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The Reactivity of Organozinc and Organocadmium Compounds in Decomposition Reactions

L.M.Dyagileva and Yu.A.Aleksandrova

The literature data on the thermal decomposition and photodecomposition of organozinc and organocadmium compounds, on the dependence of the thermal decomposition mechanism and the kinetic stability of metal alkyls in this reaction on the decomposition conditions, and also on the relation between the reactivity of the organometallic compounds and their structure are treated systematically and discussed.
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I. INTRODUCTION

The thermal decomposition reactions of organozinc and organocadmium compounds are of interest in connection with problems of the formation of zinc and cadmium coatings by chemical deposition from the gas phase.[1] Nevertheless the relevant literature data have not been subjected to systematic analysis.[1,2]

The lower alkyl derivatives of Group IIB metals are extremely unstable[3] and their use has until recently been limited.[4] However, during the last decade the dialkyl compounds of zinc and cadmium have found applications in the preparation of metallic and semiconductor coatings.[5-14] The use of metal alkyls in semiconductor technology has stimulated further research into the kinetic and thermodynamic stabilities of these organometallic compounds (OMC) and into the improvement of the methods of their synthesis[15,16] and analysis[17,18] in order to obtain specially pure compounds and also to develop conditions for the deposition and segregation of the condensed phase of the metal on thermal decomposition of the OMC.[19]

The existing reviews on the reactions involving the homolytic cleavage of organometallic compounds[20-24] are mainly concerned with OMC about the decomposition of which more reliable data are available (mercury, lead, tin, bismuth, antimony, gallium, arsenic, and titanium). It appears useful to discuss separately the results of experimental studies on the homolytic decomposition of organozinc and organocadmium compounds. This review presents a systematic account and a survey of data on the kinetic stability of the zinc and cadmium OMC in photodecomposition and thermal decomposition reactions.

II. KINETICS AND MECHANISMS OF THE DECOMPOSITION OF ORGANOZINC AND ORGANOCADMIUM COMPOUNDS

1. Decomposition of Organozinc Compounds

Although the pyrolysis of metal alkyls with formation of the corresponding metals and radicals has been known since Paneth's classical studies, the kinetic investigations of these processes began only two decades ago and have not been systematic.[1] The kinetics of the gas-phase pyrolysis of dimethylzinc in a static system have been studied over a wide range of initial reactant pressures from 15 to 580 mmHg at temperatures in the range 280–340 °C.[25,26] It has been observed[25] that the rate of decomposition diminishes with increase of the initial pressure of dimethylzinc and that there is a simultaneous increase of the yield of the main gaseous product—methane. At a single fixed initial pressure the rate of decomposition and the yield obtained increase with increasing ratio of the reactor surface area S to the reactor volume V (the so-called heterogeneous factor S/V). In the high-temperature region a narrow pressure range has been found (27–55 mmHg) in which the decomposition rate constant is invariant and corresponds to a first-order kinetic law. It has been suggested that part of the methane is produced heterogeneously, although the contribution of the heterogeneous component of the reaction has not been established and the kinetic parameters of the overall reaction have not been calculated. It has been suggested that methane and ethane are formed in the stages involving the methyl radical-induced decomposition of dimethylzinc and the dimerisation of the methyl radicals respectively. Metallic zinc and polymethylene have been detected in addition to the gaseous products.

Self-inhibition of the reaction was observed in a later study.[26] The nature of the self-inhibition was not elucidated, but, by analogy with the cracking of hydrocarbons, it was postulated that it is caused by the addition of the methyl radical to the double bond in the ethylene formed with formation of a less reactive radical. The self-inhibition coefficient is independent of pressure and temperature.

The effective decomposition rate constant depends on the initial OMC concentration but a definite relation has not been observed. The effective activation energy diminishes with increase of the dimethylzinc concentration. A radical-chain mechanism of the thermal decomposition of dimethylzinc *in vacuo* under static conditions has been proposed:

$$Me_2Zn \rightarrow Me + {}^{\cdot}ZnMe, \qquad (1)$$

$$\begin{gathered} {}^{\cdot}ZnMe \rightarrow Zn + Me, \\ Me + Me_2Zn \rightarrow CH_4 + {}^{\cdot}CH_2ZnMe, \\ {}^{\cdot}CH_2ZnMe \rightarrow :CH_2 + Zn + Me, \\ :CH_2 + Me_2Zn \rightarrow EtZnMe \rightarrow Et + {}^{\cdot}ZnMe, \\ 2Me \rightarrow C_2H_6, \\ Me + {}^{\cdot}CH_2ZnMe \rightarrow CH_4 + C_2H_4 + Zn, \\ Me + Et \begin{cases} \rightarrow C_3H_8, \\ \rightarrow CH_4 + C_2H_4. \end{cases} \end{gathered} \qquad (2)$$

The following compounds were found among the gaseous pyrolysis products (mole %): methane 88.0, ethane 4.2 to 5.5, propane 4.0–5.9, butane 1.2–1.4, ethylene 0.2–0.6, and propene 0.5–1.5.[26]

Methane is the only gaseous product of the decomposition of dimethylzinc in a sealed tube in the presence of cyclohexane (250–400 °C, pressure close to atmospheric).[27] With decrease of the fraction of cyclohexene, ethane and propane appear in the mixture of decomposition products. The following process mechanism in the presence of excess cyclohexane has been proposed:

$$Me_2Zn \rightarrow Me + ZnMe ,$$
$$Me + C_6H_{12} \rightarrow CH_4 + {}^{\cdot}C_6H_{11} ,$$
$$2{}^{\cdot}ZnMe \rightarrow ({}^{\cdot}ZnMe)_2 .$$

The activation energy for the first of these reactions has been determined as 45.5 ± 3.3 kcal mol^{-1}.

