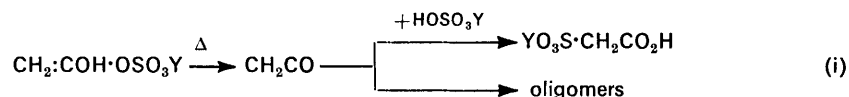# Keto–Enol Equilibria in Mixed Acetic Sulphuric Anhydrides †

By **Enzo Montoneri,** **Ezio Tempesti, Luigi Giuffrè,** and **Aldo Castoldi,** Istituto di Chimica Industriale de Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy

Mixed acetic sulphuric anhydrides obtained from both equimolar SO_3–AcOH and SO_3–Ac_2O systems in liquid SO_2 are found at low temperature ($\leqslant -20°$) in equilibrium between the keto ($CH_3 \cdot CO \cdot OSO_3Y$) and enol ($CH_2 \colon COH \cdot OSO_3Y$) forms ($Y = SO_3^-$ or Ac). At room temperature a cleavage reaction is shown to occur through the intermediacy of keten, which reacts further to yield oligomers and sulpho-derivatives [reaction (i)]. This

$$CH_2 \colon COH \cdot OSO_3Y \xrightarrow{\Delta} CH_2CO \xrightarrow{+HOSO_3Y} \begin{array}{l} \longrightarrow YO_3S \cdot CH_2CO_2H \\ \longrightarrow \text{oligomers} \end{array} \qquad (i)$$

cleavage reaction appears specifically not to involve participation of acetylium ions, whereas previously these ions were normally considered as the principal precursor of keten intermediates.

MIXED anhydrides (RCOY; $Y = NO_3$,[1] HCO_2,[2] CF_3SO_3,[3] ClO_4,[4] or halogen[5]) have been studied by numerous workers since they are known to be key intermediates in many acid-catalysed reactions. Under specific conditions some of these species[3,5] have been shown to ionize to the corresponding acylium ions

$$RCOX \rightleftharpoons RCO^+ + X^- \qquad (1)$$
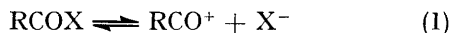
[reaction (1)]; these ions, due to the ease of preparation and relatively high stability, constitute one of the best characterized classes of stable carbocations.

For their structure a resonance hybrid of the oxonium, oxocarbenium, and 'keten-like' forms is generally assumed [equilibrium (2)]. Specifically for acetylium

$$R{-}C{\equiv}O^+ \rightleftharpoons R{-}\overset{+}{C}{=}O \rightleftharpoons \overset{+}{R}{=}C{=}O \qquad (2)$$
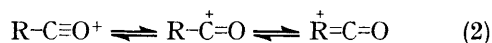
ions, participation of the 'keten-like' form has been reported to be negligible (crystalline salts)[6] or substantial (in solution)[7] according to the experimental conditions.

For pure mixed sulphuric carboxylic anhydrides ($RCO \cdot OSO_3 \cdot Y$, $Y = SO_3^-$ or RCO), which have been characterized in equimolar solutions of carboxylic acids[8] or anhydrides[9] and SO_3 in liquid SO_2, it has been also shown that on increasing the concentration of SO_3 ionization of these mixed anhydrides to acylium ions occurs.

We now report that specifically for Ac_2O–SO_3 and AcOH–SO_3 equimolar solutions in liquid SO_2 the formation of the corresponding mixed anhydrides is observed to involve at low temperature ($\leqslant -20°$) the establishment of tautomeric equilibria not previously observed. We also report that depending on the experimental conditions the enol species involved in these tautomeric equilibria are cleaved at room temperature and imply the intermediacy of keten without any significant participation by acetylium ions.

EXPERIMENTAL

Most of the experimental details have been previously reported.[8,9] In addition to i.r. and n.m.r. spectra, the Ac_2O–SO_3 and AcOH–SO_3 mixtures were analysed in other ways to supplement the spectroscopic data.

Classical Analyses.—*Analysis of sulphur derivatives.* Samples were quenched with ice and water and SO_2 was completely evaporated (as checked by iodometric titration on the resulting aqueous solution); free sulphates, organic sulphur, and total acidity were then determined as previously reported.

Olefinic double bonds. To obtain evidences of olefinic double bonds in unquenched samples chlorine (in slight excess relative to initial Ac_2O or AcOH) was added at $-70°$ to the SO_2 solutions; after quenching with ice and water, the determination of the relative concentrations of chloroacetic and acetic acid was performed either by n.m.r. spectroscopy (free acids) or by g.l.c. (butyl esters).

