APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 337-347 (1991)

Physicochemical Properties of Dimethylzinc, Dimethylcadmium and Diethylzinc

Yasuo Kuniya, Yuichi Deguchi* and Masanori Ichida†
Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Kasuga 1-13-27, Bunkyo-ku, Tokyo 112, Japan

Physicochemical properties of dimethylzinc, dimethylcadmium and diethylzinc have been investigated by means of vapor pressure measurement, mass spectroscopy and gas chromatography. The saturated vapor pressure–temperature dependence of these alkyl organometallics was determined to be as follows

For dimethyl zinc:

$$\log P_{(\mathrm{sub.})\mathrm{Torr}} = -\frac{1.752\times 10^3}{T} + 8.603$$

$$\log P_{(\mathrm{evap.})\mathrm{Torr}} = -\frac{1.461\times 10^3}{T} + 7.429$$

For dimethylcadmium:

$$\log P_{(\mathrm{sub.})\mathrm{Torr}} = -\frac{2.080\times 10^3}{T} + 8.588$$

$$\log P_{(\mathrm{evap.})\mathrm{Torr}} = -\frac{1.843\times 10^3}{T} + 7.715$$

For diethylzinc:

$$\log P_{(\mathrm{evap.})\mathrm{Torr}} = -\frac{2.012\times 10^3}{T} + 7.996$$

The temperature ranges for vapor phase decomposition for deposition of each metal were clarified, and vapor-phase species released in the decompositions were investigated. These investigations on the organometallics are to provide basic material data for the establishment of organometallic chemical vapor deposition techniques for Group IIB–VI compounds.

Keywords: Organometallic, vapor pressure, decomposition, metal vapor deposition

1 INTRODUCTION

The metal organic chemical vapor deposition (MOCVD) technique has been extensively applied to prepare single-crystal thin films of semiconductors, not only of Group III–V compounds but also of Group IIB–VI and other compounds. This technique is superior to the halide CVD technique from the viewpoint of lowering of growth temperature, higher utilization efficiency of source materials, etc., and is believed to be particularly suited for growth of thin films of multicomponent compounds.

Many studies on the growth of single-crystal thin films of Groups IIB–VI compound semiconductors such as ZnSe and CdS have been made, motivated by their practical use in the field of optoelectronics, in which methyl and ethyl compounds of Group IIB elements have been used as precursors.[1-21] However, few investigations have been made on the physicochemical properties of these alkyl metalorganic compounds, especially on their saturated vapor pressure, decomposition temperature, decomposition products and so on. The final aim of the present study is to contribute to studies on metalorganic vapor-phase deposition of Group IIB–VI compound semiconductors.

2 EXPERIMENTAL

In order to investigate the physicochemical behavior of these alkyl metalorganics, vapor pressure measurements, mass spectroscopy and gas chromatography investigations were carried out.

In the vapor-pressure measurements, a quartz Bourdon gauge with a spoon-type sensor was used to measure the temperature dependence of the saturated vapor pressure and pressure changes resulting from the decomposition of these compounds in the vapor phase. The construction and the operation of the gauge were

---

* Present address: Fujitsu Ltd, Kamikodanaka 1015, Nakahara-ku, Kawasaki 211, Japan.

† Tosoh Corporation, Tokyo Research Center, Hayakawa 2743-1, Ayase, Kanagawa 252, Japan.

0268-2605/91/040337-11$05.50

Received 17 April 1991
Revised 26 April 1991

described in detail in our previous papers[22,23] and other references.[24-27] The inner volume of the sample chamber including the spoon is about 7–8 cm^3, and 10^{-5}–10^{-6} mol cm^{-3} of each compound was loaded in the chamber. Each vapor-pressure measurement was carried out for about 70 h in the temperature range from −60 °C to 900 °C. Furthermore, similar measurements were performed on a system in which hydrogen gas was enclosed with the compound in the chamber in order to investigate the effect of hydrogen used as a carrier gas.

For mass spectroscopy, a quadrupole mass spectrometer was used to investigate the vapor-phase species resulting from the decomposition of the commpounds. The specimen was enclosed in a Pyrex glass or quartz tube of 3 mm i.d. and 6 cm long with a breakable tip under a vacuum of 3×10^{-6} Torr, and then the tube was placed in the center of a small tantalum wire-wound furnace. The furnace was placed in a vacuum chamber so that the breakable tip faced the inlet of the ionization chamber of the mass spectrometer. After the chamber was evacuated to 10^{-7} Torr and the tube was maintained at a desired temperature for about 30 min, the tip was broken with a cutter and then the gas in the tube was ejected to a slit of the inlet of the ionization chamber. The equipment used was an Anelva model GA-360 quadrupole mass spectrometer which is capable of sweeping the mass numbers from 1 to 360 in 1 s. The output signal of the spectrometer was recorded on photosensitive recording paper at a speed of 1 m s^{-1}, and the signals were recorded for 3 s. In normal mass spectroscopy, a high ionization voltage of about 70 eV is applied to an introduced gas, but considerable fragmentation of gas molecules and rearrangement of ions sometimes make identification of original molecules difficult. Therefore, low ionization voltages from 10 to 20 eV were used in this work.

In order to complement the results of mass spectroscopy, gas chromatography was conducted on a specimen which was kept at the same temperatures as those in the mass spectroscopy. The specimen was enclosed in a quartz ampoule of 8 mm i.d. and 5 cm long under a vacuum of 3×10^{-6} Torr, and was quenched in ice–water after being kept at a desired temperature in a furnace. The ampoule was broken in a glass tube which was purged with helium gas, and a fixed volume of the gas mixture was injected into the inlet of the gas chromatograph equipment (Yanagimoto Model G-180) after being sampled with the use of a microliter syringe. The system is equipped with an FID detector, and activated alumina, silica gel and Apiezon were used in its absorption columns.

Alkyl metalorganic compounds used in this work were prepared by Tosoh-Akzo Industries Ltd and used after being divided into small ampoules by two or three distillations. These ampoules were kept in a dark, cool place because these compounds tend to decompose under natural light.

3 RESULTS AND DISCUSSIONS

3.1 Dimethylzinc [$Zn(CH_3)_2$]

A typical pressure–temperature curve for dimethylzinc is shown as curve A in Fig. 1. It is observed that the saturated vapor pressure P of this compound rises at about −60 °C, and it completely vaporizes near 0 °C after which the pressure agrees with that of the ideal gas laws.

