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Products of Tetramethyllead Dealkylation with Bromine

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Abstract—Products of tetramethyllead dealkylation with bromine in the temperature interval from –20 to 20°C were analyzed by X-ray diffraction, IR spectroscopy, and spectrophotometry. Specific features of their thermal behavior were studied by differential thermal analysis and mass spectrometry.

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Stable lead isotopes find growing use in modern science and engineering [1–4]. Tetramethyllead $Pb(CH_3)_4$ is used as the working substance in separation of lead isotopes by centrifugation. The physicochemical properties of this compound have been comprehensively studied, and it has been shown to be compatible with materials of the centrifugal equipment [5].

After the production on separation cascades, isotope-enriched $Pb(CH_3)_4$ should be converted to lead metal, as this form is more convenient for storage and sale and is the starting form for preparing lead compounds with altered isotope composition. In conversion of $Pb(CH_3)_4$ to lead metal, the loss should be reduced to a minimum, the isotope dilution should be excluded, and the required chemical purity of the product should be ensured.

Thermal and photochemical processes can be used for converting $Pb(CH_3)_4$ to lead metal [6, 7]. However, both in photolysis and in thermolysis of $Pb(CH_3)_4$ lead metal is formed as dusty deposits, various films, and flakes with nonuniform distribution over the reactor surface. Therefore, the lead metal can be removed from the reactor only by mechanically scraping it off or by dissolving it in appropriate reagents. This process requires manual labor and is difficult to automate. Therefore, both procedures are characterized by low productive capacity and high processing cost.

Lead metal can be prepared from methyllead halides of types PbR_3Hal and PbR_2Hal_2, formed by dealkylation of $Pb(CH_3)_4$ with halogens [8]. These compounds are unstable and tend to disproportionate to form various lead-containing products.

Akimov et al. [9] evaluated by quantum-chemical calculations the thermodynamic probability of the reactions of $Pb(CH_3)_4$ dealkylation with halogens and substantiated the choice of bromine for $Pb(CH_3)_4$ dealkylation.

Here I report an experimental study of the products of $Pb(CH_3)_4$ dealkylation with bromine and of their chemical transformations on heating.

EXPERIMENTAL

The following chemicals were used: $Pb(CH_3)_4$ (99.5%), bromine (analytically pure grade), carbon tetrachloride (ultrapure grade), potassium tetrahydroborate (98%), ammonium hydroxide (analytically pure grade), hydrogen (99.995%), and $Pb(CH_3)_3Br$ (Aldrich).

The reaction of $Pb(CH_3)_4$ with Br_2 was performed in a CCl_4 solution in the temperature interval from –20 to 20°C. The dealkylation was performed in a KRIO-VT-06 cryostat. Tosol (aqueous ethylene glycol) was used as thermostating liquid. The temperature was maintained with an accuracy of ±0.1°C. The unchanged starting reactants were removed in a vacuum at room temperature, and the solids formed were analyzed.

The content of $Pb(CH_3)_4$ dealkylation products was determined spectrophotometrically following the procedures described in [10]. The electronic absorption spectra

