

studies in amides and the peptide linkage is believed to be $\text{NH}-\text{O}^-$ with absorption near 3.0μ if isolated but at 3.22μ if the bonds are formed in pairs. A coplanar structure is postulated for the

CONHR group which involves geometrical isomerism. This structure must be considered in any explanation of protein behavior.

URBANA, ILLINOIS

RECEIVED JULY 12, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Dissociation of Hexaphenyldiplumbane

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Molecular weight determinations by Krause and Reissaus,¹ and, more recently, by Foster, Dix and Gruntfest,² indicate that hexaphenyldiplumbane, $(\text{C}_6\text{H}_5)_3\text{Pb}-\text{Pb}(\text{C}_6\text{H}_5)_3$, is appreciably dissociated in dilute benzene solution. The assumption is that the dissociation product is triphenyllead. As triphenyllead possesses an odd number of electrons, magnetic susceptibility measurements should serve to determine the degree of dissociation with some accuracy, and possibly to determine the heat of dissociation.

Two samples of hexaphenyldiplumbane were obtained. One was prepared for this investigation by Dr. J. D. Malkemus of this University, and the other was obtained through the courtesy of Professor Laurence S. Foster of Brown University.

Experimental Part

Magnetic Measurements.—The magnetic susceptibilities were measured by means of the Gouy balance previously described.³ The only modifications were in the use of the differential method of Freed and Kasper⁴ for the investigation of dilute solutions. All measurements on solutions were carried out in the absence of air and of moisture. The amount of light reaching the samples was also restricted, and as a final precaution against decomposition, all measurements were completed within twenty-four hours of the preparation of a solution. The absence of light was necessary because a benzene solution of the diplumbane was found to decompose quickly on exposure to direct sunlight. One of the decomposition products was metallic lead which was deposited as a black mirror.

All measurements were referred to freshly distilled benzene,³ the specific susceptibility of which was assumed to be -0.7023×10^{-6} at 25° . This value is, in turn, referred to water as -0.7200×10^{-6} at 20° .

The field strength for all measurements was 13,100 oersteds.

Density Measurements.—Densities of the solutions, necessary for the magnetic susceptibilities, were deter-

mined over the temperature range 30 to 80° by means of an expansion pycnometer. The pycnometer was calibrated by reference to benzene, the density of which, at various temperatures was taken, partly by extrapolation, from the data of Smyth and Stoops.⁵

Preparation of Materials.—One of the samples (Malkemus) of the hexaphenyldiplumbane was prepared by the action of phenylmagnesium bromide on lead dichloride. The other sample (Foster) was prepared by reduction of triphenyllead iodide in liquid ammonia. As shown below, these samples in the solid state had magnetic susceptibilities differing by less than 1%. No further purification was therefore believed necessary.

Two solutions of the diplumbane in redistilled, thiophene-free benzene were used. These were prepared by shaking the benzene with the diplumbane in a completely evacuated set of bulbs which could in turn be attached to the magnetic and density tubes as desired. All transfers of solution were carried out in the complete absence of air.

Analyses of the solutions were made by evaporating to dryness at 125° and weighing the residue.

Results

The susceptibility of the powdered hexaphenyldiplumbane at several temperatures is given in Table I. The susceptibility was independent of

TABLE I

Sample	Temp., °C.	Susceptibility per g. $\times 10^6$
(Malkemus)	25	-0.408 ± 0.002
(Malkemus)	-40	-.403
(Malkemus)	-100	-.396
(Foster)	25	-.404

field strength, proving the absence of ferromagnetic impurities. These data establish the purity of the samples and set an upper limit of dissociation at 0.1%. The slight temperature dependence is probably due to paramagnetic impurities present in extremely small amount. The molar susceptibility of the diplumbane is -356×10^{-6} , as compared with -285×10^{-6} for hexaphenyldigermane.

In order to obtain the susceptibilities of the solu-

(1) Krause and Reissaus, *Ber.*, **55**, 894 (1922).

(2) Foster, Dix and Gruntfest, *THIS JOURNAL*, **61**, 1685 (1939).

(3) Selwood, *THIS JOURNAL*, **61**, 3168 (1939).

(4) Freed and Kasper, *Phys. Rev.*, **36**, 1002 (1930).