The plots of log P versus $1/T\,K^{-1}$ for the saturated vapor pressure forms two linear relationships which differ slightly in their gradients. Thus, the temperature dependences of the saturated vapor pressure for sublimation and evaporation of dimethylzinc were determined to be as follows (Eqns [1] and [2]):

For sublimation:

$$\log P_{(\mathrm{sub.})\mathrm{Torr}} = -\frac{1.752 \times 10^3}{T} + 8.603 \qquad [1]$$

For evaporation:

$$\log P_{(\mathrm{evap.})\mathrm{Torr}} = -\frac{1.461 \times 10^3}{T} + 7.429 \qquad [2]$$

The saturated vapor pressure at room temperature (25 °C) is about 336 Torr according to Eqn [2] and this suggests that the compound can be suitably used as a precursor for MOCVD growth. The following equation for the saturated vapor pressure is given in Ref. 28, without distinction between sublimation and evaporation:

$$\log P_{\mathrm{Torr}} = -\frac{1.560 \times 10^3}{T} + 7.802 \qquad [3]$$

As shown in Fig. 1, the pressure–temperature curve shows a larger increase in pressure than that

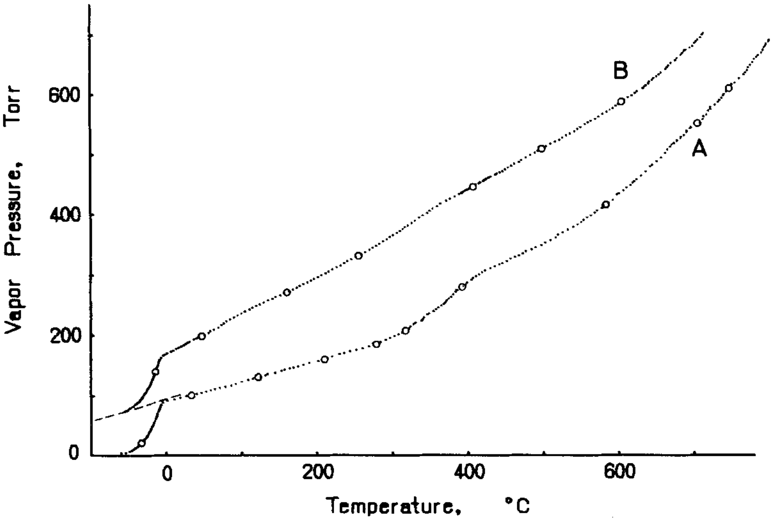

Figure 1 Pressure–temperature curves of dimethylzinc with and without hydrogen. A, without hydrogen; B, with hydrogen.

of the ideal gas law in the temperature range from 270 to 370 °C, suggesting an increase in moles of vapor species due to decomposition of the compound. Mass spectra of the vapor phases at various temperatures are shown in Figs 2(a), (b), (c) and (d).

In the spectrum at room temperature, two peak groups for monomethylzinc $[Zn(CH_3)]^+$: *m/z* 79, 81 and 83] and a parent molecule $[Zn(CH_3)_2^+$: *m/z* 94, 96 and 98] are observed, which correspond to the three isotopes of zinc, respectively. Peaks at *m/z* 15, 16, 27 and 29 are of CH_3^+, CH_4^+, $C_2H_3^+$ and $C_2H_5^+$, respectively, as a result of fragmentation of the molecule. In the spectrum at 370 °C where the increase in pressure was completed, the peak groups of $Zn(CH_3)^+$ and $Zn(CH_3)_2^+$ disappeared and only peaks for hydrocarbons were observed. On the inner surface of the tube used at 370 °C, a film-like deposit with a metallic luster was observed. Therefore, it is concluded that the increase in pressure in the temperature range from 270 to 370 °C in curve A in Fig. 1 is caused by the decomposition of dimethylzinc to deposit metallic zinc and to release hydrocarbons. In the spectrum at 370 °C, observable peaks are of CH_4^+, $C_2H_4^+$, $C_2H_6^+$, $C_3H_6^+$, $C_3H_8^+$, $C_4H_8^+$ and of ionized radicals of these hydrocarbons. Figs 3(a), (b), (c) and (d) show the results of gas chromatography on the compound with and without hydrogen at 420 and 650 °C, respectively.

At 420 °C, in addition to methane as a major species, ethane, ethylene, propane, propylene and a small amount of butane were detected, and the result shows good agreement with that of mass spectroscopy at and near the same temperature. In curve A in Fig. 1, a pressure increase with a higher increasing rate than that of the ideal gas law is observed in a wide temperature range above 450 °C. The mass spectrum at 650 °C [Fig. 2c)] shows only peaks of CH_3^+, CH_4^+ and a trace of $C_2H_5^+$ which is considered to come from residual C_2H_6. Also, in the result of gas chromatography at the same temperature [Fig. 3(b)], about 96 % of methane and only residual ethane were detected. Therefore, it is considered that decomposition of the hydrocarbons to form methane was one of the causes of increase in pressure above 450 °C. On the other hand, it should be noted that the increase in pressure above 450 °C is much higher than that estimated from the amounts of C_2, C_3 and C_4 hydrocarbons from the results of gas chromatography at 420 °C. As shown in Fig. 3(a), the vapor system contains each of these hydrocarbons by several per cent, respectively. Even if these hydrocarbons decomposed to form methane at high temperature, it seems to be impossible to explain the total pressure at about 800 °C. Decomposition of methane to carbon and hydrogen begins in the neighbourhood of 800 °C, so it cannot contribute to the total pressure at this temperature.

In order to clarify another possible cause of the above pressure increase, mass spectroscopy was carried out at 550 °C on the deposit in a tube used in mass spectroscopy at 370 °C. The tube was crushed and loaded into another glass tube, then it was sealed after evacuating under vacuum of 3×10^{-6} Torr. The result is shown in Fig. 4(a), which indicates release of various hydrocarbons from the deposit.

