[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA CITRUS EXPERIMENT STATION, RIVERSIDE]

Dichlorodiphenyltrichloroethane. I. Solubility in Various Solvents

BY FRANCIS A. GUNTHER

Dichlorodiphenyltrichloroethane, or more properly 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane, and popularly known simply as "DDT," is rapidly becoming important as an insecticidal material. Insecticidal evaluations of this compound require its efficient removal, or "stripping," from the surface of the treated objects for subsequent quantitative estimation of deposit. Furthermore, this subsequent operation usually necessitates the selection of a solvent that is readily volatile.

This report is concerned with the solubility[1] of pure DDT in several of the more common volatile organic solvents at several different temperatures. The solvents employed were purified specimens of acetone, benzene, carbon tetrachloride, chloroform, ether, 95% ethanol, and petroleum ether (30–60°). In addition, approximate data have been obtained for the solubility of pure DDT in dioxane and pyridine at several temperatures. The temperature ranges represented lay between 0 and 48° for all determinations.

Inasmuch as commercial DDT contains relatively large amounts of the *o,p'*-isomer, in addition to other contaminants, the influence which this difference in composition would have on the solubility data herein presented might be important.

Experimental

All solvents employed were of reagent quality and were redistilled prior to use. The DDT used was obtained by five-fold recrystallization from 95% ethanol of a commercial sample; it possessed a final constant m. p. of 107–108° (cor.).

Two methods were employed for the solubility determinations: the synthetic method and the residue-weight method. Both of these methods were used to determine solubility at a given temperature for each solvent. Solution temperatures were reproducible to 0.5°, and usually to 0.3°. Differences between the two methods were usually less than 2 wt. %, which was a negligible error for the intended purpose of the results. All runs were duplicated for each method, and the value finally accepted was the arithmetic mean of the four values at the temperature under consideration.

Results

In Table I are given the wt. % solubilities of pure DDT in various solvents at several temperatures. Each value reported is the arithmetic mean of four values which differed among themselves by not more than 2 wt. %.

TABLE I

WT. % SOLUBILITIES OF PURE DDT IN VARIOUS SOLVENTS AT SEVERAL TEMPERATURES

Solvent	Wt. % solubility at 0°	7.2°	24.0°	45.0°	48.0°
Acetone	21.2	27.3	40.3	..	59.0
Benzene	6.8	27.1	44.0	..	57.8
Carbon tetrachloride	9.0	10.5	18.0	34.8	..
Chloroform	18.2	21.9	31.0	47.4	..
Dioxane	8	29	46	..	61
Ether	15.0	18.9	27.5	..	..
Ethanol (95%)	0.8	1.0	2.2	..	3.9
Petroleum ether (30–60°)	1.7	2.4	4.8	..	..
Pyridine	21	36	51	..	62

Discussion

The usual plot of the wt. % solubility *vs.* the temperature is shown in Fig. 1.

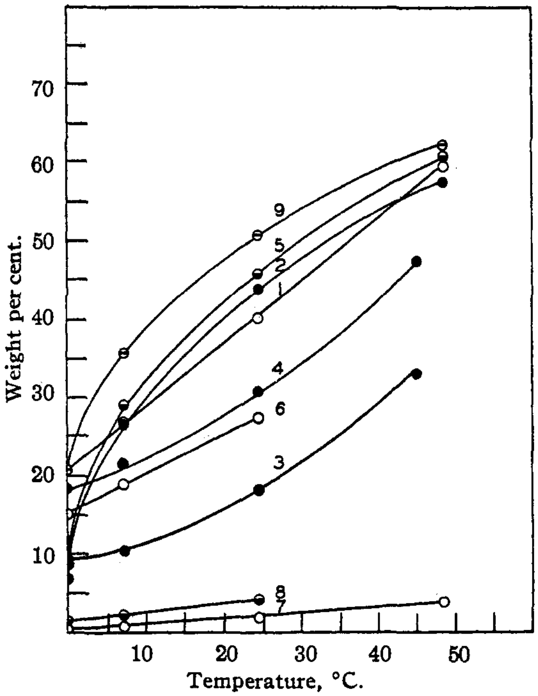

Fig. 1.—Solubility of pure DDT in various solvents: 1, acetone; 2, benzene; 3, carbon tetrachloride; 4, chloroform; 5, dioxane; 6, ether; 7, ethanol (95%); 8, petroleum ether (30–60°); 9, pyridine.

Since the purpose of the present investigation was to ascertain the best solvent for DDT under certain convenient conditions, namely, ready volatility and high solubility properties at room temperature, the discussion will be limited to those solvents fulfilling these conditions.

