THE INFRARED SPECTRA OF TIN(IV) TETRAHALIDES AND DIALKYLTIN DIHALIDES IN THE 500–50 CM^{-1} REGION

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Although the Raman spectra of the tin(IV) tetrahalides have been fully studied[1], little has been published on the infrared spectra as instrument limitations have, until recently, made it difficult to observe spectra in the lower frequency region.

The tin(IV) halides SnX_4 have T_d symmetry and therefore there are only two infrared active bands, namely ν_3 and ν_4, which have now been observed in the infrared spectra of the halides, all of which were recorded in cyclohexane solution.

TIN TETRAHALIDES

Stannic chloride

The two bands of the chloride are found at 407 (ν_3) and 127 (ν_4) cm^{-1}. The frequency for ν_3 is slightly higher than that reported[1] from the Raman spectrum (403 cm^{-1}) and recently reported[2] from the infrared spectrum of the chloride in benzene solution. The frequency of ν_4 given in the present work is lower than that obtained from Raman work (134 cm^{-1}); no previous infrared measurements are available in this region.

Stannic bromide

The ν_3 and ν_4 fundamentals occur at 280 and 86 cm^{-1}; both frequencies are in close agreement with the Raman frequencies[1]. There are in addition three weak bands which may be combination bands.

Stannic iodide

The infrared spectrum of stannic iodide in the solid state has been reported[3] but the ν_3 and ν_4 frequencies found in the present work at 219 and 71 cm^{-1} respectively are slightly higher. The corresponding Raman lines are found[4] at 216 and 63 cm^{-1}.

DIALKYLTIN DIHALIDES

The dialkyltin dihalides R_2SnX_2 have a slightly distorted tetrahedral configuration and may, at first approximation, be considered to have C_{2v} symmetry. It would be expected that discrete Sn–C and Sn–X stretching modes would be observed. In the higher dialkyltin dihalides the Sn–C bands become broad and it is probable that in these compounds the Sn–C stretching involves some C–C deformation, and/or some C–Sn–C bending. The Sn–C stretching frequencies of dialkyltin dialkoxides have recently been discussed[5] and unambiguous assigment of these modes was obtained by comparison with the corresponding dialkyltin dihalides. It is, however, significant that the order of frequencies for the Sn–C stretching modes is in the reverse order of electronegativities of the halogen atoms.

The assignment of Sn–X stretching modes can be made with complete reliance by comparing the chlorides, bromides and iodides of the same dialkyltin group. From Table 1 it can be seen that the Sn–X modes occur within the following ranges:

$$\nu_{asym}(\text{Sn–Cl})\ 355 \pm 5\ \text{cm}^{-1},\ \nu_{sym}(\text{Sn–Cl})\ 347 \pm 9\ \text{cm}^{-1},\ \delta(\text{Sn–Cl})\ 118 \pm 4\ \text{cm}^{-1}$$

$$\nu_{asym}(\text{Sn–Br})\ 253 \pm 1\ \text{cm}^{-1},\ \nu_{sym}(\text{Sn–Br})\ 240 \pm 2\ \text{cm}^{-1}$$

$$\nu_{asym}(\text{Sn–I})\ 200 \pm 2\ \text{cm}^{-1},\ \nu_{sym}(\text{Sn–I})\ 182 \pm 1\ \text{cm}^{-1}$$

The increasing separation between the asymmetric and symmetric Sn–X stretching modes, with increasing weight of halogen substituent, closely follows the increasing separation between the ν_3 and ν_1 modes of SnX_4.

TABLE 1

Sn–C AND Sn–X VIBRATIONAL FREQUENCIES OF R_2SnX_2

	R = Me		*R = Et*	*R = n-Pr*		*R = n-Bu*			*R = n-Octyl*
	X = Cl	*X = Br*	*X = Cl*	*X = Cl*	*X = I*	*X = Cl*	*X = Br*	*X = I*	*X = Cl*
Asym. Sn–C stretch	560	555	531	598	589	602	598	592	606
Sym. Sn–C stretch	524	522	497	512	501	517	510	505	518
Asym. Sn–X stretch	361	252	359	349	198	356	253	202	354
Sym. Sn–X stretch	356(sh)	241	352(sh)	338	183	340(sh)	238(sh)	182	345
Sn–X deformation	121		119	114		120			121

Edgell and Ward[6] found only one Raman line in the spectrum of dimethyltin dichloride and suggested that ν_7 (sym. Sn–Cl) and ν_{13} (asym. Sn–Cl) were degenerate and coincided at 344 cm^{-1}. In the present work both bands in the dichlorides are observed, although the lower frequency symmetric mode is only found as a shoulder; in the bromides the two bands are well resolved. Similarly the strong broad Raman lines at 135 cm^{-1} observed by these authors[6] in the spectrum of Me_2SnCl_2 was assigned to five fundamental modes. This band, now found at 121 cm^{-1} in this compound and at 118 ± 4 cm^{-1} in other chlorides, but is absent in the bromides and iodides, and must therefore be associated with a tin–chlorine vibration, rather than a Sn–C_2 bending (ν_5) mode. The Sn–Cl mode at ~ 120 cm^{-1} is very probably the $SnCl_2$ in-plane deformation (ν); this assignment is the most likely one of the Sn–Cl modes originally suggested[6] since it is usual for the in-plane deformation to be of higher frequency than rocking or torsional modes. A direct analogy may be drawn from the C–Cl modes of methylene dichloride where the in-plane deformation (ν_4) is the only bending mode observed.