Autocondensation products. The test to obtain evidence of the formation of aceto- and diaceto-acetic species in SO_3–SO_2 mixtures with AcOH or Ac_2O included quenching of samples with ethanol at $-50°$ and determination of the corresponding esters as previously reported.[7] Dehydroacetic acid was determined after quenching the samples with ice and water as reported above, extracting the aqueous solutions with CCl_4, and concentrating the organic layer. The crystalline ($-10°$) product was identified by its i.r. and n.m.r. spectra which were identical with those of an authentic sample.

Elaboration of N.m.r. Data.—*Determination of mole ratio of diacetyl sulphate enol* (II) *and keto* (I) *forms.* From relative band areas at 1.0 mole ratio (Table 2a), a tentative quantitative determination of mole ratio of (II) to (I) at equilibrium may be obtained from equation (3) where n_{CH_3}, n_{CH_2}, and n_{OH} are the numbers of methyl, methylene,

$$(3n_{CH_3} + 2n_{CH_2})/n_{OH} = A_{CH_i}/A_{OH} = 8 \qquad (3)$$

and hydroxy groups, respectively, present at equilibrium and A is the band area. The assumption that $A_{OH} = 1$ and $n_{CH_2} = n_{OH}$ [based on structure (II)] yields $n_{CH_3}/n_{CH_2} = 2$ and a (II)/(I) mole ratio of 2. Furthermore the chemical shift values for the methyl and methylene protons (δ^0 2.32 and 2.57, respectively) in species (I) and (II) may be ten-

tatively obtained. As shown for the AcOH system (Table 2d), where separate n.m.r. bands are observed for $AcOS_2O_6^-$ (δ 2.50) and $CH_2{:}COH{\cdot}OS_2O_6^-$ (δ 2.75), the methylene proton resonance (enol form) is 0.25 p.p.m. downfield from that of the methyl protons (keto-form). Assuming then the same $\Delta\delta$ for (I) and (II), from the (II)/(I) mole ratio and equations (4) and (5), where X = proton fraction of methyl

$$X_{CH_3}\delta^0CH_3 + X_{CH_2}\delta^0CH_2 = 2.38 \qquad (4)$$

$$\delta^0_{CH_3} + 0.25 = \delta^0CH_2 \qquad (5)$$

and methylene groups and 2.38 is the observed δ at 1.0 mole ratio, the δ^0 values are obtained.

Determination of the relative concentrations of the acetyl disulphate enol (VIII) *and keto* (VII) *forms and of protonated acetic acid.* From the band areas of acetyl disulphate [keto-form (VII) δ 2.50; enol form (VIII) δ 2.75] and of protonated acetic acid (δ 2.66) the relative concentrations of each species [(VIII) : (VII) : $AcOH_2^+$ = 0.4 : 0.6 : 1.0] can be obtained. Since only acetyl disulphate is involved in the tautomeric equilibrium (6) with the aid of equations (7) and (8), where n and A are the moles and band areas for each species, the mole ratios may be obtained.

$$n(_{AcOH_2^+}) = n(_{VII})^+ + n(_{VIII}) \qquad (6)$$

$$n(_{VII}) = A(_{VII})/3 \qquad (7)$$

$$3n(_{AcOH_2^+}) + 2n(_{VIII}) = A(_{AcOH_2^+}) + A(_{VIII}) \qquad (8)$$

RESULTS

The behaviour of equimolar Ac_2O–SO_3 and AcOH–SO_3 solutions in liquid SO_2 was investigated between $-78°$ and room temperature. I.r. spectra were always recorded at $-60°$ and n.m.r. spectra at $-78°$ and are reported in Tables 1 and 2, respectively. Liquid SO_2 bands are omitted from the i.r. spectra. Spectra a and c * refer to freshly

TABLE 1

I.r. frequencies (cm^{-1}) of equimolar Ac_2O–SO_3 and AcOH–SO_3 systems in liquid SO_2 at $-60°$

