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DIVINYLTIN DICHLORIDE DIHYDRATE

H. G. LANGER

The Dow Chemical Company, Eastern Research Laboratory Framingham, Massachusetts

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Abstract—The preparation of divinyltin dichloride has been reported in two independent publications, which show a discrepancy in melting points of the products.

Our duplication of the reported procedure confirmed one of the two results. An additional product in our preparation was found to be divinyltin dichloride dihydrate. Its preparation, identification and properties are reported.

Two independent publications for the preparation of divinyltin dichloride by disproportionation of tetravinyltin with tin tetrachloride show different melting points for the final product.^(1,2)

Current work in this laboratory made it necessary to prepare this compound and we observed some unexpected phenomena.

Our studies confirmed the lower melting point found by ROSENBERG *et al.*;⁽²⁾ however, we also obtained a crystalline material from the oily divinyltin dichloride after exposure to moist air.⁽³⁾

The identification of this new compound is reported in the following experimental section.

EXPERIMENTAL

After purified tetravinyltin had been reacted with tin tetrachloride, a large excess of petroleum ether (30-60°) was added and the solution treated with activated charcoal and anhydrous sodium sulphate. After removal of most of the solvent under vacuum, divinyltin dichloride formed a second layer and was separated from the remaining phase. The oil was submitted to reduced pressure (water aspirator) for several hours and allowed to crystallize in a refrigerator. The supernatant solution was cooled to approximately -5° resulting in crystallization of colourless needles. Both fractions were recrystallized from petroleum ether and the melting point of the final product was found to be 14.8 - 15.0°. (Found: C, 20.1, 19.9; H, 2.4, 2.4%. Calc. for C₄H₆Cl₂Sn: C, 19.71, H, 2.48%). Upon filtration at room temperature, these crystals melted to an oil and simultaneously reacted with condensed moisture from the air, which caused the oil to solidify. This solid crystallized from water or alcohol.

The highest melting point was found to be 43⁺ (sharp).

In dry air, especially in presence of drying agents, such as silica gel, the oily divinyltin dichloride is reformed. (Found: C, 20.1, 20.0; H, 2.5, 2.4% m.p. $14.8-15.0^\circ$). The weight loss based on the crystalline material was found to be 12.74 per cent.

The crystalline compound is obtained as prismatic needles or tablets presumably monoclinic or distorted orthorhombic. It is extremely soluble in water, alcohol and acetone, slightly soluble in chloroform and practically insoluble in nonpolar solvents such as carbon tetrachloride and benzene.

Except for two additional bands of 2.9 and 6.3 μ for the crystalline compound, the infra-red absorption spectra are the same for both oily (A) and crystalline material (B). Small shifts in some

⁽¹⁾ D. SEYFERTH and F. G. A. STONE, J. Amer. Chem. Soc. 79, 517 (1957).

⁽²⁾ S. D. ROSENBERG and A. J. GIBBONS, JR., J. Amer. Chem. Soc. 79, 2139 (1957).

⁽³⁾ In private communications, SEYFERTH explains the higher melting point as preferential crystallization of Et₂SnCl₂ and/or EtViSnCl₂ impurities formed from the ethyl bromide found to be an impurity in the starting vinyl bromide.



TRANSMITTANCE

bands and different intensities in others are most likely due to the different physical states of the two compounds.

The determination of all elements except oxygen was carried out by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. (Found: C, 17.41; H, 3.32; Cl, 25.43; O, 10.96*; Sn, 42.88. Calc. for $C_1H_8Cl_2Sn \cdot 2H_2O$: C, 17.18; H, 3.60; Cl, 25.35; O, 11.44; Sn, 42.43%).

DISCUSSION

The two bands at about 2.9 and 6.3μ in the spectrum of *B* indicated that the crystalline material is a hydrate of the oily anhydrous divinyltin dichloride. This assumption could be confirmed by analytical data. Although the percentages found for carbon, chlorine and tin are high (which could be due to loss of water between preparation and analysis), the calculated formula is still closer to the dihydrate than to a possible dimer or 1.5 hydrate. The observed weight loss of 12.74 per cent on drying the crystalline compound also corresponds to the calculated loss of 12.88 for the dihydrate.

Tin tetrachloride also shows an increased melting point for the pentahydrate: however, a decrease is reported⁽⁴⁾ when diethyltin dichloride is hydrated.[†]

No explanation can be given why other dialkyl or diaryltin dichlorides have not been found to form dihydrates, as it seems probable that the two molecules of water are used to satisfy the coordination number of six for the tetravalent tin in divinyltin dichloride dihydrate.

* By difference.

⁺ The melting point reported by SEYFERTH and STONE coincides with that of the hydrate of diethyltin dichloride, reported by PFEIFFER.

⁽⁴⁾ P. PFEIFFER, Ber. Dtsch. Chem. Ges. 35, 3306 (1902).