

A Kinetic Study of the Redistribution Reaction of $\text{Me}_{4-n}\text{Pb}[\text{M}(\text{CO})_5]_n$ ($\text{M} = \text{Mn, Re}; n = 1, 2; \text{Me} = \text{CH}_3$)

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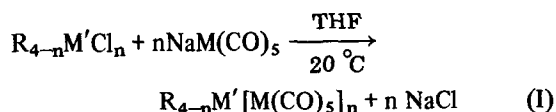
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Received October 22, 1980

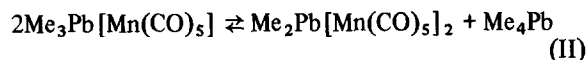
In the system $\text{Me}_4\text{Pb}/\text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]/\text{Me}_2\text{Pb}[\text{M}(\text{CO})_5]_2$ ($\text{Me} = \text{CH}_3$; $\text{M} = \text{Mn, Re}$) redistribution can occur. The single reactions involved, disproportionation of $\text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]$ ($\text{M} = \text{Mn, Re}$) and conproportionation of Me_4Pb and $\text{Me}_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ to $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]_2$ have been investigated kinetically by ^1H NMR spectroscopy in various solvents, and initial phase rate constants have been determined. Both types of reactions proceed according to a 2nd order rate law. Conproportionation is faster than disproportionation. Mn compounds redistribute faster than Re compounds. The solvent dependency of the reaction can be explained when a reaction mechanism via a bridged transition state is assumed.

Introduction

Compounds of the type $\text{R}_{4-n}\text{M}'[\text{M}(\text{CO})_5]_n$ ($\text{M} = \text{Mn, Re}$) can be prepared in good yields and high purity according to eqn. I [1, 2] ($\text{M}' = \text{Ge or Sn, R} = \text{alkyl or aryl, } n = 1, 2, 3; \text{M}' = \text{Pb, R} = \text{aryl, } n = 1, 2$):



Reaction of $\text{Alkyl}_{4-n}\text{PbCl}_n$ and $\text{NaMn}(\text{CO})_5$ in THF however does not correspond to the stoichiometry of eqn. I. Me_3PbCl ($\text{Me} = \text{CH}_3$) and $\text{NaMn}(\text{CO})_5$, e.g. react to give NaCl and a mixture of $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$ and $\text{Me}_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ [2], and additionally Me_4Pb [3]. We therefore supposed that the primary product of eqn. I, $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$, in part redistributes according to eqn. II [3],



thereby altering the overall stoichiometry of the reaction. This supposition was strengthened by our

observation during other experiments that pure $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$, [3] and $\text{Me}_3\text{Pb}[\text{Re}(\text{CO})_5]$, undergo redistribution in THF and acetone, respectively. This behaviour also would be analogous to known redistribution reactions of dialkyllead compounds R_2PbX_2 ($\text{X} = \text{e.g. halide}$) [4].

In this paper we report on kinetic investigations of the disproportionation of $\text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]$ and of the conproportionation of $\text{Me}_2\text{Pb}[\text{M}(\text{CO})_5]_2$ and Me_4Pb , continuing our efforts to determine factors influencing organolead redistribution reactions.