The use of cyclohexane in a fully deuteriated form permitted the conclusion that, under the given experimental conditions, the role of the induced decomposition reaction $Me + Me_2Zn \rightarrow CH_4 + {}^{\cdot}CH_2ZnMe$ is small even in the total absence of cyclohexane. The estimated activation energy for this reaction is ≥15 kcal mol^{-1}.[27]

The induced decomposition of dimethylzinc was fully eliminated when the reaction was carried out under flow conditions in the presence of an excess of toluene.[28] The following mechanism, analogous to the mechanisms of the decomposition of dimethylcadmium and dimethylmercury,[29] has been proposed for the decomposition of dimethylzinc under these conditions:

$$Me_2Zn \rightarrow Me + {}^{\cdot}ZnMe , \quad (1)$$

$${}^{\cdot}ZnMe \rightarrow Me + Zn , \quad (2)$$

$$Me + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2^{\cdot} , \quad (3)$$

$$2Me \rightarrow C_2H_6 ,$$
$$2C_6H_5CH_2^{\cdot} \rightarrow (C_6H_5CH_2)_2 . \quad (4)$$

Reaction (2) does not occur at temperatures below 670 °C. It begins to play an appreciable role only above 730 °C but is complicated by the decomposition of toluene. For this reason, in the temperature range 573–700 °C it was possible to investigate the kinetics of the radical initiation reaction (1). The kinetic parameters of reaction (2) were obtained after applying a correction taking into account the yield of methane resulting from the decomposition of toluene. Both rate constants, k_1 and k_2, depend appreciably on the pressure in the system. At a fixed pressure of 16 mmHg, the following expressions were obtained for the rate constants for the elementary reactions (1)–(4):[28]

$$\lg k_1, (s^{-1}) = 11.25 - (47\,200 \pm 1000)/4.58T ;$$
$$\lg k_2, (s^{-1}) = 6\,8 - 35\,000/4.58T ;$$
$$\lg (k_3/k_4^{1/2}), (mol^{-1/2})\ cm^{3/2}\ s^{-1/2} = 6.3 - 13\,000/4.58T .$$

At an overall pressure of 5 mmHg, the expression for the k_1 becomes[28]

$$\lg k_1, (s^{-1}) = 11.03 - 47\,300/4.58T .$$

If the reverse radical recombination reactions do not require an activation energy, the activation energies obtained for the forward reactions (1) and (2) can be regarded as equal to the dissociation energies D_1 and D_2 of the MeZn–Me and Zn–Me bonds respectively. It has been shown[28] that the thermochemical estimate $D_1 + D_2 = 82.9$ kcal mol^{-1} agrees with kinetic data.

The gas-phase decomposition of diethylzinc does not have the distinctive features which characterise the pyrolysis of the methyl derivative (the dependence of the rate constant and the activation parameters on the initial reactant concentration and the self-inhibition of the reaction).

In an early study of the photolysis of diethylzinc,[30] the reactivity of the ethyl radicals formed in the primary decomposition step was investigated. At a pressure of 25 mmHg and in the temperature range 45–250 °C, ethane, ethylene, butane, and traces of hydrogen, butene and higher hydrocarbons were detected in the reaction products. The study of the influence of changes in the concentration of diethylzinc, the radiation intensity, the packing of the reaction vessel comprising an inert phase, and the pressure of an inert gas on the composition of the product led to the conclusion that butane is the product of the recombination of two ethyl radicals, while ethane and ethylene are formed as a result of the interaction of ethyl radicals with a molecule of the metal alkyl. The rate of the reaction of ethyl radicals with hydrogen becomes significant above 160 °C and its activation energy has been estimated as 9 ± 2 kcal mol^{-1}. The composition of the photolysis products at high temperatures is analogous to the composition of the thermal decomposition products.

Kinetic studies of the pyrolysis of diethylzinc have been carried out in a stream of toluene[31] and an inert gas,[32] in a static system,[32,33] and in a molecular beam.[33,34]

A free-radical mechanism has been proposed for the decomposition of diethylzinc in a stream of toluene, analogous to that described above for dimethylzinc, but it is more detailed as regards the reaction of all the radicals formed in the system.[31] In the mechanism of the multistage generation of radicals of diethylzinc, the second stage ${}^{\cdot}ZnEt \rightarrow Zn + Et$ is very rapid, in contrast to the reaction ${}^{\cdot}ZnMe \rightarrow Zn + Me$. The absence of induced decomposition in a stream of toluene made it possible to determine the kinetic and activation parameters for the first stage of the homogeneous initiation of radicals via the reaction $Et_2Zn \rightarrow Et + {}^{\cdot}ZnEt$ (Table 1). The presence of zinc oxide on the reactor surface greatly accelerated this reaction, which indicates a sensitivity to the nature of the surface.

The decomposition of diethylzinc under dynamic conditions in a stream of helium in tubular reactors with the surface coated by the solid products of its pyrolysis[32] obeys the first-order kinetics. For short contact times in an open system, there is insufficient time for the development of the chain process. The experimental activation energy for the decomposition of diethylzinc in a stream of helium (47.6 kcal mol^{-1}) is close to the dissociation energy of the EtZn–Et bond which has been estimated[31] as 47.5 kcal mol^{-1}. Only the unduly large pre-exponential factor ($\lg A = 16.13$) in the expression for the rate constant for the pyrolysis of diethylzinc in a stream of helium precludes a reliable assignment of the activation parameters obtained to a specific stage of the decomposition process.

In a closed system, diethylzinc also decomposes in accordance with first-order kinetics.[32] In contrast to the methyl derivative, a wide range of pressures (50–175 mmHg) has been found for this compound in which the rate constant is invariant. On passing to atmospheric pressure, the reaction continues to be first order. An inhibiting effect by the decomposition products has not been observed. The reaction involving the formation of metallic zinc from diethylzinc in the presence of added hydrogen has been noted.

