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The Kinetic Stability of Biscyclopentadienyl and Diarene Compounds of Transition Metals in the Thermal Decomposition Reaction

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Literature data on the kinetic stability of mononuclear metallocene and diarene derivatives of transition metals are described systematically and discussed. A relation between the reactivity of the π-complexes in the thermal decomposition reaction and their structure (the nature of the central metal atom, the σ-substituent, and the π-ligand) has been discovered, surface effects and the role of the adsorption of organometallic compounds in pyrolysis are examined, and problems of macrokinetics are discussed.
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I. INTRODUCTION

The study of the thermal stability of organometallic compounds (OMC) is of great theoretical and practical interest. The kinetic stability of mononuclear metallocene and diarene derivatives of metals is, together with their volatility, the fundamental characteristic determining the possibility of their practical use for the preparation of solid fuels,[1] various coatings,[2,3] and catalysts of many chemical processes.[4,5] Furthermore, a systematic analysis of the relevant literature data has not so far been carried out; in the present review, such an attempt is made for the first time.

Four aspects of the stability of OMC in synthesis–decomposition processes have been distinguished.[2,3] They embrace the molecular and electronic structure of organometallic compounds, their state of aggregation, their dynamics, and their interaction with energy and mass fluxes: the stability of an isolated molecule and of the decomposition products (quantum-chemical aspect), the stability of the sum of the molecules in equilibrium with their decomposition products (thermodynamic aspect), the rate of change in the equilibrium of the sum of the molecules (the kinetic aspect), and the phenomenon of mass and heat transfer in assemblies of molecules (macrokinetic aspect).

The quantum-chemical aspects of the stability of the molecules of certain π-complexes of metals[2,3,6-9] as well as the thermodynamic stability of metallocene and diarene derivatives of metals[2,3,10-17] have been described in the literature. An account has been given of the ideas concerning the stability of OMC in the synthesis–decomposition processes.[18]

The present review describes systematically, and surveys, experimental data on the kinetic and macrokinetic stability of mononuclear metallocene and diarene derivatives of transition metals in the thermal decomposition reaction. Questions concerning the reactivity of the OMC and its relation with the structure (the nature of the metal and ligand), the mechanism of the decomposition process, surface effects, adsorption, and the spatial localisation of the reaction are examined. In connection with the macrokinetic studies, the thermal decomposition reaction is considered taking into acount the heat and mass exchange. The kinetic parameters of the thermal decomposition of the OMC referring to the overall process are analysed and described systematically. These data have been analysed under comparable conditions. The review does not include any data on the deposition of metallic, oxide, and composite coatings obtained by the pyrolysis of OMC by the gas-thermal method, which have already been described systematically in the specialist literature[19,20] and in reviews[21,22] and also data on the photochemical decomposition of metallocenes.[23]

II. KINETICS OF THE THERMAL DECOMPOSITION OF THE π-COMPLEXES OF TRANSITION METALS

1. The Role of the Nature of the Central Metal Atom

The systematic study of the kinetics of the gas-phase decomposition of metallocenes began two decades ago with the investigation of the thermal stability of ferrocene and its substituted derivatives.[24,25] The kinetic study of the thermal decomposition of π-complexes has been carried out under static conditions by the manometric method and under dynamic conditions by a gas-chromatographic pulse method.[26] The apparent rate constants for the overall reaction, calculated for low degrees of decomposition where the influence of the products formed can be neglected, were used as a measure of the reactivity. The kinetic parameters were compared under comparable conditions in the temperature range where the kinetic regime operates.

The pyrolysis of ferrocene,[25] ruthenocene, and osmocene[27] is strikingly autocatalytic, the metal-containing solid phase serving as the catalyst. It has been established that, in vessels treated with pyrolytic iron, the kinetic stability of metallocenes of the iron subgroup increases with increase in the average dissociation energy of the ring–metal bond in the sequence ferrocene < ruthenocene < osmocene.[28]

In contrast to the iron-subgroup metallocenes, the pyrolysis of vanadocene,[29] chromocene,[30] manganocene,[30] cobaltocene,[31] and nickelocene[32] is described satisfactorily by first-order kinetic equations.

The nature of the central metal atom determines the kinetic stability of the mononuclear metallocenes[33,34] (Table 1).

Among metallocenes of the series of 3*d* metals, ferrocene, being an 18-electron complex,[2] exhibits the highest kinetic stability. The π-complexes of metals located to the left and to the right of iron in the Periodic Table are characterised respectively by a deficiency or

an excess of electrons at the central metal atom compared with ferrocene[7-9] and are less stable (Table 2).