The figure shows that all of the alkyl radicals of dimethylzinc molecules were not released as hydrocarbon gas in the decomposition in which metallic zinc was deposited, but a fraction of them were deposited in a condensed phase in the form of highly polymerized hydrocarbon with fewer hydrogens. Therefore, it is considered that the continuous increase in pressure above 450 °C in Fig. 1 is caused not only by vapor-phase

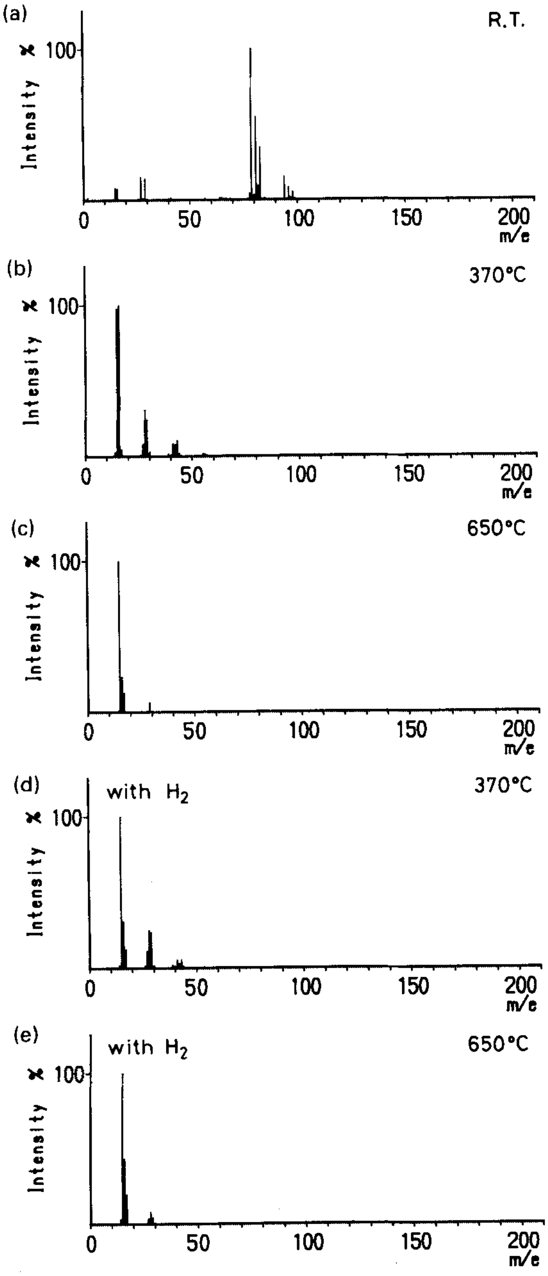

Figure 2 Mass spectra of dimethylzinc at various temperatures: (a) room temperature; (b) 370 °C; (c) 650 °C; (d) 370 °C with hydrogen; (e) 650 °C with hydrogen.

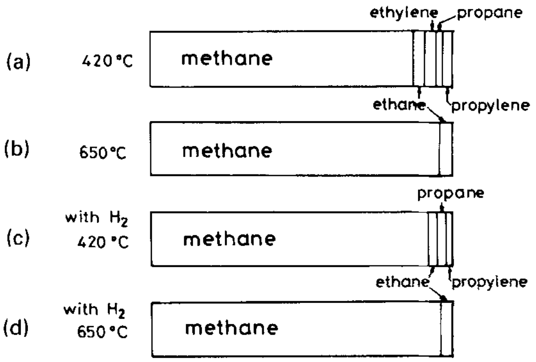

Figure 3 Gas compositions after decomposition of dimethylzinc: (a) 420 °C; (b) 650 °C; (c) 420 °C with hydrogen; (d) 650 °C with hydrogen.

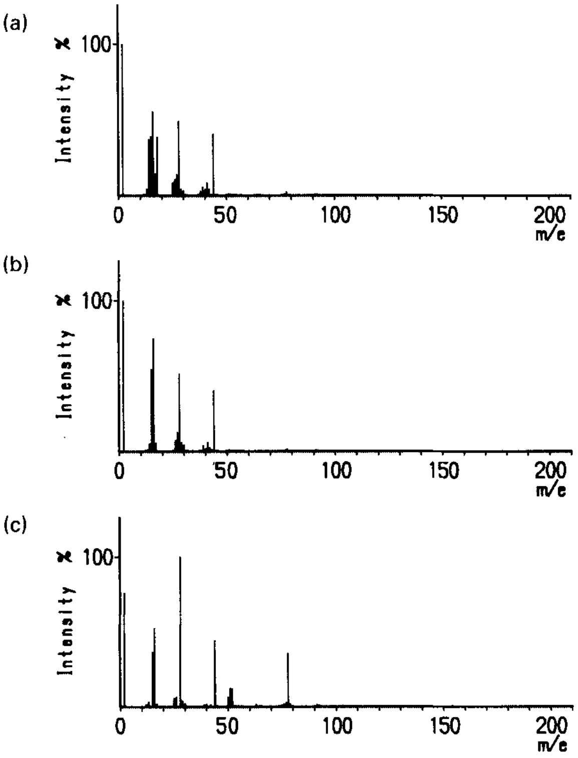

Figure 4 Mass spectra of the gases released at 550 °C from deposits after the decomposition of the following compounds: (a) dimethylzinc, decomposed at 370 °C; (b) dimethylcadmium, decomposed at 320 °C; (c) diethylzinc, decomposed at 320 °C.

decomposition of hydrocarbons which have already been released at 370 °C, but also by release of hydrocarbons from the above polymer in the condensed phase. A similar behavior of pressure was also clearly observed in the decomposition of trimethyl compounds such as trimethylaluminum and trimethylgallium,[29] and the polymer will therefore cause carbon contamination of growing crystals in MOCVD.

When dimethylzinc is used as a precursor in MOCVD, its vapor is usually supplied to the deposition zone by hydrogen as a carrier gas, and the influence of hydrogen on the decomposition of the compound should be considered. Therefore, similar measurements were performed on the system of dimethylzinc–hydrogen. A typical example of the pressure–temperature curve of the above system is shown as curve B in Fig. 1. Almost the same amount of the compound as that for curve A was loaded in the sample chamber of a gauge, but it was found that the increase in pressure in the decomposition temperature range from 270 to 370 °C is much lower than that in curve A. Figures 2(d) and 3(c) show the results of mass spectroscopy and of gas chromatography, respectively, at a temperature just above decomposition. In mass spectroscopy, the spectrum differs from that without hydrogen shown in Fig. 2(b), in that peaks of C_2 and C_3 hydrocarbons have become relatively lower compared with those of CH_3^+ and CH_4^+ and that peaks of C_4 hydrocarbons have disappeared. Also gas chromatography at the same temperature showed a relative increase of CH_4 and a decrease of C_2H_4 and C_3H_8. These results suggest the hydrogenation of hydrocarbons with a C═C bond and probably formation of CH_4 by hydrocracking of hydrocarbons with C–CH_3 bonds. These addition reactions of hydrogen result in consumption of the added hydrogen, and thus the increase in moles of vapor species would be kept relatively lower. The increase in pressure above 450 °C is also lower than that without hydrogen as shown in Fig. 1. this should come also from consumption of added hydrogen through the hydrogenation and hydrocracking to form CH_4 from C_2 and C_3 hydrocarbons in the system. Another cause for the lower increase in pressure is the loss of hydrogen from the sample chamber by diffusion through the thin walls of the quartz spoon. According to our pressure measurement on hydrogen gas, the pressure decrease due to diffusion of hydrogen becomes appreciable at approximately 550 °C and more considerable with increasing temperature.

