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SHORT COMMUNICATIONS

Complexes of organometallic compounds

XIV. The coordination of tin and lead atoms in triphenyltin (IV) and triphenyllead (IV) oxinates

In an earlier paper[1] we investigated the absorption spectrum of triphenyltin (IV) oxinate in 95% aqueous ethanol, and showed it to correspond with that of 8-quinolinol in the same solvent. Then we suggested that triphenyltin (IV) oxinate was not a chelate complex in 95% ethanol, so that the tin atom in the undissociated molecule should be tetra-coordinated, bound only to the oxygen atom of the 8-quinolinol.

Our conclusions have recently been commented on as follows:

(1) Lack of chelation in 95% ethanol does not preclude chelation at the solid state[2]. Solid triphenyltin (IV) oxinate has a yellow colour, which is inconsistent with a lack of chelation[3].

(2) From the absorption spectra of triphenyltin (IV) oxinate in cyclohexane it is inferred that the compound is a chelate complex both in this solvent and (probably) in the solid state[3].

(3) The correspondence between triphenyltin (IV) oxinate and 8-quinolinol spectra in 95% aqueous ethanol may be due to the hydrolysis of the organotin compound[3]; the species $(C_6H_5)_2SnOH$ and C_9H_6NOH may be formed[2].

We did not infer anything about the solid state from solution data. On the other hand, the yellow colour of a solid oxinate is not a definite evidence of chelation: sodium oxinate is yellow too, but can hardly be considered to be chelated.

As to the formation of a chelate triphenyltin (IV) oxinate in cyclohexane[3], we had earlier reported that the absorption spectrum in benzene solution of triphenyllead (IV) oxinate (a compound which shows properties very similar to those of the corresponding organotin derivative) corresponds to the presence of a chelate complex[4].

The hypothesis that the spectrum in 95% aq. ethanol corresponds to that of 8-quinolinol, owing to complete hydrolysis of the organotin complex, implies that the tetra-coordinated species does not exist under these conditions. We carried out the investigations described below in order to elucidate the nature of the triorganometal oxinates of tin and lead in solution in such a way as to enable a decision on the existence of tetra-coordinated species to be made.

The absorption spectra of triphenyltin (IV) oxinate have been recorded in dry benzene and methanol, and in benzene-methanol, and are shown in Fig. 1. The complex seems to be chelated in benzene solution, so that a penta-coordination of the tin atom could be assumed in this solvent. The spectrum in dry methanol corresponds to that in wet methanol and ethanol, and to the spectrum of 8-quinolinol in both solvents. The presence of a not-chelated, tetra-coordinated complex, or of solvolysed species, can be assumed in these solvents.

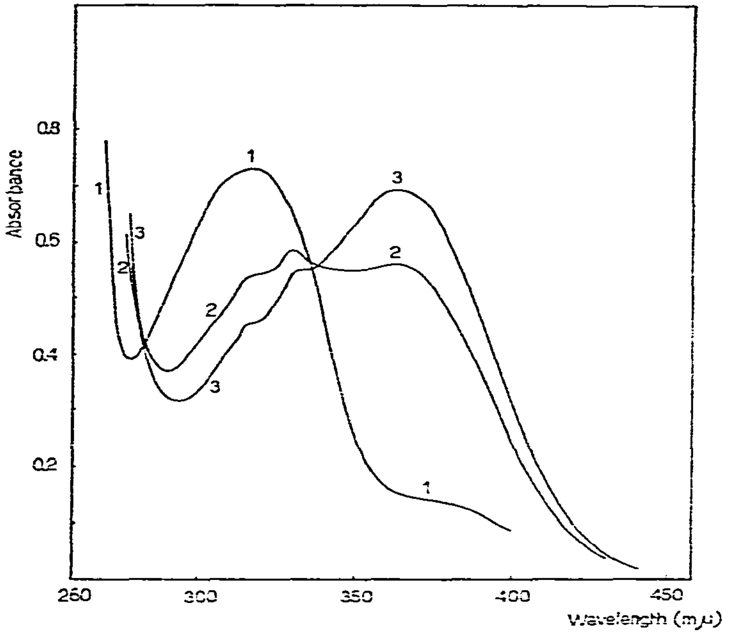


Fig. 1. Absorption spectra at 25° of triphenyltin oxinate 3×10^{-4} M in the following solvents: curve 1, anhydrous methanol; curve 2, benzene + 1 % methanol (v/v); curve 3, benzene.

