

## 227. *The Methanesulphonic Acid-Sulphur Trioxide Complex : Detection by Raman Spectroscopy.*

By I. SANDEMAN.

The Raman spectra and crystallising points of solutions of sulphur trioxide of varying concentration in methanesulphonic acid have been measured. It is concluded that a mixed anhydride of methanesulphonic and sulphuric acids is formed, and this forms the complex  $\text{Me}\cdot\text{SO}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}\cdot 2\text{Me}\cdot\text{SO}_3\text{H}$ . The Raman spectrum of oleum is also reported.

VICARY and HINSHELWOOD (*J.*, 1939, 1372), in studying the kinetics of the sulphonation of nitrobenzene by sulphur trioxide, concluded that the reaction was of the second order with respect to the trioxide and was strongly retarded by the formation of a complex between it and the sulphonic acid. Their data indicate a 1 : 1 complex. A similar conclusion was reached by Wadsworth and Hinshelwood (*J.*, 1944, 469) in studying the kinetics of the sulphonation by sulphur trioxide of *p*-nitrotoluene and chlorobenzene. It is important for the interpretation of the kinetics of sulphonation to determine whether complexes are formed between sulphur trioxide and sulphonic acids. With this end in view, an attempt was made to study the Raman spectrum of toluene-*p*-sulphonic acid solutions in oleum. This attempt had, however, to be abandoned, because it proved impossible to obtain solutions of sufficient clarity for investigation of their spectra. Satisfactory results were, however, obtained with solutions of sulphur trioxide in methanesulphonic acid.

Pyrosulphuric acid is known from Chédin's work (*Ann. Chim.*, 1937, 8, 243) to have a Raman spectrum entirely distinct from that of sulphuric acid, and the changes resulting from the treatment of sulphuric acid with increasing quantities of the trioxide can be followed spectroscopically. Briefly, what happens is that in oleum of low trioxide content the Raman lines of concentrated sulphuric acid are observed, but increase of trioxide causes decreasing intensity, and new lines due to pyrosulphuric acid appear. As the equimolecular stage of concentration is reached (about 45%  $\text{SO}_3$  by wt.), the sulphuric acid spectrum fades out, and only that of pyrosulphuric acid is left. At still higher concentrations new lines traceable to free trioxide appear superimposed on the pyrosulphuric acid spectrum. If sulphonic acids form analogous compounds with sulphur trioxide, similar changes should occur in the Raman spectra of their solutions with the trioxide.

As the principal desideratum in handling the methanesulphonic acid solutions of sulphur trioxide was to minimise contact with moisture and dust-laden air, the apparatus used was designed for preparing the solutions and introducing them into the Raman tube entirely under glass. When air was rigidly excluded, the solution in the Raman tube showed only a very faint pink colour when the tube was viewed in daylight through the optical flat closing its end. The Raman tube was surrounded with a heating coil which could be used to prevent the contents from solidifying.

*The Raman Spectra.*—The spectrum of sulphuric acid is shown in Table 1, that of methanesulphonic acid in Table 2, and the spectra of pyrosulphuric acid and the complex formed between methanesulphonic acid and sulphur trioxide side by side in Table 3. These tables give approximate visual estimates of intensity based on the best exposures.

The Raman spectrum was taken with a Hilger E 612 spectrograph. A filter containing solutions of sodium nitrite and praseodymium nitrate was used, which served to clarify the spectrum on the long-wave side of the exciting mercury line 4358 Å as well as to reduce the intensity of the 4047 Å line. The lamp-head consisted of four Osira lamps under-run at 20–60 volts. Exposures of  $14\frac{1}{2}$  hours were made with a slit of about 25 μ. As the spectra studied were diffuse, it is only possible to claim an accuracy of about  $\pm 6 \text{ cm.}^{-1}$  for the Raman shifts, that of the stronger lines averaged over a considerable number of plates being better than this (cf. the measurements of sulphuric acid in Table 1 with literature values). Wave-lengths were calculated from the comparison spectrum of a small neon lamp by Hartmann interpolation.

To obtain the spectrum of pyrosulphuric acid, oleum of various weight concentrations of trioxide up to 56% was used. The results of this work confirmed those of Chédin (*loc. cit.*), and the general conclusions were the same, *viz.*, those recorded on p. 1135, but there are differences in detail. Chédin gives pyrosulphuric acid lines at the following wave-numbers : 300, 327, 480, 735, 960, and 1250  $\text{cm}^{-1}$ . The first two are components of the doublet given in Table 3 as 311  $\text{cm}^{-1}$ . The next three correspond to those at 465, 729, and 944  $\text{cm}^{-1}$ .