The results of mass spectroscopy and gas chromatography at 650 °C are shown in Figs 2(e) and 3(d), respectively. Both results show that the vapor phase in the system is almost completely occupied by methane, and it is found that these results are very similar to those without hydrogen [Figs 2(c) and 3(b)]. Considering leakage of residual hydrogen from the spoon of the gauge, it is reasonable that the increasing rate in pressure above 500 °C in curve B in Fig. 1 is not so high as that in curve A.

3. Dimethylcadmium [$Cd(CH_3)_2$]

A typical example of a pressure–temperature curve of dimethylcadmium is shown as curve A in Fig. 5. The saturated vapor pressure (P) rises in the neighborhood of −30 °C and it agrees with the pressure of the ideal gas law after the condensed phase disappears.

The log P versus $1/T\,K^{-1}$ plots for the range of saturated vapor pressure gave two linear relationships which intersect each other at 271.5 K. The temperature dependences of sublimation and evaporation were found to be as shown in [Eqns [4] and [5].

For sublimation:

$$\log P_{(\text{sub.})\text{Torr}} = -\frac{2.080\times 10^3}{T} + 8.588 \qquad [4]$$

For evaporation:

$$\log P_{(\text{evap.})\text{Torr}} = -\frac{1843\times 10^3}{T} + 7.715 \qquad [5]$$

The following equations are given in references, only for evaporation.

$$\log P_{\text{Torr}} = -\frac{1.850\times 10^3}{T} + 7.764 \text{ (Ref. 28)} \qquad [6]$$

$$\log P_{\text{Torr}} = -\frac{1126.36}{T + 201.07} + 6.490 \text{ (Ref. 30)} \qquad [7]$$

The increase in pressure in the temperature range from 180 °C to 290 °C is considered to be caused by decomposition of the compound in which metallic cadmium is deposited. The mass spectrum at 320 °C where the decomposition is complete is shown in Fig. 6(b), with the spectrum at room temperature in Fig. 6(a).

In the spectrum at room temperature, peaks for CH_4^+, fragments such as CH_3^+ and hydrocarbons

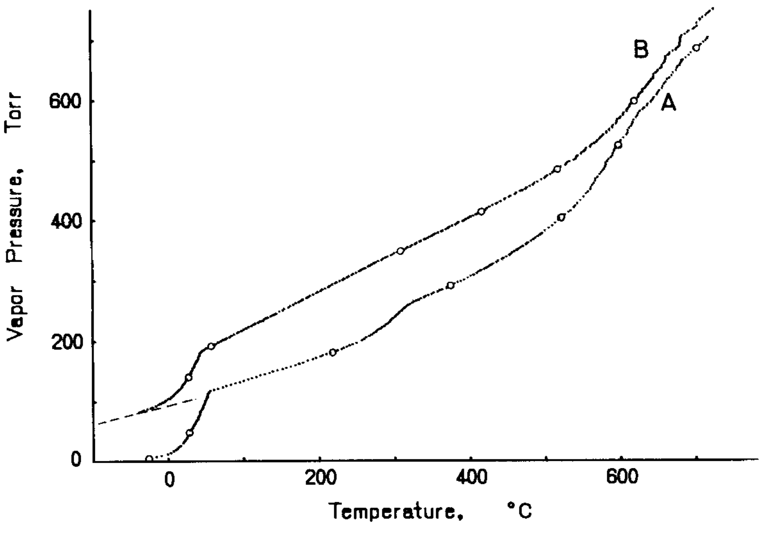

Figure 5 Pressure–temperature curves of dimethylcadmium with and without hydrogen. A, without hydrogen; B, with hydrogen.

by rearrangement of ionized radicals were observed in addition to two peak groups of $Cd(CH_3)^+$ (m/z 125, 126, 127, 128, 129, 130 and 131) and of $Cd(CH_3)_2^+$ (m/z 140, 141, 142, 143 and 144). In the spectrum at 320 °C, these two peak groups of $Cd(CH_3)^+$ and $Cd(CH_3)_2^+$ had disappeared and those of C_1, C_2, C_3 and C_4 hydrocarbons were observed. The results of gas chromatography on dimethylcadmium with and without hydrogen are shown in Fig. 7(a), (b), (c) and (d).

As shown in Fig. 7(a), 83% of methane, 10% of ethane, 5% of propane and 2% of n-butane were detected at 320 °C. The pressure increase from 320 to 700 °C in curve A in Fig. 5 can not be explained by only the increase of vapor species through the decomposition of the above C_2, C_3 and C_4 hydrocarbons. Another vapor-phase species which makes an important contribution to the increase in pressure in the above temperature range is considered to be gaseous cadmium vaporized from the deposited metallic cadmium. Only a trace of Cd^+ was seen in mass spectroscopy at 650 °C, because most cadmium released in the decomposition was deposited in the tip of the tube, which is at a low temperature, and the vapor pressure of cadmium in the tube is very low. The saturated vapor pressure of metallic cadmium is given by Eqn [8].[31]

$$\log P_{\mathrm{Torr}} = -\frac{5.763 \times 10^3}{T} + 12.282 - 1.28 \log T \qquad [8]$$

According to the above equation, the saturated vapor pressures of metallic cadmium are 1.25 Torr at 400 °C and 82.6 Torr at 600 °C. Therefore, it is estimated that, in the pressure increase between 320 and 700 °C in curve A in Fig. 5, the saturated vapor pressure should augment on the pressure increase by decomposition of C_2, C_3 and C_4 hydrocarbons and by release of hydrocarbons from the condensed polymer mentioned below.

Hydrocarbons, released from the condensed phase deposited in the decomposition of the compound, are also one of the causes of pressure increase in the above temperature range, in the same manner as that of dimethylzinc. Figure 4(b) shows a mass spectrum of fragments of the crushed tube at 550 °C which was used for the spectroscopy at 320 °C in Fig. 6(b). As seen in the figure, the spectrum is similar to that of dimethylzinc shown in Fig. 4(a), and it can be said that, in the decomposition of dimethylcadmium also, polymer with less hydrogen was deposited and hydrocarbons were released from the polymer in the above temperature range.