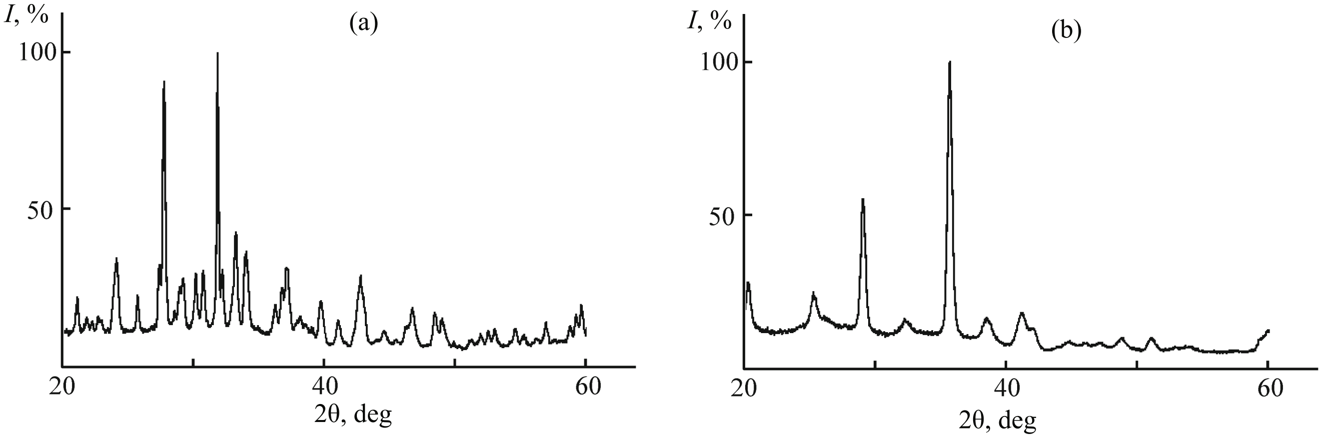

Fig. 1. Diffraction patterns of products of $Pb(CH_3)_4$ dealkylation with bromine at 20°C. (*I*) Intensity and (2θ) Bragg angle. $Br_2 : Pb(CH_3)_4$: (a) 0.5 and (b) 2.5.

were recorded with an Evolution 600 spectrophotometer using a 1-cm quartz cell.

The diffraction patterns were recorded with a D8 Discover diffractometer (CuK_α radiation, $\lambda = 1.54056$ Å).

The IR spectra of samples prepared as KBr pellets were recorded with a Nicolet 6700 Fourier IR spectrometer in the range 400–4000 cm^{-1} at room temperature.

Thermal gravimetric studies were performed with an SDT Q600 analyzer in the temperature interval 20–400°C in a nitrogen stream at a heating rate of 10 deg min^{-1}. The released gases were analyzed with a ProLab mass spectrometer in the *m*/*e* interval from 2 to 200 with unity resolution.

The mass spectra of thermolysis products were also studied with a TRACE DSQ gas chromatograph–mass spectrometer equipped with a direct sample inlet system. Ions were recorded in the *m*/*e* interval 40–400 with unity resolution at a heating rate of 50 deg s^{-1}.

RESULTS AND DISCUSSION

To find the optimum conditions for dealkylation of $Pb(CH_3)_4$ with bromine and reduce to a minimum the loss of isotope-enriched lead, we studied the products of the reaction of $Pb(CH_3)_4$ with Br_2 at –20, –10, –5, 0, 5, 10, and 20°C. At each temperature, a solution of Br_2 in CCl_4 was added to a solution of $Pb(CH_3)_4$ in CCl_4, with the reactant molar ratio varied from 0.1 to 2.5. Colorless crystalline precipitates were obtained.

The IR spectra of the dealkylation products obtained at the examined molar ratios and temperatures are identical. They were compared to the spectra of methyllead bromides described previously [11].

The IR spectra showed that the substances formed at the $Br_2 : Pb(CH_3)_4$ molar ratios from 0.1 to 1 corresponded to trimethyllead bromide $Pb(CH_3)_3Br$. In the IR spectra of the substances obtained at the molar ratios from 1 to 2, the bands of $Pb(CH_3)_3Br$ disappeared, and the bands of dimethyllead bromide $Pb(CH_3)$ appeared. The IR spectra of the precipitates obtained on adding excess bromine contained only the absorption bands characteristic of $Pb(CH_3)_2Br_2$.

The frequencies of the vibration band maxima and the band assignment in the IR spectra of the dealkylation products formed in the reaction of $Pb(CH_3)_4$ with Br_2 at 10°C and different molar ratios of the reactants are given as example in the table.

