ACTA CHEMICA SCANDINAVICA 26 (1972) 1591–1598

Hydrogen Bond Studies

55.* Infrared Study of 2,5-Dichlorobenzenesulfonic Acid Trihydrate and 2,5-Dibromobenzenesulfonic Acid Trihydrate

ANDERS ERIKSSON and JAN LINDGREN

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

Infrared spectra of the trihydrates of 2,5-dichlorobenzenesulfonic acid and 2,5-dibromobenzenesulfonic acid have been recorded. The X-ray diffraction studies of these acids indicated the existence of aggregates described as $H_2O\cdots H_3O^+\cdots OH_2$. These results are confirmed by the present study. The spectra of the corresponding dihydrates of the acids are also shown.

Several infrared and Raman investigations of the hydrated proton in the solid state have been reported in the literature.[1–10] From these studies the spectrum of the oxonium ion, H_3O^+, are well established. When higher hydrates with two or more water molecules are considered, the increased number of different possible structural arrangements complicates the interpretation of the spectra. It is therefore necessary to perform parallel studies using both spectroscopic and diffraction techniques.

The present paper deals mainly with the infrared spectra of the hydrated proton in the normal and deuterated trihydrates of 2,5-dichlorobenzenesulfonic acid and 2,5-dibromobenzenesulfonic acid. X-Ray diffraction studies of these acids have recently been carried out.[11,12] Relatively isolated aggregates described as $H_2O\cdots H_3O^+\cdots OH_2$ or $H_7O_3^+$ have been shown to exist (Fig. 1).

The spectra of the corresponding dihydrates are also presented, but in these cases the structure determinations have yet to be performed.

EXPERIMENTAL

The acids were prepared using a method described by de Crauw.[13] This description only deals with the chloro-compound but it was also found applicable to the bromo-compound. The deuterations were carried out by successive recrystallizations in heavy water (99.98 %).

* Part 54: *J. Solid State Chem.* **4** (1972) 255.

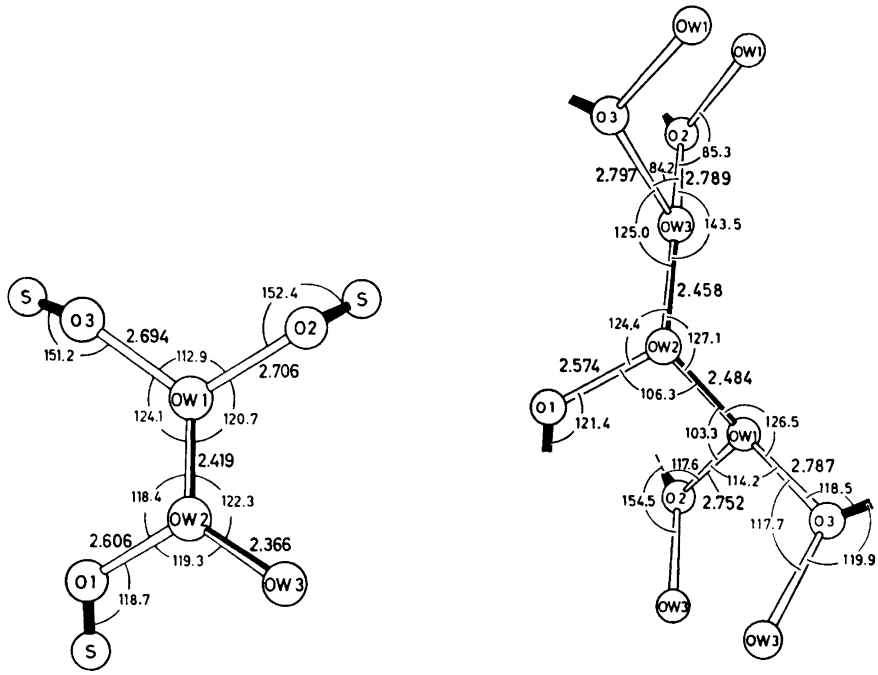

Fig. 1. Distances and angles within and around the $H_7O_3^+$ ion in $C_6H_3Cl_2SO_3H.3H_2O$ (a) $C_6H_3Br_2SO_3H.3H_2O$ (b). Hydrogen bonds within $H_7O_3^+$ are half filled and other hydrogen bonds are open. Covalent bonds are filled. (Drawings and data from Lundgren.[11,12])

In order to obtain a series of well defined hydrates, hygrostats with varying relative humidities were used. The trihydrates and the dihydrates were obtained in this way. These were stable over saturated aqueous solutions of sodium bromide and calcium bromide, respectively. The relative humidities at 25°C over these solutions are 57 % and 17 %.[14] The hydrates were analysed by gravimetry and by acidimetry. As an independent check the chloro-compound stable over a calcium bromide solution was also analysed at the Central Analytical Laboratory at this institute. The analysis gave 27.42 % C, 3.04 % H, and 26.83 % Cl. The calculated values for $C_6H_3Cl_2SO_3H.2H_2O$ were 27.39 %, 3.07 % and 26.95 %, respectively. On commencing the spectroscopic work, it soon became clear that the positions of the C–H out-of-plane bending vibrations gave an excellent *in situ* test of the purity of the hydrates (*cf.* Tables 1 and 2, and Figs. 2 and 3).

