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Adducts of Organotin Halides with some Sulphoxides

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The preparation and properties of eighteen stable adducts of organotin halides with both aliphatic and aromatic sulphoxides are reported here. Eight of the adducts are being reported for the first time, whereas the others have only been partially studied before. Thermogravimetry as well as infrared spectroscopy were used as a probe of some of their bonding and structural features.

Experimental

Preparation of the Adducts

The organotin halide and the sulphoxide were dissolved in CCl_4 and the two solutions mixed. Heating followed by slow cooling yielded white crystalline precipitates which were recrystallised either from CCl_4, hexane, or cyclohexane.

In some cases the addition of a polar solvent (usually water) was necessary to promote the formation of the precipitate. When one or both of the parent compounds were liquid they were simply stirred together and the other procedures followed as above. The molar acid:base ratio used was of the order of 1:3. Some of the products were obtained in high purity even without recrystallisation. They were all dried in a desiccator over calcium chloride. Their C, H elemental analyses and melting points are as follows.

1. $(Ph)_3SnCl\cdot(p\text{-}Cl\text{-}C_6H_4)_2SO$-m.p. = 102–105 °C (106–108 °C)[a]
   C = 63.24%, H = 4.80% (exp.); C = 62.41%; H = 4.76% (calc.)
2. $(Ph)_3SnCl\cdot(PhCH_2)_2SO$-m.p. = 108–110 °C (91 °C)[a]
   C = 62.07%, H = 4.83% (exp.); C = 62.41%, H = 4.76% (calc.)
3. $(Ph)_3SnCl\cdot(Ph)_2SO$-m.p. = 103–105 °C (102–104 °C)[a], (97 °C)[b]
   C = 61.99%, H = 4.35% (exp.); C = 61.30%, H = 4.30% (calc.)
4. $(Ph)_3SnCl\cdot(CH_3)_2SO$-m.p. = 113–116 °C (113–115 °C)[a], (112 °C)[c]
   C = 51.60%, H = 4.48% (exp.); C = 51.81%, H = 4.58% (calc.)
5.* $(Ph)_3SnCl\cdot(n\text{-}C_4H_9)_2SO$-m.p. = 81–83 °C
   C = 57.42%, H = 6.05% (exp.); C = 57.00%; H = 6.08% (calc.)
6.* $(Ph)_3SnCl\cdot(n\text{-}C_3H_7)_2SO$-m.p. = 72–74 °C
   C = 55.53%, H = 5.63% (exp.); C = 55.46%, H = 5.64% (calc.)
7. $(CH_3)_2SnCl_2\cdot 2(p\text{-}CH_3\text{–}C_6H_4)_2SO$-m.p. = 86.5–88.5 °C (79–81 °C)[d]
   C = 53.39%, H = 4.98% (exp.); C = 52.95%, H = 5.05% (calc.)
8. $(CH_3)_2SnCl_2\cdot 2(PhCH_2)_2SO$-m.p. = 102–105 °C
   C = 52.73%, H = 5.03% (exp.); C = 52.95%, H = 5.05% (calc.)
9. $(CH_3)_2SnCl_2\cdot(PhCH_2)_2SO$-m.p. = 119–122 °C (117–119 °C)[e]
   C = 42.56%, H = 4.36% (exp.); C = 42.70%, H = 4.49% (calc.)
10. $(CH_3)_2SnCl_2\cdot 2(Ph)_2SO$-m.p. = 100–103 °C
    C = 50.20%, H = 4.24% (exp.); C = 50.02%, H = 4.21% (calc.)
11. $(CH_3)_2SnCl_2\cdot 2(CH_3)_2SO$-m.p. = 111–114 °C (112–113 °C)[b], (113 °C)[c], (110–110.5 °C)[g]
    C = 18.89%, H = 4.68% (exp.); C = 19.17%, H = 4.84% (calc.)
12. $(CH_3)_2SnCl_2\cdot 2(n\text{-}C_4H_9)_2SO$-m.p. = 88–91 °C
    C = 39.49%, H = 7.67% (exp.); C = 39.71%, H = 7.79% (calc.)
13. $(CH_3)_2SnCl_2\cdot 2(n\text{-}C_3H_7)_2SO$-m.p. = 106–109 °C
    C = 34.50%, H = 6.94% (exp.); C = 34.44%, H = 7.03% (calc.)

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*Ref. 8 reports these adducts but only with respect to the Mössbauer study.

[a]Ref. 1. [b]Ref. 2. [c]Ref. 3. [d]Ref. 4. [e]Ref. 5. [f]Ref. 6. [g]Ref. 7.

TABLE I. Thermogravimetric and Infrared Data (absorptions in cm^{-1}).