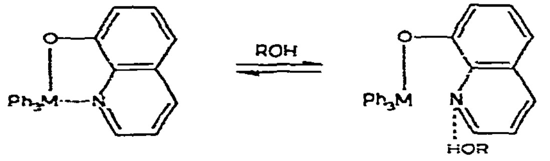
The effect of the addition of 1 % (v/v) anhydrous methanol to benzene is shown in Fig. 1. It has been found that the addition of increasing amounts of dry methanol to benzene gradually changes the spectrum of the chelate to that of 8-quinolinol.

Water is not very effective in changing the spectrum of a solution of the organotin chelate complex, and the spectra in dry benzene (reported in Fig. 1), and in benzene saturated with water at 25°, differ very little. The same can be said for solutions in cyclohexane and cyclohexane saturated with water at 25°. The solubilities of water in benzene and cyclohexane at 20° are 2.47×10^{-2} and 0.55×10^{-2} molal[5], respectively; they are about 100 to 10 times higher than the concentration of the oxinate (3×10^{-4} M).

The behaviour of triphenyllead(IV) oxinate is described in ref. 4, Figs. 3, and it seems that a chelated complex, with a five-coordinated lead atom, is present in benzene. We found that the spectrum in dry methanol is identical with that in dry ethanol[4].

Both spectra correspond to the spectrum of 8-quinolinol, so that a non-chelated tetracoordinated complex, or solvolysed species, can be assumed to exist in these solvents. The effect of the addition of 1% (v/v) dry methanol to benzene is very similar to that of the addition of 1% (v/v) dry ethanol to chloroform, as it is shown in Fig. 3 of ref. 4. Again the addition of increasing amounts of dry methanol to benzene gradually changes the spectrum of the chelate to that of 8-quinolinol. The use of benzene and cyclohexane saturated with water at 25° does not alter very much the absorption spectrum of the chelate.

The changes in the spectra of the two organometal(IV) oxinates, observed by replacing benzene and cyclohexane with dry or wet alcohols as solvents, can, then, be generally ascribed to solvolysis. The breakage of the metal-nitrogen bond might take place:



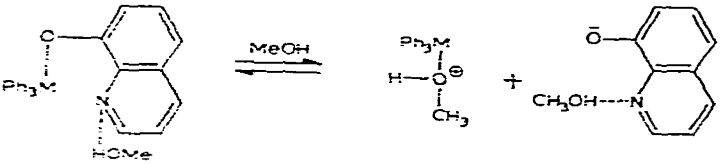
(1)

(M= Sn, Pb; R = H,Me,Et)

A similar hypothesis was advanced by Janssen *et al.*[6] to explain the depolymerization by ethanol of associated N-(tributylstannyl) imidazole.

Even the metal-oxygen bond of the oxinates must undergo partial dissociation, because the 3×10^{-4} *M* solutions in anhydrous methanol at 25° conduct electricity. The equivalent conductances increase in the order: $(C_6H_5)_3SnOx < (C_6H_5)_2PbOx <$ NaOx (Ox = oxinate).

The dissociation could be due to alcoholysis:



(2)

It can be assumed that solvolysis will not proceed till the complete fission of the O–H bond, with formation of methoxy or ethoxy compounds and, perhaps, 8-quinolinol. Triorganolead halides do not undergo complete alcoholysis[7], and for triorganotin halides complete alcoholysis seems to be rare[7,8]. Recrystallization of triphenyltin (IV) oxinate and triphenyltin(IV) hydroxide from ethanol[4,9] gives unchanged compounds.

The extent of the dissociation in methanol [which may be represented as in eqn. (2)] has been investigated by vapor-pressure measurements carried out using a Mechrolab Osmometer Model 302, and the results are shown in Table 1. The ΔR reading is proportional to the difference in temperature between a drop of solvent and one of solution, and then also to the difference in their vapor pressures. It can be assumed that deviations of the solvent from Raoult's law (other than those due to

