

bands have been observed in the ranges 520-525 and 555-580 cm^{-1} (refs. 10, 11).

The $\text{As}=\text{O}$ and $\text{As}\begin{smallmatrix} \diagup \\ \text{O} \\ \diagdown \end{smallmatrix}$ of the AsO_3 group undergo changes after compound formation. The $\text{As}=\text{O}$ band shifts upwards by 5-50 cm^{-1} in some of the arylarsonates (when X is H, CH_3 , OCH_3 and $o\text{-NH}_2$) and shows a downward shift by 15-30 cm^{-1} in other arylarsonates (when X is $p\text{-Cl}$, $p\text{-Br}$ and $o\text{-NO}_2$). The upward shift may be due to coupling of the arsenic-oxygen and metal-oxygen modes on coordination of $\text{As}=\text{O}$ oxygen to tin(IV) ion. The downward shift may be due to coordination of the oxygen of the $\text{As}=\text{O}$ group to tin(IV) ion which would result in decreasing the $d\pi\text{-}p\pi$ double bond character of $\text{As}=\text{O}$ bond. Splitting observed in the $\text{As}=\text{O}$ stretching frequency may also be attributed to the coordination of oxygen with tin(IV). The ν_s and $\nu_{\text{as}}(\text{As}\begin{smallmatrix} \diagup \\ \text{O} \\ \diagdown \end{smallmatrix})$ modes of the arylarsonic acids also undergo changes on compound formation with tin(IV)^{2,12}. An increase in $\text{As}-\text{C}$ frequency by 5-20 cm^{-1} can be explained on the basis of an increase in electron density between arsenic and carbon when $\text{As}=\text{O}$ and $\text{As}\begin{smallmatrix} \diagup \\ \text{O} \\ \diagdown \end{smallmatrix}$ groups take part in bond formation.

In the spectra of the compounds with X = $p\text{-OCH}_3$ and $o\text{-NH}_2$, an increase in $\nu\text{C}-\text{OCH}_3$ and $\nu\text{N}-\text{C}$ frequencies suggests coordination of $p\text{-OCH}_3$ and $o\text{-NH}_2$ groups to tin(IV). In the compound with X = $o\text{-NH}_2$, coordination from nitrogen to metal is further supported by a decrease in νNH frequency on compound formation¹³. An increase in NO stretching frequency (58 cm^{-1}) of the nitro group on compound formation indicates the coordination of the nitro group. We conclude that the tridentate AsO_3 group acts as a bridging group in a polymeric structure in which the tin atom is six coordinated.

Thermal stabilities of all the arylarsonates have been studied with the help of DTA and TGA. In DTA and TGA, the compounds were heated from room temperature to about 800° at the rate of 10°/min and 7°/min respectively except in the case of o -nitrophenylarsorotdiberzyltin(IV) which exploded at about 400° with the evolution of obnoxious smelling gases. Percentage loss, corresponding to peaks obtained in the DTA thermograms, has been calculated approximately from the TGA data. The compounds probably lose water and carbon dioxide along with other gases and an arsenic compound is formed endothermally during heating in the ranges 100-200° and 200-400°, respectively. More of carbon dioxide and water are formed in the temperature range 500-700°. In the region 700-800°, the weight of the residue formed remains constant and it corresponds approximately to that calculated for SnO_2 .

The author is thankful to Prof. S. S. Sandhu, Head, Chemistry Department, Guru Nanak Dev University for providing research facilities.

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Reaction of Liquid Sulphur Trioxide with Diethyl Ether

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Received 16 August 1977; revised 28 June 1978;
accepted 7 July 1978

Addition of liquid sulphur trioxide to diethyl ether at low temperature results in the separation of a liquid adduct of stoichiometry $\text{SO}_3 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$. Plots of the log of viscosity (η) and log of molar conductivity (μ) of the addition compound versus reciprocal of absolute temperature are linear. The activation energies of viscous flow (E_η) and ionic migration (E_μ) have been calculated from these plots and the ratio E_η/E_μ has been found to be 2.73. Degree of dissociation (α) of the complex as obtained from the relation $\alpha = \mu\eta^{1/m}$ is nearly 2.3%. Electrolysis and infrared spectral data as well as its Friedel-Craft reaction with benzene and toluene suggest the complex to exist in the following equilibrium: $\text{SO}_3 \cdot 2(\text{C}_2\text{H}_5)_2\text{O} \rightleftharpoons (\text{C}_2\text{H}_5)_3\text{O}^+ + (\text{C}_2\text{H}_5\text{OSO}_3)^-$.