Table 1. Kinetic parameters of the pyrolysis of the metallocenes Cp_2M (Cp = cyclopentadienyl) under static conditions*.[33,34]

t, °C	Cp_2V		Cp_2Cr		Cp_2Mn		Cp_2Co		Cp_2Ni	
	p_0, mmHg	$10^3 k$, s^{-1}	p_0, mmHg	$10^3 k$, s^{-1}	p_0, mmHg	$10^3 k$, s^{-1}	p_0, mmHg	$10^3 k$, s^{-1}	p_0, mmHg	$10^3 k$, s^{-1}
550	51	1.03	60	3.80	—	—	—	—	—	—
540	81	0.69	—	—	—	—	—	—	—	—
520	38—180	0.31	45—78	2.10	—	—	—	—	—	—
500	59	0.14	36—196	1.34	175	7.20	117	3.30	—	—
480	—	—	105	0.85	261	4.40	130	2.15	—	—
470	—	—	—	—	—	—	71	1.70	—	—
460	—	—	94	0.48	139	2.50	—	—	—	—
450	—	—	—	—	—	—	45—280	1.17	—	—
440	—	—	—	—	92	1.30	—	—	—	—
420	—	—	—	—	103	0.84	—	—	151	5.78
380	—	—	—	—	—	—	—	—	150	2.36
360	—	—	—	—	—	—	—	—	120—200	1.55
350	—	—	—	—	—	—	—	—	149	1.00
340	—	—	—	—	—	—	—	—	151	0.76

*The activation energy (E, kcal mol^{-1}) and the pre-exponential factor [lg $A(s^{-1})$] are respectively 50.5 ±0.66 and 10.41 ±0.18 for Cp_2V, 27.3 ± 0.8 and 4.87 ± 0.23 for Cp_2Cr, 29.3 ± 1.2 and 6.61 ± 0.35 for Cp_2Mn, 23.1 ± 1.0 and 4.04 ± 0.31 for Cp_2Co, and 21.4 ± 0.2 and 4.52 ± 0.37 for Cp_2Ni.

Table 2. Thermodynamic parameters and comparative kinetic stabilities of metallocenes in their decomposition in a glass reactor under static conditions (at 500 °C).[16,17,33]

Compound	$\bar{D}$(M-Cp), kcal mol^{-1}	ΔS(M-Cp), cal mol^{-1} K^{-1}	ΔG(M-Cp), kcal mol^{-1}	r (M—C), Å	$10^3 k$, s^{-1}
Cp_2V	88	47	74	2.280	0.14
Cp_2Cr	67	40	55	2.169	1.34
Cp_2Mn	51	35	40	2.383	7.20
Cp_2Fe	72	41	60	2.064	0.01
Cp_2Co	64	41	52	2.119	3.30
Cp_2Ni	60	37	49	2.196	29.50
Cp_2Fe *	72	41	60	2.064	11.8
Cp_2Ru *	99	—	—	2.208	1.90
Cp_2Os *	109	—	—	2.220	0.77

*The walls of the glass reactor were coated by the solid products of the pyrolysis of ferrocene.

For the electron-deficient complexes of 3*d* metals (vanadocene > chromocene > manganocene), the thermodynamic characteristics of the dissociation of the ring—metal atom bond (the average Gibbs free energy $\Delta\bar{G}$ and the average dissociation energy $\bar{D}$) and the kinetic stability vary in parallel. The contribution of the entropy change $\Delta\bar{S}$ to $\Delta\bar{G}$ is insignificant.[16] For the complexes of the metals in the iron triad, the decrease in thermal stability in the sequence ferrocene > cobaltocene > nickelocene is correlated with the decrease in the average dissociation energy in the above bond and with the population of the antibonding orbitals of the metallocene. In ferrocene, these orbitals are unoccupied, in cobaltocene they contain one electron, and in nickelocene they contain two electrons.[7]

Thus a monotonic variation of the kinetic stability of the metallocenes in the 3*d* series has not been observed:

$$Cp_2V > Cp_2Cr > Cp_2Mn \ll Cp_2Fe \gg Cp_2Co > Cp_2Ni.$$

In the Group VIII of the Periodic System, the kinetic stability of the metallocenes of the iron subgroup increases with increase in the atomic number of the metal.

The kinetic stability of the metallocene is not correlated with characteristics of the electronic structure such as the negative charge on the metal atom, the M—C bond indices,[9] and the number of unpaired electrons[8] and also no correlation is observed with the molecular structure (the M—C bond length[8]) and with the so called "decomposition temperature" which has no definite physical significance.[28,35]

The thermal stability of the diarene complexes of chromium, molybdenum, and vanadium increases with increase in the average dissociation energy of the six-membered ring—metal atom bond[36-38] (Table 3).

Table 3. Kinetic parameters of the gas-phase pyrolysis of diarene complexes of chromium, molybdenum, and vanadium.[36—38]

Compound	t, °C	E, kcal mol^{-1}	lg A (s^{-1})	$10^3 k$, s^{-1} (380 °C)
Dibenzenechromium	340—400	23.5±0.5	—	1.55
Di(ethylbenzene)chromium	320—400	25.0±1.0	5.7±0.4	2.26
(Ethylbenzene)(diethylbenzene)chromium	320—380	41.0±0.5	11.2±0.23	2.95
Di(ethylbenzene)molybdenum	340—400	42.1±0.6	10.9±0.2	0.69
Di(diethylbenzene)molybdenum	340—380	31.9±2.1	7.7±0.7	0.90
(Ethylbenzene)(diethylbenzene)molybdenum	340—400	36.9±1.4	9.4±0.5	0.93
Di(ethylbenzene)vanadium	360—480	22.3±0.5	3.8±0.4	0.22

The kinetic stability of the diarene derivatives of metals corresponds to the average dissociation energy, found by the thermochemical method, of the bond between the metal atom and the six-membered ring, which diminishes along the first series of transition elements and increases along the Group with increase in the atomic number of the transition metal.[12,13]

2. The Influence of the Substituent in Cyclic π-Ligands

The nature of the substituents in aromatic rings influences the kinetic stability of metallocene[25,35,39,40] and diarene derivatives of metals[37,38,41] (Tables 3 and 4). The activity of ferrocenes is attributed to the polar influence of the substituents and also to the stability of the radical formed on homolysis of the cyclopentadienyl ring—substituent bond. The influence of electron-donating alkyl substituents on the reactivity of the ferrocene nucleus is inductive in character, like the transfer of this influence via the iron atom to the other ring.[25] Little is known about the character of the influence of electron-accepting substituents on the thermal stability.