TABLE 1

OSMOMETRIC MEASUREMENTS FOR METHANOLIC SOLUTIONS AT 37°

Oxinate	*Molar concn.* $(\times 10^2)$	*ΔR readings*		*i*
		Oxinate	*Benzil*	
Ph_3Sn	0.53	1.88	1.30	1.45
	0.75	2.57	1.78	1.44
	0.86	2.94	2.02	1.45
	1.06	3.48	2.45	1.42
Ph_3Pb	0.53	2.08	1.30	1.60
	0.67	2.54	1.60	1.59
	0.80	2.99	1.89	1.58
	1.47	5.17	3.34	1.55
Na	0.50	2.43	1.22	1.97
	0.70	3.40	1.68	2.02
	0.80	3.90	1.89	2.06
	1.28	5.92	2.93	2.02

solute dissociation) are negligible for the diluted solutions here investigated, and that the reference compound here employed (benzil) behaves almost ideally. If the latter holds true, the ratio of the readings for the oxinates to those for benzil, at a given solute concentration, will be a measure of the Van 't Hoff "*i*" factor, which in our case should approximate the value 2 for complete dissociation [if eqn. (2) holds]. From Table 1 it appears that "*i*" factors change in the series: $(C_6H_5)_3SnOx < (C_6H_5)_3PbOx < NaOx \simeq 2$. These findings are in qualitative accordance with the conductivity measurements, which refer to methanolic solutions of the oxinates at the concentration and temperature employed in the determination of the absorption spectra. In the methanolic solutions 3×10^{-4} *M* of the two organometal oxinates there are then present the tetra-coordinated molecule (with metal–oxygen bonds) and the solvated ions $(C_6H_5)_3M(ROH)_n^+$ and $C_9H_6NO(ROH)_n^-$. The absorption spectrum of the latter could be assumed to correspond to that of sodium oxinate in anhydrous methanol. Since even sodium oxinate in dry methanol shows a spectrum very similar to that of 8-quinolinol, both the tetra-coordinated organometal oxinates and the dissociated part of the molecule will contribute in the same spectral region to the spectra in anhydrous methanol. This explains the values of the absorbances at 315 mμ (Fig. 1 and ref. 4, Fig. 3), which correspond to the total ligand present.

We believe that the present researches support our previous conclusions[1] about the existence of the tetra-coordinated triphenyltin(IV) oxinate, and at the same time reveal some factors influencing the change from chelated triphenyltin(IV) and triphenyllead(IV) oxinates to the non-chelated and to the dissociated species.

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Improved direct synthesis of methylgermanium halides

An improvement of the "Direct Synthesis"[1,*] of organogermanium halides involving the use of germanium and copper of smaller particle size and increased alkyl halide flow rate is reported. These modifications result in considerably larger amounts of crude reaction product produced per unit time than reported previously.

Experimental

Materials. Germanium powder (99.99 %) was obtained from A. D. Mackay, Inc., 198 Broadway, New York 38, N.Y., and exhibited an average particle diameter by microscopy of 0.02 to 0.05 mm, with high uniformity of size. Copper powder of electrolytic grade was purchased from Fisher Scientific and its particle size was the same as that of germanium. Methyl chloride and methyl bromide were supplied by the Matheson Company and methyl iodide was obtained from Fisher Scientific.

Apparatus and procedure. The methyl chloride or methyl bromide was passed (flow rate *ca.* 400–600 cc/min) through two wash bottles containing concentrated sodium hydroxide solution and concentrated sulfuric acid respectively and via a mercury safety valve into the reaction tube. The latter was a 25 mm I.D. Pyrex tube containing an intimate mixture of germanium powder and copper powder (weight ratio 10:4) distributed on glass wool. The 50 cm long tube was heated at 400 ± 10° in a 30 cm tube furnace. The methyl iodide was introduced at a rate of 100 drops per min directly into the reaction tube by means of a dropping funnel. The resulting liquid products were collected in a flask and the gaseous products separated in a dry-ice trap. The liquid materials were fractionated over a 100-cm heated column packed with glass helices.

The following boiling points were observed (at 750 mm): CH_3GeCl_3, 111°; $(CH_3)_2GeCl_2$, 122°; $(CH_3)_2GeBr_2$, 153°; CH_3GeBr_3, 170°; $(CH_3)_2GeI_2$, 62–64°/2 mm, CH_3GeI_3, 83–85°/12 mm, recrystallized from petroleum ether, m.p. 47°. The crude reaction products were assayed by proton nuclear-magnetic-resonance (NMR) spectroscopy of the neat liquids. The following chemical shifts were observed (in ppm relative to tetramethylsilane): CH_3Cl, −2.950; CH_3GeCl_3, −1.667; $(CH_3)_2GeCl_2$,

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[*] For a review of the "Direct Synthesis", see ref. 2.