A satisfactory interpretation of the results has been achieved on the assumption of a radical-chain mechanism of the decomposition:[32]

$$Et_2Zn \rightarrow Et + {}^{\cdot}ZnEt , \quad (5)$$

$${}^{\cdot}ZnEt \rightarrow Et + Zn , \quad (6)$$

$$Et + Et_2Zn \rightarrow C_2H_6 + C_2H_4 + {}^{\cdot}ZnEt . \quad (7)$$

$$Et \rightarrow C_2H_4 + H^{\cdot}, \quad (8)$$

$$H^{\cdot} + Et_2Zn \rightarrow C_2H_6 + {}^{\cdot}ZnEt, \quad (9)$$

$$2Et \rightarrow C_4H_{10} \text{ (or } C_2H_6 + C_2H_4). \quad (10)$$

The experimental effective rate constant is $k_{eff} = k_8 \cdot (k_5/k_{10})^{1/2}\ s^{-1}$. The initiation stage (5) can occur on the surface, since zinc oxide has been found to have an accelerating effect, but the process is propagated in the bulk phase (because the ratio S/V has not effect and acceleration of the reaction by added hydrogen is not observed).

In order to account for the overall first order of the reaction, it is necessary to assume that the initiation reaction (5) in the gas phase is of second order, although it is known that zinc alkyls are not associated in the gas phase.[35] However, it has been observed in the liquid-phase autoxidation of dimethylzinc[36] that the initiation of the radicals does indeed take place as a result of the interaction of two dimethylzinc molecules.

In contrast to the liquid-phase pyrolysis,[32,37] in the gas-phase pyrolysis the contribution of the disproportionation reactions to the formation of ethane and ethylene is small[38] and their rate is 0.11–0.14 of the rate of recombination of ethyl radicals.

It has been observed[32] that the ethylene formed can be consumed in secondary reactions involving insertion in the C–Zn bond in diethylzinc. Thus the hydrolysis in heavy water of the condensed residue after the interaction of diethylzinc with ethylene yielded, together with monodeuteriomethane, also monodeuteriobutane. At the same time, the absence of dideuterioethane in the same experiment shows that the intramolecular and intermolecular decomposition of diethylzinc via the α-disproportionation of the ethyl groups does not occur under the given experimental conditions. It was postulated[32] that in a closed system the main gaseous product, namely ethane, is formed preferentially in the induced diethylzinc decomposition reaction (7).

The following compounds were detected in the gaseous products of the total decomposition of diethylzinc under static conditions at 270 °C [32] (in moles per mole of the substance decomposed): octane 0.0010, octene 0.0023, hexane 0.0085, hexene 0.0142, butane 0.2219, butene 0.0619, ethane 1.0443, ethylene 0.2709, and hydrogen 0.1072. Metallic zinc was found in the solid phase.

High pressures (from tens mmHg to atmospheric pressure) and low degrees of decomposition favour the abstraction of hydrogen from the diethylzinc molecule by the ethyl radical formed in the primary decomposition step.[33] Decrease of the pressure to 10^{-4} mmHg tends to decrease the kinetic stability of zinc dialkyls.[34] Under dynamic conditions, on passing from atmospheric pressure in a stream of helium to a high vacuum, the temperature of the total decomposition of diethylzinc decreases on the zinc coating from 310° to 130 °C and on zinc oxide from 310° to room temperature. The lines due to the molecular ions in the mass spectrum of dimethylzinc decomposing under high vacuum conditions on the solid products of its pyrolysis disappear already at 230 °C. The apparent activation energies in the temperature range 100 to 300 °C are 7.7 ± 1.5 and 6 ± 1.0 kcal mol^{-1} for dimethylzinc and diethylzinc respectively. The composition of the products changes significantly in the pyrolysis of diethylzinc *in vacuo*[34] and the gas phase becomes enriched to the extent of approximately 70% in ethylene as a consequence of the vigorous dehydrogenation of ethane on pyrolytic zinc at the instant of formation.

In a high vacuum, where contact of OMC molecules with one another and also with the thermal decomposition products and the carrier gas is ruled out, the reactant decomposes heterogeneously in the adsorbed state on the catalytic centres of the reactor surface.[34] It has been suggested that, under dynamic conditions in a high vacuum, zinc alkyls decompose intramolecularly in accordance with the following mechanism:

$$Me_2Zn \xrightarrow{\text{recombination}} C_2H_6;$$
$$Me_2Zn \xrightarrow{\alpha\text{-disproportionation}} CH_4 + CH_2{:}Zn;$$
$$Et_2Zn \xrightarrow{\beta\text{-disproportionation}} C_2H_4 + C_2H_6 + Zn_{abs}.$$

Table 1. Activation parameters of the stages in the gas-phase pyrolysis of zinc dialkyls.

Condition	Stage	E, kcal mol^{-1}	lg$A$	Refs.
	Dimethylzinc			
16 mmHg, 573–700°, toluene stream	$Me_2Zn \rightarrow Me + ZnMe$	47.2±1.0	11.25	[28]
5 mmHg, 573–700°, toluene stream	$Me_2Zn \rightarrow Me + ZnMe$	47.3	11.03	[28]
16 mmHg, 730–825°, toluene stream	$Me \rightarrow Me + Zn$	35.0	6.8	[28]
1 atm, 250–400°, in the presence of cyclohexane, static system	$Me_2Zn \rightarrow Me + ZnMe$	45.5±3.3	—	[27]
580 mmHg, 280–338°, static system	overall process	35.0±1.5	9.63±0.02	[26]
10^{-4} mmHg, 170–230°, molecular beam	overall process	7.7±1.5	—	[34]
	Diethylzinc			
15 mmHg, 440–473°, toluene stream	$Et_2Zn \rightarrow Et + ZnEt$	49.0±2.0	14.3±0.6	[31]
Ditto	$Et_2Zn \rightarrow Et + ZnEt$ *	24.0±5.0	7.6±1.6	[31]
150–175 mmHg, 270–310°, static system	overall process	28.3±0.3	8.44±0.13	[32]
1 atm, 310–340°, helium stream	overall process	47.6±2.5	16.13±0.93	[32]
10^{-4} mmHg, 80–130°, molecular beam	overall process	6.0±1.0	—	[34]

*In the presence of zinc oxide.

Table 2. The influence of the reaction conditions on the mechanism of the gas-phase decomposition of zinc dialkyls.