Compound	ΔH_v (kJ/mol)	$\Delta\nu_{SO}$	ν_{Sn-C}	ν_{Sn-Cl}	ν_{Sn-O}
$(C_6H_5)_3SnCl$			275(s)	340(s)	
$(C_6H_5)_3SnCl\cdot(p\text{-}CH_3-C_6H_4)_2SO$	100	65	276(s)	258–248(sh)	400(m)
$(C_6H_5)_3SnCl\cdot(C_6H_5-CH_2)_2SO$	112	26	279(s)	263(m)	410(sh)
$(C_6H_5)_3SnCl\cdot(C_6H_5)_2SO$	83	60	279(s)	255(w)	425(m)
$(C_6H_5)_3SnCl\cdot(CH_3)_2SO$	78	83	275(s)	–	405(m)
$(C_6H_5)_3SnCl\cdot(n\text{-}C_4H_9)_2SO$	–	70	277(s)	270–260(sh)	410(m)
$(C_6H_5)_3SnCl\cdot(n\text{-}C_3H_7)_2SO$	–	49	278(s)	260(m)	400(m)
$(CH_3)_2SnCl_2$			553(m), 520(m)	335(s), 316(s)	
$(CH_3)_2SnCl_2\cdot 2(p\text{-}CH_3-C_6H_4)_2SO$	–	35, 54	580(m)	–	400(m)
$(CH_3)_2SnCl_2\cdot 2(C_6H_5-CH_2)_2SO$	–	46	580(w)	325(m)	405(m)
$(CH_3)_2SnCl_2\cdot(C_6H_5-CH_2)_2SO$	–	48	580(w)	323(s)	405(m)
$(CH_3)_2SnCl_2\cdot 2(C_6H_5)_2SO$	–	30, 50	584(m)	–	435(m)
$(CH_3)_2SnCl_2\cdot 2(CH_3)_2SO$	–	85	581(m)	318(m), 308(sh)	421(s)
$(CH_3)_2SnCl_2\cdot 2(n\text{-}C_4H_9)_2SO$	87	90	580(m)	–	427(s)
$(CH_3)_2SnCl_2\cdot 2(n\text{-}C_3H_7)_2SO$	85	75	580(m)	310(w)	423(s)
CH_3SnCl_3			560(m)	–	
$CH_3SnCl_3\cdot(n\text{-}C_4H_9)_2SO$	–	125	590–540(m)	340(s), 335(s)	480(s)
$(CH_3)_3SnBr$					
$(CH_3)_3SnBr\cdot(n\text{-}C_4H_9)_2SO$	93	93			
$(CH_3)_3SnBr\cdot(CH_3)_2SO$	66	–			
$(CH_3)_3SnCl$			551(s)	330(s)	
$(CH_3)_3SnCl\cdot(n\text{-}C_4H_9)_2SO$	91	90	570(s)		428(s)
$(CH_3)_3SnCl\cdot(n\text{-}C_3H_7)_2SO$	82	72	580(s)		432(s)

14. $CH_3SnCl_3\cdot(n\text{-}C_4H_9)_2SO$-m.p. = 192–195 °C (d.)
C = 27.18%, H = 5.10% (exp.); C = 26.86%, H = 5.27% (calc.)
15. $(CH_3)_3SnBr\cdot(n\text{-}C_4H_9)_2SO$-m.p. = 103–105 °C
C = 34.14%, H = 6.54% (exp.); C = 32.53%, H = 6.72% (calc.)
16. $(CH_3)_3SnBr\cdot(CH_3)_2SO$-m.p. = 60–63 °C (63–64 °C)^f
C = 18.12%, H = 4.51% (exp.); C = 18.65%, H = 4.71% (calc.)
17. $(CH_3)_3SnCl\cdot(n\text{-}C_4H_9)_2SO$-m.p. = 88.5–89 °C
C = 38.88%, H = 7.47% (exp.); C = 36.53%, H = 7.54% (calc.)
18. $(CH_3)_3SnCl\cdot(n\text{-}C_3H_7)_2SO$-m.p. = 104–105 °C
C = 34.58%, H = 6.84% (exp.); C = 32.40, H = 6.96% (calc.)

Thermogravimetry

Thermograms of the adducts were run in a PE TGS 1 thermobalance operated under a steady flow of N_2.

Infrared Spectroscopy

Infrared spectra of the adducts were obtained from a PE 467 spectrophotometer using CsI pellets. All spectra were calibrated with a polystyrene film.

Results and Discussion

The adducts are insoluble in the polar solvents usually employed in conductimetric measurements, which is taken as an indication of their character as nonelectrolytes.

Since the adducts are easily volatilized, it was possible to use them for thermogravimetric determinations. Volatilization always took place at least 30 °C above the melting point of the adducts. In all cases the weight loss was greater than 90% below 275 °C, suggesting that the adducts are monomeric molecular species. The calculated enthalpies of volatilization (ΔH_v) refer to a process occurring in the melt, which includes the enthalpy of vapourization plus a second term dependent on the dissociation of the vapour. The values of ΔH_v tend to increase with the molecular weight of the adduct, but no clear relationship was found between ΔH_v and the molecular weight. Some of the adducts strongly decomposed upon vapourization and the corresponding thermograms are very complex. They are not reported here. Table I shows the mean ΔH_v values for ten of the adducts. Each of these mean values was obtained from three different heating rates of 2.5, 5.0, and 10.0 °C/min, respectively, and the data were processed by a Burroughs B 6700 computer.