In the spectrum at 650 °C, major species in the system are CH_3^+ and CH_4^+ and a small amount of C_2 hydrocarbon species (m/z 28 and 29), and furthermore, in the spectrum at 800 °C, only CH_3^+ and CH_4^+ were observed except for a trace of ethane. Gas chromatography at 650 °C gave only 4 % of ethane in addition to 96 % of methane as the major species.

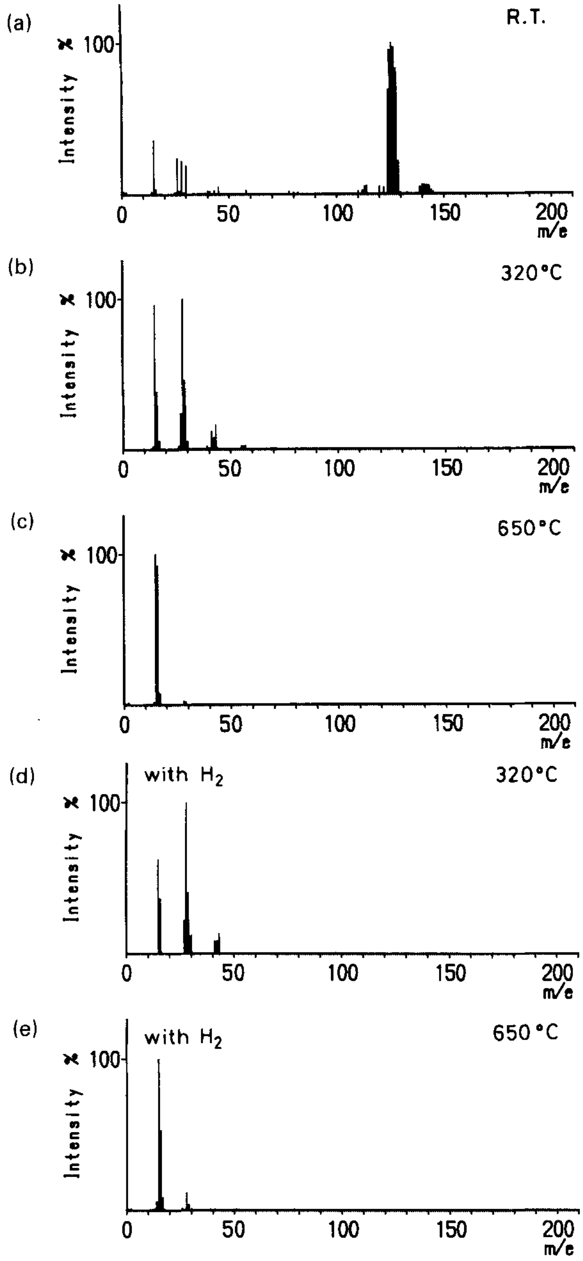

Figure 6 Mass spectra of dimethylcadmium at various temperatures: (a) room temperature; (b) 320 °C; (c) 650 °C; (d) 320 °C with hydrogen; (e) 650 °C with hydrogen.

A pressure–temperature curve of dimethylcadmium in coexistence with hydrogen gas is shown as curve B in Fig. 5. Increase in pressure by decomposition of the compound in the temperature range from 180 to 280 °C is scarcely observed, in contrast to that without hydrogen.

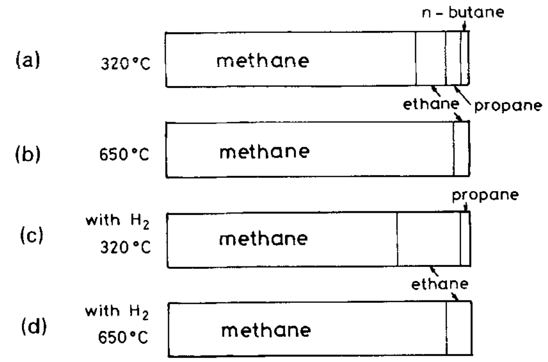

Figure 7 Gas compositions after decomposition of dimethylcadmium. (a) 320 °C; (b) 650 °C; (c) 320 °C with hydrogen; (d) 650 °C with hydrogen.

The results of mass spectroscopy and gas chromatography at 320 °C are given in Figs 6(d) and 7(c), respectively. The system with hydrogen shows an apparently lower content of methane than that without hydrogen in both measurements of mass spectroscopy and gas chromatography [see Figs 6(b), 7(a), 6(d) and 7(c)]. In the results of gas chromatography of the system with hydrogen, differences from that without hydrogen include higher content of ethane, lower content of propane and no detection of n-butane. These results, of course, indicate that hydrogen was consumed to form ethane through hydrogenation of n-butane and propane.

It is found that, in mass spectroscopy at 320 °C, peaks of methane were lower than those of ethane regardless of the presence of hydrogen while, in gas chromatography, methane was the major species in both systems with and without hydrogen. It is considered that this fact comes from insufficient ionization of methane by the low ionization voltage (10 eV) used in the present work.

At 650 °C, patterns similar to those without hydrogen were obtained in both mass spectroscopy and gas chromatography. Thus, the total pressure in the system continues to increase, even above 700 °C, with increase of methane.

3.3 Diethylzinc $[Zn(C_2H_5)_2]$

One of the problems with MOCVD using alkyl metalorganic compounds as precursors is carbon contamination of the growing crystal. Diethylzinc has been sometimes used[17–21] in spite of its lower saturated vapor pressure, because it gives less carbon contamination.

A typical pressure–temperature curve for diethylzinc is shown in Fig. 8. The saturated vapor pressure begins to rise at about −20 °C and it is about 20 Torr at room temperature.

From the log P versus $1/T\,\mathrm{K}^{-1}$ plots, the temperature dependence of the saturated vapor pressure was found to be as shown in Eqn [9].

For evaporation:

$$\log P_{(\text{evap.})\text{Torr}} = -\frac{2.012\times 10^{3}}{T} + 7.996 \qquad [9]$$

In the above plots, a break which corresponds to the melting point of this compound was not clearly found. The melting point of the compound has been reported to be −28 °C, but it was almost impossible to determine it in the above plots and to obtain the temperature dependence of the saturated vapor pressure for sublimation, because very few readings of pressure could be taken at such a low pressure range. Equations [10] and [11] have been reported for evaporation of this compound.

$$\log P_{\text{Torr}} = -\frac{2.190\times 10^{3}}{T} + 8.280 \text{ (Ref. 28)} \qquad [10]$$

$$\log P_{\text{kPa}} = -\frac{2.109\times 10^{3}}{T} + 7.405 \text{ (Ref. 33)} \qquad [11]$$

It is seen that the vapor pressure agrees with that of the ideal gas law after evaporation and the compound decomposes in the vapor phase in the temperature range 170–225 °C. Figure 9 shows the results of mass spectrography of the compound with and without hydrogen at various temperatures.

