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ORGANOMETALLIC OXIDES, ALKOXIDES AND PEROXIDES II*. PHENYLMERCURIC HYDROXIDE AND OXIDE

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SUMMARY

The existence of the discrete compounds phenylmercuric hydroxide, PhHgOH, and phenylmercuric oxide, $(PhHg)_2O$, is shown by a combination of thermogravimetric analysis and infrared spectroscopy. The method is also shown to be applicable in distinguishing between triphenyltin hydroxide and oxide.

DISCUSSION

The controversy surrounding the melting point of substances described as methylmercuric hydroxide was cleared up by the work of Grdenić and Zado[2]. They showed that all such materials were mixtures of methylmercuric oxide, $(MeHg)_2O$, m.p. 139° and the oxonium salt $[(MeHg)_3O]^+OH^-$, m.p. 88°.

Melting points between 200° (with decomposition)[3,4] and 230–232° (ref. 5) have been reported for substances referred to as phenylmercuric hydroxide. Other values are 216° (ref. 6), 224–225° (ref. 7), 225–227° (ref. 8), and 226–227° (ref. 9). It might be assumed that a situation similar to that for methylmercuric hydroxide obtains here, but, in contrast, this work shows the existence of discrete compounds of stoichiometry PhHgOH and $(PhHg)_2O$. Phenylmercuric oxide has not been reported previously; its properties and those of phenylmercuric hydroxide, and the interconversion of these compounds are now described.

Phenylmercuric hydroxide is best prepared by treating phenylmercuric acetate in hot benzene with 5–10% sodium hydroxide solution. The benzene is evaporated off and the crude product separates as small white crystals. These may be recrystallised from hot water (solubility at 100° is approximately 35 g/l), washed with acetone, and dried at 0.1 mm for several hours. The snowy white crystals melt on a micro-heating stage at 234–237°, although this is probably the melting point of the oxide (see below). The infrared spectrum shows a strong, broad absorption centred near 3250 cm^{-1}, attributable to the hydroxyl group.

Accurately weighed samples were analysed thermogravimetrically. Whilst no weight loss was observed between 30° and 80° and between 110° and 180°, between

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* For Part I see ref. 1.

80° and 110° a loss in weight was observed which was equivalent to 95% of that calculated for the interconversion:

$$2\ PhHgOH \rightarrow (PhHg)_2O + H_2O\uparrow$$

The infrared spectrum of a sample removed from the oven at 140° and cooled in a desiccator showed complete loss of the hydroxyl band at 3250 cm^{-1}, with simultaneous appearance of a new, intense band at 675 cm^{-1}. This new band may be assigned reasonably to the mercury–oxygen–mercury asymmetric stretching vibration in $(PhHg)_2O$. The analogous ν_{as}(M–O–M) band in bis(triethyltin) oxide (M = Sn) occurs at 778 cm^{-1}, and in bis(triethyllead) oxide[10] (M = Pb), at 625 cm^{-1}.

A similar change in infrared spectrum was observed by Kushlefsky, Simmons and Ross[11] during the interconversion of triphenyltin hydroxide to bis(triphenyltin) oxide by azeotropic dehydration in toluene. As well as the appearance of ν_{as}(Sn–O–Sn) at 774 cm^{-1}, they observed loss of δ(OH) at 910 and 897 cm^{-1}. In the conversion of phenylmercuric hydroxide to oxide, we also observed the loss of two weak bands at 925 and 910 cm^{-1}, possibly due to δ(OH).

The information derived from the thermogravimetric analysis of phenylmercuric hydroxide was used in a large-scale conversion of hydroxide into oxide. A bulk sample of hydroxide was simply suspended in a bath of boiling water while being evacuated at about 0.1 mm for three to four hours. This procedure yielded a white crystaline product, m.p. (microheating stage) 235–238°, which was superior to that obtained by azeotropic dehydration in cyclohexane. The latter method provided a pale yellow product, the colouration probably arising from decomposition brought about by local overheating of the solid.

Phenylmercuric oxide was unaffected by exposure to the air for 18 h. Unlike the triphenyltin compound, it could not be reconverted to the hydroxide by recrystallisation from 95% ethanol, but required the use of water.

It has often been difficult to distinguish effectively between some organometallic hydroxides and oxides. Triphenyltin hydroxide and oxide were identified by their reaction with the Karl Fischer reagent where one mole of iodine is used up per g-atom of tin[11]:

$$Ph_3SnOH + I_2 + SO_2 + MeOH \rightarrow Ph_3SnI + HI + HSO_4Me$$

$$(Ph_3Sn)_2O + I_2 + SO_2 + MeOH \rightarrow 2\ Ph_3SnI + HSO_4Me$$

A parallel behaviour might be expected for the mercury compounds. In methanolic pyridine, which is the medium for the Karl Fischer titration, we found that the phenyl–mercury bond of phenylmercuric iodide is cleaved by iodine,

$$PhHgI + I_2 \rightarrow PhI + HgI_2$$

However the reaction appears to be rapid and quantitative so that we still expected to be able to distinguish between phenylmercuric oxide and hydroxide by the Karl Fischer titration, but meaningful results could not be obtained.