System	Ac_2O–SO_3		AcOH–SO_3		
Spectrum	a	b	c	d	e
	2 950w,br	3 000s,br	2 800m,br	2 850s,br	2 850s,br
			1 875w,br	1 875w,br	
	1 820s		1 805ms	1 805w	
		1 725s,br			1 710m,br
	1 680w				
	1 600m	1 580s,br	1 612s	1 612s	1 612s
	1 555m	1 545s,br	1 545s	1 545s	1 545s
	1 416s		1 405s	1 405w	
	1 375s	1 365s,br	1 370m	1 370m	1 370s,br
	1 230m				
	1 218s				
	1 185ms	1 170s,br	1 200s,br	1 200s,br	1 212s,br
	1 045m	1 030s,br	1 045m	1 040m	1 040m
	998ms		995m		
	940m	925s,br	930m	940m	935s
	850s	885sh	850m	892w	895sh
	802s	810m,br			795s
	765m		760s	775ms	705m

prepared (at $-60°$) mixtures; the other spectra were recorded after the mixtures had been left at $-20°$ for 48 h (spectrum d) and at room temperature for 90 min (spectra b and e). The spectra (which are not reported in the Tables)

* The values reported in column c are taken from ref. 8. The bands at 1405 and 1370 cm^{-1} appear as shoulders of the SO_2 band at 1340 cm^{-1}, which in this system is quite broad.

of freshly prepared 0.0 and 0.5 SO_3 : Ac_2O mole ratio mixtures contained the following bands: δ 2.18; ν 1 821s, 1745s, 1 430m, 1 375ms, 1 230w, 1 045w, 1 000ms, 900m, 810w, and 780w cm^{-1} (0.0 mole ratio); δ 2.30 (19 H) and 15.10 (1.0 H) (0.5 mole ratio). Dehydroacetic acid formation (10 and 1% w/w yields relative to initial Ac_2O and AcOH, respectively) and loss of free sulphate (75 and 50%

TABLE 2

Proton chemical shifts (δ values, tetramethylsilane as internal standard) of Ac_2O–SO_3 and AcOH–SO_3 system in liquid SO_2

System	Ac_2O–SO_3		AcOH–SO_3		
Spectrum	a	b	c	d	e
	2.38	2.0	2.61	2.50	2.15
	(8.0 H)	(2.5 H)	(3.0 H)	(0.85 H)	(0.14 H)
		2.24		2.66	2.66
		(0.15 H)		(1.6 H) *	(0.83 H)
		2.62		2.75	3.41
		(0.15 H)			(0.10 H)
		4.10			4.40
		(1.3 H)			(0.28 H)
					5.04
					(0.03 H)
					5.38
					(0.05 H)
					5.80
					(0.05 H)
	15.13	12.65	14.47	14.52	13.49
	(1.0 H)	(1.0 H)	(1.0 H)	(1.0 H)	(1.0 H)

* The integrated intensity refers to both δ 2.66 and 2.75 bands since they were both broad and separate values could not be obtained. The latter band was however much weaker.

mol per mol relative to initial SO_3 in the Ac_2O and AcOH systems, respectively) and of organic acidity (15 and 25% relative to initial Ac_2O and AcOH, respectively) occurred only in mixtures from which spectra b and e are derived. Addition of Cl_2 to yield chloroacetic acid (MCA) occurred only in mixtures from which spectra a and d are derived with 30 and 25% mol per mol yields (relative to initial Ac_2O and AcOH), respectively. No evidence of the formation of aceto- and diaceto-acetic species was obtained.

DISCUSSION

(a) *Tautomerization of Mixed Acetic Sulphuric Anhydrides.*—(1) *The* Ac_2O–SO_3 *system at low temperature* ($\leqslant -20°$). The establishment of tautomeric equilibria involving mixed acetic sulphuric anhydrides has been thoroughly investigated in this work starting from a mixture of Ac_2O and SO_3 in SO_2 in order to eliminate spectroscopic interferences due to the presence of acid protons (*e.g.* in AcOH–SO_3). The equimolar addition of SO_3 to Ac_2O at $-60°$ leads quantitatively to diacetyl sulphate formation [reaction (9)] on the basis of the

$$Ac_2O + SO_3 \rightleftharpoons (AcO)_2SO_2 \qquad (9)$$
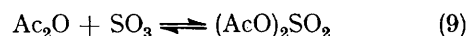
following spectroscopic evidence. The absence of Ac_2O C=O bands (ν 1 745 and 1 821 cm^{-1}) in the i.r. spectrum (Table 1a) shows that the conversion of acetic anhydride is complete. The absorptions at ν 1 820 (C=O), 998 and 1 045 (C–O), 1 416 and 1 218 (S=O), and 765—850 (S–O) cm^{-1} are characteristic of diacetyl sulphate (I), and similar to those previously reported for biscyclohexylcarbonyl sulphate.[9] Two additional bands (1 600 and 1 555 cm^{-1}) indicated however, the presence of