Thin films of mulls in nujol or hexachlorobutadiene were examined between plates of KBr or CaF_2. The samples of the dihydrates and the deuterated compounds were prepared in a dry box. The deuterated trihydrates required an artificial atmosphere of heavy water to prevent them from decomposing during preparation. This was achieved by boiling a suitable amount of heavy water in the dry box before the preparation.

The spectra were recorded using a Leitz IR III G double beam grating spectrometer calibrated with gas bands from HCl, H_2O, NH_3, and CO_2. Spectra between 2.5 μ (4000 cm^{-1}) and 18.5 μ (540 cm^{-1}) were obtained. To assist in identifying the bands from the hydrates, the spectra of the anhydrous acids and the sodium salts were also recorded. All spectroscopic studies were carried out at 27°C.

RESULTS AND DISCUSSION

The spectra are presented in Figs. 2 and 3. Band assignments and wave numbers are listed in Tables 1 and 2. These assignments in terms of group frequencies are not to be taken too literally since strong couplings certainly exist between the different modes in aromatic systems. Since the aim of the present study is to obtain spectroscopic data and complementary information as to the structure of the $H_7O_3^+$ aggregates, no discussion of bands arising from the anions will be given. In the following the chloro- and bromo-compounds are discussed together.

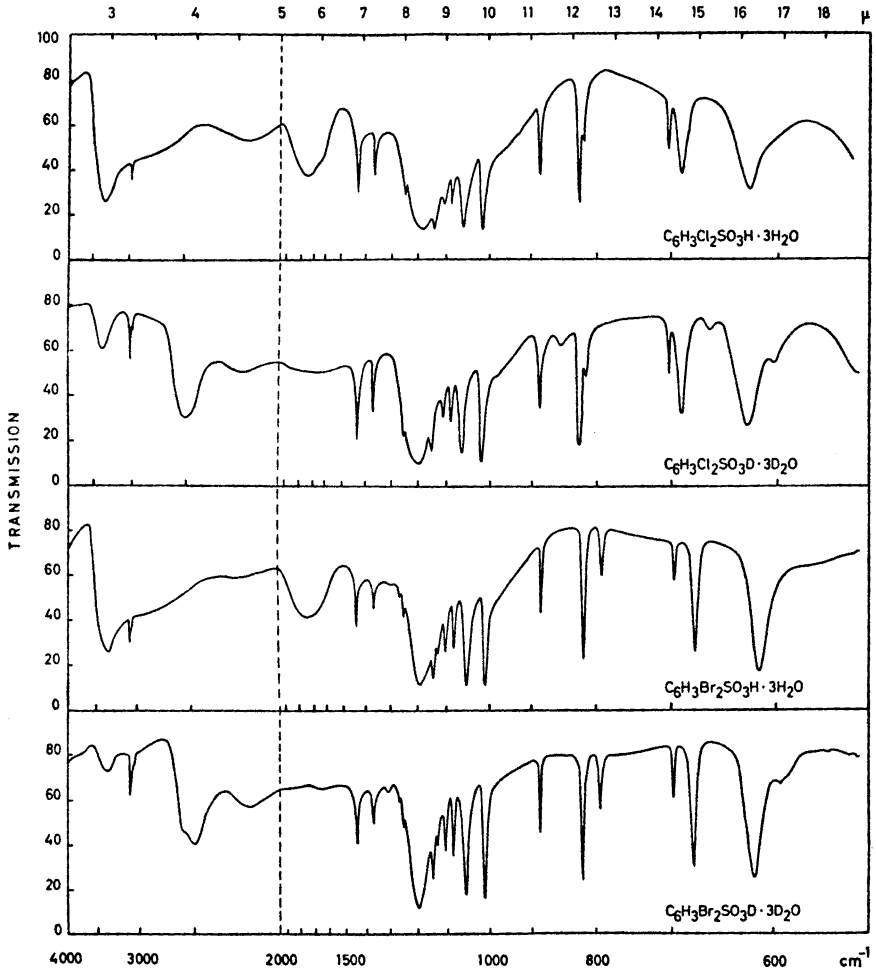

Fig. 2. Infrared spectra of the trihydrates combined from recordings with mulls in nujol and hexachlorobutadiene.