Under both static and dynamic conditions, the thermal stability of ferrocene increases with increase in the thermodynamic stability of the groups formed when the side chain is split off homolytically. The accumulation of t-butyl groups in the ferrocene nucleus increases the thermal decomposition rate constant to a much greater extent than the replacement of one alkyl group by another. This effect is especially pronounced on passing from heteroannular tri-t-butyl- and tetra-t-butyl-ferrocenes, in which the t-butyl groups are in different cyclopentadienyl rings of the ferrocene nucleus. Thus substitution of two hydrogen atoms by t-butyl groups in one cyclopentadiene ring of ferrocene increases the rate constant by a factor of 15, while the introduction of a further two t-butyl groups in the other ring increases the rate constant by a factor of 300. A similar relation can be traced also for ferrocenes with electron-accepting substituents. Evidently steric effects also play a decisive role in the kinetic stability of polysubstituted ferrocenes.

Analysis of data obtained shows that both electron-donating (alkyls) and electron-accepting (acetyl) substituents accelerate the decomposition of ferrocene. Here the introduction of one electron-accepting group lowers the thermal stability of ferrocene to a much greater extent than the introduction of any electron-donating group. Heteroannular polysubstituted ferrocenes with electron-accepting substituents are thermally the most stable. The introduction of an alkyl substituent into the cyclopentadienyl ring of nickelocene influences the reactivity to a lesser extent than in the case of ferrocene, the rate constant for the thermal decomposition of substituted nickelocene increasing by less than a factor of two.

The kinetic stability of the bisarene derivatives of chromium and molybdenum investigated hardly changes in the thermal decomposition reaction on passing from the diethyl to the triethyl and tetraethyl derivatives. This agrees well with the conclusion[13] that the influence of the alkyl substituent in the benzene ring of bisarene derivatives of metals on the average dissociation energy of the metal atom–ring bond is within the limits of experimental error.

Table 4. The influence of the substitutent on the rate of pyrolysis of metallocenes in closed and open systems.[34,36-38]

Compound	t, °C	$10^3\,k$, s^{-1}	V^*_{rel}
Closed system			
Ferrocene	550	0.01	1
Ethylferrocene	550	0.05	5
Butylferrocene	560	0.11	—
"	550	0.07	7
Di-t-butylferrocene	560	0.16	—
"	550	0.15	15
1,1',3-Tri-t-butylferrocene	550	2.00	200
"	510	0.34	—
"	450	0.03	—
1,1',3,3'-Tetra-t-butylferrocene	550	3.02	300
"	500	0.32	—
"	480	0.12	—
Acetylferrocene	560	1.40	—
"	550	1.00	100
"	530	0.52	—
1,1'-Diacetylferrocene	550	4.47	447
"	520	1.50	—
"	500	0.67	—
Nickelocene	380	2.36	—
"	360	1.60	—
Diisopropylnickelocene	380	3.50	—
"	360	2.11	—
Open system			
Ethylferrocene	500	66	—
"	450	9	1
Diethylferrocene	500	79	—
"	450	18	2
t-Butylferrocene	500	97	—
"	450	36	4

* V_{rel} is the ratio of the [pyrolysis?] rate constant to the rate constant for the decomposition of ferrocene at 550 °C.

3. The Influence of the Nature of the Cyclic π-Ligand

The reactivity of π-complexes of chromium is determined by the character of the ring linked to the metal atom. A comparative study has been made[42] of the kinetics of the thermal decomposition of the π-complexes of chromium with six-membered and five-membered cyclic π-ligands. It was shown that dibenzenechromium is less stable than chromocene. Thus dibenzenechromium and chromocene decompose at almost equal rates at 360° and 460 °C respectively (the rate constants are 0.35×10^{-3} and 0.48×10^{-3} s^{-1} respectively). It is known[16] that not only the average dissociation energy but also other thermodynamic characteristics of the metal–ligand bond dissociation ($\Delta\bar{G}$ and $\Delta\bar{S}$) diminish on passing from $(C_5H_5)_2Cr$ to $(C_6H_6)_2Cr$, the contribution of $\Delta\bar{S}$ to $\Delta\bar{G}$ being insignificant. Furthermore, these compounds decompose via different pathways: the radical pathway for $(C_2H_5)_2Cr$ and the molecular pathway for $(C_6H_6)_2Cr$. The latter pathway leads to the formation of chromium in an active state and to the autocatalytic acceleration of the decomposition of dibenzenechromium.

