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TRIMETHYLLEAD CHLORIDE DISSOCIATION IN AQUEOUS AND METHANOLIC SOLUTIONS

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Summary

The dissociation constants of $(CH_3)_3PbCl$ at 26°C in water and in methanol have been determined to be 0.51 mol/l and 4.65×10^{-4} mol/l, respectively, from the variations of Pb NMR chemical shifts (by INDOR) with concentration. Chemical shifts relative to $(CH_3)_4Pb$ have been obtained for $(CH_3)_3PbCl$, for solvated $(CH_3)_3Pb^+$, and for a possible dimer $[(CH_3)_3PbCl]_2$ formed in methanol.

Introduction

Some time ago we reported [1] results on the complexation of methylmercuric halides obtained from the variation of ^{199}Hg NMR chemical shift (by INDOR), and employed these data to assist in the understanding of anion catalysis of reactions of these species. The INDOR procedure has again been employed to follow the change in ^{207}Pb chemical shift due to the dissociation of trimethyllead chloride. Evidence for this dissociation has previously been obtained from studies of the reaction of trimethyllead chloride with hexamethyldilead [2]. Similar behaviour was also found for the reaction of trimethyltin chloride with hexamethylditin [3,4].

Experimental

The ^{207}Pb NMR spectra (given in Tables 1 and 2) were obtained in the INDOR mode by irradiation of the high field component of the methyl group doublet in the proton spectrum [5]. The PS-100 spectrometer was operated in the frequency sweep mode with the field locked on the solvent protons (CH_3 for

TABLE 1

LEAD-207 CHEMICAL; TRIMETHYLLEAD CHLORIDE IN WATER (26°C)

	$[(PH_3)_3PbCl]$ (mol/l)	ν_5 (Hz)	ν_6 (Hz)	δ (ppm)
1	0.031	20 928 870	20 928 790	482.1
2	0.070	680	602	473.1
3	0.097	620	544	470.25
4	0.129	559	482	467.3
5	0.162	503	426	464.5
6	0.193	466	387	462.8
7	0.224	424	347	460.85
8	0.255	387	310	459.1
9	0.285	356	279	457.5
10	0.318	326	248	456.15
11	0.374	275	196	453.7
12	0.433	220	143	451.1
13	0.489	180	104	449.2
14	0.545	140	064	447.3
15	0.600	103	026	445.5

(Ref. (in expt. no 1) 20 918 739 Hz. Ref. (in expt. no. 15) 20 918 739 Hz.)

methanol). The irradiation frequency was derived from a Rohde and Schwarz BNB4444803 Synthsizer swept by a ramp voltage from a Hewlett-Packard HP3304A unit and monitored by a Hewlett-Packard HP5244L Counter. Tetramethyllead (85% in toluene) in a capillary was used as an external reference in the highest and lowest concentrations of each series.

TABLE 2

LEAD-207 CHEMICAL SHIFTS: TRIMETHYLLEAD CHLORIDE IN METHANOL (26°C)

	$[(CH_3)_3PbCl]$ (mol/l)	ν_5 (Hz)	ν_6 (Hz)	δ (ppm)
1	0.039	20 926 077	20 925 996	347.3
2	0.063	007	926	343.95
3	0.081	20 925 968	894	342.25
4	0.102	945	865	341.0
5	0.121	924	844	340.0
6	0.163	897	817	338.7
7	0.199	885	805	338.15
8	0.241	867	787	337.3
9	0.294	857	779	336.85
10	0.388	843	764	335.9
11	0.470	838	758	335.9
12	0.554	836	755	335.8
13	0.637	834	752	335.65
14	0.715	831	752	335.6
15	0.771	832	752	335.6
16	0.863	834	754	335.7
17	0.932	836	756	335.8
18	1.000	838	759	335.9

(Ref. (in expt. no. 1) 20 918 771 Hz. Ref. (in expt. no. 18) 20 918 771 Hz.)

Results and discussion

Results for aqueous and for methanolic solutions of trimethyllead chloride, both at 26°C, are given in Tables 1 and 2 respectively. The reference resonance occurs at the same frequency 20 918 739 Hz (H_2O solution) and 20 918 771 Hz (CH_3OH solution) for both observations in each set of experiments, but at different frequencies for these sets due to different locked fields. The frequency for the reference at a field strength corresponding to the protons of tetramethylsilane at exactly 100 MHz is 20 920 516 Hz in both cases. McFarlane [6] reports 20 920 680 Hz for a neat sample.