a new species. If we assume that a donor (carbonyl and not ether oxygen [9])–acceptor complex, such as $Ac_2O \cdot SO_3$ is formed (see *e.g.* the donor–acceptor complexes of carboxylic anhydrides with metal halides),[10] then we would expect to find additional S=O absorptions at wavelengths lower than 1 390 and 1 065 cm^{-1} (free SO_3),[11] respectively. The two bands, instead, which have been identified as additional S=O absorptions fall at 1 375 and 1 185 cm^{-1}. Since a broad band is also observed around 2 950 cm^{-1} (which is reminiscent of a strong hydrogen-bonded OH function) [12] the formation of a new enolic species $CH_2\!:\!COH \cdot OSO_2Ac$ * in equilibrium with the keto-form (I) seems plausible.

Referring again to the new bands at 1 600 and 1 555 cm^{-1}, it is known that these are frequently indicative of

(I)   (II)

(III)   (IV)
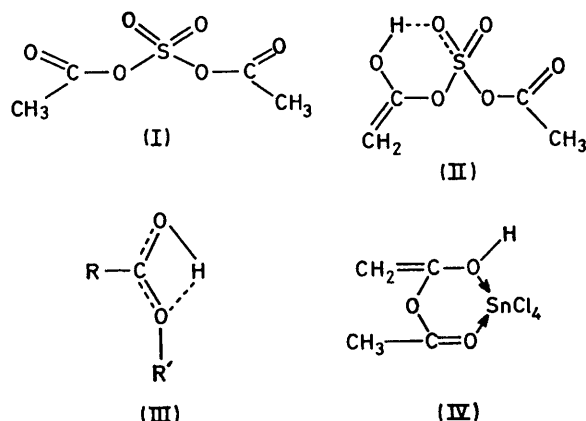
enolic compounds. In β-diketo-compounds, for instance, strong absorptions in this range (1 640—1 540 cm^{-1}) have been assigned to the C=O (chelated) and C=C stretching vibrations.[14] A pair of absorptions in this range, however, does not necessarily require a β-diketo-structure; in fact it may also be due to protonated C=O groups as in (III) where intramolecular interaction between the proton formally attached to the carbonyl oxygen atom and hydroxy (R' = H) or ether (R' = alkyl) oxygen atoms may occur.[15] Furthermore Hunt and Satchell [16] suggested that in some cases, even if a β-diketo-chelated structure is present (*e.g.* the enolic form of the Ac_2O–$SnCl_4$ donor–acceptor complex), the absorption between 1 630 and 1 500 cm^{-1} would rise from the cyclic chelated structure (IV) and not from C=O stretching vibrations.

Based on these findings, the 1 600 and 1 555 cm^{-1} absorptions in Table 1a can be due to the enolic form of diacetyl sulphate (I) where strong intramolecular hydrogen bonding of the chelate ring structure (II) occurs.†

Accordingly, the remaining new bands reported in Table 1a, may be assigned as follows. The broad absorption (in the 3 400—2 300 cm^{-1} range) centred at 2 950 cm^{-1} relates to the bonded hydroxy-group in the chelated form,[12] while the 1 375 ‡ and 1 185 cm^{-1} bands may be attributed to hydrogen-bonded sulphuryl groups ($S \cdots O \cdots H$). The latter frequencies, which are almost equally displaced from the free S=O [as in (I)] absorptions, exhibit absorption shifts of the same magnitude as observed from hydrogen-bonding studies with sulphones and sulphoxides.[19] Finally the weak band at 1 680 cm^{-1} could be tentatively assigned to the stretching vibration of the C=C bond § in (II) by analogy with the corresponding absorption (1 672 cm^{-1}) in isopropenyl acetate.[21]

Further information on structure (II) can be obtained from n.m.r. spectroscopy. The high-field resonance dependent on the SO_3 mole ratio between 0.0 and 1.0 may be attributed to the carbon protons of fast exchanging Ac_2O, (I), and (II) species. The value (δ 2.38) at 1.0 mole ratio (Table 2a) is, however, due to exchange of species (I) and (II) only since conversion of Ac_2O is shown to occur quantitatively from the i.r. spectrum.