III. SURFACE REACTIONS IN THE PYROLYSIS OF ORGANOMETALLIC COMPOUNDS

1. The Spatial Localisation of the Reaction

Features characteristic of a homogeneous-heterogeneous process have been observed in the study of the pyrolysis of metallocenes[43] and bisarene derivatives of metals.[44] The rate of thermal decomposition of metallocenes of the iron triad (especially ferrocene and its alkyl derivatives) depends greatly on non-controllable changes in the state of the walls of the glass reaction vessel.

The metal-containing products of the pyrolysis of metallocenes exhibit an autocatalytic activity. The autocatalytic character of the decomposition of the iron subgroup metallocenes was noted above.[32,35] The rate constant for the pyrolysis of ferrocene on its own decomposition products is higher by three orders of magnitude than in clean glass vessels.[25]

The catalytic activity of the metal-containing solid phase segregated in the pyrolysis of metallocenes depends on the nature of the central metal atom. Pyrolytic osmium accelerates the thermal decomposition of osmocene to a greater extent than pyrolytic ruthenium accelerates the decomposition of ruthenocene, while pyrolytic iron is more active in the decomposition reaction of ferrocene than is osmium in the decomposition of osmocene. The catalytic activity of the pyrolytic metals in relation to the decomposition of ferrocene falls in the sequence osmium > iron > ruthenium.[27]

The solid products of the pyrolysis of vanadocene, chromocene, manganocene, cobaltocene, and nickelocene are less active and their catalytic effect is small and disappears during the experiment as a result of adsorption of cyclopentadiene on the active centres produced in the reaction. The absence of the autocatalytic acceleration in the thermal decomposition of the cyclopentadienyl derivatives of vanadium, chromium, manganese, cobalt, and nickel in clean glass vessels can be accounted for precisely by the decrease in the catalytic activity of the surface during the experiment.[34]

It has been shown[43] that, under static conditions, the heterogeneous decomposition of metallocenes on solid metal-containing products does not occur and the role of the heterogeneous processes reduces to initiating the gas-phase reaction, developing subsequently within the volume of the reactor. An analogous investigation of the surface effect in the pyrolysis of bisarene derivatives of metals[44] has demonstrated an appreciable dependence of the rate of reaction on both the nature and the area of the surface.

Coatings obtained by the pyrolysis of ditoluenechromium iodide, ferrocene, and carbonylruthenium chloride are the most active, accelerating the decomposition of the bisarene derivatives of chromium, molybdenum, vanadium by a factor of 30–50. The solid products of the pyrolysis of the diarene derivatives themselves and the nickel–carbon coating obtained by the decomposition of diisopropylnickelocene are less active coatings, accelerating the decomposition by a factor of only 3–5.

The rate of decomposition of the diarene derivatives of metals, except dibenzenechromium, depends to a large extent on the surface

area of the reaction vessel (Table 5). The effective rate constant for the decomposition of (ethylbenzene) (diethylbenzene)-chromium increases linearly with increase in the ratio of the surface area of the reactor to its volume.[37,44,45] The contribution of the homogeneous component to the overall process increases with increase in temperature and with decrease in the surface to volume ratio, while the contribution of the heterogeneous component actually falls under these conditions. The purely heterogeneous course of the process and a decrease in the kinetic stability of the diarene derivatives of metals have been observed when the thermal decomposition was carried out in a high vacuum.[45]

Table 5. The influence of the surface area on the rate constants for the pyrolysis of diarene complexes of metals in glass vessels.[37,44,45]

Compound	t, °C	S/v, cm^{-1}	$10^3 k$, s^{-1}
Dibenzenechromium	380	1.5	1.55
	380	18.0	1.55
	380	18.0*	1.55
Di(ethylbenzene)chromium	360	1.8	1.06
	360	2.5	2.65
	380	1.8	2.26
	380	2.5	4.40
(Ethylbenzene)(diethylbenzene)chromium	320	1.8	0.12
	320	2.5	0.32
	320	6.8	1.53
	320	8.5	2.61
	320	11.5	3.50
	320	25.0	8.20
Di(ethylbenzene)molybdenum (mixture of isomers and homologues)	340	1.5	0.10
	340	12.8	3.30
	380	1.5	0.69
	380	12.8	5.10
(Ethylbenzene)(diethylbenzene)molybdenum	340	1.8	0.16
	340	8.0	7.10
	380	1.8	0.98
	380	8.0	7.10
Di(ethylbenzene)molybdenum	360	1.8	0.50
	360	7.2	1.50
	360	9.0	6.70
Di(ethylbenzene)vanadium (mixture of isomers and homologues)	450	1.5	1.10
	450	12.8	1.22

* "Packing" coated with pyrolytic chromium.

The kinetics of the heterogeneous thermal decomposition reaction of the diarenechromium π-complexes have been investigated in a stream of carrier gas[46,47] and also in closed and circulation systems.[48] In the kinetic region (305–350 °C), the order of the reaction changes from first to zero with increase in the OMC concentration, while in the diffusion region (360–600 °C) the reaction is first order. From the kinetic data presented,[48] one may conclude that the reactivity of the diarenechromium complexes changes little on passing from dibenzenechromium to its ethyl derivatives.