System	Reaction conditions	Decomposition mechanism	Refs.
		Dimethylzinc	
Static*	305–340°, 13–270 mmHg	radical, with selfinhibition	[25]
	280–338°, 580 mmHg	radical, with selfinhibition	[26]
	250–400°, atmospheric pressure, in the presence of cyclohexane	radical	[27]
Toluene stream**	573–700°, 16 mmHg	radical, $k_{exp} = k_1$ (s^{-1}) (c^{-1})	[28]
	730–825°, 16 mmHg	radical, $k_{exp} = k_2$ (s^{-1}) (c^{-1})	[28]
Molecular beam	170–230°, 10^{-4} mmHg	intramolecular heterogeneous (recombination and α-disproportionation); $E_{app} \ll E_{hom}$	[24]
		Diethylzinc	
Static*	270–310°, 50–170 mmHg	radical-chain: k_{exp} (s^{-1}) $= k_8 (k_5/k_{10})^{1/2}$; k_5 – second order reaction	[32]
Toluene stream**	440–483°, 15 mmHg	radical non-chain: homogeneous $k_{exp} = k_5$ (s^{-1}); heterogeneous (on ZnO) $k_{exp} = k_5$ (s^{-1}); k_5 – first order reaction	[31]
Helium stream**	310–340°, atmospheric pressure	radical non-chain: k_{exp} – first order reaction	[32]
Molecular beam	90–150°, 10^{-4} mmHg	intramolecular heterogeneous (β-disproportionation); $E_{app} \ll E_{hom}$	[33,34]

*In a glass reactor.
**The reactor walls were coated by the solid pyrolysis products.

The kinetic stability and mechanism of the pyrolysis of zinc alkyls depend on the decomposition conditions. The free-radical mechanism operates at reduced and atmospheric pressures, while the molecular mechanism, characteristic of the adsorbed state, operates in a high vacuum (Table 2).

The homolytic reactions of organozinc compounds (the methyl, ethyl and phenyl derivatives) in the liquid phase and in solution in benzene in the course of their thermal decomposition and photodecomposition have been described.[39–44] The decomposition proceeds via a free-radical mechanism and is accompanied by the formation of a metallic mirror and the segregation of radical reaction products. The radical disproportionation and dimerisation reactions are characteristic of the photolysis (20–30 °C). The thermal decomposition of the OMC in the absence of a solvent entails, apart from the above reactions, the interactions of the alkyl radicals with the hydrocarbons and the initial OMC. In the solvent, the reaction takes place mainly via the mechanism involving the homolytic substitution of hydrogen in the solvent molecules by the alkyl or phenyl radicals formed.

The disproportionation and recombination reactions of the alkyl radicals are the most characteristic of the liquid-phase decomposition of the OMC, in contrast to the gas-phase decomposition, the contribution of the disproportionation to the thermal decomposition increasing with increase in the complexity of the radical on going from ethyl[45] to pentyl[46] radicals.

A method has been proposed for the preparation of zinc and cadmium coatings with a thickness up to tens of microns by the decomposition of zinc dialkyls (at 310–330 °C) and cadmium dialkyls (at 230–290 °C) by a gas-thermal method.[47] The coatings constitute a dense polycrystalline film with a grain size of approximately 1–5 μm.

2. Decomposition of Organocadmium Compounds

The gas-phase pyrolysis of dimethyl cadmium has been investigated under static conditions[48,49] in a stream of toluene[29] and benzene.[50] In an early study[48] measurements were made of the initial rates of formation of the principal gaseous pyrolysis products—methane and ethane. A poor reproducibility of the results was noted and considerable surface effects were observed, although the cadmium and polymethylene formed did not alter the rate of reaction. The increase of the heterogeneous factor (i.e. the increase of S/V) diminishes the rate of formation of ethane and methane, while the addition of hydrogen, nitrogen, helium, and nitric oxide increases them. As an alternative to the generally accepted free-radical mechanism, observed in the photolysis and thermolysis of metal alkyls, a mechanism involving the intramolecular disproportionation of the methyl groups as they approach one another, resulting from the deformation of the molecule, has been proposed:[48]

$$Me_2Cd \rightarrow CH_4 + Cd{:}CH_2 .$$

However, under the experimental conditions employed (150–200 mmHg, 212–327 °C), the role of the radical pathway should be considerable. This is indicated both by the poor reproducibility of the results, which can be accounted for by the uncontrolled change in the state of the vessel walls in the presence of impurities and by the increase of the yield of ethane with increasing temperature. The latter takes place as a consequence of the increase of the concentration of methyl radicals and the increase of the yield of their recombination product—ethane. Such findings are more likely to indicate a significant contribution of the free-radical pathways to the mechanism of the pyrolysis of

dimethylcadmium rather than the occurrence of an intramolecular rearrangement via the scheme presented by Heller and Taylor.[48]

A free-radical mechanism has been proposed[51] for the photolysis of dimethylcadmium, according to which the induced decomposition reaction

$$Me_2Cd + Me \rightarrow CH_4 + {}^{\cdot}CH_2CdMe$$

is the only source from which methane is formed.

It is believed that the mechanisms of the pyrolytic and photolytic decomposition of the majority of metal alkyls are the same. Thus a mechanism, equally probable for both pyrolysis and photolysis, has been proposed in a study[49] of the gas-phase decomposition of dimethylcadmium in a static system at a fixed initial reactant pressure of 150 mmHg and a temperature of 258 °C:

$$Me_2Cd \rightarrow Me + {}^{\cdot}CdMe \ ; \quad (11)$$

$$^{\cdot}CdMe \rightarrow Cd + Me \ ; \quad (12)$$

$$2Me \rightarrow C_2H_6 \ ; \quad (13)$$

$$Me + C_2H_6 \rightarrow CH_4 + Et \ ; \quad (14)$$

$$Me + Et \rightarrow C_3H_8 \ ; \quad (15)$$

$$Me + C_3H_8 \rightarrow CH_4 + Pr \ ; \quad (16)$$

$$Pr \rightarrow Me + C_3H_6 \text{ (polymerisation, etc.)} \quad (17)$$

It has been suggested that reaction (12) is faster than reaction (11) and that stages (13)–(16) have comparatively low activation energies and are rapid at the given temperature.