The spectrum at room temperature [Fig. 9(a)] (that is, the cracking pattern) is characterized by three groups of peaks at *m*/*z* 64–70, 93–99 and 122–128 which correspond to Z_n^+, $Zn(C_2H_5)^+$ and $Zn(C_2H_5)_2^+$, respectively. As shown in Fig. 9(b), these peaks completely disappeared at 250 °C and a thin film with metallic luster was observed on the inner surface of the used tube. Therefore, the pressure increase in the above temperature range is considered to be caused by decomposition during which metallic zinc is deposited. In the mass spectrum at 250 °C, considerable peaks for C_2 hydrocarbons with *m*/*z* 26–30 are observed together with peaks for C_3 hydrocarbons with *m*/*z* 39–44 and C_4 hydrocarbons with *m*/*z* 55–58. Figure 10 shows the results of gas chromatography of this compound with and without hydrogen at various temperatures.

At 250 °C, as shown in Fig. 10(a), ethane and n-butane were detected as major species together with small amounts of ethylene, *trans*-2-butene and *cis*-2-butene. Considering tht C_2H_5 is the alkyl radical released from the compound, it would be reasonable to estimate formation (i) of ethane by addition of hydrogen to the radical and (ii) of n-butane by coupling of two radicals. In Fig. 9(b), peaks for C_3 hydrocarbons were observed, but not from the results of gas chromatography shown in

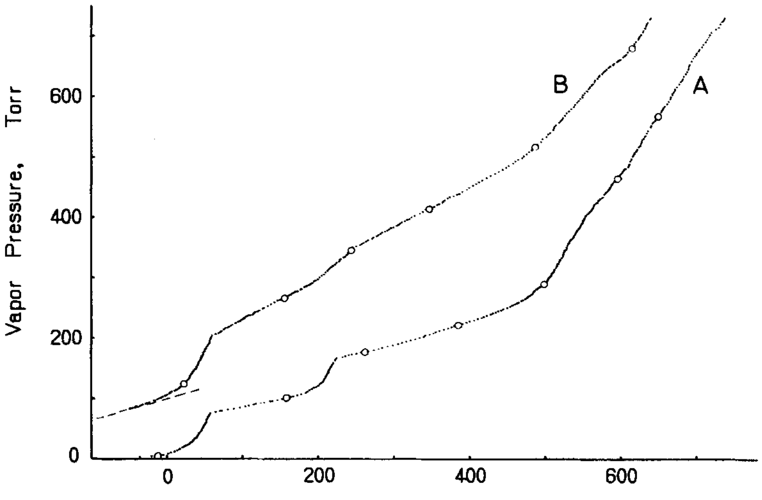

Figure 8 Pressure–temperature curves of diethylzinc with and without hydrogen: A, without hydrogen; B, with hydrogen.

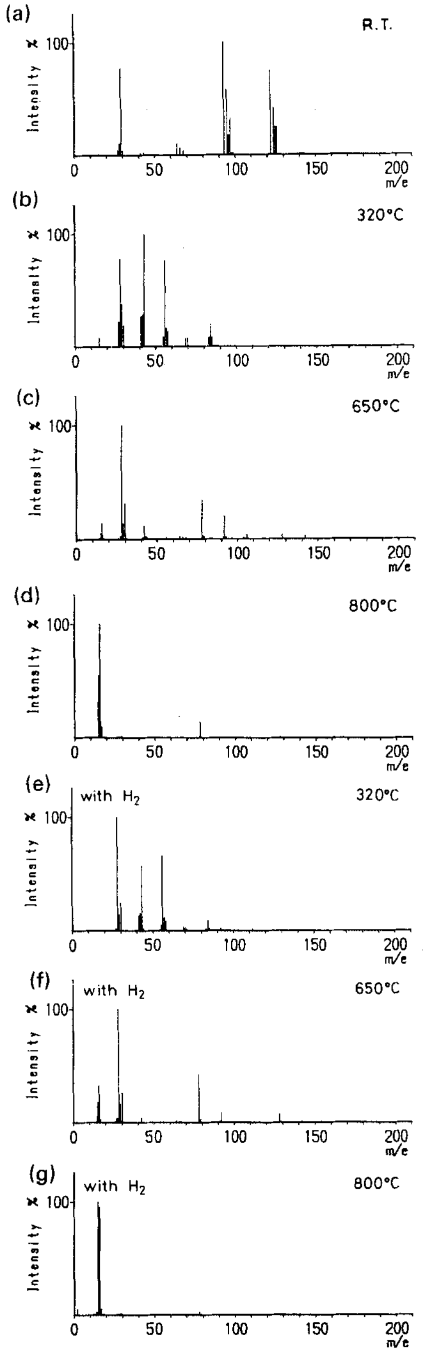

Figure 9 Mass spectra of diethylzinc at various temperatures: (a) room temperature; (b) 320 °C; (c) 650 °C; (d) 800 °C; (e) 320 °C with hydrogen; (f) 650 °C with hydrogen; (g) 800 °C with hydrogen. (f) (g)

Fig. 10(a). Although the peak at *m*/*z* 41 corresponds to $-CH{=}CH-CH_3^+$, *m*/*z* 42 to $CH_3-CH{=}CH_2^+$, *m*/*z* 43 to $-CH_2-CH_2-CH_3^+$ and *m*/*z* 44 to $CH_3-CH_2-CH_3^+$, respectively, these fragment ions are considered to come from rearrangement of fragments of n-butane, *trans*-2-butene and *cis*-2-butene.

After the decompositions mentioned above, the pressure shows agreement with that of the ideal gas law with a gradually larger increase above 300 °C followed by a rapid increase above 450 °C. In the results from mass spectroscopy at 650 °C [Fig. 9(c)], peaks of C_3 and C_4 hydrocarbons almost disappeared and those for CH_3^+, CH_4^+ and $C_2H_4^+$ grew considerably. The result of gas chromatography at 580 °C [Fig. 10(b)] supports the above measurement, i.e. n-butane and butenes were not detected and methane, ethane and ethylene occupied the larger part in the system in order of content. In vapor pressure measurements on n-butane, *trans*-2-butene and *cis*-2-butene, it was observed that a rapid increase in pressure by decompositions of these hydrocarbons began in the neighbourhood of 450 °C, and it is reasonable to conclude that the rapid increase in pressure above 450 °C in curve A in Fig. 8 is caused by the decomposition of these hydrocarbons in the system. The saturated vapor pressure of metallic zinc is not considered to contribute to the total pressure of the system at 580 °C, because it is about 10 Torr at 600 °C. At 650 °C, peaks of C_2 hydrocarbons became highest and peaks of benzene (*m*/*z* 78), toluene (*m*/*z* 92) and naphthalene (*m*/*z* 128) appeared as shown in Fig. 9(c).