It should be noted that, according to the IR spectra, $Pb(CH_3)_2Br_2$ decomposes at room temperature within 1 day to form $Pb(CH_3)_3Br$, but below 0°C $Pb(CH_3)_2Br_2$ is fairly stable. The $Pb(CH_3)_2Br_2$ decomposition rate increases with temperature. $Pb(CH_3)_3Br$ is stable and suitable for prolonged storage. Apparently, the $Pb(CH_3)_2Br_2$ decomposition is associated with lower strength of the Pb–CH_3 bond in the compound containing two bromine atoms, compared to the compound containing only one bromine atom.

The purity of the compounds obtained at the $Br_2 : Pb(CH_3)_4$ molar ratios of 0.5 and 2.5 was proved by X-ray diffraction analysis. As seen from the diffraction patterns (Figs. 1a, 1b), each compound has a set of specific interplanar spacings differing from each other. Comparison of the diffraction pattern of the compound formed at the molar ratio of 0.5 with that of the reference compound, $Pb(CH_3)_3Br$ (Aldrich), showed that they were identical.

Figure 2 shows how the yields of $Pb(CH_3)_3Br$ and $Pb(CH_3)_2Br_2$ at 20 and –20°C (determined spectropho-

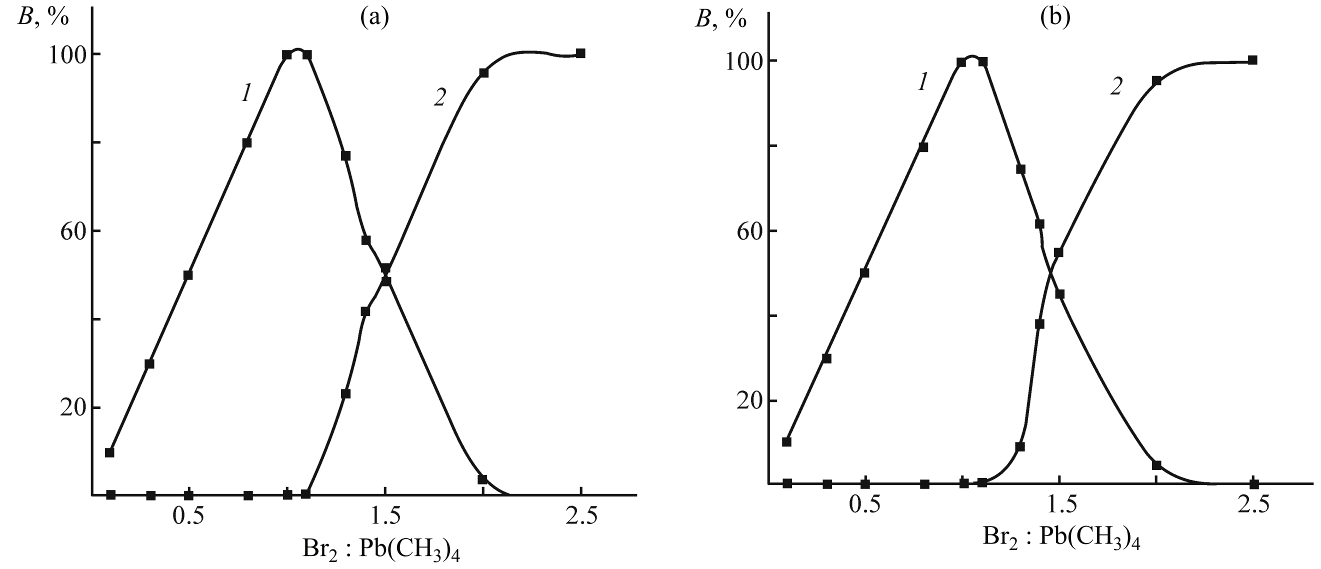

Fig. 2. Yield B of (*1*) $Pb(CH_3)_3Br$ and (*2*) $Pb(CH_3)_2Br_2$ in reaction of $Pb(CH_3)_4$ with Br_2 at (a) 20 and (b) –20°C as a function of the reactant molar ratio.

tometrically) depend on the $Br_2 : Pb(CH_3)_4$ molar ratio. $Pb(CH_3)_3Br$ is formed when Br_2 is in deficiency, with the highest yield attained at the $Br_2 : Pb(CH_3)_4$ molar ratio of 1. In the range of molar ratios from 1 to 2.1, the yield of $Pb(CH_3)_3Br$ decreases and that of $Pb(CH_3)_2Br_2$ increases, i.e., a mixture of the reaction products is formed. At molar ratios higher than 2.1, $Pb(CH_3)_2Br_2$ is the only reaction product.

