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Mercury(6^3P_1)-Photosensitized Decomposition of Tetramethyllead

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(Received November 28, 1991)

Synopsis. Mercury(6^3P_1)-photosensitized decomposition of tetramethyllead was investigated at 393 K and at pressures from 260 to 6700 Pa. Ethane and methane were detected as gaseous products. From the pressure dependences of the yields of ethane and methane, and from the effects of O_2 and H_2 on the yield of ethane, it was deduced that the main initial reactions involve Pb–C bond cleavage.

It has been reported that the main product in mercury-photosensitized reactions of neopentane (NP),[1,2] tetramethylsilane (TMS),[3,4] and tetramethylgerman (TMG)[5] was hydrogen and the primary process in these reactions is C–H bond cleavage. Recently we found, however, that the main products were ethane and methane and hydrogen was a minor product in the mercury-photosensitized reaction of tetramethyltin (TMT); this shows that the major primary processes of this reaction involve Sn–C bond cleavage.[6]

In this study we investigated the mercury-photosensitized decomposition of tetramethyllead (TML) in order to obtain further information on the mercury-photosensitized reactions of tetramethyl compounds of group-14 elements.

Experimental

Apparatus and techiniques for the mercury-photosensitized reaction were similar to those used previously.[6] The mercury-photosensitized reaction of TML was carried out at 393 K. Mercury vapor of constant volume and pressure was admitted into the reaction vessel with various amounts of TML ($[Hg]=9.3\times10^{-7}$ mol dm^{-3}). The light intensity absorbed by mercury atoms at 253.7 nm was determined by means of *cis*-2-butene actinometry[7] ($I_{abs}=4.5\times10^{-9}$ mol s^{-1}).

Product analysis was carried out by measurements with a gas buret and gas chromatography after fractionation at 77 and 184 K. The first portion, noncondensable at 77 K, was collected with a Toepler pump, and analyzed by combustion over copper(II) oxide at 553 K. The second portion, which was not condensable at 184 K, was anlayzed by gas chromatography using a 6-m colum of VZ-7 (Gasukuro Kogyo Co., Ltd.) at 273 K.

TML (TRI Chemical Laboratory Inc.; nominal purity 99.9999%) was used without further purification.

Results and Discussion

Thermal decomposition and direct photolysis of TML were negligible under the present conditions. The gaseous products detected in the mercury-photosensitized reaction were ethane and methane. Hydrogen, being a major product from NP, TMS, and TMG and a minor product from TMT, was not detected. The yields of ethane and methane increased linearly with time.

The quantum yields of these products are shown in Fig. 1 as a function of the TML pressure. The effects of added O_2 and H_2 on the yield of ethane are shown in Figs. 2 and 3, respectively. The yield of ethane decreases with an increase in the O_2/TML and H_2/TML ratios.

The quenching cross section of TML was obtained from the competitive rates of the mercury-photosensitized reactions of TML and N_2O in a manner similar to that used previously.[6] A value of $\sigma_Q(\mathrm{TML})=151\times10^{-16}$ cm^2 was obtained ($\sigma_Q=k_Q(8RT/\pi\mu)^{-1/2}$; k_Q is the quenching rate constant and μ is the reduced mass). This value is larger than that for TMT (63.7×10^{-16} cm^2) and much larger than those for NP (4.4×10^{-16} cm^2) and TMS (15.7×10^{-16} cm^2).

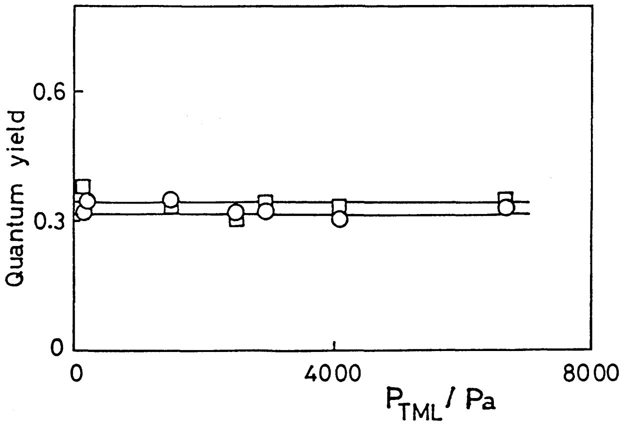

Fig. 1. Pressure dependences of the quantum yields of ethane (○) and methane (□) in the mercury-photosensitized reaction of TML at 393 K.