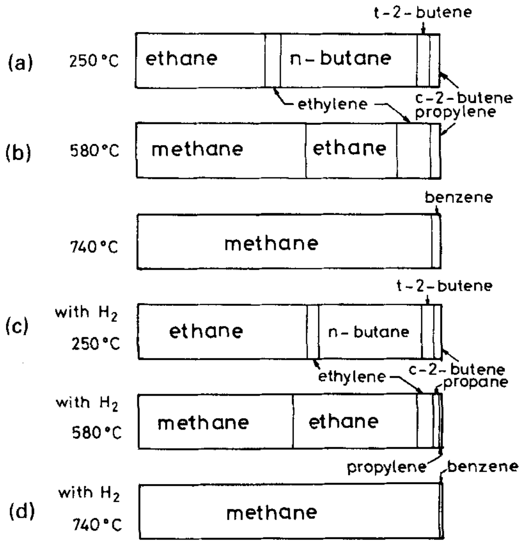

Figure 10 Gas compositions after decomposition of diethylzinc: (a) 250 °C; (b) 580 °C; (c) 740 °C; (d) 250 °C with hydrogen; (e) 580 °C with hydrogen; (f) 740 °C with hydrogen.

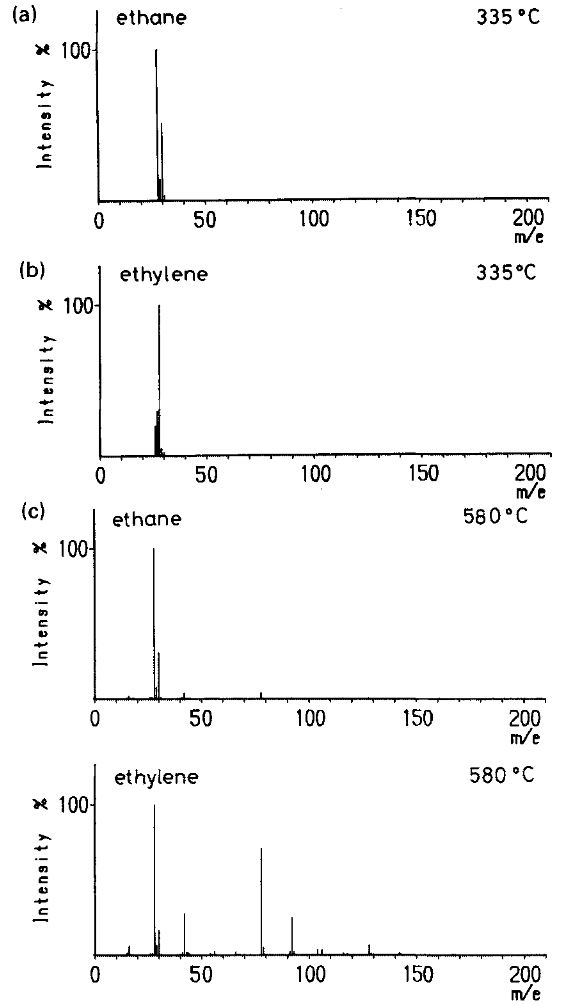

Figure 11 Mass spectra of ethane and ethylene at 335 and 580 °C: (a) ethane at 335 °C; (b) ethylene at 335 °C; (c) ethane at 580 °C; (d) ethylene at 580 °C.

These aromatic hydrocarbons come from chain hydrocarbons having a C═C bond such as ethylene and propylene.[34] The results of mass spectroscopy on ethane and ethylene at 335 and 580 °C are shown in Figs. 11(a), (b), (c) and (d).

It is seen that reactors of ethylene resulted in the aromatic hydrocarbons mentioned above at 580 °C, whilst the spectrum of ethene at 580 °C was not so different from that at 335 °C. The spectrum of ethane at 335 °C is characterized by two high peaks at *m/z* 28 and 30. From these spectra, the relative peak heights at *mz* 26, 27 and 28. From these spectra, the relative peak heights at *m/z* 26–30 at 320 °C in Fig. 9(b) suggest coexistence of ethane and ethylene, and those at 650 °C [Fig. 9(c)] suggest a decrease of ethylene by the formation of aromatic hydrocarbons.

As seen in Fig. 9(d), the spectrum at 800 °C shows only peaks of CH_3^+, CH_4^+ and a small amount of benzene, and in gas chromatography at 740 °C [Fig. 10(c)], the greater part of the vapor phase in the system is occupied by methane. The saturated vapor pressure of zinc at 740 °C is about 118 Torr and it should be a component of the total pressure of the system although it does not appear in the gas chromatography.

The pressure–temperature curve on a mixed system of diethylzinc and hydrogen is shown as curve B in Fig. 8. The pressure increase by decomposition of the compound began at about 200 °C whereas it began at about 170 °C without hydrogen, and the mole ratio of vapor phases before and after decomposition is clearly lower than that in curve A. These facts suggest that the compound reacts with hydrogen as soon as it begins to decompose and hydrogen is consumed in the hydrogenation of radicals.

Figures 9(e), (f) and (g) show the results of mass spectroscopy on the compound in the presence of hydrogen at 320, 650 and 800 °C, respectively. At 320 °C, it is seen that the relative intensities of peaks for C_3 hydrocarbons of *m/z* 41, 42 and 43, and C_4 hydrocarbons of *m/z* 55, 56, 57 and 58 became lower and those for peaks of *m/z* 27, 28, 29 and 30 became higher, compared with those without hydrogen at the same temperature [Fig. 9(b)]. This indicates that hydrogenation of radicals of C_2 hydrocarbons took place to form more ethane and ethylene when n-butane and butenes decomposed. In Fig. 9(e), the highest peak is at *m/z* 28 which correspond to C_2H_4, but ethane also gives the highest peak at *m/z* 28. As shown in Fig. 11(a) and (b), both ethane and ethylene gave fragment patterns in which the highest peak is at *m/z* 28, and the peak pattern of ethylene was characterized by a very low relative intensity of the peak at *m/z* 30. Accordingly, these spectra suggest that ethylene coexists with a large amount of ethane in the system with hydrogen at 320 °C. The result of gas chromatography is shown in Fig. 10(d), in which the system is in a similar state to that for Fig. 9(e), although the temperature is a little lower. It is seen that the relative amount of ethane was increased while that of ethylene did not change, comparing with that without hydrogen [Fig. 10)a)], and the decrease in intensity of n-butane reflects its decomposition and hydrocracking to form ethane.