TABLE 1. *Raman spectrum of sulphuric acid.\**

$\Delta\nu$ , $\text{cm}^{-1}$	Previous work : †		$\Delta\nu$ , $\text{cm}^{-1}$	Previous work : †		$\Delta\nu$ , $\text{cm}^{-1}$	Previous work : †	
	A	B		A	B		A	B
411 (3)	410 (1b)	381	911 (5)	916 (8)	910	1136 (3)	1140 (4)	1121
Doublet		417	969 (1b) ‡		978	1187 (0)		1195
561 (4b)	564 (5b)	555	1049 (2)	1045 (0)		1365 (1b)	1364 (1)	

\* b = Broad.

† A = Angus and Leckie, *J.*, 1939, 1372. B = Woodward and Horner, *Proc. Roy. Soc.*, 1934, *A*, 144, 129.

‡ This line was difficult to measure owing to its nearness to the barium line 4554 Å, a trace of which appeared on all the plates, owing to the fact that the electrodes of Osira lamps are coated with barium oxide.

TABLE 2. *Raman spectrum of methanesulphonic acid,  $\Delta\nu(\text{cm}^{-1})$ .*

335 (3b),\* 502 (2), 535 (4), 769 (6), 895 (1), 1179 (4), 1413 (3), 2945 (5), 3030 (3), 3125 (3).

\* Doublet with components about 324 and 341.

Notes : (i) b = Broad.

(ii) Besides the above there were traces of lines at 253, 292, and 980  $\text{cm}^{-1}$ .

(iii) The lines at 769 and 2945  $\text{cm}^{-1}$  come very near lines observed in the complex with  $\text{SO}_3$ . In the case of 2945  $\text{cm}^{-1}$  this is not surprising since  $\text{CH}_3$  stretching vibrations would not be expected to vary very much between the sulphonic acid and its complex with  $\text{SO}_3$ .

TABLE 3. *Raman spectra of pyrosulphuric acid and of  $\text{CH}_3\cdot\text{SO}_3\text{H}\cdot\text{SO}_3$  complex,  $\Delta\nu(\text{cm}^{-1})$ .*

$\text{H}_2\text{S}_2\text{O}_7$	Complex	$\text{H}_2\text{S}_2\text{O}_7$	Complex	$\text{H}_2\text{S}_2\text{O}_7$	Complex
234 (1) *	230 (1) *	498 (1)	—	810 (0)	772 (1)
271 (1)	261 (2)	527 (2)	513 (4)	901 (5)	922 (0)
311 (4b) †	309 (5b) ‡	682 (1)	655 (2)	944 (1) *	944 (1) *
334 (1)	372 (2)	729 (4) *	691 (4)	—	1177 (5)
465 (1) *	469 (1) *	798 (1)	731 (2) *	—	2945 (3)

Notes : (i) b = Broad.

(ii) A few very faint lines observed in only one plate are omitted from the lists.

\* These lines occur at about the same wave-number in both complexes.

† Doublet with components about 298 and 327.

‡ Doublet with components about 301 and 317.

|| These lines come very near those of gaseous  $\text{SO}_3$ .

The last was not observed, unless it corresponds to the trioxide line at 1226  $\text{cm}^{-1}$ . Chédin also identified trioxide lines at 245, 535, 688, and 1075  $\text{cm}^{-1}$ . These correspond to lines found at 234, 527, 682, and 1068  $\text{cm}^{-1}$ . It seems likely that only the last is an actual line of the trioxide. Measurements of the Raman lines of gaseous trioxide are now available from the work of Gerding and Nijveld (*Rec. Trav. chim.*, 1940, 59, 1206). It seems at this stage safest to classify as lines due to the trioxide only those which appear in its solutions in both sulphuric acid and methanesulphonic acid of high trioxide concentration at wave-numbers agreeing with the literature values for the Raman spectrum of the trioxide. When this is done, only five lines observed in the spectra of these solutions can be allocated with certainty to sulphur trioxide, *viz.*, at 123 (0), 166 (1), 1068 (6), 1226 (4, sharp), and 1390 (3, diffuse doublet). Lines found in the spectra of pyrosulphuric acid and the methanesulphonic acid-trioxide complex (but not in both) which come near the literature values for trioxide lines are indicated in Table 3.