Thus the localisation of the reaction in space is determined by the experimental conditions on which depends the purely homogeneous, heterogeneous, or homogeneous-heterogeneous course of the process. Such conditions include the initial pressure and the concentration of the initial diarene derivatives of the metal,[45,48,49] the heterogeneous factor S/V (the ratio of the internal surface area of the reactor to its volume),[44,45] and the nature of the surface and the methods used to produce it.[44]

For the thermal decomposition of the diarene derivatives of chromium, molybdenum, and vanadium at the metal–ligand bond in a reactor of limited size with walls exhibiting a catalytic activity, a kinetic model has been proposed in which it is suggested that the reaction proceeds via a unimolecular mechanism complicated by phenomena involving the association of the OMC molecules or the formation of their complexes with the molecules of catalytic additives.[51] This model makes it possible to explain the experimentally observed dependence of the effective rate constant for the process on the initial pressure, the S/V ratio, the chemical activity of the surface of the reactor, and the degree of complex formation with the molecules of the catalytic additives.[52]

2. Adsorption Effects in Thermolysis

The high adsorption capacity of the OMC is widely known.[3,53] The adsorption of organometallic compounds and their decomposition products is one of the stages of the heterogeneous process influencing the rate and mechanism of the decomposition.

Two forms of adsorption have been observed by direct IR spectroscopic studies of the adsorption complexes of OMC[54-56] on surfaces modified by pyrolytic chromium: physical adsorption resulting from the ligand–surface interaction, chemical adsorption which is a consequence of the formation of a metal–surface or CO–surface (for OMC with carbonyl ligands) bond. On chemisorption, ferrocene forms charge-transfer complexes in the form of ferricenium[53,56] and ferrocenonium[56] cations.

A mechanism has been proposed for the catalytic decomposition of 1,1'-diethylferrocene on alumina involving its adsorption on the active surface centres with formation of the alkylferrocenium cation and its subsequent decomposition in the adsorbed state with segregation of an iron-containing solid phase having a polymeric structure.[57] The formation of σ- and π-complexes of cyclopentadiene following its adsorption on Group VIII metals has been observed spectroscopically.[58] The strong specific interaction of the surface chromium atoms, obtained by the decomposition of diarenechromium, with the six-membered rings of the substituted benzenes involving the formation of π-complexes has been demonstrated by gas chromatography.[59]

The influence of the adsorption of the OMC and of their decomposition products in the absence and presence of various additives on the rate of deposition and the properties of the resulting coating have been described in a number of studies.[60-64] The character of the intermolecular interaction of alkylferrocenes and (ethylbenzene) (diethylbenzene)chromium with the metallated and non-metallated surfaces under conditions approaching those in the thermal decomposition has been studied.[65] At temperatures above 200 °C on surfaces metallated by pyrolytic chromium, the contribution of the specific interaction of the diarenechromium molecules with the surface, leading to chemisorption, increases. Thus the isosteric heat of adsorption of (ethylbenzene) (diethylbenzene)-chromium on pyrolytic chromium at low degrees of coverages reaches 46 kcal mol^{-1}, while after the attainment of 20% coverage it falls to the limiting value of 27.5 kcal mol^{-1}. On the other hand, after its adsorption on quartz only non-specific adsorbate—adsorbent interactions (the isosteric heat of adsorption at 10% coverage is 1 kcal mol^{-1}) or weak interactions of the adsorbed diarenechromium molecules with one another (the isosteric heat of adsorption at a coverage above 10% is 5 kcal mol^{-1}) were observed. The following series based on the adsorption capacity of the compounds has been obtained from the heats of adsorption: (ethylbenzene) (diethylbenzene)chromium > ethylferrocene > ethylbenzene > benzene.[65]

Comparison of the adsorption capacities of ethyl- and butylferrocenes on quartz, pyrolytic iron, and chromium showed that the isosteric heats of adsorption at high coverages (starting from 20%) are similar (13.0 ± 0.5 kcal mol^{-1}), which is characteristic of physical adsorption.[65] Only at low coverages (5–10%) are strong specific interactions manifested between ethylferrocene (19.5 kcal mol^{-1}) and the most active centres on the surface metallated by pyrolytic iron, probably occurring with formation of charge-transfer adsorption complexes.

IV. MACROKINETICS OF THE THERMAL DECOMPOSITION

The study of the macrokinetics of the thermal decomposition of OMC has been undertaken in view of the practical interest in such compounds as sources of metallic and composite coatings.

In the decomposition of diarenechromium on a support in an open system at a constant rate of evacuation, the phenomenon of "peak" (maximum) rate of deposition of the coating, due to the change in the partial pressure of the OMC near the support owing to the increase in the concentration (pressure) of the volatile products liberted, has been observed.[3,6] The causes of the decrease in the rate of deposition are also the endothermicity of the thermal decomposition process and the decrease in the temperature of the support.[66-69]

There exist two types of conditions for the deposition of coatings from the vapour phase in the thermal decomposition of OMC[3,6,69-71]—monotonic and vibrational (including the conditions in a closed system)—which have been revealed by the changes in the pressure, the temperature of the support, and the rate of deposition of the coating. The vibrational phenomena and the causes of their appearance have been examined in detail.[3] The vibrational conditions lead to the appearance of a layered structure of the film with alternation of layers of the metal or metal carbide with different contents of carbon-containing products.