IR characteristics of products formed in reaction of Br_2 solutions with $Pb(CH_3)_4$ at 10°C

Absorption maximum, cm^{-1}, for indicated compound					Band assignment
$Pb(CH_3)_3Br$ [11]	$Pb(CH_3)_2Br_2$ [11]	product formed at indicated $Br_2 : Pb(CH_3)_4$ molar ratio			
		0.5	1.5	2.5	
3023	3020	3021	3022	3020	$\nu_a(CH_3)$
2928	2920	2925	2928	2920	$\nu_s(CH_3)$
2774	–	2773	–	–	$2x\delta_a(CH_3)$
2288	2323	2286	2286	2324	$2x\delta_s(CH_3)$
1641	–	1641	1639	–	
1609	–	1610	1610	–	$2x\rho(CH_3)$
1396	1414	–	–	–	$\delta_a(CH_3)$
	1397	1391	1391	1390	
1167	1160	1167	1165	1164	$\delta_s(CH_3)$
1154	1154	1150	1154	–	
1149					
784	821	777	780,797	825	$\rho(CH_3)$
655	602	–	–	–	
–	523	–	–	–	$\nu_a(PbC_2)$
492	–	493	493	–	$\nu_a(PbC_3)$
463	–	460	–	–	$\nu_s(PbC_3)$

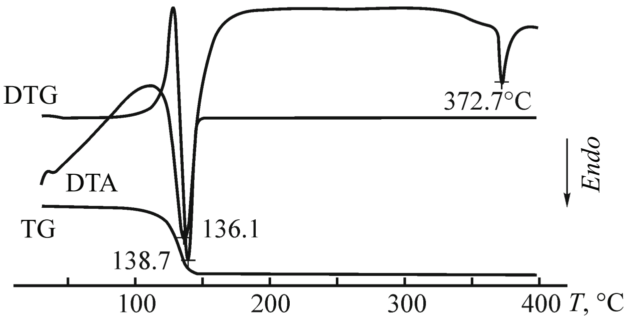

Fig. 3. Thermogram of $Pb(CH_3)_3Br$. (*T*) Temperature; the same for Fig. 4.

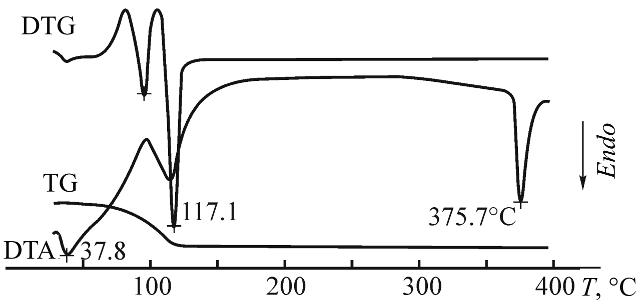

Fig. 4. Thermogram of $Pb(CH_3)_2Br_2$.

Thus, the data obtained by spectrophotometry, IR spectrometry, and X-ray diffraction suggest that the dealkylation of $Pb(CH_3)_4$ with bromine occurs with replacement of one or two methyl groups, yielding in the examined temperature interval two compounds, $Pb(CH_3)_3Br$ and $Pb(CH_3)_2Br_2$, depending on the molar ratio of the reactants.

Thermolysis of $Pb(CH_3)_4$ occurs with the formation of lead metal [7]. We found no data in the literature on transformations of $Pb(CH_3)_3Br$ and $Pb(CH_3)_2Br_2$ on heating; therefore, we studied the products of their thermolysis.