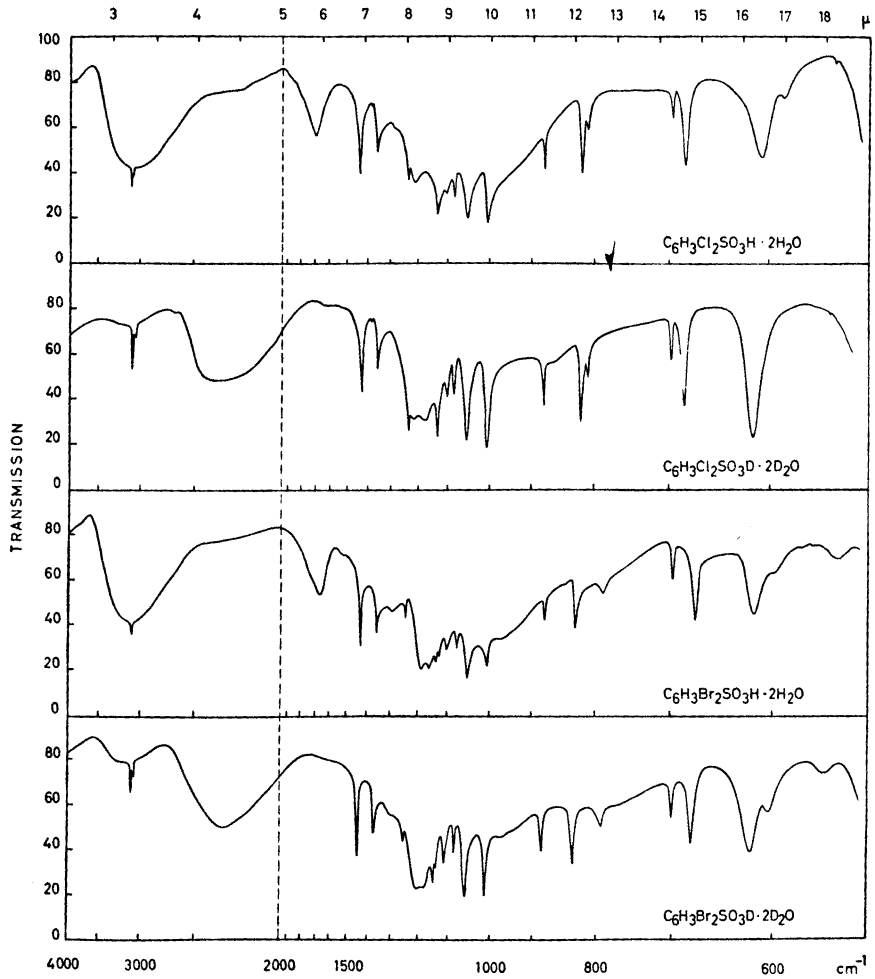

Fig. 3. Infrared spectra of the dihydrates combined from recordings with mulls in nujol and hexachlorobutadiene.

The trihydrates. No hydrogen atom positions from the $H_7O_3^+$ aggregates were obtained in the structure determinations.[11,12] However, the O···O distances (Fig. 1) gave clear evidence for the existence of such aggregates. The two oxygen atoms OW1 and OW3 were shown to be connected to the central oxygen atom OW2 by two very short hydrogen bonds. This implies that the spectra may be regarded as a superposition of bands from $H_7O_3^+$ ($D_7O_3^+$) and the anions. The question thus arises as to whether the hydrogen atoms in the OW1···OW2 and OW3···OW2 bonds are located close to the centre of these bonds or nearer to OW2. The latter would result in an

Table 1. Assignments of the bands of $C_6H_3Cl_2SO_3H.3H_2O$, $C_6H_3Cl_2SO_3D.3D_2O$, $C_6H_3Br_2SO_3H.3H_2O$ and $C_6H_3Br_2SO_3D.3D_2O$.