Features characteristic of the homogeneous–heterogeneous process have been observed in the pyrolysis of dimethylcadmium in a static system.[49] Extrapolation to $S/V = 0$ yielded the rate constant for the homogeneous dissociation of the first Cd–C bond: $k_{11} = 1.43 \times 10^{-5}$ s^{-1} at 258 °C. The activation energy for this reaction, estimated as 43.5 ± 1.2 kcal mol^{-1}, has been identified with the dissociation energy of the first MeCd–Me bond. This value is close to $E_{11} = 45.8 \pm 1.0$ mol^{-1}, calculated[29] for the process in a stream of toluene. The dissociation energy of the second bond, calculated using thermochemical data, is $E_{12} = D_{12} =$ 21.4 kcal mol^{-1}.[49]

When dimethylcadmium was pyrolysed in a stream of benzene,[50] a range of initial pressures was observed (80 to 163 mmHg) in which the rate constant was invariant, which corresponds to a first-order kinetic law; on the other hand, in the range of low initial pressures (10–20 mmHg), the rate constant increases with increasing pressure.[29] The mechanism of the decomposition of dimethylcadmium in toluene and benzene streams is analogous to that described above for the pyrolysis of zinc alkyls and includes, apart from the initiation stage, also reactions involving the abstraction of hydrogen from toluene and benzene by the methyl radical formed and subsequent recombination reactions of the benzyl and phenyl radicals. The kinetic and activation parameters for the individual stages of the above reaction have been published.[29,49,50] Activation energies in the range from 43.5 to 48.8 kcal mol^{-1} and logarithms of the pre-exponential factor ranging from 11.9 to 13.4 have been obtained for reaction (11). The activation energy for reaction (12) has been estimated as 21.4 ± 4.0 kcal mol^{-1}.

The results of thermochemical studies, according to which the overall dissociation energy of the metal–carbon bonds in diethylcadmium is 52.9 ± 2 kcal mol^{-1}, suggest that diethylcadmium is thermally less stable than dimethyl cadmium.[1] The decomposition of gaseous diethylcadmium has been noted even at room temperature. However, detailed kinetic studies on the thermolysis of diethylcadmium and higher cadmium alkyls have not been made.

The kinetics of the deposition of metallic cadmium in the heterogeneous decomposition of gaseous diethylcadmium (temperature of the support 250–290 °C, temperature of the evaporator 19–50 °C) and di-isopentylcadmium (temperature of the support 240–250 °C, temperature of the evaporator 70–80 °C) have been investigated.[52] The amount of cadmium produced on the support depends on the temperature of the latter. The cadmium films obtained, with a thickness ranging from several microns to several tens of microns, constitute a light-coloured coating with a metallic lustre and satisfactory adhesion to the material of the support. The content of metallic cadmium in the coating is 99.5%. The microstructure and phase composition of the cadmium produced have been described.[46,47]

Solid dicylcohexylcadmium decomposes with liberation of metallic cadmium even at room temperature and for this reason the thermal decomposition has been studied in solution in benzene (100°, 30 h).[53] It was observed that the photodecomposition and thermal decomposition of dicyclohexylcadmium in benzene are accompanied by the formation of cyclohexane, cyclohexene, and bicyclohexyl.

A free-radical mechanism, in which the disproportionation of the radical formed predominates over the recombination and which is common to all metal alkyls, has been adopted for the pyrolysis of dicyclohexylcadmium [53] and di-isopentylcadmium [46] in solution and in the liquid phase in the absence of a solvent. It has also been suggested that the reaction involving the induced decomposition of the reactant via the abstraction of a hydrogen atom from the OMC molecule by the radical formed takes place. When solutions of diphenylcadmium in benzene are irradiated,[54] biphenyl and cadmium are formed preferentially, the contribution by the reaction with the solvent being small. On the other hand, the reaction involving the abstraction of hydrogen by the phenyl radical from the solvent molecule predominates in the photolysis of diphenylcadmium in dioxan.

III. REACTIVITY AND STRUCTURE

Despite the fact that the experimental data for the kinetics of the pyrolysis of organozinc and organocadmium compounds refer solely to derivatives of lower alkyls, one can already reach certain conclusions about the reactivity of the above OMC in the decomposition reaction.

Under identical experimental conditions, the kinetic stability of the organometallic compounds formed is determined by the nature of the initial OMC, i.e. the nature of the metal atom and the radical. The kinetic stability of the lower alkyl and aryl compounds of zinc and cadmium varies in parallel with the variation of the average dissociation energy of the metal–radical bond ($\bar{D}$), although the initial step in the decomposition of the MR_2 molecules is their dissociation into R$^{\cdot}$ and $^{\cdot}$MR with the activation energy equal to the dissociation energy D_1. The second stage of the radical initiation reaction $^{\cdot}MR \rightarrow M + R^{\cdot}$ involving different compounds proceeds at different rates, as described above for zinc dialkyls. The dissociation energies of individual bonds and the average bond dissociation energies are listed in Table 3, from which it follows that, for the same metal, the energy of the abstraction of the first radical D_1 is greater than the energy of the abstraction of the second radical D_2 and the average dissociation energy of the metal–radical bond diminishes as the radical becomes more complex. The latter energy diminishes on passing from organozinc to organocadmium compounds.

With increase of the atomic number of the metal in Group IIB, the kinetic stability of the metal alkyls and metal aryls decreases, the thermal stability of the latter

being higher than that of the former.[1] The thermodynamic stability of the above OMC varies in the same sequence. It is known from thermochemical investigations that the average dissociation energy of the M–C bond for the OMC of transition elements within a single Group in Mendeleev's Periodic Table decreases with increase of the atomic number of the element.[55] For each individual element, the values of $\bar{D}$ can then be arranged in the following sequence:

$$M—Me > M—Et \cong M - n\text{-}Pr \cong M - n\text{-}Bu.$$

According to Voevodskii's rule,[60] the kinetic stability of the OMC decreases with increase of the thermodynamic stability of the radical liberated in the homolytic cleavage of the metal–radical bond. The ethyl derivatives of each metal are therefore less stable than its methyl derivatives. The thermal stability of the zinc alkyls decreases when the methyl group is replaced by the ethyl group to a lesser extent than for cadmium derivatives.