The kinetics of the growth of the layer of pyrolytic chromium in the decomposition of diarenechromium derivatives in a stream of an inert gas have been investigated[41] taking into account heat and mass exchange. The rate of growth was calculated with the aid of the model proposed by Patankar and Spalding[72] and Popov and Rabinovich[73] using the rate constants for the decomposition of the diarene derivatives of chromium in a stream of helium.[41] With increase in temperature in the deposition zone from 350° to 500 °C, the rate of growth of the chromium layer also increases, but the non-uniformity of the distribution along the length of the channel diminishes (the deviation from the uniform distribution increases from 2.6% to 36% respectively). With increase in the concentration of the diarene derivatives of chromium, the rate of growth also increases and the uniformity of the growing layer is improved. On the other hand, an increase in the flow rate of the gas mixture diminishes the rate of growth of chromium but the uniformity of its distribution along the length of the channel also improves. In order to attain high rates of growth of the coating, it is necessary to raise the concentration of the OMC introduced at a temperature in the deposition zone in the range 350°–400 °C and for the optimum flow rate of the gas mixture.

The influence of various factors (channel temperature, flow rate of gas mixture, concentration of the initial substance) on the distribution of the solid products of the pyrolysis of ethylferrocene along the length of the channel has been investigated analogously and the rates of growth of the layer of the iron-cross-linked polymer on the surface have been determined.[40] With increase in the pyrolysis temperature from 400° to 550 °C, an increase in the rate of growth and a decrease in the uniformity of the growing layer along the length of the channel are observed. An increase in the concentration of the ethylferrocene introduced leads to an increase in the rate of growth virtually without change in the uniformity of the growing layer along the deposition zone. An increase in flow rate of the gas mixture tends to decrease the rate of growth of the layer but improves significantly its uniformity (at flow rates of 1 and 3 litre min^{-2}, the deviation from uniformity at 400 °C is 8.4 and 0.1% respectively). The highest rate of growth of the coating combined with the best uniformity of the distribution is attained at 500 °C and for a flow rate of the gas mixture of 2 litre min^{-1}. These conclusions apply only to the given specific dimensions of the reactor, gas flow conditions, and the composition of the gas mixture.

V. THE MECHANISM OF PYROLYSIS

1. Thermal Decomposition Products and Pathways

The thermal decomposition of the π-complexes of transition metals is accompanied by the homopolar dissociation of the metal–ligand bond with formation of the metal and radicals or the metal and ligand molecules.[2,3] OMC whose ligands have an odd number of bonding electrons decompose via the radical pathway, while those having an even number of such electrons decompose via the molecular pathway.[64] The pyrolysis is usually a multistage process, the ease of the occurrence of which and the pathway followed are determined by the nature of the OMC, the metal–ligand bond dissociation energy, the ratios of this energy to the C–C and C–H bond dissociation energies in the ligand, the polarity of the metal–ligand bond,[2,3,6] and also the degree of shielding of the central metal atom by the ligands, i.e. by steric effects.[74]

A free radical mechanism, involving the homolytic cleavage of the metal–ligand bonds and the C–C and C–H bonds in the ligand, is usually proposed for the decomposition of the mononuclear cyclopentadienyl compounds of transition metals.

The main product of the non-extensive gas-phase pyrolysis of ferrocene is hydrogen, methane and carbon monoxide are formed from acetylferrocene, and ethane is formed from ethylferrocene. This agrees with the hypothesis that a hydrogen atom is initially abstracted from the ferrocene nucleus in the unsubstituted ferrocene and that the side chain (CH_3CO and C_2H_5) is split off from the cyclopentadienyl ring in the substituted ferrocenes.[25] The dependence of the yield of the main pyrolysis products of ferrocenes on the nature of the surface and on its area and also on the added inhibitors shows that the heterogeneous stages of the free-radical mechanism of the decomposition reaction are both the generation and destruction of the radicals.

The thermal decomposition of ferrocene in the condensed phase at relatively low temperatures is accompanied by the dissociation of the C–H bonds with formation of the pyrolysis product—biferrocenyl.[75] The same mechanism of the decomposition reaction—not at the metal—ligand bond but at the C–C and C–H bonds—has been proposed also for the decomposition of alkylferrocenes by electron impact.[76] At high temperatures, in the pyrolysis of ferrocene above 800 °C, the cleavage of the ring–metal atom bond is observed with formation of the cyclopentadienyl radical, which has been detected spectroscopically.[77] Indeed, cyclopentadiene has been found together with methane and ethylene in the products of the pyrolysis of ferrocene above 600 °C.[28]

The pyrolysis products of ruthenocene and osmocene have not been investigated. Only the existence of the dimeric forms of ruthenocene and osmocene in the gas phase has been established.[78] The main gaseous products of the pyrolysis of other metallocenes for low degrees of decomposition are cyclopentadiene, hydrogen, and methane.[33] The composition of the volatile products depends on the temperature and the degree of decomposition.

Apart from cyclopentadiene, naphthalene, and nickel, 9,10-dihydrofulvalene, which is the product of the recombination of the cyclopentadienyl radicals, has been found among the products of the pyrolysis of nickelocene[79] *in vacuo* under pulse conditions at 950 °C. The cyclopentadienyl dimer has also been detected[28] in the decomposition of cyclopentadienylcarbonylman- ganese. The main products of the decomposition of nickelocene in a stream of hydrogen[80] were cyclopentadiene, cyclopentene, and cyclopentane. The purity of the nickel segregated was 83–93%.