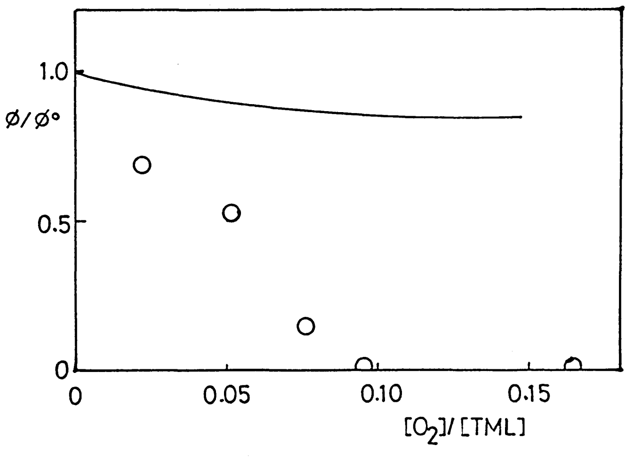

Fig. 2. Quantum yield of ethane formation in the mercury-photosensitized reaction of TML at 393 K in the presence of O_2. For solid curve, see text.

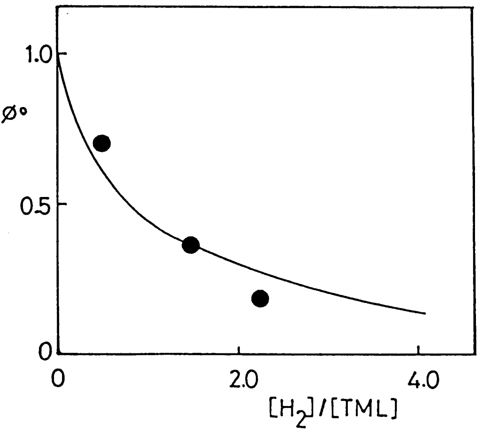

Fig. 3. Quantum yield of ethane formation in the mercury-photosensitized reaction of TML at 393 K in the presence of H_2. For solid curve, see text.

The solid curves in Figs. 2 and 3 are the relative yields calculated from the following relative quenching efficiencies ($k_Q(O_2)/k_Q(\mathrm{TML})=0.84$ and $k_Q(H_2)/k_Q(\mathrm{TML})=1.36$ obtained from $\sigma_Q(O_2)=62.5\times10^{-16}$ cm^2,[8] $\sigma_Q(H_2)=27\times10^{-16}$ cm^2,[8] and $\sigma_Q(\mathrm{TML})=151\times10^{-16}$ cm^2).

The decrease in the yield of ethane in the presence of O_2 is much steeper than that expected for the competitive quenching of the triplet mercury atoms by O_2 and TML. This shows that O_2 has an additional effect (probably radical scavenging) on the formation of ethane. In contrast, the decrease in the yield of ethane in the presence of H_2 can be roughly explained in terms of a competitive quenching by H_2 and TML. These effects of O_2 and H_2 on the yield of ethane are very similar to those observed in the mercury-photosensitized decomposition of TMT. The pressure dependences of the yields of ethane and methane are also similar to those observed in the mercury-photosensitized decomposition of TMT at 393 K.

From the observations that ethane and methane were the major products with no hydrogen formation, and that a 10% level of O_2 completely suppressed the ethane formation (Fig. 2), the following reactions are proposed for the formation of ethane:

$$\mathrm{Hg(^3P_1)+TML\longrightarrow Hg+CH_3+Pb(CH_3)_3,} \tag{1}$$
$$\mathrm{CH_3+CH_3\longrightarrow C_2H_6.} \tag{2}$$

As mentioned previously for the Hg–TMT system,[6] the effect of H_2 on the yield of ethane shown in Fig. 3 eliminates the possibility of atom cracking shown by Reactions (3) and (4) for the formation of methyl radical:

$$\mathrm{H+CH_2Pb(CH_3)_3\longrightarrow TML^*,} \tag{3}$$
$$\mathrm{TML^*\longrightarrow CH_3+Pb(CH_3)_3.} \tag{4}$$

If the atom cracking contributes to the formation of methyl radical, one would expect that the yield of ethane increases with increasing the ratio of H_2/TML, because of the large efficiency of the formation of H atom for the H_2-triplet mercury atom system. As shown in Fig. 3, however, the yield decreases with increasing the ratio of H_2/TML, and this decrease can be explained only in terms of the competitive quenching by H_2 and TML.