Table 3. The bond dissociation energies and the average metal–radical bond dissociation energies in metal alkyls (kcal mol^{-1}).

D_1	D_2	$\bar{D}$	Refs.
	Dimethylzinc		
47.0±2.0	—	43.1±0.5	[56]
47.2	35.0	41.1	[28]
47.2±1.0	36.8±3.0	42.0±1.5	[57]
—	—	41.0	[58]
—	—	42.7±2.2	[55]
	Diethylzinc		
—	—	34.4	[58]
—	—	34.6±2.2	[55]
47.5	22.2	34.8	[31]
	Di-n-propylzinc		
—	—	37.8±5.1	[55]
	Di-n-butylzinc		
—	—	37.8±5.2	[55]
	Dimethylcadmium		
45.8±1.0	21.0	33.4	[29]
44.7±2.0	—	35.2±0.5	[56]
45.8±1.0	20.8±2.0	33.3±1.0	[57]
43.5±1.2	—	—	[59]
—	—	32.9	[58]
—	—	34.4±1.6	[55]
	Diethylcadmium		
—	—	26.5	[58]
—	—	26.4±1.6	[55]

The kinetic stability of organometallic compounds in the decomposition process can be estimated from the reaction rate constants measured under comparable conditions for the entire OMC reaction series. Depending on the decomposition conditions, the measured rate constant can be an effective quantity representing a combination of the rate constants for the elementary reactions or (for example, when the process is carried out in a stream of toluene) it is the true rate constant for the elementary stage limiting the rate of the overall decomposition. The rate-limiting stage is usually the elementary radical initiation reaction. Only in the latter case is the experimental rate constant for the elementary reaction in the free-radical non-chain process determined by the activation energy for this stage, since isotypical elementary reactions are then compared.[60]

However, there are no experimental data for such a comparison, because there have been no kinetic studies of the decomposition of series of compounds with successively altered structures. In certain cases the role of the steric effect can be significant.

The structure of the organometallic compound determines not only the dissociation energy of the metal–carbon bond but also the steric accessibility of the metal to possible attack in bimolecular collisions. It has been noted in a series of studies[61–63] that an increase of the degree of steric shielding of the metal atom in the OMC increases the kinetic stability of the latter. A method has been proposed[62,63] for the estimation of the degree of shielding of the reaction centre M in the OMC molecule by the organic group with the aid of the solid angles formed by the substituents at the metal on cylindrical projections of the OMC molecules. The degree of steric shielding of the reaction centre determines the effectiveness of the molecular collisions and can therefore serve as a criterion for the comparison of the contributions of the entropy term to the OMC decomposition rate constant. In order to eliminate the influence of electronic effects, the degree of shielding was estimated quantitatively and compared with experimental data for compounds with the same metal atom and with different substituents.[62,63] It was shown that the degree of steric shielding of the metal atom by the substituents is the dominant factor, which determines the kinetic stability of compounds of the type MR_n, where M = Hg or Cd.

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Thus it has been shown for lower zinc and cadmium alkyls and aryls that the mechanism of the thermal decomposition and photodecomposition varies with the decomposition conditions. At atmospheric and reduced pressures in a closed system and in a stream of the accompanying gas, the OMC investigated decompose via a free-radical mechanism, whilst under high vacuum conditions they decompose intramolecularly in an adsorption layer.

Although the general kinetic features of the thermal decomposition of the organozinc and organocadmium compounds as well as the kinetic and activation parameters of the radical initiation reaction in the homolytic cleavage of the first and second metal–carbon bonds have been established, systematic kinetic studies have not been made for an entire series embracing a large range of compounds with substituents of different lengths and with different degrees of branching. This limits to some extent the validity of the conclusions concerning the relation between the reactivity of the OMC considered, on the one hand, and their structure and the known thermodynamic characteristics of the dissociation of the given bond, on the other. The latter are represented in the literature only by the average metal–carbon bond dissociation energies and in certain cases the dissociation energies of specific ruptured bonds. On the other hand, there are so far no data on the average bond dissociation energies and enthalpies.

The causes of the self-inhibition of the decomposition of dimethylzinc have not so far been investigated. It is therefore important to study its decomposition under conditions which rule out self-inhibition. It is no less interesting to establish the order of the radical initiation reaction in the pyrolysis of diethylzinc in a closed system, which would help in determining the mechanism of the most difficult initial stage of the process investigated.

Complete quantitative analysis of the decomposition products for low degrees of reaction, which is essential for the determination of the detailed process mechanism and of

the role of the induced decomposition stage, has also not been carried out so far. Whereas the existence of the free-radical pathway to the decomposition of the zinc and cadmium OMC has been established unambiguously and gives rise to no doubts, additional studies are needed to solve the problem of the involvement of the intramolecular or intermolecular disproportionation reactions of the alkyl groups in the mechanism of the primary decomposition process.