It has been suggested that the pyrolysis of metallocenes involves the abstraction of hydrogen from the cyclopentadienyl ring and the subsequent polyrecombination of the metal-containing radical. The metal-containing radicals formed are also capable of being dehydrogenated and of undergoing subsequent condensation, affording ultimately carbide-like structures.[2,32]

Apart from the metal-containing phases, substances have been detected in the pyrolysis products which appear as a result of the condensation of five-membered rings (ranging from the cyclopentadiene dimer to the pentamer) and also naphthalene, anthracene, phenanthrene, pyrene, and perylene.[32] Volatile products containing metal–carbon phases, tentatively assumed to be polymeric in nature, are also formed.[25,57]

The main reactions leading to the decomposition of unsubstituted metallocenes involve the cleavage of the ring–metal atom bond and the dehydrogenation of the metallocene, the contribution of the dehydrogenation reaction increasing in the sequences Cp_2Ni < Cp_2Co < Cp_2Fe and Cp_2Mn < Cp_2Cr < Cp_2V. The decrease in the contribution by the dehydrogenation reaction takes place in parallel with the decrease in the kinetic stability of the 3*d* metal metallocenes.[33]

The mechanism of the decomposition of the diarene derivatives of transition metals on heating[2,64,81-91] in a strong electric field,[92] in a high-frequency discharge,[93] and under the influence of electron impact[94] has been discussed widely in the literature. It is suggested that the process takes place almost quantitatively via a molecular mechanism involving the abstraction of ligands and the segregation of the metal.[2,3,64]

Gaseous compounds (hydrogen, methane, and C_2–C_5 paraffinic and olefinic hydrocarbons), liquid compounds (benzene, and ethyl-, diethyl-, and triethyl-benzenes), and solid compounds (biphenyl, terphenyl, ethyldiphenylcyclohexanes, carbon, metal carbides, and the metal) have been found in the products of the thermal decomposition of the diarene derivatives of vanadium, chromium, and molybdenum under static conditions. The main process involving the decomposition of the metal–ligand bond is accompanied by secondary ligand decomposition reactions[95,96] via catalytic dehydrogenation stages[87,88,95] and the subsequent formation of carbon-containing condensed products. It also proceeds via the elimination of methylene from the ligand side groups (for example, ethylbenzene), whose subsequent reaction leads to the formation of methane, carbon, and hydrogen.

In a flow system,[87,88,97] the primary ligand conversion reaction is also their dehydrogenation accompanied by the formation of aryl radicals whose recombination leads to the formation of biphenyls and other condensed substances which are dehydrogenated to carbon in the presence of the metal. Graphite has been detected in the condensation products by electron diffraction.[66] The amount of gaseous products in an open system is smaller by an order of magnitude than in a static system, the only gaseous product being hydrogen.

Thermographic and gas-chromatographic studies have shown[81] that the thermal decomposition of dibenzenechromium at the metal-ligand bond at reduced pressures takes place stepwise with the consecutive elimination of ligands, the energy of the abstraction of the first ligand being greater than that of the second.

Together with the preferential molecular decomposition of diarene derivatives of metals at the metal–ligand bond, radical decomposition takes place to some extent, proceeding via the $\pi-\sigma$ rearrangement of the initial compound[97,98] with formation of a hydrogen atom and aryl radicals. The formation of aryl radicals from the diarene derivatives of chromium, vanadium, and molybdenum has been demonstrated by their fixation on anthracene and ferrocene. A radical chain mechanism of the pyrolysis of di(ethylbenzene)chromium has also been proposed by Dudorov et al.[99]

2. Elementary Steps in the Thermal Decomposition Reaction

The common features of the radical and molecular mechanisms of the thermal decomposition of OMC proceeding with retention of the orbital symmetry (the Woodward–Hoffmann rule) and of the total spin of the system (the Wigner–Witmer rule) have been examined in detail by Razuvaev and co-workers.[2,3] A common feature of the radical and molecular decomposition pathways from the standpoint of the conservation rules, is that the most favourable activated state of the OMC molecule is the OMC triplet dissociating via the metal–ligand bond with formation of either a pair of radicals in the triplet state or ligand molecules and the metal in the excited triplet state.

A quantum-chemical description of the elementary step in the thermal decomposition at the metal–ligand bond has been achieved for diarenechromium[3,6,100] within the framework of the method of one-electron molecular orbitals. The dissociation of the metal–ligand bond can occur in an OMC molecule in an excited electronic state, arising when a light quantum is absorbed or as a result of the interaction with the medium. For dibenzenechromium, the energetically most favourable course of this reaction is via the triplet state of the OMC molecule with formation of the arene in the triplet state and of a chromium atom in a state other than the ground state. The possible pathways leading to the molecular decomposition of diarenechromium with migration of energy and the formation of the corresponding multiplet states have been examined[2] (p.105). The formation of excited chromium atoms imparts surface activity to the solid phase formed, which is manifested by the autocatalytic character of the decomposition of dibenzenechromium, improved adhesion of the chromium segregated to the material of the support, and its increased adsorption capacity. The decomposition of the arene in the triplet state (for example, to a carbene) induces secondary reactions.[3]

The metals segregated (especialy W, Mo, Re, Cr, and V) are capable of being coordinated to olfefins, arenes, and carbenes, forming intermediate complexes which undergo further reactions,[3] leading ultimately to metal carbide structures.[101-103] For example, carbene complexes can disproportionate to a carbyne complex with a metal–carbon triple bond and further to methane and the $-M\equiv C-$ carbide species.