(5) Smyth and Stoops, *THIS JOURNAL*, **51**, 3320 (1929).

tions it was necessary to know the susceptibility of benzene at several temperatures. These data are given in Table II and show, rather surprisingly, some dependence of susceptibility on temperature.

Temp., °C.	Susceptibility per g. $\chi \times 10^6$
30	-0.7024 ± 0.0007
40	.7039
50	.7060
60	.7082
70	.7107
80	.7136

It should be noted, however, that, according to the method of Freed and Kasper, the data for benzene affect only the absolute and not the relative values for the diplumbane reported below.

In the following tables T is the temperature, d the density, χ_s the susceptibility of the solution, and $\chi_{\text{calcd.}}$ the apparent susceptibility of the diplumbane in solution calculated according to Wiedemann's law, from χ_s and the percentage composition.

Table III gives the data for a 0.02265 molal solution of the Malkemus sample containing 19.88 g. of diplumbane per 1000 g. of benzene.

T	d	$\chi_s \times 10^6$	$\chi_{\text{calcd.}} \times 10^6$
30	0.8784	-0.6952 ± 0.0007	-0.33 ± 0.05
40	.8659	-.6980	-.40
50	.8559	-.6993	-.37
60	.8451	-.7013	-.35
70	.8343	-.7037	-.35
80	.8231	-.7068	-.37

Table IV gives the data for a 0.01547 molal solution of the Foster sample containing 13.58 g. of diplumbane per 1000 g. of benzene.

T	d	$\chi_s \times 10^6$	$\chi_{\text{calcd.}} \times 10^6$
30	0.8746	-0.6974	-0.33
40	.8636	.6990	-.34
50	.8526	.7012	-.35
60	.8418	.7034	-.31
70	.8309	.7059	-.35
80	.8197	.7090	-.37

In order to obtain the degree of dissociation from the above data it is necessary to know the susceptibility of undissociated diplumbane and of triphenyllead. The first may be taken as -0.406×10^{-6} at room temperature, with probably little variation up to 80°. The susceptibility of triphenyllead is assumed to be given by $a/T + b$ where a is the Curie constant, T the absolute tem-

perature, and b the diamagnetic correction. The molar paramagnetism produced by a single unpaired electron spin is about 1270×10^{-6} at room temperature. Hence for triphenyllead the paramagnetic part of the susceptibility is about $(1270 \times 298 \times 10^{-6}) / (T \times 438)$ per gram. The diamagnetic correction is, to a first approximation, the same, gram for gram, as the susceptibility of the hexaphenyldiplumbane. Hence the specific susceptibility of triphenyllead at 30° is probably about

$$\left(\frac{1270 \times 298}{303 \times 438} - 0.406 \right) \times 10^{-6} = 2.34 \times 10^{-6}.$$

With the above information the fraction, p , of triphenyllead present may be calculated by an application of Wiedemann's law. The degree of dissociation, α , is related to p by $p = 2\alpha / (1 + \alpha)$. The data are summarized in Table V.

TABLE V
APPARENT PERCENTAGE DISSOCIATION OF HEXAPHENYLDIPLUMBANE IN BENZENE SOLUTION

Temp., °C.	0.02265 M α	0.01547 M α
30	1.3%	1.3%
40	0.1	1.2
50	.6	1.1
60	1.0	1.1
70	1.2	1.1
80	0.8	0.8

Although the apparent percentage dissociation is in all cases positive, it should be borne in mind that paramagnetic impurities present in extremely small amount would show the observed effect, while diamagnetic impurities would be negligible. The results therefore set upper limits of dissociation, which are in all cases under 1.4%. It is also to be noted that the dissociation would be expected to increase with increasing dilution and rising temperature. This effect is not observed.

Inasmuch as the concentrations employed in this work approach those of Krause and Reissaus, and definitely overlap those of Foster, Dix and Gruntest, it may be concluded that, within the above upper limits, triphenyllead is not one of the dissociation products of hexaphenyldiplumbane.

Summary

Magnetic measurements on hexaphenyldiplumbane set upper limits of dissociation into triphenyllead at 0.1% in the solid and 1.4% in a benzene solution within the temperature range 30 to 80°, and the concentrations 0.02265 M and 0.01547 M .