Wave numbers cm^{-1}				Assignment
$C_6H_3Cl_2SO_3H.3H_2O$	$C_6H_3Cl_2SO_3D.3D_2O$	$C_6H_3Br_2SO_3H.3H_2O$	$C_6H_3Br_2SO_3D.3D_2O$	
$H_7O_3^+$	$D_7O_3^+$	$H_7O_3^+$	$D_7O_3^+$	
~3400 (broad)	~3400 (broad)	~3480 (shoulder) ~3370 (broad)	~3370 (broad)	O–H stretching of H_2O or HDO
~2950 (broad)		~2950 (broad)		O–H stretching of H_3O^+
	~2550 (broad)		~2580 (shoulder) ~2500 (broad)	O–D stretching of D_2O
	~2200 (broad)		~2160 (broad)	O–D stretching of D_3O^+
~2150 (broad)		~2200 (broad)		Overtone to the band at 1100 cm^{-1} or a combination band.
~1770 (broad)		~1770 (broad)		Antisymmetric bending of H_3O^+
~1650 (shoulder)		~1650 (shoulder) 1175 (shoulder)		Bending of H_2O
~1100 (very broad)		~1100 (very broad)		Symmetric bending of H_3O^+
	855, 651			
$C_6H_3Cl_2SO_3^-$	$C_6H_3Cl_2SO_3^-$	$C_6H_3Br_2SO_3^-$	$C_6H_3Br_2SO_3^-$	
3090	3090, 3060	3090	3090	C–H stretching
1453, 1377, 1252	1453, 1377, 1252	1445, 1370, 1264, 1249	1445, 1370, 1264, 1249	Stretching vibrations of the benzene ring
1200	1200	1195	1195	Antisymmetric S–O stretching in the $-SO_3^-$ group
1152, 1119, 1065, 1017	1152, 1119, 1098, 1065, 1017	1149, 1135, 1110, 1087, 1055, 1008	1149, 1135, 1110, 1087, 1055, 1008	C–H in-plane bending
893, 825	893, 825	890, 817	890, 817	C–H out-of-plane bending
818	818	790	790	Ring vibration with participation of C–Cl (C–Br) stretching
703, 688	703, 688	695, 672	695, 672	Ring vibrations
620	620	611	614	S–O bending in the $-SO_3^-$ group or a ring vibration

H_3O^+ ion strongly hydrogen-bonded to two water molecules. Spectra of isolated H_3O^+ ions [1-5,7] and H_2O molecules in the solid state are already well determined. On the other hand, IR studies of compounds having a hydrogen

Table 2. Assignments of the bands of $C_6H_3Cl_2SO_3H.2H_2O$, $C_6H_3Cl_2SO_3D.2D_2O$, $C_6H_3Br_2SO_3H.2H_2O$ and $C_6H_3Br_2SO_3D.2D_2O$.

Wave numbers (cm^{-1})				Assignment
$C_6H_3Cl_2SO_3H.2H_2O$	$C_6H_3Cl_2SO_3D.2D_2O$	$C_6H_3Br_2SO_3H.2H_2O$	$C_6H_3Br_2SO_3D.2D_2O$	
$H_3O^+.H_2O$ (?)	$D_3O^+.D_2O$ (?)	$H_3O^+.H_2O$ (?)	$D_3O^+.D_2O$ (?)	
~3150 (broad)	~3150 (broad)	~3100 (broad)	~3100 (broad)	O–H stretching of H_3O^+ (HD_2O^+) and H_2O (HDO)
	~2350 (broad)		~2300 (broad)	O–D stretching of D_3O^+ and D_2O
~2270 (weak)		~2270 (weak)		A combination band or O–H stretching of H_3O^+ (symmetric?)
~1700 (broad)		~1690 (broad)		O–H bending of H_3O^+ and H_2O
	~1195			
~1000 (very broad)		~1000 (very broad)		Symmetric bending of H_3O^+
	~880 (weak)			
$C_6H_3Cl_2SO_3^-$	$C_6H_3Cl_2SO_3^-$	$C_6H_3Br_2SO_3^-$	$C_6H_3Br_2SO_3^-$	
3090	3090, 3060	3090	3090, 3060	C–H stretching
1453, 1377, 1252	1453, 1377, 1252	1447, 1374, 1252	1447, 1374, 1252	Stretching vibrations of the benzene ring
1230	1230	1195, 1170	1205, 1180	Antisymmetric S–O stretching in the $-SO_3^-$ group
1151, 1122, 1100, 1064, 1012	1151, 1122, 1100, 1064, 1012	1149, 1140, 1115, 1087, 1057, 1007	1149, 1140, 1115, 1087, 1057, 1007	C–H in-plane bending
891, 826	891, 826	886, 832	886, 832	C–H out-of-plane bending
815	815	790	790	Ring vibration with participation of C–Cl (C–Br) stretching
701, 686	701, 686	679, 673	679,673	Ring vibrations
610	617	616	616	S–O bending in the $-SO_3^-$ group or ring vibration

atom centred in an O···O bond in aggregates of the type $H^+ \cdot nH_2O$ have so far been carried out only for the cases of perchloric acid dihydrate, $H_5O_2^+ClO_4^-$,[9,10] and sulfuric acid tetrahydrate, $(H_5O_2^+)_2SO_4^{2-}$.[15] On comparing these two kinds of spectra with those obtained in the present study it must be concluded that our spectra are best interpreted in terms of a strongly hydrogen-bonded H_3O^+ and two H_2O molecules.