REFERENCES

1. G.A.Razuvaev, B.G.Gribov, G.A.Domrachev, and B.A.Salamatin, "Metalloorganicheskie Soedineniya v Elektronike" (Organometallic Compounds in Electronics), Izd.Nauka, Moscow, 1972.
2. J.Boersma, J.Organomet.Chem., 1981, **207**, 1.
3. N.I.Sheverdina and K.A.Kocheshkov, "Metody Elementoorganicheskoi Khimii. Tsink, Kadmii" (Methods in Organoelemental Chemistry. Zinc and Cadmium), Izd.Nauka, Moscow, 1964, p.145.
4. J.H.Harwood, "Industrial Applications of the Organometallic Compounds: A Literature Survey" (Translated into Russian), Izd.Khimiya, Leningrad, 1970, p.56.
5. G.A.Razuvaev (Editor), "Osazhdenie Plenok i Pokrytii Razlozheniem Metalloorganicheskikh Soedinenii" (Deposition of Films and Coatings by the Deposition of Organometallic Compounds), Izd. Nauka, Moscow, 1981, p.214.
6. H.M.Manasevit and W.I.Simpson, J.Electrochem.Soc., 1969, **116**, 1725.
7. P.Blanconnier, M.Cerclet, and P.J.Henoc, Thin Solid Films, 1978, **55**, 375.
8. W.Stutius, Appl.Phys.Letters, 1978, **33**, 656.
9. P.I.Kuznetsov, L.A.Zhuravlev, I.N.Odin, V.V.Shemet, and A.V.Novoselova, Izv.Akad.Nauk SSSR, Ser.Neorg.Materialy, 1982, 18.
10. P.I.Kuznetsov, V.V.Shemet, I.N.Odin, and A.V.Novoselova, Dokl.Akad.Nauk SSSR, 1979, **248**, 879.
11. P.I.Kuznetsov, M.Safaev, V.V.Shemet, I.N.Odin, and A.V.Novoselova, Izv.Akad.Nauk SSSR, Ser. Neorg.Materialy, 1983, **19**, 875.
12. G.G.Devyatykh, G.A.Domrachev, B.V.Zhuk, B.S.Kaverin, A.I.Lazarev, V.K.Khamylov, and M.F.Churbanov, Dokl.Akad.Nauk SSSR, 1982, **266**, 1403.
13. B.V.Zhuk, V.K.Khamylov, B.S.Kaverin, and G.A.Domrachev, Poverkhnost', 1982(7), 112.
14. P.I.Kuznetsov, V.F.Dvoryankin, V.V.Shemet, I.N.Odin, A.P.Porotikov, and A.V.Novoselova, Dokl.Akad.Nauk SSSR, 1980, **252**, 115.
15. V.Ya.Egurnov, E.E.Grinberg, A.A.Efremov, and Yu.M.Fetisov, Elektron.Tekhnika.Ser.Materialy, 1978, **4**, 36.
16. T.S.Pochekutova, B.V.Zhuk, V.K.Khamylov, G.A.Domrachev, and N.M.Semenov, "Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov. Tezisy Dokladov IV Vsesoyuznogo Soveshchaniya" (Application of Organometallic Compounds in the Preparation of Inorganic Coatings and Materials. Abstracts of Reports at the IV All-Union Conference), Izd.Nauka, Moscow, 1983, p.132.
17. N.D.Grishnova, V.A.Krylov, A.N.Moiseev, Yu.M.Salganskii, and G.V.Sokolova, "Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov. Tezisy Dokladov IV Vsesoyuznogo Soveshchaniya" (Application of Organometallic Compounds in the Preparation of Inorganic Coatings and Materials. Abstracts of Reports at the IV All-Union Conference), Izd.Nauka, Moscow, 1983, p.137.
18. L.G.Novotorova, I.L.Agafonov, T.L.Spirina, and Z.K.Borisova, Symposium, "Khimiya Elementoorganicheskikh Soedinenii (Gor'k.Univ.)" [The Chemistry of Organoelemental Compounds (Gorky University)], 1982, p.95.
19. V.G.Kuleshov, B.V.Zhuk, and I.V.Lomakova, "Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov. Tezisy Dokladov IV Vsesoyuznogo Soveshchaniya" (Application of Organometallic Compounds in the Preparation of Inorganic Coatings and Materials. Abstracts of Reports at the IVth All-Union Conference), Izd.Nauka, Moscow, 1983, p.40.
20. K.C.Bass, Lab.Practice, 1965, **14**(1), 47.
21. K.C.Bass, Lab.Practice, 1965, **14**(2), 145.
22. G.A.Razuvaev, Symposium, "Trudy po Khimii i Khimicheskoi Tekhnologii (Gor'kii)" [Studies in Chemistry and Chemical Engineering (Gorky)], 1963, No.2, p.278.
23. N.S.Vyazankin and O.A.Kruglaya, "Trudy po Khimii i Khimicheskoi Tekhnologii (Gor'kii)" [Studies in Chemistry and Chemical Engineering (Gorky)], 1966, No.1, p.3.
24. S.F.Zhil'tsov and A.A.Lavrent'ev, "Trudy po Khimii i Khimicheskoi Tekhnologii (Gor'kii)" [Studies in Chemistry and Chemical Engineering (Gorky)], 1979, No.7, p.20.
25. R.Ganesan and L.M.Yeddanapalli, J.Madras.Univ., 1961, **B31**(2), 127.
26. A.K.Sokolovskii and A.K.Baev, Zhur.Obshch.Khim., 1984, **54**, 2559.
27. I.Lambert, J.Chim.phys.et phys.-chim.biol., 1965, **62**, 516.
28. A.N.Dunlop and S.J.W.Price, Canad.J.Chem., 1970, **48**, 3205.
29. S.J.W.Price and A.F.Trotman-Dickenson, Trans. Faraday Soc., 1957, **53**, 939.
30. W.J.Moore and H.S.Taylor, J.Chem.Phys., 1940, **8**, 396.
31. A.A.Koski, S.J.W.Price, and B.C.Trudel, Canad.J. Chem., 1976, **54**, 482.
32. L.M.Dyagileva, I.I.Didenkulova, E.I.Tsyganova, and Yu.A.Aleksandrov, Zhur.Obshch.Khim., 1984, **54**, 861.
33. L.M.Dyagileva, I.I.Didenkulova, E.I.Tsyganova, Yu.A.Aleksandrov, and R.F.Galiullina, "Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov. Tezisy Dokladov IV Vsesoyuznogo Soveshchaniya" (Application of Organometallic Compounds in the Preparation of Inorganic Coatings and Materials. Abstracts of Reports at the IVth All-Union Conference), Izd. Nauka, Moscow, 1983, p.43.
34. V.I.Faerman, I.L.Agafonov, L.M.Dyagileva, and Yu.A.Aleksandrov, "Primenenie Metallorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov. Tezisy Dokladov IV Vsesoyuznogo Soveshchaniya" (Application of Organometallic Compounds in the Preparation of Inorganic Coatings and Materials. Abstracts of Reports at the IVth All-Union Conference), Izd.Nauka, Moscow, 1983, p.44.