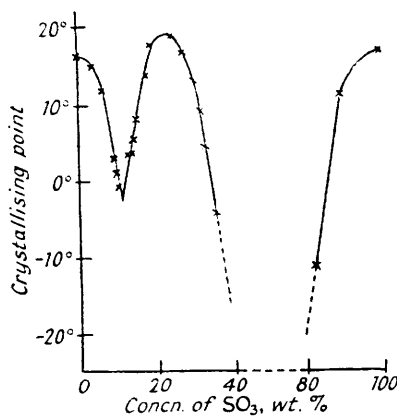
The Raman spectrum of solutions of the trioxide in methanesulphonic acid was obtained for various weight-concentrations up to 67%. The results showed that the spectrum of the parent liquid fades with increase of trioxide and is replaced by that of the complex, just as in the case of oleum, except that the onset of the spectrum of the complex here appears

to take place at a lower concentration of trioxide. As with oleum, the lines of the trioxide begin to appear when it reaches a high concentration.

*Crystallising Points of Solutions of Sulphur Trioxide in Methanesulphonic Acid.*—The apparatus used consisted of a tube about 30 cm. long, in two parts joined by a cone and socket. By rotating the top part in the course of taking crystallising points it was possible to alter the position of the thermometer and so facilitate readings. The lower part of the tube was fitted with a spiral stirrer actuated by a handle in a side-arm. Cone and socket joints were lubricated with methanesulphonic acid. To decrease the rate of cooling, a cork and outer tube were fitted to interpose an air space between the solution and the cooling-bath. Crystallising points were found by slow cooling and noting the highest temperature indicated by the thermometer after solidification had set in. At points on the low-concentration side of the first eutectic, *viz.*, those for which methanesulphonic acid came out of solution on freezing, this method may yield low results since extensive supercooling was possible. The figure shows a graph of crystallising point plotted against weight-concentration of trioxide. For concentrations between 37% and 83% the liquid became very viscous and crystallising points could not be measured.

*Discussion.*—The Raman spectra show that a complex is formed between methanesulphonic acid and sulphur trioxide and the m. p. diagram, which has a peak about con-

Concentration of  $\text{SO}_3$  (by wt.) in  $\text{Me}\cdot\text{SO}_3\text{H}$  solution plotted against crystallising point.

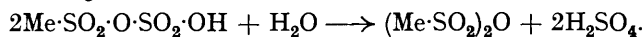


centration 21%, shows that the compound solidifying from solution contains 3 molecules of methanesulphonic acid to one of sulphur trioxide. The configuration of such a complex would appear at first sight to be a hydrogen-bonded one, since any other configuration than this would involve the placing of too many oxygen atoms round the central sulphur atom of the trioxide molecule entering into the complex. The Raman spectrum of the complex, which differs from that of methanesulphonic acid and resembles that of pyrosulphuric acid, is, however, not easy to reconcile with a hydrogen-bonded configuration.

Vicary and Hinshelwood's data (*loc. cit.*) for the kinetic behaviour of the sulphonation of nitrobenzene have been examined and found inconsistent with the assumption of a 3 : 1 complex  $3\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}\cdot\text{SO}_3$ . In considering the facts of the case one must take into account a chemical property of solutions of the trioxide in methanesulphonic acid, *viz.*, that, if a solution containing up to about 40% of trioxide is poured into water, a white precipitate is formed in small yield which appears to be methanesulphonic anhydride.

The above facts are all consistent with an initial reaction of methanesulphonic acid with sulphur trioxide to give the mixed anhydride  $\text{Me}\cdot\text{SO}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$ , followed by the attachment of two molecules of methanesulphonic acid by hydrogen bonding. As far as the Raman spectrum is concerned this view would explain why spectra of solutions of sulphur trioxide in methanesulphonic acid are so different from that of methanesulphonic acid and resemble that of pyrosulphuric acid. It would also explain why the spectrum of the trioxide begins to appear only at a concentration of about 50% and why some traces of the methanesulphonic acid spectrum are found at concentrations about 20%. With regard

to the crystallising-point curve, the view would explain why a peak occurs at a concentration of about 21%. (The theoretical peak concentration for  $\text{Me}\cdot\text{SO}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$ ,  $2\text{Me}\cdot\text{SO}_3\text{H}$  would be 21.7%.) The absence of a peak at 45.5% (theoretical peak concentration for  $\text{Me}\cdot\text{SO}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$ ) would also be explained, since amounts of pure methanesulphonic acid and sulphur trioxide must be presumed present which would depress the crystallising point. The view would also be consistent with the evidence for 1 : 1 complexes in the case of aromatic sulphonic acids and would explain the formation of methanesulphonic anhydride when solutions of the trioxide in methanesulphonic acid are poured into water, since the function of the water would be to remove the hydrogen-bonded  $\text{Me}\cdot\text{SO}_3\text{H}$  molecules, the reaction then proceeding :



IMPERIAL CHEMICAL INDUSTRIES LIMITED, RESEARCH LABORATORIES,  
HEXAGON HOUSE, MANCHESTER, 9.

[Received, November 27th, 1952.]

---