Tentative chemical shift values for pure methyl (δ^0 2.32) and methylene (δ^0 2.57) protons in species (I) and (II) have been obtained (see Experimental section). The methyl proton shift in diacetyl sulphate is 0.14 p.p.m. deshielded relative to the value observed for pure methyl protons in Ac_2O. This deshielding is well within the range observed for other mixed carboxylic sulphuric anhydrides when they are compared with the corresponding pure carboxylic species.[8,9]

The low-field band (δ 15.13) indicates a substantially deshielded exchangeable proton associated with at least two oxygen atoms such as those of a very strong acid or a strong intramolecularly hydrogen-bonded species. The behaviour of this band is quite peculiar; although the relative intensity of the low- to high-field proton bands increases from 0.0 to 0.12 upon changing the mole ratio from 0.0 to 1.0, indicating increasing concentration of hydroxy-protons, the hydroxy-proton chemical shift is constant. This may be assumed to be consistent [22] with a strong intramolecular-hydrogen-bonded hydroxy-proton such as in (II), whose chemical shift is not dependent on concentration.

(2) *The Ac_2O–SO_3 system at room temperature.* Starting from Ac_2O and H_2SO_4 (or AcOH and SO_3) the room temperature formation of a stable sulphur derivative, sulphoacetic acid, is known. This sulphonation reaction has been assumed [23] to proceed through the intermediacy of both acetylsulphuric acid and diacetyl sulphate. While evidence for the existence of acetylsulphuric acid has been reported [8,24] no direct observation of diacetyl sulphate is known. We have shown here that at low

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* Only the keto-form was observed at low temperature [≤ −20°) for biscyclohexylcarbonyl sulphate [9] and propionyl sulphate.[13]

† Stable six-membered chelate ring systems have been experimentally established in carbohydrates [17] and in enolized systems.[18]

‡ Although intense methyl absorptions may also occur at 1375 cm^{-1} (*e.g.*, that of Ac_2O), it may reasonably be assumed from the following discussion that in this case the band is due to ν_{as} ($S \cdots O \cdots H$).

§ The presence of an olefinic double bond has been confirmed by chlorination as indicated above; the formation of MCA occurs immediately at low temperature, while it is known that, normally,[20] starting from AcOH, high temperatures and long induction periods are required.

temperature diacetyl sulphate is indeed formed from an Ac_2O–SO_3 equimolar mixture and is in equilibrium between a keto and an enol form.

We now report that at room temperature diacetyl sulphate ultimately leads to a predominant sulphonation product (sulphoacetic acid) with concomitant formation, not previously observed, of keten oligomers.

The n.m.r. spectrum of an equimolar Ac_2O–SO_3 solution, which contains at low temperature a single low field proton band (δ 2.38), yields at room temperature two main bands at δ 2.0 and 4.1 and two weak bands at δ 2.24 and 2.62 (Table 2b). These latter were identified as the methyl proton bands of dehydroacetic acid, which was recovered from the reaction mixture with a yield in agreement with its spectroscopic concentration. This oligomerization may occur through thermal cleavage of (II) to acetylsulphuric acid and keten [reaction (10)]

$$(I) \rightleftharpoons (II) \rightleftharpoons AcOSO_3H + CH_2CO \qquad (10)$$

which may further react by (11) and (12). Thermal cleavage of other mixed sulphuric carboxylic anhydrides [25] (e.g. $RCO \cdot OSO_2R'$) to ketens has been previously reported at 80°, but the role of the enol form of the mixed anhydrides has not been recognized. Subsequent sulphonation rather than acetylation of keten by $AcOSO_3H$ [equation (11)] is more likely since acetylsulphuric acid is known to be a sulphonating rather than an acetylating agent.[26] Furthermore the formation of the sulpho-derivative (VI) can be assumed to proceed through the interaction of a cyclic compound [27] with AcOH.

On this basis the two main bands at δ 2.0 and 4.10 could be tentatively assigned to (VI).* As a result of reactions (10)—(12) the acid-proton concentration increases as shown by the increased ratio of the lowest-field band ($\delta \geqslant 12.65$) area to the higher-field band ($\delta \leqslant 4.10$) area sum from 0.12 in spectrum a to 0.25 in spectrum b. Although this indicates a shift of equilibrium between (I) and (II) towards (II), the acid protons are mostly accounted for by the presence of (VI), since no evidence of olefinic double bonds was obtained.

The i.r. spectrum of a room temperature sample (Table 1b) changed (relative to spectrum a) in accord with the n.m.r. data. The characteristic bands for (I)

* This assignment is also confirmed by sulphur analyses performed on the reaction mixture: ca. 75% of initial SO_3 is converted into organic sulphur.