Experimental

Compounds $\text{Me}_{4-n}\text{Pb}[\text{M}(\text{CO})_5]_n$ ($n = 1, 2; \text{M} = \text{Mn}$ [2], $\text{M} = \text{Re}$ [5]) were prepared freshly for each set of experiments. Me_4Pb was obtained from Associated Octel Ltd. London (84.7% solution in toluene). The kinetic behaviour was studied in acetone- d_6 , methanol- d_4 and pyridine solution by ^1H NMR measurements (60 MHz, Varian A 60 D) using sealed glass tubes at definite temperatures given in the tables. Signals were recorded every 30 min. Due to low solubilities nearly saturated solutions of $\text{Me}_{4-n}\text{Pb}[\text{M}(\text{CO})_5]_n$ had to be used to obtain NMR signals, which could be evaluated with sufficient accuracy. Actually the solubility of $\text{Me}_2\text{Pb}[\text{M}(\text{CO})_5]_2$ in methanol was too low to measure reliable signals. Precipitation of small amounts of $\text{Me}_2\text{Pb}[\text{M}(\text{CO})_5]_2$ during disproportionation of $\text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]$ prevented determination of rate constants beyond the initial phase of the reaction. ^1H NMR spectra of the methyl lead species (Table I) taking part in the redistribution show proportionality between concentration of the appropriate compound and peak area of its methyl main signal, provided the measurements were done sufficiently far from the saturation energy of a resonance signal. To ensure this an estimation was made before each measurement. Furthermore the peak area of each species was correlated with the peak area of a reference (Me group in toluene or residual ^1H atoms in acetone- d_6) to balance instabilities of the spectro-

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TABLE I. ^1H NMR Chemical Shifts (ppm) of $\text{Me}_{4-n}\text{Pb}[\text{M}(\text{CO})_5]_n$ ($n = 0, 1, 2$) in Different Solvents (Reference Me_4Si , $T = 40^\circ\text{C}$).

Solvent	$n = 0$	$n = 1$ $\text{M} = \text{Mn}$	$n = 1$ $\text{M} = \text{Re}$	$n = 2$ $\text{M} = \text{Mn}$	$n = 2$ $\text{M} = \text{Re}$
CD_3COCD_3	0.75	1.20	1.07	1.58	1.52
CD_3OD	0.95	1.40	^a	1.75	^a
$\text{CD}_3\text{OD/KCl}$	0.95	1.40	^a	1.76	^a
$\text{CD}_3\text{OD/D}_2\text{O}$	0.95	1.42	^a	1.76	^a
$\text{CD}_3\text{OD}/(\text{COOH})_2$	0.98	1.43	1.25	1.78	1.68

^aInsufficient solubility.TABLE II. Rate Constants (with standard deviations) of Redistribution Reactions in the System $\text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]/\text{Me}_2\text{Pb}[\text{M}(\text{CO})_5]_2/\text{Me}_4\text{Pb}$ ($\text{M} = \text{Mn, Re}$) in different Solvents (k_d = rate constant of disproportionation reaction, k_c = rate constant of conproportionation reaction).

Compound	$T [^\circ\text{C}]$	$k_d [\text{l mol}^{-1} \text{h}^{-1}]$	$T [^\circ\text{C}]$	$k_d [\text{l mol}^{-1} \text{h}^{-1}]$
$\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$	CD_3COCD_3		$\text{CD}_3\text{OD/KCl}^{\text{a}}$	
	40	1.2(1)	37	11.4(4)
	46	2.4(3)		
	50	3.6(1)		
	CD_3OD		$\text{CD}_3\text{OD/D}_2\text{O}^{\text{b}}$	
	37	12.7(9)	37	18.1(7)
	44	15.2(5)		$\text{CD}_3\text{OD/Hox}^{\text{c}}$
	Pyridine		37	19.0(6)
	45	0.99(5)		
$\text{Me}_3\text{Pb}[\text{Re}(\text{CO})_5]$	CD_3COCD_3		$\text{CD}_3\text{OD/Hox}^{\text{c}}$	
	40	0.13(1)	37	3.1(4)
	50	0.25(2)		
	$T [^\circ\text{C}]$	$k_c [\text{l mol}^{-1} \text{h}^{-1}]$		
$\text{Me}_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ and Me_4Pb	CD_3COCD_3			
	40	9.9		
	46	20.5		
	50	27.1		

^a0.2 M KCl. ^b $\text{CD}_3\text{OD}:\text{D}_2\text{O} = 10:1$. ^c0.2 M oxalic acid (= Hox).