The bands from H_3O^+ and H_2O are easily identified since they are the only ones which move appreciably on deuteration. Some of the bands are not

found after deuteration because of overlapping bands from the anions combined with large intensity decrease. Their broadness which is characteristic of hydrogen-bonded systems is also useful for identification purposes.

The positions of the stretching bands of the H_3O^+ ions in the present case relative to those of less strongly bonded H_3O^+ ion are, as expected, shifted towards smaller wave numbers. On the same reasoning the bands of the antisymmetric bending vibrations of H_3O^+ are found at somewhat larger wave numbers.

The bands of the symmetric bending mode of H_3O^+ are unusually broad. They appear to extend from about 1350 cm^{-1} to 850 cm^{-1}. In the X-ray studies [11,12] it was noticed that the thermal ellipsoids of the atoms OW2 were very extended in the direction perpendicular to the plane approximately described by the four oxygen atoms OW1, OW2, OW3, and O1 (Fig. 1). This was discussed in terms of a disordered oxygen atom arrangement. Such a disorder would evidently contribute to the broadness of the bands. However, it is of interest here to consider a theoretical *ab initio* calculation of a free H_3O^+ ion carried out by Almlöf.[16] He has calculated the potential energy of an H_3O^+ ion (C_{3v} symmetry) as a function of the H – O – H angle. This resulted in a strongly anharmonic potential with an energy minimum at 117°. The potential energy increased rapidly for H – O – H angles below 117°. A small barrier to inversion was obtained ($\sim$0.3 kcal/mol). If such a potential situation still persists in the solid state or is only slightly modified a broadening caused by the anharmonicity will occur.

The dihydrates. Since no structure determinations have been carried out for the dihydrates, no detailed discussion of the spectra is possible. The spectra again seem to indicate, however, that the H_3O^+ ions are present. The bands from the remaining H_2O then have to be overlapped by bands from H_3O^+. The H_2O molecules evidently have to be strongly hydrogen-bonded for this to occur. From the spectra, however, it is not possible to ascertain whether or not the H_3O^+ ions and the H_2O molecules are connected.

Acknowledgements. The authors wish to thank Prof. S. Claesson at the Institute of Physical Chemistry at this university for the use of his IR spectrometer. We are also indebted to Prof. I. Olovsson for the facilities he has placed at our disposal and to Dr. J.-O. Lundgren for the structural data he has made available to us.

This work has been supported by grants from the *Swedish Natural Science Research Council* which are hereby gratefully acknowledged.

REFERENCES

1. Bethell, D. E. and Sheppard, N. *J. Chim. Phys.* **50** (1953) 744.
2. Bethell, D. E. and Sheppard, N. *J. Chem. Phys.* **21** (1953) 1421.
3. Ferriso, C. C. and Hornig, D. F. *J. Chem. Phys.* **23** (1955) 1464.
4. Mullhaupt, J. T. and Hornig, D. F. *J. Chem. Phys.* **24** (1956) 169.
5. Taylor, R. C. and Vidalle, G. L. *J. Am. Chem. Soc.* **78** (1956) 5999.
6. Rudolph, J. and Zimmermann, H. *Z. physik. Chem. (Frankfurt)* **43** (1964) 311.
7. Savoie, R. and Giguère, P. A. *J. Chem. Phys.* **41** (1964) 1640.
8. Gillard, R. D. and Wilkinson, G. *J. Chem. Soc.* **1964** 1640.
9. Pavia, A. C. and Giguère, P. A. *J. Chem. Phys.* **52** (1970) 3551.
10. Chemouni, E., Fournier, M., Rozière, J. and Potier, J. *J. Chim. Phys.* **67** (1970) 517.
11. Lundgren, J.-O. and Lundin, P. *Acta Cryst.* **B 28** (1972) 486.

12. Lundgren, J.-O. *Acta Cryst.* **B 28** (1972) 475.
13. de Crauw, T. *Rec. Trav. Chim.* **50** (1931) 53.
14. Kolthoff, I. M. and Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., Macmillan, New York 1952, p. 142.
15. Lindgren, J. *Acta Chem. Scand.* **26** (1972). *In press.*
16. Almlöf, J. and Wahlgren, U. *Theoret. Chim. Acta. In press.*

Received September 1, 1971.