[ν(C=O) 1 820 and ν(S=O) 1 416 and 1 218 cm^{-1}] are absent at room temperature; strong bands are, however, evident at 1 725 and at 1 365 and 1 170 cm^{-1}. These bands may respectively be assigned to the carbonyl (ν 1 725 cm^{-1}) and sulphuryl (ν 1 365 and 1 170 cm^{-1}) absorptions in (VI).[24b]

The 1 600—1 540 cm^{-1} bands, which at low temperature have been assigned to (II), increase significantly as a result of increasing acid-proton concentration in the system and therefore as a result of chelation [28] and/or protonation of C=O groups in (VI). Also the weak band 1 680 cm^{-1}, which at low temperature was assigned to the olefinic double bond in (II), is absent. Finally the typical bands of dehydroacetic acid between 1 550 and 1 720 cm^{-1} are confused with those of (VI).

(3) The AcOH–SO_3 system at low temperature ($\leqslant$ −20°). With an SO_3 concentration $\leqslant$15% w/w a freshly prepared equimolar mixture of SO_3 and AcOH in SO_2 is sufficiently stable at low temperature to observe spectroscopically equimolar concentrations of $AcOS_2O_6^-$ and $AcOH_2^+$, which are the main species present. Together with these species the formation of diacetyl sulphate had been previously hypothesized to occur according to reactions (13)—(15) with a low concentration of $(AcO)_2SO_2H^+$ at equilibrium.

Due to the findings reported above for the Ac_2O–SO_3 system we may now report that keto–enol equilibria are

$$2AcOH + SO_3 \rightleftharpoons AcOSO_3^- + AcOH_2^+ \qquad (13)$$

$$AcOSO_3^- + SO_3 \rightleftharpoons AcOS_2O_6^- \qquad (14)$$

$$AcOS_2O_6^- + AcOH_2^+ \rightleftharpoons \qquad \qquad (AcO)_2SO_2H^+ HSO_4^- \qquad (15)$$

also involved in the AcOH–SO_3 system; specifically in this case however we have found that these equilibria refer mainly to acetyl disulphate rather than acetyl or diacetyl sulphate.

In fact starting from an equimolar mixture of AcOH and SO_3 in SO_2, after several hours at −20°, the initial (Table 1c) C=O absorption of $AcOS_2O_6^-$ (1 805 cm^{-1}) decreases (Table 1d) and the 1 612—1 545 cm^{-1} bands (assigned before low temperature conditioning to $AcOH_2^+$ only) increase markedly relative to the 1 805 cm^{-1} band intensity. This is probably due to the establishment of the tautomeric equilibrium (16); thus the

$$CH_3COOS_2O_6^- \rightleftharpoons CH_2\!:\!COH \cdot OS_2O_6^- \qquad (16)$$
$$\text{(VIII)} \qquad \qquad \text{(VII)}$$

intensity increase of the 1 612—1 545 cm^{-1} bands (at the expense of that due to $AcOS_2O_6^-$) corresponds to the formation of the enol form (VIII) of the disulphate species absorbing at the same wavelengths reported for (II) and $AcOH_2^+$. Coherently with the formation of (VIII), the 1 370 [ν_{as}(S $\cdots$ O $\cdots$ H)] to 1 405 [ν_{as}(S=O)] cm^{-1} relative intensity increases; no modification is observed at 1 200 cm^{-1} since ν_s(S $\cdots$ O $\cdots$ H) and ν_s(S=O) bands could not be observed separately even in the freshly prepared mixture.
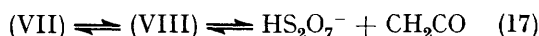
In this system the participation of diacetyl sulphate in

tautomerization cannot be established unambiguously due to its low concentration. No appreciable modification is indeed observed in the weak 1 875 cm^{-1} band, which in the freshly prepared mixture had been previously assigned to sulphur–oxygen protonated diacetyl sulphate.

Finally neither AcOSO$_3^-$ nor AcOH$_2^+$ appear involved in tautomerization equilibria since no changes are observed in the 0.5 mole ratio spectra on standing at $-20°$.
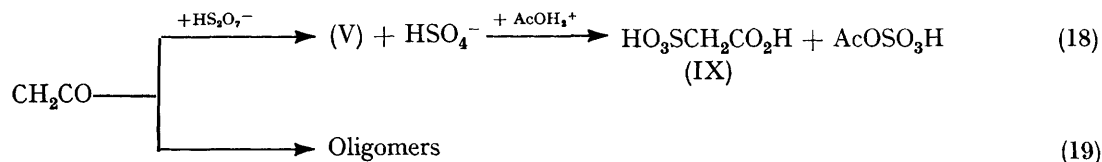
The modifications observed in the i.r. spectra are in fair agreement with those observed in the n.m.r. spectra. At a SO$_3$/AcOH mole ratio of 1.0, the n.m.r. spectrum (Table 2c) of the freshly prepared mixture contains a single high-field proton band at δ 2.61, which has been previously justified with the rapid exchange of equimolar AcOS$_2$O$_6^-$ and AcOH$_2^+$ species. At $-20°$, however, this band splits (Table 2d) and the ratio of the high-field ($\delta \leqslant 2.75$) band area sum to the low-field ($\delta \geqslant 14.47$) band area decreases from 3 to 2.45 (spectra c and d, respectively), indicating increasing concentration of acid protons. The δ 2.50 chemical shift is in fair agreement with that previously extrapolated [8] for the methyl protons of acetyl disulphate. The other bands may be assigned to the methyl protons of AcOH$_2^+$ (δ 2.66) and to the methylene * protons of CH$_2$:COH·OS$_2$O$_6^-$ (δ 2.75).