Mass spectroscopy at 650 °C [Fig. 9(f)] gave a similar result to that without hydrogen shown in fig. 9(c), in which the relative intensity of ethane is higher than that without hydrogen. In gas chromtography with and without hydrogen at 580 °C, methane is the major species in these systems, as seen in Figs 10(b) and (e), whilst peak heights of CH_3^+ and CH_4^+ are far lower than those of ethane and ethylene in the mass spectra in Figs 9(c) and (f). This discrepancy is considered to be caused by the low ionization voltge (10 eV) which was not sufficient to ionize methane.

At 800 °C, with or without hydrogen, the system was almost entirely occupied by methane [Figs. 9(d) and (g)] and the results are supported by gas chromatography at 740 °C as shown in Figs 10(c) and (f).

4 CONCLUSION

Physicochemical properties of dimethylzinc, dimethylcadmium and diethylzinc were investigated by means of vapor pressure measurement, mass spectroscopy and gas chromatography. The temperature dependences of the saturated vapor pressure of these compounds were determined. The saturated vapor pressure of sublimation of diethylzinc is less than 1 Torr and it was impossible to determine its temperature dependence with good accuracy.

Dimethylzinc decomposes in the vapor phase in the temperature range 270–370 °C, releasing methane as a major species with small amounts of ethane, ethylene, propane and propylene. Dimethylcadmium decomposes in the range 180–290 °C, releasing methane as a major species with small amounts of ethane, propane and n-butane. Diethylzinc decomposes in the range 170–225 °C, releasing ethane and n-butane as major species with small amounts of ethylene, *trans*-2-butene and *cis*-2-butene.

In the decomposition of these compounds, polymers with less hydrogen were deposited together with metals. These polymers decompose to release a few lower hydrocarbons at higher temperature.

Hydrogen gas reacts with these compounds as soon as they begin to decompose and promotes the formation of methane with increasing temperature through hydrogenation and hydrocracking of the various hydrocarbons released.

Acknowledgement The authors wish to thank Messrs H. Minato, H. Ban, T. Mori and H. Kurita for their assistance during this work.

REFERENCES

1. Cockayne, B and Wright, P J *J. Crystal Growth*, 1984, 68: 223
2. Stutius W, *Appl. Phys. Lett.*, 1978, 33: 656
3. Wright, P J, Griffiths, R J M and Cockayne, B *J. Crystal Growth*, 1984, 66: 26
4. Roth, A P and Williams, D F *J. Electrochem. Soc.*, 1980, 127: 1843
5. Smith, F T J *Appl. Phys. Lett.*, 1983, 43: 1108
6. Solanki, R and Collins, G J *Appl. Phys. Lett.*, 1983, 42: 662
7. Mullin, J B, Irvine, S J C and Ashen, D J *J. Crystal Growth*, 1982, 55: 92
8. Hoke, W E and Traczewski, R *J. Appl. Phys.*, 1983, 54: 5087
9. Schmit, J L *J. Crystal Growth*, 1983, 65: 249
10. Kuznetsov, P I, Zhuravlev, L A, Odin, I N, Shemet, V V and Novoselova, A V *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1982, 18: 930
11. Sataev, M, Kuznetov, P I, Shemet, V V and Karimov, I A *Dokl. Akad. Nauk Uzb. SSSR*, 1983, 2: 23
12. Kuznetov, P I, Shemet, V V, Odin, I N and Novoseleva, A V *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1981, 17: 791
13. Kuznetov, P I, Shemet, V V, Odin, I N and Novoseleva, A V *Dokl. Akad. Nauk SSSR*, 1979, 248: 879
14. Fujita, S, Matsuda, Y and Sasaki, A *J. Crystal Growth*, 1984, 68: 231
15. Yoshikawa, A, Yamaga, S, Tanaka, K and Kasai, H *J. Crystal Growth*, 1985, 72: 13
16. Cockayne, B, Wright, P J, Skolnick, M S, Pitt, A D and Williams, J D *J. Crystal Growth*, 1985, 72: 17
17. Manasevit, H M and Simpson, W I *J. Electrochem. Soc.*, 1971, 118: 644
18. Ghandi, S K, Field, R J and Shealy, J R *Appl. Phys. Lett.*, 1980, 37: 449
19. Roth, A P and Williams, D F *J. Electrochem. Soc.*, 1981, 128: 2784
20. Lan, C K, Tiku, S K and Lakin, K M *J. Electrochem. Soc.*, 1980, 127: 1843
21. Fujita, S, Tomomura, Y and Sasaki, A *Japan J. Appl. Phys.*, 1983, 22: L583
22. Kuniya, Y and Chino, T *Denki-Kagaku*, 1972, 40: 858
23. Kuniya, Y *Oyo-Butsuri*, 1986, 55: 1051
24. Nitsche, R and Richman, D *Z. Elektrochem.*, 1962, 66: 709
25. Fergusson, R and Gabor, T *J. Electrochem. Soc.*, 1964, 111: 585
26. Silvestri, V J and Lyons, V *J. Electrochem. Soc.*, 1962, 109: 963
27. Kirwan, D J *J. Electrochem. Soc.*, 1970, 117: 1572
28. *Alfa Products Catalogue, 1989*, Morton Thiokol Inc., p 36
29. Kuniya, Y *Handotai Kenkyu*, vol 31, no 4, Nishizawa, J, (ed) Kogyo Chosaki Publishing Co Ltd, Tokyo, 1989, pp 115–136

30. *The Vapor Pressures of Pure Substances*, Boublik, T, Fried, V and Hâla, E (eds) Amsterdam, 1973, Elsevier, p 94
31. Braune, H, *Z. Anorg. Allgem. Chem.*, 1920, 111: 109
32. Hota, N K *J. Organomet. Chem.*, 1967, 9: 169
33. Stephenson, R M and Malanowski, S (eds) *Handbook of the Thermodynamics of Organic Compounds*, Elsevier, New York, 1987, p 495
34. Kunugi, T, Sakai, T, Soma, K and Sasaki, Y, *Indi. Eng. Chem. Fundamentals*, 1969, 8: 374