The possibility of the decomposition of the OMC triplet into a singlet molecule (toluene from diethylbenzenechromium) and a carbene complex of the metal via the scheme

$$(CH_3CH_2C_6H_5)_2M \rightarrow 2CH_3C_6H_5 + CH_2{:} \rightarrow M \leftarrow {:}CH_2 \rightarrow$$
$$\rightarrow CH_3{-}M\equiv CH \rightarrow CH_4 + {-}M\equiv C{-}$$

has not been ruled out.[3,64]

The heterogeneous decomposition of the OMC of *d* metals on the surface in accordance wit the spin conservation rule (an analogue of the Wigner rule) takes place on active centres (AC) having unpaired electrons.[3] Such centres may be absorbed metal atoms, whose role is similar to that of free radicals in the homogeneous decomposition.

The decomposition of ferrocene with formation of iron in the ground state is possible when triplet AC, which may be chemisorbed iron atoms, are present on the surface:[3,63]

$$Fe(C_5H_5)_2(S) + AC(T) \rightarrow (C_5H_5)_2(S) + Fe(^5D_4) + AC(T),$$

where S is the singlet, T the triplet, and $^5D_4$ the ground state of iron.

The chemisorbed iron atoms, which are effective dehydrogenation catalysts, promote the formation of iron-cross-linked polymers, which has been frequently observed experimentally.[25,57] By suppressing the dehydrogenation reaction by adding hydrogen, it has been possible to obtain α-iron from 1,1'-diethylferrocene,[57] nickel from nickelocene,[80] and ruthenium from ruthenocene.[2]

Either the chemisorption of atomic chromium, or the cleavage of the benzene ring, or the dehydrogenation of the latter are necessary for the retention of the multiplicity of the OMC–AC system in the heterogeneous decomposition of the diarene derivatives of chromium.[63] In the presence of a catalyst (iodine, bromine, and sulphur),[3] which removes the spin prohibition, the decomposition of diarene-chromium proceeds with segregation of pure chromium and ethylbenzene without the cleavage of the latter.

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The above analysis of the literature data revealed regularities in the variation of the kinetic parameters of the mechanism of the thermal decomposition of the test compounds as a function of the nature of the metal and the ligand and also the reaction conditions. The rate and mode of the thermal decomposition of the OMC investigated are determined by the nature of the reactant, mainly by its electronic temperature, the metal–ligand bond dissociation energy, and the ratios of this energy to the C–C and C–H bond dissociation energies in the ligand. Nor are there any grounds for the exclusion of the influence of steric factors on the kinetic thermal stability of the test compounds. The steric effect of the ligand on the stability of the complex, especially its quantitative aspect, have not been described in the literature. Nevertheless, in estimating the stability of the compound, it is essential to take into account also the steric effect together with the electronic influence.[104]

The decomposition reactions of the classes of comounds considered have not been found to be the same. A free radical pyrolysis mechanism via the homolytic cleavage of the metal–ligand bonds and the C–C and C–H bonds in the ligand has been proposed for mononuclear cyclopentadienyl compounds of transition metals. Predominantly molecular decomposition, involving the dissociation of the ring–metal bond or the elimination of a carbene and its stabilisation via coordination to the segregated metal and subsequent conversion of the carbene complex via known schemes, is characteristic of diarene compounds. The π–σ rearrangement, leading to the formation of radicals takes place to a slight extent in the decomposition of the diarene derivatives of metals.[105] It may be that the C–H bond dissociation process in the metallocenes is also preceded by the π–σ rearrangement, which has been detected for ferrocene by NMR.[106] However, from the standpoint of the conservation rules for the orbital symmetry and the total spin of the system, common features are observed in the radical and molecular mechanisms of the decomposition and also an analogy between the homogeneous and heterogeneous decomposition pathways.[3]

In recent years, a new field of study has begun to develop—the study of the adsorption of OMC and their volatile decomposition products on various surfaces, which determine the character of the interaction of the test compounds with the surface, and also the establishment of a correlation between the structure of the OMC and its adsorption capacity in relation to the metal-containing solid products of its own decomposition. However, these studies have only just begun, the range of compounds investigated is inadequate, and the nature of the adsorption complexes obtained has not been established. The importance of expanding the adsorption investigations is dictated by the fact that adsorption is one of the stages in the heterogeneous-catalytic decomposition which makes a definite contribution to the kinetics of the overall process.

In conclusion, it must be emphasised that the range of kinetic studies on the thermal decomposition of OMC is fairly narrow. Furthermore, the use of OMC is very promising in practice. The needs of modern technology for new materials in fact make it necessary to develop further the theoretical and experimental studies designed to determine the kinetics of the thermal decomposition of various OMC, whose knowledge is essential for the optimisation of the process leading to the formation of inorganic coatings and materials.

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