Finally the relative equilibrium concentration of (VIII), (VII), and AcOH$_2^+$ can be obtained (see Experimental section).

(4) *The* AcOH–SO$_3$ *system at room temperature.* While no changes are observed at the SO$_3$/AcOH 0.5 mole ratio, thus indicating that AcOSO$_3^-$ is stable even at room

$$(\text{VII}) \rightleftharpoons (\text{VIII}) \rightleftharpoons \text{HS}_2\text{O}_7^- + \text{CH}_2\text{CO} \quad (17)$$

temperature, at the SO$_3$/AcOH 1.0 mole ratio at the same temperature we found that AcOS$_2$O$_6^-$ undergoes thermal cleavage † to keten [reaction (17)] which may further react by (18) and (19).

1 805 cm^{-1} band of (VII) while two strong bands at 1 612 and 1 545 cm^{-1} can be assigned to both AcOH$_2^+$ and AcOSO$_3$H. Finally the absorptions at 795 and 705 cm^{-1} are due to HS$_2$O$_7^-$,[29] which is not completely converted through equation (18) since (19) occurs too.

(b) *Effect of Excess of* SO$_3$ *on the Tautomerization of Mixed Acetic Sulphuric Anhydrides.*—Both systems (Ac$_2$O– or AcOH–SO$_3$) upon increasing the SO$_3$ mole ratio above 1.0 evolve unequivocally towards the formation of acetylium ions. The complex equilibria involved in this case will be dealt with in a subsequent paper.

(c) *Mechanistic Considerations on the Acetylating (and/ or Sulphonating) Properties of Acetyl Sulphates.*— Acetylation performed with acetyl sulphates [23] are known to exhibit complications since, depending on the experimental conditions, these species may also induce intra- or inter-molecular sulphonation.[24] With other acylating systems (acyl and metal halides) [5] it has been shown that, according to the system considered, acylations may occur with or without acylium ion participation; in the former case the involvement of ' keten-like ' species has been considered as in (2).[6] In agreement with this assumption, starting from acids or anhydrides in sulphuric media, due to the complications reported above, previous investigators have not considered the possibility of the involvement of keten species without the unequivocally established participation of acetylium ions.[30]

The involvement of keten in sulphuric acid reactions [31] may, however, occur on raising the temperature (80°). In this case it has been inferred that the active precursor of a keten intermediate [26,27b] is a mixed carboxylic sulphonic anhydride (RCOY; R = cyclohexyl, Y = 1-carboxycyclohexanesulphonate). It has now been found that starting from mixed carboxylic sulphuric anhydrides such as acetyl sulphates, even at lower temperatures keten oligomers may be isolated without evident particpation of acetylium ions. This may be


$$\text{CH}_2\text{CO} \begin{cases} \xrightarrow{+ \text{HS}_2\text{O}_7^-} (\text{V}) + \text{HSO}_4^- \xrightarrow{+ \text{AcOH}_2^+} \underset{(\text{IX})}{\text{HO}_3\text{SCH}_2\text{CO}_2\text{H}} + \text{AcOSO}_3\text{H} \qquad (18) \\ \\ \xrightarrow{\phantom{+ \text{HS}_2\text{O}_7^-}} \text{Oligomers} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (19) \end{cases}$$

The n.m.r. bands initially (Table 2d) assigned to (VII) (δ 2.50) and (VIII) (δ 2.75) are absent from the spectrum (Table 2e) of the room temperature sample, whereas a major band at δ 4.4 ‡ is observed and can be assigned to the methylene protons of sulphoacetic acid (IX). The δ 2.66 band may be common to both AcOH$_2^+$ and AcOSO$_3$H; the other bands at δ 2.15, 3.41, and 5.0—5.5 may be due to other oligomerization products which, except for dehydroacetic acid, were not identified.