SOME reactions of liquid sulphur trioxide with a few oxy bases are reported in literature¹⁻³. Conductometric studies of mixtures of liquid sulphur trioxide and diethyl ether have indicated compound formation between them⁴. A detailed physico-chemical investigation of the complex, $\text{SO}_3 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, is being reported here.

Diethyl ether (BDH, AR) was distilled over sodium wire and redistilled over phosphorus(V) oxide and the fraction (b.p. 33.5°/750 mm) was taken for use. Liquid sulphur trioxide was obtained as described before³.

Reaction of liquid sulphur trioxide with diethyl ether — Diethyl ether (50 ml) was taken in a three-necked round bottom flask (250 ml) fitted with a reflux condenser having silica gel guard tube and nitrogen inlet tube. Liquid sulphur trioxide was

distilled into the flask which was maintained at the temperature of ice-salt mixture (1 hr) and in an atmosphere of dry nitrogen. The reaction mixture was stirred continuously by a magnetic stirrer. Since the reaction was highly exothermic, liquid sulphur trioxide was added slowly. A colourless viscous compound separated out which was isolated under dry nitrogen, washed with carbon tetrachloride, dried *in vacuo* and analysed (Found: C, 42.3; H, 9.0; S, 14.3. $C_8H_{20}O_5S$ requires: C, 42.4; H, 8.8; S, 14.02%).

Conductance of the complex was measured (conductivity bridge, Toshniwal CL 01/01) at different temperatures using an electrically controlled constant temperature bath (accuracy $\pm 0.05^\circ$). Cell constant of the dip-type cell (0.361 ± 0.002) was determined by the standard method and was periodically checked⁵. Specific conductance at 24° was found to be $3.70 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$.

Viscosity of the compound was determined at different temperatures using a modified Ubbelohde capillary type viscometer⁶ fitted with silica gel guard tubes. Carbon tetrachloride (BDH, AR, b.p. 78.2° ; η , $9.019 \times 10^{-3} P$; and d , 0.9970 g ml^{-1}) and freshly distilled benzene (BDH, AR, m.p. 5.51° ; η , $5.996 \times 10^{-3} P$; and d , 0.8737 g ml^{-3}) were used as reference liquids. Viscosity of the compound at 24° was found to be $0.382 P$.

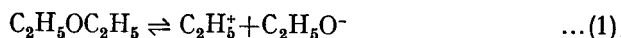
Density of the compound was determined at different temperatures using bicapillary type pycnometer which was calibrated with doubly distilled mercury. The density of the compound was found to be 1.3478 g ml^{-1} at 24° .

Refractive index of the complex was measured using Abbe's refractometer ASCO No. 528 and was found to be 1.438 at 24° .

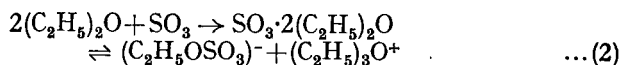
Friedel-Craft reaction of $SO_3 \cdot 2(C_2H_5)_2O$ -- The sulphur trioxide-diethyl ether complex (27 g, 20 ml) obtained above was added to freshly distilled benzene or toluene (50 ml) maintained under dry nitrogen and the reaction mixture was stirred for 1 hr at room temperature. The mixture was then warmed to $45-50^\circ$ for 1 hr. It was decomposed with dil. sodium carbonate solution, washed with water and extracted with ether. The extract was dried over anhydrous sodium sulphate and distilled. After removing the solvent, the first fraction obtained on distillation was unreacted benzene (42 ml, 85%) or toluene (45 ml, 90%). The second fraction was ethyl benzene (b.p. $135^\circ/750 \text{ mm}$; 8 ml, 15%) or ethyl toluene (b.p. $159.5^\circ/750 \text{ mm}$; 5 ml, 10%) as identified by infrared spectroscopy. The formation of the sulphonate product was carefully checked and no such product was obtained in the reaction.