meter. To obtain rate laws in each set of experiments measurements at three different concentrations of the educts $\text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]$ (for disproportionation) and $\text{Me}_2\text{Pb}[\text{Mn}(\text{CO})_5]_2/\text{Me}_4\text{Pb}$ (for conproportionation) were made. Samples were prepared by dissolving a measured amount of organolead compound in the appropriate solvent in a 1 ml volumetric flask. Concentration of $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$ was about 0.3 mol l^{-1} in acetone- d_6 and pyridine, and 0.08–0.10 mol

l^{-1} in methanol- d_4 ; concentration of $\text{Me}_3\text{Pb}[\text{Re}(\text{CO})_5]$ was 0.05–0.07 mol l^{-1} . For evaluation of the measured data it was assumed that the disproportionation reaction (eqn. II) is of 2nd order with respect to $\text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]$ ($\text{M} = \text{Mn, Re}$), and that the conproportionation is also a 2nd order reaction being 1st order with respect to $\text{Me}_2\text{Pb}[\text{M}(\text{CO})_5]_2$ and to Me_4Pb . Then, for the initial phase of each reaction and not regarding the backward reaction the follow-

ing equations [6] can be applied for graphical evaluation:

$$\frac{1}{C_A} - \frac{1}{C_A^0} = k_d \cdot t \quad (1)$$

(C^0 = molar concentration at t (h) = 0; C = molar concentration at t (h) = t ; $A = \text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]$) and (since essentially equal starting concentrations – ca. 0.15 mol l^{-1} – of Me_4Pb and $\text{Me}_2\text{Pb}[\text{M}(\text{CO})_5]_2$ have been used) [6, 7]

$$\frac{1}{C_B^0 - x} - \frac{1}{C_B^0} = k_c \cdot t \quad (2)$$

($C_B^0 = \frac{1}{2} (C^0\text{Me}_4\text{Pb} + C^0\text{Me}_2\text{Pb}[\text{M}(\text{CO})_5]_2)$ at t (h) = 0; x = conversion variable at t (h) = t).

Insertion of the measured kinetic data into the appropriate equations and graphical evaluation gave linear relations of $1/C_A - 1/C_A^0$ and t (h) (example, see Fig. 1) and of $1/(C_B^0 - x) - 1/C_B^0$ and t (h) for the initial phase. The rate determining step therefore is of 2nd order.

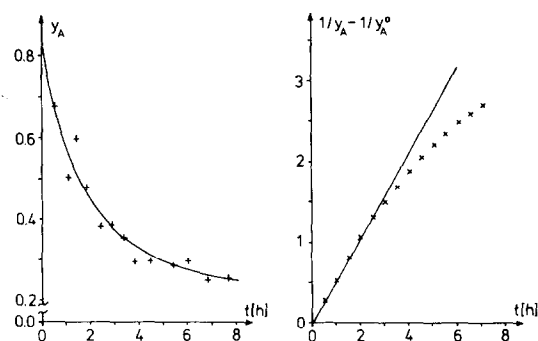


Fig. 1. Redistribution of $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$ (A) in acetone- d_6 ; measurement at 40°C (y_A = relative concentration of $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$ based on peak areas of methyl main ^1H NMR signal). a) Decrease of concentration of $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$ (+ = measured values). b) Determination of k_d according to Initial Rate Method (x = graphically evaluated values of Fig. 1 a).

The rate constants k_d and k_c at different temperatures and in different solvents are presented in Table II. The accuracy of determinations of k_d and k_c was checked according to ref. [6].

Discussion

From the kinetic data gained during the initial phase of the disproportion of $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$ in acetone- d_6 (k_d) it follows that this reaction is about ten times slower than the conproportionation of $\text{Me}_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ and Me_4Pb (k_c). The equilibrium state (equation II) could not be determined, since $\text{Me}_{4-n}\text{Pb}[\text{Mn}(\text{CO})_5]_n$ species ($n = 1, 2$) precipi-

tated before equilibrium was attained; besides, after more than 4 h, undefined decomposition reactions evidently gained importance.

