Tetra-n-alkylammonium Bisulphites: a New Example of the Existence of the Bisulphite Ion in Solid Compounds

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Liquid sulphur dioxide reacts with aqueous NR_4OH (R = Et, Bu^n, or n-pentyl) solutions to form the corresponding bisulphite. I.r. studies indicate that the compounds contain the bisulphite ion with structure $H{-}SO_3^-$, having essentially C_{3v} symmetry. The preparative method used is that which leads to the formation of tetramethylammonium pyrosulphite when tetramethylammonium hydroxide is treated with sulphur dioxide. Tetra-n-propylammonium hydroxide, on treatment with sulphur dioxide, yields tetra-n-propylammonium pyrosulphite. The i.r. spectra of the tetra-alkylammonium bisulphites and pyrosulphites are recorded and discussed.

THIS paper reports the preparation of three solid tetra-n-alkylammonium bisulphites. The bisulphite ion can have two possible structures: first where the hydrogen is bonded to the sulphur atom, HSO_3^-, and second where the hydrogen is bonded to an oxygen atom, $HO{\cdot}SO_2^-$. The HSO_3^- ion is expected to have C_{3v} symmetry, whereas the $HO{\cdot}SO_2^-$ ion should have C_s symmetry. Raman studies on solutions of bisulphites by Simon [1,2] show that the HSO_3^- ion has C_{3v} symmetry. In aqueous solutions, both forms can exist in a tautomeric equilibrium. Until now, only two bisulphites, namely those of caesium and rubidium, have definitely been shown to exist in the solid state [3,4] and the i.r. spectra recorded for these two compounds are in accord with their containing the HSO_3^- ion of C_{3v} symmetry. In the five solid bisulphites now definitely known, the bisulphite ion has the HSO_3^- structure of C_{3v} symmetry.

Despite the many reported preparations of solid bisulphites, notably those of sodium and potassium, no *X*-ray structure determinations have been made. When i.r. spectra of some of the reported alkali-metal bisulphites were recorded, they were found to be pyrosulphites. Contary to statements in many textbooks, the bisulphites of lithium, sodium, and potassium have never been obtained as solids. Rocchiccioli [5] attempted to prepare solid sodium bisulphite, by a number of methods, for an i.r. study of the ion. He could, however, only obtain the pyrosulphite or sulphite, both of which were easily identified by their i.r. spectra. Similarly, Herlinger and Long [6] observed that there was a change in the i.r. spectrum on concentrating a solution of potassium bisulphite, and no evidence has been obtained for the formation of solid sodium bisulphite.

I.r. studies show that the methods given for preparing bisulphites are not generally applicable. A survey of some of the older literature reporting bisulphite preparations shows that often bisulphite was assumed to have been formed merely from stoicheiometric requirements. For example, when solutions of equimolar amounts of sodium hydroxide and sulphur dioxide in water were mixed, it was assumed that the addition of ethanol would precipitate the product of the reaction: $NaOH + SO_2 \longrightarrow NaHSO_3$. Analytical figures were seldom quoted for the reported bisulphites, and when they were, any deviations of analyses from the theoretical values were usually attributed to difficulties in obtaining a pure sample. Despite the general acceptance that bisulphites could readily be prepared, a number of workers did express doubts before i.r. studies were carried out. Foerster,[7] in a study of the sulphito-compounds of sodium and potassium, questioned the existence of solid bisulphites of these metals, and it was later suggested [8] that sodium pyrosulphite was more stable than the bisulphite and that the former compound was obtained when sodium bisulphite solutions were evaporated. The validity of these comments has been established by i.r. studies, and of the alkali metal bisulphites, only those of

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[1] A. Simon and K. Waldmann, *Z. anorg. Chem.*, 1955, **281**, 113, 135.

[2] A. Simon and K. Waldmann, *Z. anorg. Chem.*, 1956, **284**, 36.

[3] A. Simon and K. Waldman, *Naturwiss*, 1957, **44**, 33.

[4] A. Simon and W. Schmidt, *Z. Electrochem.*, 1960, **64**, 737.

[5] C. Rocchiccioli, *Ann. Chim.*, 1960, **5**, 999.

[6] A. W. Herlinger and T. V. Long, *Inorg. Chem.*, 1969, **8**, 2661.

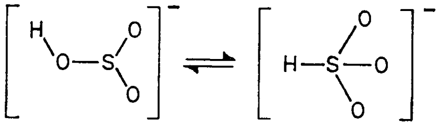
[7] F. Foerster, A. Brosche, and C. Norberg-Schultz, *Z. phys. Chem.*, 1924, **110**, 435.

[8] *Chemical Trade Journal*, 1932, **90**, 433.

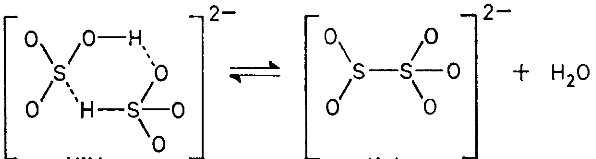
caesium and rubidium have been obtained in the solid state.

The effect of concentration on solutions of sodium pyrosulphite/bisulphite has been studied by Simon[1,2] using Raman spectroscopy and by Golding[9] using u.v. spectroscopy.

In aqueous solution, the pyrosulphite and bisulphite ions are related to each other through a series of equilibria dependent on hydrogen-bonding interaction, and the positions of these equilibria are profoundly affected by concentration. A dilute (3×10^{-3}M) solution of sodium bisulphite contains bisulphite ions in the two isomeric forms (i) and (ii),


(i) (ii)

At higher concentrations (>10^{-2}M), these two tautomers interact by hydrogen-bonding to give species (iii), which in turn is in equilibrium with the pyrosulphite ion (iv).