The frequencies of the central pair (ν_5 and ν_6) of the ^{207}Pb decet are listed. The mean of these is the lead chemical shift (relative to the tetramethyllead capillary and positive to low field) which is the weighted average of all rapidly exchanging trimethyllead species in the system.

If the only process taking place in solution is the dissociation represented by eqn. 1 then the observed lead chemical shift, δ_{obs}, at some stoichiometric con-

$$(CH_3)_3PbCl \overset{K_D}{\rightleftharpoons} (CH_3)_3Pb^+(solv) + Cl^- \qquad (1)$$

centration m of trimethyllead chloride is given by

$$\delta_{obs} = \alpha\delta_B + (1-\alpha)\,\delta_A = \delta_A + \alpha(\delta_B - \delta_A) \qquad (2)$$

where δ_A and δ_B are the chemical shifts of $(CH_3)_3PbCl$ and $(CH_3)_3Pb^+(solv)$ respectively and α is the degree of dissociation given by:

$$\alpha = \frac{-K_D + \sqrt{K_D^2 + 4mK_D}}{2m} \qquad (3)$$

If K_D were sufficiently small relative to m the chemical shift data could be fitted to the quadratic eqn. 4. Least-squares fitting of δ_{obs} and $m^{-1/2}$ gives values for δ_A, δ_B and K_D. However, these do not properly reproduce the δ_{obs} values and a full numerical solution of eq. 3 is required to obtain α-values for

$$\delta_{obs} = \delta_A + (\delta_B - \delta_A)\,K_D^{1/2}\cdot m^{-1/2} - \tfrac{1}{2}(\delta_B - \delta_A)K_D \cdot m^{-1} \qquad (4)$$

insertion in eq. 2. A modified version of the "pit-mapping" program of Sillen [7] was employed to minimize the error square sum, $\Sigma_i(\delta_{obs} - \delta_{calc})^2$, and the following were obtained:

	Aqueous solution (26°C)
K_D	0.51 mol/l
δ_A	20 926 995 Hz = 394.6 ppm
δ_B	20 928 841 Hz = 482.9 ppm

Figure 1 shows the correspondence between observed and calculated chemical shift values.

This value of K_D is in excellent agreement with the value (0.48 ± 0.05 mol/l) obtained by Pilloni and Magno [8] by a potentiometric method for aqueous solution (1 M ClO_4^-) at 25°C.

In the case of methanolic solution K_D is sufficiently small for eq. 4 to be fol-

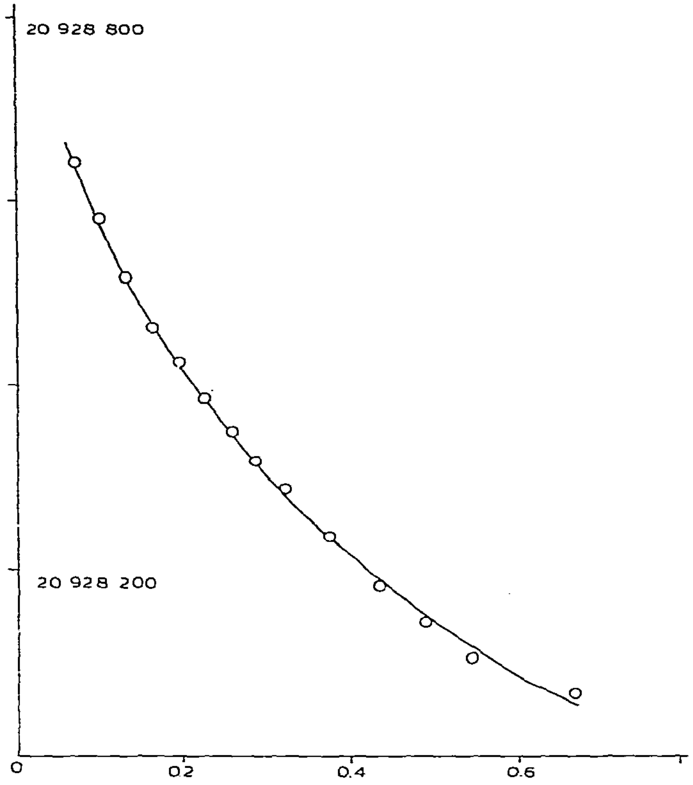


Fig. 1. ^{207}Pb chemical shift vs. concentration (aqueous solution).