Acetone, benzene, dioxane, and pyridine were

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[1] It has been brought to the attention of the author that Campbell and West [*Chem. Trade J. and Chem. Eng.* (London), **115**, 195 (1944)], in a paper entitled, "DDT, Synthetic Insecticide—Its Properties and Potentialities," have discussed certain solubility properties of DDT. The unavailability of this journal has prevented the inclusion of a review of this work in the present report.

roughly comparable in solvent power at room temperature (24°) according to the curves shown in Fig. 1. Of these four, however, benzene is the only solvent which is immiscible with water, a factor of much importance when the strip solution has to be evaporated to near dryness before its content of DDT can be determined. Furthermore, since DDT may decompose above its melting point,[2] dioxane and pyridine become doubly impracticable because of the proximity of their boiling points to the melting point of DDT. Thus, we may conclude that benzene is an ideal stripping solvent for pure DDT at room temperature.

Summary

The wt. % solubilities of pure DDT in various common organic solvents have been determined for certain temperatures between 0 and 48° and rough solubility curves have been plotted. From the data so obtained, it is concluded that benzene is the most efficient "stripping" solvent for pure DDT at room temperature.

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[2] Zeidler, *Ber.*, **7**, 1180 (1874).

[Contribution from the Chemical Research Laboratory of the Ethyl Corporation]

The Preparation of Alkyllead Salts

By George Calingaert, F. J. Dykstra and Hymin Shapiro

Alkyllead salts are usually prepared by one of three general methods: (a) reaction of an acid with a tetraalkyllead compound or trialkyllead hydroxide; (b) interaction of an inorganic salt and an alkyllead salt; and (c) for the halides, reaction of a halogen with a lead tetraalkyl.[1] Since each of these general methods is not applicable for the preparation of all alkyllead salts, it is necessary to select the proper method and conditions for each salt in order to obtain a satisfactory yield of pure product. This Laboratory has made a large number of preparations of organolead compounds, and we have found that some of the methods reported in the literature for alkyllead salts are unsatisfactory, since they give impure products. For example, we have found that preparations of trialkyllead bromides and dialkyllead dichlorides by reaction of lead alkyls with hydrogen bromide and hydrogen chloride,[2] respectively, are badly contaminated with lead bromide and lead chloride, respectively.

In the course of our work, improved methods of preparation of several alkyllead salts were developed. This paper presents these methods and also the syntheses of several salts heretofore undescribed.

Trialkyllead Chlorides.—Trialkyllead chlorides containing like alkyl groups may be prepared in good purity and yield by treating a 5–10% solution of lead tetraalkyl in hexane at room temperature with hydrogen chloride. The trialkyllead chlorides precipitate, and successive crops of product may be removed by filtration at intervals, thus precluding their further and slow conversion to dialkyllead dichlorides. This method gave consistently higher yields of purer products than the treatment of lead tetraalkyls with concentrated aqueous hydrochloric acid,[3] or reaction with chlorine in an inert solvent,[4] or treatment with hydrogen chloride in ether.[2,5] The use of hexane as a solvent has two distinct advantages over the use of ether: no special effort need be made to dry the solvent, and excess hydrogen chloride has no adverse effect on the nature or yield of the product, unless the time of reaction is excessive.

Reaction of mixed methylethyllead alkyls with hydrogen chloride usually resulted in oils instead of crystalline products, and both the analyses and the appearance of the R_3PbCl products were indicative of mixtures. Apparently both methyl and ethyl radicals were cleaved because of the small difference in electronegativity[6] of the two groups, or the initial R_3PbCl produced underwent redistribution[7] to yield a mixture of R_3PbCl compounds.

In the reaction of hydrogen chloride with trimethylethyllead in hexane solution, pure dimethylethyllead chloride was isolated from the crude product by careful handling and recrystallization.

Trialkyllead Iodides.—These compounds are readily synthesized by interaction of lead alkyls with iodine in ether at −65°.[8] The trialkyllead iodides are less stable than the other trialkyllead halides but may be isolated in a fair state of purity. Triethyllead iodide, described in the literature[9] as an oil of low stability which cannot be obtained pure, was obtained as a clear liquid, freezing at 19–20°, stable to diffused light, and unchanged for months on storage at about 5°.

Alkyllead Hydroxides and Carbonates.—Many attempts, in this Laboratory and by

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[1] Calingaert, *Chem. Rev.*, **2**, 43 (1925).

[2] Gilman and Robinson, This Journal, **52**, 1975 (1930).

[3] (a) Browne and Reid, *ibid.*, **49**, 830 (1927); (b) Cahours, *Ann.*, **122**, 48 (1862).

[4] Grüttner and Krause, *Ber.*, **49**, 1415 (1916).

[5] (a) Pfeiffer, Truskier and Disselkampf, *ibid.*, **49**, 2445 (1916); (b) Buckton, *Ann.*, **112**, 220 (1859).

[6] Kharasch and Marker, This Journal, **48**, 3130 (1926).

[7] (a) Calingaert, Beatty and Hess, *ibid.*, **61**, 3300 (1939); (b) Calingaert, Soroos and Shapiro, *ibid.*, **62**, 1104 (1940).

[8] Calingaert and Soroos, *J. Org. Chem.*, **2**, 537 (1938).

[9] (a) Löwig, *Ann.*, **88**, 318 (1853); (b) Klippel, *Jahresber.*, 380 (1860); (c) Klippel, *J. prakt. Chem.*, **81**, 286 (1860).