(iii) (iv)

The existence of these equilibria explains why solid sodium bisulphite cannot be obtained by concentrating an aqueous solution of this salt, since removal of the water only causes the formation of pyrosulphite by shifting the final equilibrium to the right.

In non-aqueous solutions the positions of these equilibria many vary according to the nature of the solvent. In the solid state, the magnitude of the lattice energy may play a dominant part.

The tetra-alkylammonium bisulphites were prepared in a similar way to tetramethylammonium pyrosulphite.[10] It appears that the larger cations stabilise HSO_3^- ion relative to $S_2O_5^{2-}$ ion, and it seems in this case that the lattice energy of tetra-alkylammonium bisulphite is sufficient to overcome the tendency of the dimeric ion (iii) to lose water to form the pyrosulphite ion. We find the position with regard to the tetra-n-propyl compound is anomalous, however.

The effect of cation size on the stability of bisulphite relative to pyrosulphite in the tetra-alkylammonium series is not fully understood. The larger cations are not spherical, and a comparison with the alkali-metal compounds would suggest that, since the tetramethylammonium ion is larger than the rubidium ion, it might stabilise bisulphite relative to pyrosulphite in the solid. However, in the absence of structural information, a correlation of relative stabilities with lattice energy cannot be made.

The i.r. bands of the tetra-alkylammonium bisulphites are listed in the Table, and are compared with those of the tetra-alkylammonium pyrosulphites.

Infrared bands due to the sulphito-anion in tetra-alkylammonium pyrosulphites and tetra-alkylammonium bisulphites * (cm^{-1})

$(R_4N)_2S_2O_5$	$R^1_4NHSO_3$	
430		
463w		
	502s	asym S–O bend
505s	508s	
520sh		
550s		
579w		
619w	627s	sym S–O bend
651s		
952s		
960s		
974s		
	999w	
	1020w	
1051m	1048s	sym S–O stretch
1100m	1101m	asym S–H bend
	1115m	
	1145m	
1165sh		
1180s	1175sh	
1198sh	1205s	asym S–O stretch
	1230s	
	2435m	sym S–H stretch

* R = Me, Pr^n; R^1 = Et, Bu^n, n-pentyl.

A comparison of the two types of spectra, between 700 and 400 cm^{-1} in particular, indicates that the compounds contain completely different anions. Strong evidence for a bisulphite ion of C_{3v} symmetry comes from the band at 2435 cm^{-1} which can be assigned to the S–H stretching frequency. For a bisulphite ion of C_{3v} symmetry, six bands should be observed.[2] Probable band assignments for the tetra-alkylammonium bisulphites are given in the Table.

Since the degeneracies have been lifted, a certain amount of interaction must occur in the solid state, which lowers the symmetry of the anion, but it is concluded that the bisulphite ion in the tetra-alkylammonium bisulphites has the structure $H\text{-}SO_3^-$, with essentially C_{3v} symmetry.

An examination of the i.r. spectra of aqueous solutions of tetraethylammonium bisulphite and tetramethylammonium pyrosulphite indicates that the solutions contain a mixture of pyrosulphite ion and bisulphite ion.

It was not possible to convert the bisulphites to the corresponding pyrosulphites by heating, according to the method used by Simon,[2] since the tetra-alkylammonium bisulphites decompose below the temperature required for the conversion.

EXPERIMENTAL

Tetraethylammonium Bisulphite.—Excess of liquid sulphur dioxide was slowly added to 40% aqueous tetraethylammonium hydroxide solution (100 ml). After 48 h, the resultant yellow solution was pumped to dryness to yield a white solid (Found: C, 45·3; H, 10·0; N, 6·55; SO_2, 30·25. $C_8H_{21}NO_3S$ requires C, 45·5; H, 9·95; N, 6·65;

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[9] R. M. Golding, *J. Chem. Soc.*, 1960, 3711.

[10] R. E. Johnson, T. H. Norris, and J. L. Huston, *J. Amer. Chem. Soc.*, 1951, **73**, 3052.

SO_2, 30·35%). Similarly prepared were ***tetra-n-butylammonium bisulphite*** (Found: C, 59·25; H, 11·1; N, 4·5; SO_2, 19·6. $C_{16}H_{37}NO_3S$ requires C, 59·4; H, 11·4; N, 4·35; SO_2, 19·8%), *tetra-n-amylammonium bisulphite* (Found: C, 64·0; H, 11·85; N, 3·5; SO_2, 16·9. $C_{20}H_{45}NO_3S$ requires C, 63·35; H, 11·9; N, 3·7; SO_2, 16·9%), and *tetra-n-propylammonium pyrosulphite* (Found: C, 55·5; H, 10·7; N, 5·5; SO_2, 12·25. $C_{24}H_{56}N_2O_5S_2$ requires C, 55·8; H, 10·85; N, 5·4; SO_2, 12·4%).

Physical Measurements.—I.r. spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer as Nujol mulls. Since the compounds handled were moisture-sensitive, the mulls were prepared by grinding the solids finely and mixing them with sodium-dried Nujol in a dry bag. The mull was placed between potassium bromide discs, and a lead washer (0·05 mm thickness) used to provide a seal to exclude atmospheric moisture.

Sulphur dioxide was determined by titration of the bisulphite with iodine. Carbon, hydrogen, and nitrogen were determined by Mr. A. Hedley of this department.

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