.8 mole ratios, at −78°. Different experiments were made with anisole in equimolar amounts, relative either to SO_3, or acetic acid, or their sum. After 20 min at the mixing temperature, water was added and the system allowed to reach room temperature. When SO_2 evolution ceased, the aqueous solution was extracted with diethyl ether, which was then washed with sodium hydrogen carbonate, dried (Na_2SO_4), and evaporated. Only acetic acid and anisole were identified in the residue. When free sulphuric acid was present in the aqueous solution, a white precipitate formed. In this case, the solution was filtered before extraction. The solid was identified as *p*-methoxybenzenesulphonic acid. In order to obtain a complete material balance, a different procedure was used. After addition of water to the reaction mixture and SO_2 evaporation, the last traces of SO_2 were removed under vacuum at room temperature. Overall acidity (with 0.1N-NaOH and phenolphthalein as indicator), free H_2SO_4 (with $BaCl_2$), and total sulphur (with Eschka's mixture and $BaCl_2$) were determined on the aqueous solution. It was shown by this procedure that anisole reacts quantitatively with SO_3 and yields the corresponding sulphonic acid, and that all initial acetic acid is recovered unchanged.

In blank runs (solutions of acetic acid and SO_3 in SO_2, which did not contain anisole), no organic sulphur was found, showing that no sulphoacetic acid forms under these conditions.

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[25] H. P. Leftin and N. N. Lichtin, *J. Amer. Chem. Soc.*, 1957, **79**, 2475.

[26] G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *J. Amer. Chem. Soc.*, 1962, **84**, 2733.

[27] P. N. Gates and D. Steel, *J. Mol. Structure*, 1967—1968, **1**, 349.