Thermogravimetric analysis between 30° and 140° of triphenyltin hydroxide coupled with infrared spectra before and after the measured weight loss, enabled us to confirm the conclusions of Kushlefsky *et al.*[11] in a simple and rapid way. Indeed this combination of techniques seems particularly suited to the general problem of distinguishing between organometallic oxides and hydroxides, and avoids the difficulties associated with use of the Karl Fischer reagent.

EXPERIMENTAL

Infrared spectra were recorded as mulls in hexachlorobutadiene using Unicam SP 200 or Perkin–Elmer 337 instruments. Thermogravimetric analyses were carried out with a Stanton thermal balance at a heating rate of 200°/h. Carbon and hydrogen analyses were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, West Germany.

Mercury analysis was performed by converting a sample (ca. 0.4 g) into mercuric sulphate by boiling for 1 h in a Keldjahl flask with ANALAR sulphuric acid (20 ml). After the mixture was cooled, the organic material was oxidised by adding concentrated nitric acid (1 ml) and boiling for a further 1 h. The cold colourless solution was diluted with distilled water to about 150 ml, then titrated with standard ammonium thiocyanate using ferric ammonium sulphate as indicator. I thank Dr. D. H. Ballard for carrying out these determinations.

Preparation of phenylmercuric hydroxide

Sodium hydroxide solution (6%, 100 ml) was stirred into a solution of phenylmercuric acetate (34 g) in boiling benzene (250 ml). The benzene was evaporated off at a steam bath and the aqueous layer allowed to cool. The crude product was filtered off, recrystallised from boiling water, washed with acetone (50 ml) and dried at 0.1 mm for 5 h (23 g); ν_{max} 3250 br, s [ν(OH)], 3050 sh, m [ν(CH)], 1485 m, 1440 m, 1065 w, 1025 m, 925 w, 910 w, 730 s [δ(CH)], 695 s [δ(CH)] cm^{-1}. (Found: C, 24.33; H, 2.18; Hg, 68.1. C_6H_6HgO calcd.: C, 24.46; H, 2.04; Hg, 68.08%.)

Preparation of phenylmercuric oxide

Phenylmercuric hydroxide (18.15 g) was heated at 100° under a pressure of 0.3 to 0.05 mm for 3.5 h to yield phenylmercuric oxide (17.5 g); ν_{max} 3050 m [ν(CH)], 1485 m, 1435 m, 1065 w, 1025 m, 730 s [δ(CH)], 695 s [δ(CH)], 675 s [ν_{as}(Hg–O–Hg)] cm^{-1}. (Found: C, 25.10; H, 2.03; Hg, 70.5. $C_{12}H_{10}Hg_2O$ calcd.: C, 25.23; H, 1.77; Hg, 70.3%.)

Thermogravimetric analysis

(a). Phenylmercuric hydroxide. Run 1. Phenylmercuric hydroxide (0.6024 g) showed a weight loss of 0.017 g between 80° and 110° (calcd. for $2\,C_6H_6HgO \rightarrow C_{12}H_{10}Hg_2O + H_2O\uparrow$: 0.0184 g). A steady weight loss was observed above 180°, 0.240 g being lost between 180° and 300°. The infrared spectrum of the pale yellow residue indicated that some decomposition had occurred. *Run* 2. Phenylmercuric hydroxide (0.6622 g) showed a weight loss of 0.019 g between 80° and 110° (calcd. 0.020 g). At 140° the white crystalline product was removed rapidly from the oven and allowed to cool in a desiccator. The infrared spectrum showed that this was pure $(PhHg)_2O$.

(b). Triphenyltin hydroxide. Triphenyltin hydroxide (0.78563 g) showed a weight loss of 0.019 g between 80° and 110° [calcd. for $2\,Ph_3SnOH \rightarrow (Ph_3Sn)_2O + H_2O\uparrow$: 0.0193 g]. At 140° the molten sample was transferred rapidly to a desiccator to cool, when it resolidified. The infrared spectra and melting points of the starting hydroxide and product were in agreement with those previously reported[11] for triphenyltin hydroxide and bis(triphenyltin) oxide respectively.

Reaction of phenylmercuric oxide, hydroxide and iodide with iodine

(*a*). Methanol (50 ml) was added to phenylmercuric oxide (1.029 g; 1.8 mmole) and the solution titrated with methanolic iodine (79.87 g/l); 3.4 mmole were required. Filtration gave lustrous crystals (1.20 g) which were washed with methanol then light petroleum, dried under suction, and then recrystallised from boiling acetone, m.p. 259–261°, mixed m.p. with phenylmercuric iodide prepared by the method of Cowperthwaite and Warhurst[12], 258–262°.

(*b*). Phenylmercuric hydroxide (2.8 mmole) similarly reacted with iodide (2.6 mmole) in methanol to precipitate phenylmercuric iodide in high yield.

(*c*). Phenylmercuric iodide (3.23 mmole) in pyridine (25 ml) was titrated with methanolic iodine to a permanent golden colour which could be discharged with sodium thiocyanate; 3.47 mmole iodine were required.

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