35. A.K.Baev and A.K.Sokolovskii, Zhur.Obshch.Khim., 1984, **54**, 103.
36. S.A.Lebedev, N.V.Kuznetsova, Yu.A.Aleksandrov, and V.E.Lelekov, Zhur.Obshch.Khim., 1979, **49**, 2263.
37. S.F.Zhil'tsov, G.A.Razuvaev, and A.V.Shabanov, "II Vsesoyuznaya Konferentsiya po Metalloorganicheskoi Khimii. Tezisy Dokladov" (The II All-Union Conference on Organometallic Chemistry. Abstracts of Reports), Gorky, 1982, p.39.
38. K.J.Laidler, "Kinetics of Organic Reactions" (Translated into Russian), Izd.Mir, Moscow, 1966, p.143.
39. G.A.Razuvaev, G.G.Petukhov, R.F.Galiullina, and T.N.Brevnova, Zhur.Obshch.Khim., 1961, **31**, 2348.
40. G.A.Razuvaev, R.F.Galiullina, G.G.Petukhov, and N.V.Likhovidova, Zhur.Obshch.Khim., 1963, **33**, 3358.
41. G.A.Razuvaev, G.G.Petukhov, R.F.Galiullina, and N.N.Shabanova, Zhur.Obshch.Khim., 1964, **34**, 3812.
42. R.F.Galiullina, O.N.Druzhkov, G.G.Petukhov, and G.A.Razuvaev, Zhur.Obshch.Khim., 1965, **35**, 1164.
43. R.F.Galiullina, N.N.Shabanova, and G.G.Petukhov, Zhur.Obshch.Khim., 1966, **36**, 1920.
44. G.A.Razuvaev, R.F.Galiullina, and G.G.Petukhov, Zhur.Obshch.Khim., 1968, **38**, 3.
45. R.F.Galiullina, Abstract of Candidate's Thesis in Chemical Sciences, Gorky State University, Gorky, 1968, 17 pp.
46. G.G.Petukhov, R.F.Galiullina, Yu.N.Krasnov, and B.S.Kaverin, Symposium, "Trudy po Khimii i Khimicheskoi Tekhnologii (Gor'kii)" [Studies in Chemistry and Chemical Engineering (Gorky)], 1963, No.2, p.113.
47. R.F.Galiullina, Yu.N.Krasnov, G.G.Petukhov, B.S.Kaverin, and L.M.Dyagileva, "Vsesoyuznoe Soveshchanie 'Metalloorganicheskie Soedineniya dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii'. Tezisy Dokladov" (All-Union Conference on 'Organometallic Compounds for the Preparation of Metallic and Oxide Coatings'. Abstracts of Reports), Gorky, 1974, p.47.
48. C.A.Heller and H.A.Taylor, J.Phys.Chem., 1953, **57**, 226.
49. C.M.Laurie and L.H.Long, Trans.Faraday Soc., 1957, **53**, 1431.
50. M.Krech and S.J.W.Price, Canad.J.Chem., 1965, **43**, 1929.
51. R.D.Anderson and H.A.Taylor, J.Phys.Chem., 1952, **56**, 498.
52. L.M.Dyagileva, A.K.Kazhaeva, Yu.A.Aleksandrov, and B.F.Surin, Symposium, "Trudy po Khimii i Khimicheskoi Tekhnologii (Gor'kii)" [Studies in Chemistry and Chemical Engineering (Gorky)], 1973, No.2, p.144.
53. G.A.Razuvaev, V.N.Pankratova, and A.M.Bobrova, Zhur.Obshch.Khim., 1968, **38**, 1723.
54. G.A.Razuvaev and V.N.Pankratova, Zhur.Obshch. Khim., 1966, **36**, 1702.
55. V.I.Tel'noi, Symposium, "Trudy po Khimii i Khimicheskoi Tekhnologii (Gor'kii)" [Studies in Chemistry and Chemical Engineering (Gorky)], 1974, No.1, p.28.
56. G.Distefano and V.H.Dibeler, Int.J.Mass Spectrom. and Ion Phys., 1970, **4**, 59.
57. H.A.Skinner, "Advances in Organometallic Chemistry" (Edited by F.Stone), New York–London, 1964, Vol.2, p.360.
58. A.S.Carson, K.Hartley, and H.A.Skinner, Trans. Faraday Soc., 1949, **45**, 1159.
59. V.I.Vedeneev, L.V.Gurvich, V.N.Kondrat'ev, V.A.Medvedev, and E.L.Frankevich, Handbook, "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu" (Chemical Bond Dissociation Energies, Ionisation Potentials, and Electron Affinities), Izd.Akad.Nauk SSSR, Moscow, 1962, p.30.
60. V.V.Voevodskii, "Fizika i Khimiya Elementarnykh Khimicheskikh Protsessov" (The Physics and Chemistry of Elementary Chemical Processes), Izd.Nauka, Moscow, 1969, p.57.
61. G.A.Domrachev, L.N.Zakharov, and Yu.A.Shevelev, Uspekhi Khim., 1985, **54**, 1260 [Russ.Chem.Rev., 1985(8)].
62. L.N.Zakharov and G.A.Domrachev, "III Vsesoyuznoe Soveshchanie po Primeneniyu Metalloorganicheskikh Soedinenii dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii. Tezisy Dokladov" (The III All-Union Conference on the Application of Organometallic Compounds in the Preparation of Metallic and Oxide Coatings. Abstracts of Reports), Gorky, 1980, p.12.
63. L.N.Zhakharov, G.A.Domrachev, and Yu.T.Struchkov, Zhur.Strukt.Khim., 1983, **24**(3), 75.

Institute of Chemistry at the
Gorky State University