Sulphur trioxide diethyl ether complex [$SO_3 \cdot 2(C_2H_5)_2O$] is insoluble in most of the organic solvents and hence its molar conductance and molecular weight could not be determined. The adduct slowly reacts with water but rapidly with alcohols to produce alkyl hydrogen sulphate. It is unreactive towards alkali metal salts. It changes to diethyl sulphate on long standing at room temperature. The decomposition of the complex starts at 80° . An attempted distillation even in high vacuum ($\approx 0.5 \text{ mm}$) gave only diethyl sulphate.

Specific conductances of diethyl ether⁷ ($3 \times 10^{-13} \Omega^{-1} \text{cm}^{-1}$), sulphur trioxide⁸ ($1 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$) and diethyl sulphate in diethyl ether⁸ ($1 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$) are much less than that of the adduct ($3.7 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$). Jander *et al.*⁹ have shown that ether ionizes as shown in Eq. 1.



Since sulphur trioxide is a well-known Lewis acid, it may combine with the anion to give ethyl sulphate anion and thus increase the ionisation of ether. Alternatively, a donor-acceptor bond may be formed between ethereal oxygen and sulphur trioxide followed by the separation of ethyl ion (Eq. 2).



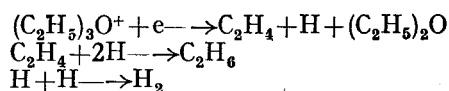
The additional ether molecule solvates ethyl ion which results in further separation of the ions and thus causes greater ionisation and conductivity of the adduct.

The specific conductance of the adduct increases with increase in temperature and the relative temperature coefficient ($1/K \cdot \frac{dK}{dt}$) has been found to be

2.8% degree⁻¹. Plots of log of molar conductivity (μ) and log of viscosity (η) versus reciprocal of absolute temperature ($1/T$) are linear. Energies of activation of ionic migration (E_μ) and of viscous flow (E_η) have been obtained from the slopes of these plots⁸. The value of E_η (12.69 kcal mole⁻¹) is higher than that of E_μ (4.65 kcal mole⁻¹) and the ratio (m) of the two energies is 2.73:1.

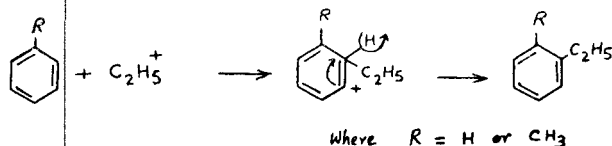
Greenwood *et al.* have suggested that for 1:1 electrolytes, when E_η is greater than E_μ , their degree of dissociation (α) can be approximately determined from the relation $\alpha = \mu\eta^{1/m}$. Assuming the dietherate to be a 1:1 electrolyte, α , as calculated from this relation comes out to be 2.3%.

In order to investigate further the nature of the complex, electrolysis of the etherate was carried out at moderate potentials (70 volts dc) for 1.5 hr using the procedure reported earlier³. Whereas the gaseous product obtained at the cathode (4 ml), as shown by infrared spectroscopy and elementary analysis is a mixture of ether (1.0 ml, 25%), hydrogen (0.7 ml, 17.3%)* and ethane (1.0 ml, 25%), no gas was produced at the anode. But the colour of the compound around the anode turned dark brown. In view of the small quantity of gas analysed, it is not possible to exactly describe the reactions occurring at the cathode. However, from the analytical data of the gases obtained, the reaction may be represented with some certainty as shown below:



An analogous mechanism has been proposed for boron trifluoride etherate⁷ also. The reaction at

*Remaining hydrogen seems to have been consumed in ethane formation.



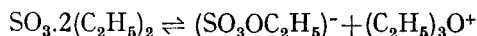
Scheme 1

the anode cannot be predicted with confidence. The change of colour may be due to some polymerization reactions. The reaction of higher ethers with sulphur trioxide results in the formation of gum like products which resisted exact analysis and hence no further work was possible.

A comparison of the infrared spectra (band positions in cm^{-1}) reveals that the prominent bands of the reacting species shift to the lower spectral range on complex formation. For example, ν_{CO} mode of diethyl ether suffers a negative shift of about 80 while $\nu_{\text{as}} \text{SO}$ of liquid sulphur trioxide¹¹ changes by 60. Another $\nu_{\text{as}} \text{SO}$ band also appeared at 1120. $\nu_{\text{s}} \text{SO}$ changed from 1065 to 915 on adduct formation. δOSO modes occurring at 652 and 532 in liquid sulphur trioxide¹¹ merge into a single band occurring at 550. A weak band occurs at 1095 in the spectrum of the complex which may be due to the oxonium ion, $(\text{C}_2\text{H}_5)_3\text{O}^+$, while a second weak band at 845 is perhaps due to the presence of small amounts of diethyl sulphate 8 formed during the reaction. An absorption at 1560 could not be explained with certainty but the possibility of occurrence of combination or overtone bands can not be ruled out completely.