Sulphoxides present two possible basic sites, the oxygen or the sulphur atoms. When a sulphoxide bonds to an 'a' (or 'hard') type acid, the donor is oxygen, sulphur being the donor atom only in bonds to 'b' (or 'soft') type acids [2, 9, 10]. In all our adducts we observed a negative shift in the infrared stretching vibration of the SO bond, which is indicative of a bond through oxygen, insofar as such a shift implies a weakening of the $(p \rightarrow d)\ \pi$ bond in the SO group, thus making oxygen less likely to donate electron density to the sulphur atom. Indeed an estimation of the SO bond order by means of Szmant's Rule [11] gave values ranging from 127.7 pm for $CH_3SnCl_3 \cdot (n\text{-}C_4H_9)_2SO$ to 142.5 pm for $(C_6H_5)_3SnCl \cdot (C_6H_5{-}CH_2)_2SO$, whereas in the free sulphoxides all estimated SO bond orders are above 144.0 pm. The infrared data, given in terms of $\Delta\nu_{SO}$, are shown in Table I.

The Mulliken-Jaffé electronegativities of the organic groups in the sulphoxides are:

$$\chi_{p\text{-}CH_3-C_6H_4} = 7.90 + 0.94q^{h} \qquad \text{eqn. 1}$$

$$\chi_{C_6H_5-CH_2} = 7.90 + 0.95q^{i} \qquad \text{eqn. 2}$$

$$\chi_{C_6H_5} = 8.03 + 1.21q^{h} \qquad \text{eqn. 3}$$

$$\chi_{CH_3} = 7.37 + 3.24q^{h} \qquad \text{eqn. 4}$$

$$\chi_{n\text{-}C_4H_9} = 7.41 + 1.00q^{h} \qquad \text{eqn. 5}$$

$$\chi_{n\text{-}C_3H_7} = 7.41 + 1.30q^{h} \qquad \text{eqn. 6}$$

where χ_n stands for the electronegativity of group n and q is the electric charge on n.

Inspection of Table I shows that the order of decreasing basicity of the sulphoxide, as given by $\Delta\nu_{SO}$, is not that of increasing group electronegativity, as one might expect. Dibenzyl sulphoxide, for example, appears to be far less basic than the electronegativity of the benzyl group would suggest. One also might expect di-n-butyl sulphoxide always to be the most basic donor, closely followed by di-n-propyl sulphoxide. It seems that stereochemical effects play a very important role in this respect, and that the basicity exhibited by the sulphoxide is not always what one would expect due to such steric hindrance. In the dibenzyl sulphoxide case, in addition to the steric effect one might also point out the impossibility of electronic assistance by the aromatic rings due to blocking by the methylene groups. In the five-coordinate adducts, a likely structure is that of a distorted trigonal bipyramid, as already determined for some similar compounds, [14, 15] with the most electronegative ligands on the axial positions, as predicted by Bent's Rule. Mössbauer data for our 1:1 adducts are consistent with a structure approaching a trigonal bipyramidal geometry but with its symmetry lowered with respect to the parent organotin halide.* It is interesting to note that in the triphenyltin chloride series, dimethyl sulphoxide appears to be more basic than the sterically hindered di-n-butyl sulphoxide. This situation is inverted for the six-coordinate adducts, with the stronger acid dimethyltindichloride. If one fixes the base (*e.g.* $(n\text{-}C_4H_9)_2SO$) and varies the acid, one can see the effect of acid strength on the value of $\Delta\nu_{SO}$. The latter will depend directly upon the strength of the acid. Two of the 1:2 adducts, namely those formed between dimethyltindichloride and di-*p*-tolylsulphoxide and diphenyl sulphoxide, respectively, show a split band due to the shifted SO stretching. This could be attributed to a symmetry lowering caused by the fact that the two sulphoxide molecules occupy nonequivalent sites in the six-coordinate complex unit (*e.g. cis* and *trans*) or to some crystal effect. Moreover, in addition to the 1:2 complex, dibenzyl sulphoxide also formed a well defined 1:1 adduct with dimethyltindichloride, not reported previously, and showing a totally different melting point and elemental analysis from the 1:2 adduct. The infrared spectra of the two adducts are, however, very similar, which suggests that their crystal structures must also be closely alike.

The infrared absorptions below 600 cm^{-1} show that the Sn–C absorptions are practically constant for each group of adducts and close to the values for the uncomplexed acid. The Sn–Cl bonds are more ionic than the Sn–C bonds, hence their occurrence towards lower frequencies as compared to the latter and also their in some cases significant negative shifts upon complexation with the base. The new medium to strong band occurring was 400 cm^{-1} is attributed to the Sn–O stretching.

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[h] Ref. 12. [i] Calculated according to the method in ref. 13.

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