As for the formation of ethane, the following reactions were proposed for the mercury-photosensitized reaction of TMT:

$$\mathrm{CH_3+TMT\longrightarrow CH_4+CH_2Pb(CH_3)_3,} \tag{5}$$
$$\mathrm{Hg(^3P_1)+TMT\longrightarrow CH_4+CH_2{=}Sn(CH_3)_2.} \tag{6}$$

The formation of methane shown by Reaction (6) was suported by the effect of O_2 on the yield of methane (the formation of methane was not completely suppressed).

Although the effect of O_2 on the yield of methane was not examined and the evidence for the molecular process was not obtained in the present system, the similarity of the pressure dependences of the yields of ethane and methane for TML to those observed for TMT at 393 K suggests that the reaction mechanism for TML is similar to that for TMT.

From these considerations, the mechanism for the photosensitized decomposition of TML could be expressed by the following scheme:

$$\mathrm{Hg(^3P_1)+TML\longrightarrow Hg+CH_3+Pb(CH_3)_3,} \tag{1}$$
$$\mathrm{Hg(^3P_1)+TML\longrightarrow Hg+CH_4+CH_2{=}Pb(CH_3)_2,} \tag{7}$$
$$\mathrm{CH_3+CH_3\longrightarrow C_2H_6,} \tag{2}$$
$$\mathrm{CH_3+TML\longrightarrow CH_4+CH_2Pb(CH_3)_3.} \tag{8}$$

The primary process in the mercury-photosensitized decompositions of NP, TMS, and TMG is C–H bond cleavage, as is the case for mercury-photosensitized decompositions of many alkanes. Contrary to the mercury-photosensitized reactions of NP, TMS, and TMG, the main initial reactions for TMT and TML involve M–C bond cleavage (the formation of methyl radical and the molecular formation of methane) and C–H bond rupture is very minor. In this respect these reactions are similar to the direct photolysis of TMT[9] and TML[10,11] and also to the mercury-photosensitized reactions of acetaldehyde[12] and acetone,[12] which reportedly proceed through the formation of excited triplet molecules[8] (these carbonyl compounds have low-lying triplet states). The triplet energy of TMT and TML are not yet known, but they are probably lower than those of NP, TMS, and TMG, because the absorption bands of TMT and TML appear at longer wavelengths as compared to NP, TMS, and TMG.[13] Probably the triplet energy transfer occurs from $\mathrm{Hg(^3P_1)}$ to TMT or TML to promote the latter into the triplet state. The large cross sections for the quenching of triplet mercury atom by TMT and TML are in line with this view: The quenching cross section of TML is comparable to those for acetaldehyde (129×10^{-16} cm^2) and acetone (166×10^{-16} cm^2).[8] Such an effective energy transfer for TMT and TML explains the essential difference in the reaction feature between the group of TMT and TML and that of NP, TMS, and TMG.

The authors thank Dr. N. Shimo of Idemitsu Kosan Co., Ltd. for generous donation of TML.

References

1) R. J. Norstron, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, **43**, 2140 (1964).

2) E. Furimsky and K. J. Laidler, *Can. J. Chem.*, **50**, 1115, 1120, 1129 (1972).

3) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965).

4) P. Potzinger, B. Reimann, and R. S. Roy, *Ber. Bunsen-Ges. Phys. Chem.*, **85**, 1119 (1981).

5) J. Duval and Y. Rousseau, *Can. J. Chem.*, **51** , 3062 (1973).

6) S. Yamamoto, S. Inoue, Y. Sueishi, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **64**, 2872 (1991).

7) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

8) R. J. Cvetanovic, *Prog. React. Kinet.*, **2**, 39 (1964).

9) P. Borrell and A. E. Platt, *Trans. Faraday Soc.*, **66**, 2286 (1970).

10) P. A. Leighton and R. A. Mortensen, *J. Am. Chem. Soc.*, **58**, 448 (1936).

11) J. G. Clouston and C. L. Cook, *Trans. Faraday Soc.*, **54**, 1001 (1957).

12) F. P. Lossing, *Can. J. Chem.*, **35**, 305 (1957).

13) H. W. Thompson and J. W. Linett, *Proc. R. Soc. London, Ser. A*, **156**, 108 (1936).