lowed at least for the data of experiments 1—9 but thereafter deviations are observable. One possibility to account for these deviations is the equilibrium (eq. 5) utilising chloride generated through dissociation (eq. 1). However the data

$$(CH_3)_3PbCl + Cl^- \rightleftharpoons (CH_3)_3PbCl_2^- \tag{5}$$

cannot be fitted to the pair of equilibria 1 and 5 with reasonable values of K_5 and δ for $(CH_3)_3PbCl_2^-$. On the other hand a dimerization reaction (eq. 6) with

$$2(CH_3)_3PbCl \rightleftharpoons [(CH_3)_3PbCl]_2 \tag{6}$$

an equilibrium constant, K_6, and yielding a product with chemical shift, δ_c, leads to the expressions 7 and 8, where

$$\delta_{obs} = \alpha_A\delta_A + \alpha_B\delta_B + \alpha_c\delta_c \tag{7}$$

where

$$\alpha_A = \frac{[(CH_3)_3PbCl]}{m}; \quad \alpha_c = 2K_D\,\frac{[(CH_3)_3PbCl]^2}{m}; \quad \alpha_B = 1 - \alpha_A - \alpha_C\,.$$

$$2K_6[(CH_3)_3PbCl]^2 + \sqrt{K_D[(CH_3)_3PbCl} + [(CH_3)_3PbCl] = m \tag{8}$$

The approximate expression 4 and the "pit-mapping" method yield the following results:

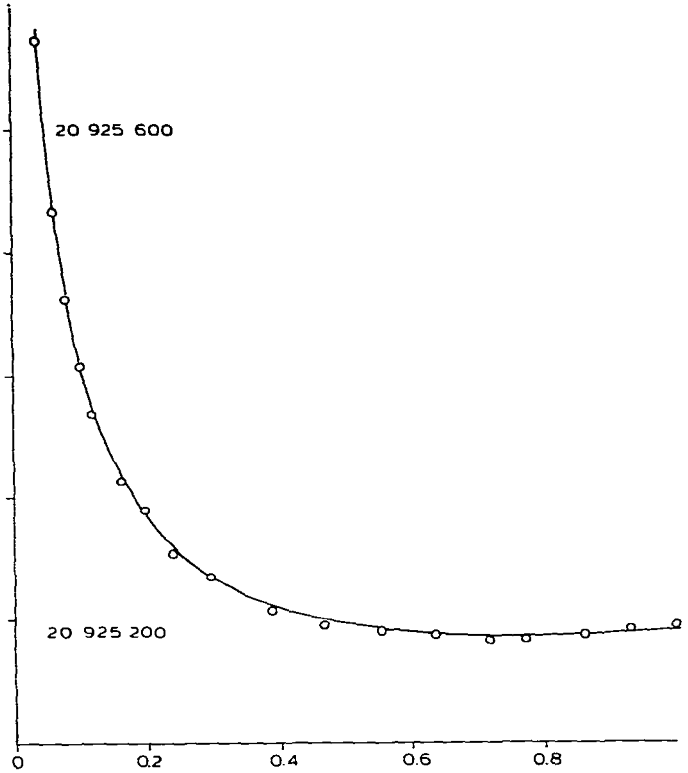


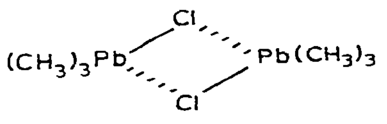
Fig. 2. ^{207}Pb chemical shift vs. concentration (methanol).

Methanol solution (26° C)

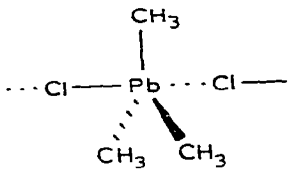
	Equation 4	"Pit-mapping"
K_D	3.64×10^{-4}	4.65×10^{-4} mol/l
K_6	—	7.8×10^{-2} l/mol
δ_A	20 925 679	20 925 652 Hz ≡ 329.9 ppm
δ_B	20 929 577	20 929 400 Hz ≡ 508.1 ppm
δ_C	—	20 926 238 Hz ≡ 356.9 ppm

Figure 2 shows the correspondence between observed and calculated shift values.

The dimer which appears to be present in concentrated methanolic solutions of trimethyllead chloride can presumably be formulated as in I, and is a conse-



(I)



(II)

quence of the Lewis acidity of the monomeric species. This is reminiscent of the behaviour of trialkyltin halides, which in the solid state may have structures similar to II above [9]. Strong interactions of the Lewis acid-base type may well be responsible for the marked solvent effects on the chemical shifts of the monomeric species and the cation evident in the present results.

Pb chemical shifts have been reported for a number of organolead compounds [10] in particular $(CH_3)_3PbCl$ in $CDCl_3$ solution at 374.8 ppm to low field of external $(CH_3)_4Pb$ (80% in toluene) (This reference is at 20 920 657 ± 2 Hz). The structure in this case may be best represented by II.

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