The i.r. evidence agrees with the n.m.r. data. A new broad band at 1 710 cm^{-1} (Table 1e), which may be assigned to HO$_3$SCH$_2$CO$_2$H,[24b] appears in place of the

due to the higher (relative to mixed carboxylic sulphonic anhydrides) electron-withdrawing effect of AcOSO$_3$ or S$_2$O$_6^-$ moieties present in (I) and (VII) respectively, which through an evident enolization step facilitates the mechanism of thermal cleavage [reaction (20].

On the basis of this finding it becomes necessary to reconsider some controversial aspects related to other acylating systems. For Ac$_2$O–SnCl$_4$, the formation of condensation products (oligomers) has been suggested by Hunt and Satchell [16] as a consequence of preliminary

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* The presence of an olefinic double bond inferred from spectroscopic data has been further supported through chlorination experiments.
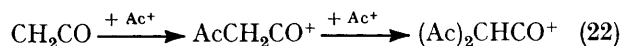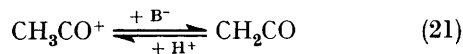
† The participation of diacetyl sulphate, however, cannot be rigorously excluded.

‡ A medium effect may be responsible for the 0.35 p.p.m. low-field-shifted value relative to that (δ 4.05) reported for the Ac$_2$O system.[24b]
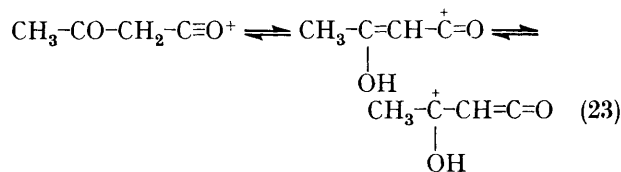
enolization * of the active acetylating intermediate (the donor–acceptor complex Ac_2O–$SnCl_4$; based on i.r. data, no mention is made of Ac^+ participation). On the other hand, starting from AcCl and $AlCl_3$,[7] a plausible mechanism has recently been reported for the formation of

$$\longrightarrow^{\Delta} \quad CH_2CO + YOSO_3H \quad (20)$$

$$Y = SO_3^- \text{ or } Ac$$
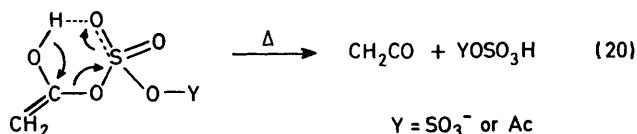
diacetoacetylium ions in which the rate-limiting step is assumed to be the deprotonation (at low acidities) of acetylium ions [reactions (21) and (22)]. Although

$$CH_3CO^+ \underset{+ H^+}{\overset{+ B^-}{\rightleftharpoons}} CH_2CO \quad (21)$$

$$CH_2CO \xrightarrow{+ Ac^+} AcCH_2CO^+ \xrightarrow{+ Ac^+} (Ac)_2CHCO^+ \quad (22)$$

equilibrium (21) seems justified on the basis of the time dependent i.r. absorption intensity of Ac^+ (2 300 cm^{-1}), no such evidence was reported for a very similar system ($AcBr$–$AlBr_3$)[33] though diacetoacetylium ions were again shown to be present. Furthermore, referring again to equilibrium (21), while the deprotonation of the acetoacetylium ion has been observed directly in superacid systems[34] through an enolization step which seems necessary in terms of charge delocalization [reaction (23)], no such observation has been reported directly for

$$CH_3\text{–}CO\text{–}CH_2\text{–}C\equiv O^+ \rightleftharpoons CH_3\text{–}C\text{=}CH\text{–}\overset{+}{C}\text{=}O \rightleftharpoons$$
$$\underset{OH}{|}$$
$$CH_3\text{–}\overset{+}{C}\text{–}CH\text{=}C\text{=}O \quad (23)$$
$$\underset{OH}{|}$$

acetylium ions. Although basicity of the system may be necessary for the establishment of equilibrium (21), other arguments also come into consideration. So far as our system is concerned, we have to admit that the involvement of 'keten-like' species mainly implies the enolization of acetyl sulphates without evident participation of acetylium ions.

* Somewhat confusing evidence of enolization in 1 : 1 acetyl–metal halide complexes leading to the formation of the 'Illari' compound, $CH_2{:}CClO{\cdot}AlCl_2$, has been produced.[32]

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