Figure 3 shows the thermogram of $Pb(CH_3)_3Br$, in which there are two endothermic effects at 138 and 372°C. The first endothermic effect is associated with the decomposition of $Pb(CH_3)_3Br$. The results of X-ray diffraction analysis show that the final thermolysis product is $PbBr_2$, with the endothermic effect in the DTA curve at 372°C corresponding to its melting.

In the mass spectrum of the gas phase, peaks of ions with the mass numbers *m*/*e* of 14, 15, 16, 28, 29, 30, 40, 44, and 94 (hereinafter, for ^1H, ^{12}C, and ^{79}Br) were detected. These peaks belong to the fragment ions CH_2^+, CH_3^+, $C_2H_5^+$, and $C_3H_4^+$ and to the molecular ions CH_4^+, $C_2H_4^+$, $C_2H_6^+$, $C_3H_8^+$, and CH_3Br^+. The CH_3^+ and CH_2^+ ions are detected from the very beginning of heating of $Pb(CH_3)_3Br$. This means that the decomposition starts with cleavage of the Pb–CH_3 bond, and other gaseous products are formed in secondary reactions.

The relative amount of the residue in thermolysis of $Pb(CH_3)_3Br$ is 31.9%. The calculated amount assuming the formation of $PbBr_2$ is 56.6%. This fact indicates that a part of lead passes into the gas phase in the course of decomposition. The lead loss may be due to volatilization of the starting compound $Pb(CH_3)_3Br$ or to formation of a gaseous lead-containing product in the course of decomposition.

The IR spectra of $Pb(CH_3)_3Br$ and of the substance deposited on the capsule walls in the course of isothermal heating of $Pb(CH_3)_3Br$ at 130°C are identical. This fact confirms partial sublimation of $Pb(CH_3)_3Br$ on heating.

According to [8], decomposition of alkyllead halides should be accompanied by the formation of tetraalkyllead compounds, $Pb(CH_3)_4$ in our case. It can be formed via the following pathways:

$$2Pb(CH_3)_3Br \rightarrow PbBr_2 + Pb(CH_3)_4 + 2CH_3^{\cdot}, \quad (1)$$

$$3Pb(CH_3)_3Br \rightarrow PbBr_2 + 2Pb(CH_3)_4 + CH_3Br. \quad (2)$$

To confirm these pathways, $Pb(CH_3)_3Br$ was studied by mass spectrometry with direct sample inlet. In the mass spectrum obtained, the strongest peaks belong to ions with the following mass numbers *m*/*e* (the relative intensity, %, is given in parentheses): 317 (100) $Pb(CH_3)_2Br^+$, 208 (82.5) Pb^+, 287 (72.6) $PbBr^+$, 223 (61.2) $PbCH_3^+$, 94 (55.1) CH_3Br^+, and 253 (54.3) $Pb(CH_3)_3^+$.

Also, the following less intense peaks were detected, *m*/*e* (relative intensity, %): 383 (13.9) $PbCH_3Br_2^+$, 302 (10.1) $PbCH_3Br^+$, 238 (8.2) $Pb(CH_3)_2^+$, 268 (7.1) $Pb(CH_3)_4^+$, 79 (6.3) Br^+, 57 (1.3) $C_4H_9^+$, and 43 (3.5) $C_3H_7^+$.

The presence of the strong Pb^+ fragment peak and of the $Pb(CH_3)_4{}^+$ molecular peak suggests the formation of $Pb(CH_3)_4$ in the course of thermolysis. Under electron impact, this molecule undergoes radical decomposition [12]:

$$Pb(CH_3)_4 \rightarrow Pb^+ + 4CH_3^{\cdot}. \quad (3)$$

Thus, the thermolysis of $Pb(CH_3)_3Br$ is accompanied by its partial sublimation and decomposition.