With a view to obtaining further evidence for the existence of C_2H_5^+ ion in the complex, Friedel-Craft reactions of the etherate with benzene and toluene were carried out. The products isolated and identified on the basis of their IR spectra include ethylbenzene (15%) and 1-methyl-2-ethylbenzene (10%). The reaction may be represented as in Scheme 1.

It may be thus concluded that sulphur trioxide forms an adduct with diethyl ether at low temperature which ionizes as:



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Reactions of Tetraorganotin Derivatives with Chlorosulphonic Acid

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Received 23 January 1978; revised and accepted 7 June 1978

Facile and specific cleavage of tin-carbon bond(s) in tetraorganotins, R_4Sn ($\text{R} = \text{Bu}$, Ph , p -tolyl) and Bu_2SnAr_2 ($\text{Ar} = \text{Ph}$, p -tolyl) employing chlorosulphonic acid has been studied with a view to establishing their synthetic utility for the preparation of organotin esters, $\text{R}_n\text{Sn}(\text{SO}_3\text{R})_{4-n}$ or $\text{Bu}_2\text{Sn}(\text{SO}_3\text{Ar})_2$ in a simple one step procedure. Sn-Ar bond is cleaved in preference to Sn-Bu bond in Bu_2SnAr_2 .

REACTIONS of tetraorgano derivatives of group IVB metals, R_4M ($\text{M} = \text{Si}$, Ge , Sn , Pb) with various electrophilic reagents have been extensively studied both from synthetic and mechanistic point of view¹. However, not much work has been reported on the cleavage of M-C bond(s) with halosulphonic acids, viz. HSO_3X ($\text{X} = \text{F}$, Cl , Br)^{2,3}.

In continuation of our work on electrophilic cleavage of M-C bond(s) ($\text{M} = \text{Ge}$, Sn , Pb) with halogens⁴, interhalogens⁵, and pseudohalogens⁶, we now report some reactions of tetraorganotin derivatives, R_4Sn ($\text{R} = \text{butyl}$, phenyl and p -tolyl) and Bu_2SnAr_2 with chlorosulphonic acid. The main object of this work was to (i) study the extent and relative ease of cleavage of an organic group from R_4Sn compounds with HSO_3Cl , (ii) develop one step synthesis of triorgano or diorganotin arylsulphonates, $\text{R}_n\text{Sn}(\text{SO}_3\text{R})_{4-n}$ or $\text{Bu}_2\text{Sn}(\text{SO}_3\text{Ar})_2$ and (iii) study the preferential cleavage of Bu-Sn or Ph-Sn bond(s). The previous routes for the formation of organotin esters of sulphonic acid involved solvolysis of tetramethyltin and methyltin chlorides by sulphonic acid³, ligand redistribution between methyltin(IV) chlorides and methyltin(IV) sulphonates⁷, functional group exchange between a diorganotin oxide and the trimethylsilyl ester of an arylsulphonic acid⁸ and more recently the azeotropic dehydration of the organotin oxide and the arylsulphonic acid in boiling benzene⁹.

Tetraorganotins (n -butyl, phenyl, p -tolyl)¹⁰, di-butyltin diphenyl⁵ and silver salts of aryl sulphonic acids¹¹ were synthesized by the reported procedures. Chlorosulphonic acid (E. Merck) was used as such. All the solvents employed were of reagent grade distilled twice and dried before use.

Infrared spectra were recorded on a Perkin-Elmer 177 grating spectrometer, elemental analysis were performed at CDRI, Lucknow, and the melting points were taken in sealed capillary tubes.

All preparations were carried out under nitrogen atmosphere excluding moisture rigorously.

Representative experiments are described below. Further details are given in Table 1.

Reaction of Ph_4Sn and HSO_3Cl —To a chilled (-10°) solution of tetraphenyltin (4.27 g, 0.01 mol)

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