The influence of the solvent was studied in another series of experiments. Besides acetone- d_6 methanol- d_4 and pyridine were suitable, however $\text{Me}_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ was not sufficiently soluble to give evaluable ^1H NMR signals to establish k_c in these two solvents. Rate constants k_d (Table II) increase in the sequence pyridine < acetone- d_6 < methanol- d_4 at comparable temperatures. Since pyridine has been shown to be a stronger donor for organolead compounds than acetone [8], it seems reasonable to assume that the increase of k_d indicates a decrease of coordinative stabilization of $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$ species by the different solvent molecules.

In non polar solvents like benzene no reaction occurred during 3 days at 50°C . The higher rate of disproportionation in methanol- d_4 than in acetone- d_6 has also to be considered under the aspect of the protic properties of methanol- d_4 . Actually addition of water or oxalic acid to methanol- d_4 and thereby increasing the protic strength of the solvent led to further increase of k_d (Table II). Increase of the ionic strength by dissolving salts in methanol- d_4 , e.g. KCl, showed no appreciable effect (Table II).

To study the influence of the transition metal M in $\text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]$ on the rate of disproportionation the redistribution of the Re- and of the Mn-compound was compared. The disproportionation of $\text{Me}_3\text{Pb}[\text{Re}(\text{CO})_5]$ was slower in acetone- d_6 during the initial phase; the conproportionation of $\text{Me}_2\text{Pb}[\text{Re}(\text{CO})_5]_2$ and Me_4Pb was much slower. Also – according to a qualitative experiment (low solubility of $\text{Me}_2\text{Pb}[\text{Re}(\text{CO})_5]_2$) – the conproportionation of $\text{Me}_2\text{Pb}[\text{Re}(\text{CO})_5]_2$ and Me_4Pb was slower than the disproportionation of $\text{Me}_3\text{Pb}[\text{Re}(\text{CO})_5]$. The differences in the reaction rate of Re and Mn compounds can be correlated – assuming comparable Me–Pb bond strengths – with the increase of strength of the bonds Pb–Mn < Pb–Re [9].

The results explain why Me_3PbCl reacts with $\text{NaMn}(\text{CO})_5$ to give a mixture of $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$ and $\text{Me}_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$, and with $\text{NaRe}(\text{CO})_5$ to give only $\text{Me}_3\text{Pb}[\text{Re}(\text{CO})_5]$ [2, 4]: in the first case fast disproportionation of the primary product $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$ leads to $\text{Me}_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ and Me_4Pb , while in the second case no appreciable amounts of $\text{Me}_2\text{Pb}[\text{Re}(\text{CO})_5]_2$ are produced, since the disproportionation of $\text{Me}_3\text{Pb}[\text{Re}(\text{CO})_5]$ is too slow.

All observations regarding influences on the disproportionation of $\text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]$ can be correlated with the assumption of a reaction mechanism, which according to Fig. 2 involves formation of a 4-centre transition state. Its formation is disfavoured if $\text{Me}_3\text{Pb}[\text{M}(\text{CO})_5]$ forms rather stable complexes with solvent molecules L, and if the Pb–M bond is rather strong.

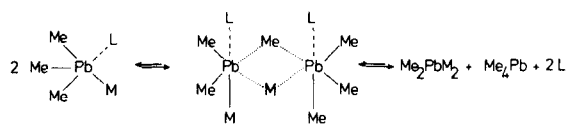


Fig. 2. Proposed reaction pathway (M = Mn(CO)₅, L = solvent molecules).

Using the Arrhenius equation an activation energy of disproportionation of $\text{Me}_3\text{Pb}[\text{Mn}(\text{CO})_5]$ in acetone-d₆ of $89 \pm 5 \text{ kJ mol}^{-1}$ was evaluated; the activation enthalpy $\Delta H^\ddagger$ then is $86.5 \pm 5 \text{ kJ mol}^{-1}$.

Acknowledgement

We thank Fonds der Chemischen Industrie for assistance.

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