The thermolysis of $Pb(CH_3)_2Br_2$ follows more complex pattern and is characterized by three endothermic effects at 37, 117, and 375°C (Fig. 4). The thermolysis of $Pb(CH_3)_2Br_2$ starts at a lower temperature than that of $Pb(CH_3)_3Br$, suggesting thermodynamic instability of the former. As in thermolysis of $Pb(CH_3)_3Br$, the final decomposition product of $Pb(CH_3)_2Br_2$ is $PbBr_2$; therefore, the endothermic peak in the DTA curve at 375°C corresponds to its melting. The relative amount of the residue for $Pb(CH_3)_2Br_2$ is 60.33%, and theoretically it should be 92.4%, which also confirms partial volatilization of lead.

In the mass spectra of gaseous thermolysis products, we detected peaks of ions with *m*/*e* 14, 15, 79, and 80, belonging to fragment ions CH_2^+, CH_3^+, and Br^+ and to the molecular ion HBr^+. The generation of CH_3^+ ions is characterized by two maxima at 37 and 117°C, whereas CH_2^+ ions are recorded only at 117°C. The Br^+ and HBr^+ ions appear in the mass spectrum only at 362°C, with melting of $PbBr_2$.

The IR spectra of the substance obtained by isothermal heating of $Pb(CH_3)_2Br_2$ at 40°C and of the sublimate deposited on the capsule walls in the course of $Pb(CH_3)_2Br_2$ heating are identical to that of $Pb(CH_3)_3Br$. $Pb(CH_3)_3Br$ may be formed via the following pathway:

$$2Pb(CH_3)_2Br_2 \rightarrow Pb(CH_3)_3Br + PbBr_2 + CH_3Br. \qquad (4)$$

The absence of CH_3Br in the mass spectrum, however, indicates that the decomposition pattern of $Pb(CH_3)_2Br_2$ is more complex. $Pb(CH_3)_3Br$ can be formed in the following reactions:

$$Pb(CH_3)_2Br_2 \rightarrow PbBr_2 + 2CH_3^{\bullet}, \qquad (5)$$

$$Pb(CH_3)_2Br_2 + CH_3^{\bullet} \rightarrow Pb(CH_3)_3Br + Br^{\bullet}, \qquad (6)$$

$$Pb(CH_3)_2Br_2 + Br^{\bullet} \rightarrow PbBr_2 + HBr + CH_3^{\bullet} + CH_2^{\bullet}. \qquad (7)$$

The removal of $Br^{\bullet}$ and HBr at high temperatures indicates that these species are adsorbed by the $PbBr_2$ surface, and their excess amount is associated with the deficiency of lead, which partially sublimes in the form of $Pb(CH_3)_3Br$.

In the electron impact mass spectra of $Pb(CH_3)_2Br_2$, there are peaks observed in the course of $Pb(CH_3)_3Br$ decomposition and belonging to the following ions, *m*/*e* (relative intensity, %): 317 (100) $Pb(CH_3)_2Br^+$, 253 (70.2) $Pb(CH_3)_3^+$, 223 (43.7) $PbCH_3^+$, 287 (46.1) $PbBr^+$, 208 (40.4) Pb^+, 302 (8.4) $PbCH_3Br^+$, 238 (7.5) $Pb(CH_3)_2^+$, and 268 (1.1) $Pb(CH_3)_4^+$. A distinctive feature is the absence of ions with *m*/*e* 94 CH_3Br^+, 79 Br^+, 57 $C_4H_9^+$, and 43 $C_3H_7^+$.

CONCLUSIONS

(1) In the temperature interval from –20 to 20°C, the dealkylation of $Pb(CH_3)_4$ with bromine occurs with replacement of one or two methyl groups and formation of trimethyllead bromide $Pb(CH_3)_3Br$ and dimethyllead dibromide $Pb(CH_3)_2Br_2$.

(2) The thermolysis of $Pb(CH_3)_3Br$ and $Pb(CH_3)_2Br_2$ is accompanied by the formation of gaseous products and lead bromide $PbBr_2$. $Pb(CH_3)_2Br_2$ decomposes via formation of $Pb(CH_3)_3Br$.

(3) Thermal decomposition of methyllead bromides is not an efficient route to isotope-enriched lead metal because of probable increase in the loss of the isotope-enriched material due to high volatility of $Pb(CH_3)_3Br$ on heating.

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