EXPERIMENTAL

The stannic chloride and bromide were redistilled before use. The preparation of the dialkyltin dihalides by reactions:

$$R_4Sn + 2BX_3 \longrightarrow R_2SnX_2 + 2RBX_2,$$

where $X = Cl$ and Br, has been described[7]. Stannic iodide and dialkyltin diiodides were prepared by reaction[8]:

$$Y_2SnCl_2 + 2NaI \longrightarrow Z_2SnI_2 + 2NaCl$$

where $Y = Z = R$ or $Y = Cl$ and $Z = I$. The analytical data of the halides used, but not previously given, are shown in Table 2.

TABLE 2

PHYSICAL DATA OF DIALKYLTIN DIHALIDES*

R_2SnX_2	(m.p.) b.p.	Found (%)				Calculated (%)			
		C	H	Sn	X	C	H	Sn	X
n-Pr_2SnBr_2	(51°)	19.6	3.7	33.2	44.2	19.7	3.9	32.5	43.8
n-Pr_2SnI_2	150–151°/10 mm	15.5	3.2	25.9	55.1	15.7	3.1	25.9	55.3
n-Bu_2SnI_2	142–144°/0.7 mm	19.5	3.6	24.0	51.7	19.7	3.7	24.3	52.1

* Data for other dialkyltin dihalides given in Ref. 7.

The spectra in the 600–400 cm^{-1} region were recorded in carbon disulphide solution using KBr or KCl cells on a Perkin–Elmer 137 Spectrometer with KBr optics. The spectra in the region 500–20 cm^{-1} were recorded in cyclohexane solution using a Michelson interferometer which has previously been described[9]; the observations thus obtained were converted to spectra by Fourier Transformation using the N.P.L. A.C.E. computer. The liquid cell used in the interferometer was a modified FHOl cell, supplied by Research and Industrial Instruments Co., fitted with Rigidex (low pressure polythene, made by British Resin Products) windows (40 thou.) and using P.T.F.E. spacers to give path lengths between 0.5 and 3.00 mm; these cells were satisfactory for working in the evacuated sample chamber. The effective spectral resolution with the interferometer was 4 cm^{-1}.

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SUMMARY

The infrared spectra of tin(IV) tetrahalides SnX_4 (X = Cl, Br and I) have been recorded, in cyclohexane solution, using a Michelson interferometer and the ν_3 and ν_4 fundamentals assigned.

Investigation of the infrared spectra of a series of dialkyltin dihalides R_2SnX_2 (X = Cl, Br and I) in the 600–50 cm^{-1} region has permitted unambiguous assignment of Sn–C and Sn–halogen modes.

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Short Communication

A cyclic tetramer of di-tert-butyltin

It is now becoming clear that the so-called "dialkyltins" and "diaryltins" are mixtures of polymers[1]. These contain both straight and branched chains, but when prepared by certain routes, well-defined cyclic compounds are also present. Thus a cyclic 6-mer and 9-mer have been isolated from crude "diethyltin"[2], and cyclic 5- and 6-mers from "diphenyltin"[2]. We now report a cyclic 4-mer of di-*tert*-butyltin, which was formed unexpectedly during attempts to prepare tetra-*tert*-butyltin.

Krause and Weinberg studied the reaction of *tert*-butylmagnesium chloride with tin(IV) chloride in diethyl ether, and obtained a red ethereal solution, which they supposed to contain "di-*tert*-butyltin", since on addition of bromine, di-*tert*-butyltin dibromide was formed. In our hands the same reaction, but carried out in tetrahydrofuran solvent, gave a good yield of di-*tert*-butyltin dichloride, without formation of a red solution. Traces of a bright yellow crystalline by-product were noticed, however, and this became the main product when di-*tert*-butyltin dichloride was allowed to react with an excess of *tert*-butylmagnesium chloride in boiling tetrahydrofuran.

Elementary analysis showed the yellow compound had empirical formula $C_8H_{18}Sn$. On heating, the substance decomposed without melting at *ca.* 205°C; it also proved to be only sparingly soluble in the usual solvents at room temperature.

An X-ray analysis of the crystal showed that the unit cell is monoclinic (a = 18.42 Å, b = 12.70 Å, c = 9.53 Å, β = 115° 2′) and contains 8 monomer ($C_8H_{18}Sn$) units. Systematic absences indicate a C centred cell, and allow $C2$, Cm and C^2_m as possible spacegroups. It follows that di-*tert*-butyltin may be monomeric, dimeric, or tetrameric; it is not possible to have molecules larger than tetramers.