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REACTIVITY OF THE FIRST TRANSITION ROW METALLOCENES IN THERMAL DECOMPOSITION REACTION

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Summary

The thermal decomposition of vanadium, chromium, manganese, iron, cobalt and nickel metallocenes in vacuum has been studied. Kinetic parameters of the process have been calculated. It was established that the thermal stability of the electron-deficient π-complexes of metals to the left of the Periodic System changes in parallel with the thermodynamic functions of the metal—ring bond dissociation and decreases in the order: $Cp_2V > Cp_2Cr > Cp_2Mn$. Thermal stability of metallocene analogues of iron-triad, governed more by electronic structure than thermodynamic factors, decreases in the order: $Cp_2Fe > Cp_2Co > Cp_2Ni$. It has been found that metallocene pyrolysis in a closed system is a homogeneous—heterogeneous process occurring both in a volume and on a surface. The catalytic activity of solid decomposition products has been observed.

Introduction

Earlier works have shown that the decomposition of $(\pi\text{-Cp})_2M(\sigma\text{-R})_2$ (M = Ti, Zr, V; R = Me, Ph) proceeds via cleavage of M—R σ-bonds [1—3]. π-Cp ligands take part in decomposition, however, homolysis of the stronger π-Cp—M bonds occurs negligibly. Therefore, it seemed advisable to investigate the manner and conditions of π-Cp—M bond cleavage in compounds which do not contain substituents σ-bonded to the metal. The first row transition metallocenes were chosen as such compounds.

Not many pyrolytic reactions of metallocenes, i.e. ferrocene [4,5], diindenylcobalt [6], nickelocene [7,8] and ruthenocene [9] have been described. The formation of cyclopentadienyl radicals on pyrolysis of ferrocene occurring above 800°C [4] and indenyl radicals on diindenyl—cobalt pyrolysis [6] was

TABLE 1

KINETIC PARAMETERS OF METALLOCENE PYROLYSIS
(V = 60 ml, S/V = 1.5 cm^{-1})

T (°C)	Cp_2V [a]		Cp_2Cr [b]		Cp_2Mn [c]		Cp_2Co [d]		Cp_2Ni [e]	
	P_0 (mmHg)	$K \times 10^3$ (s^{-1})	P_0 (mmHg)	$K \times 10^3$ (s^{-1})	P_0 (mmHg)	$K \times 10^3$ (s^{-1})	P_0 (mmHg)	$K \times 10^3$ (s^{-1})	P_0 (mmHg)	$K \times 10^3$ (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	1.16		
440					92	1.30				
420					103	0.84			151	5.78
380									150	2.36
360									120—220	1.55
350									149	1.00
340									151	0.76

[a] $E = 50.5 \pm 0.66$ kcal mol^{-1}, log $k_0 = 10.41 \pm 0.18$. [b] $E = 27.3 \pm 0.8$ kcal mol^{-1}, log $k_0 = 4.87 \pm 0.23$. [c] $E = 29.3 \pm 1.2$ kcal mol^{-1}, log $k_0 = 6.15 \pm 0.35$. [d] $E = 23.1 \pm 1.0$ kcal mol^{-1} log $k_0 = 4.04 \pm 0.31$. [e] $E = 21.4 \pm 0.2$ kcal mol^{-1}, log $k_0 = 4.52 \pm 0.37$.

shown by spectroscopic methods. An exception to this was ferrocene pyrolysis in condensed phase [5], where the ferrocene structure was not destroyed and formation of the pyrolysis product diferrocenyl was explained by abstraction of a hydrogen atom from the cyclopentadienyl ring.

In addition to cyclopentadiene, naphtalene and carbon-containing nickel, 9,10-dihydrofulvalene, which is a product of cyclopentadienyl radical recombination, was found on impulse vacuum pyrolysis of nickelocene [7,8]. Appearance potentials for nickel, cyclopentadienyl, and cyclopentadienyl nickel ions, generated from nickelocene on electron impact, were obtained. These, in combination with the corresponding ionization potentials, lead to estimates of the dissociation energies of nickelocene to cyclopentadienyl nickel and cyclopentadienyl radicals or to nickel and cyclopentadienyl radicals. The results imply that thermal fragmentation of nickelocene occurs on the reactor walls [8].

The method of preparation of pure ruthenium metal (99.99%) by ruthenocene pyrolysis at 595°C in a hydrogen flow has been described [9]. Although products other than the metallic film have not been analysed, the authors proposed that the mecanism of ruthenocene decomposition proceeded via ring—metal bond cleavage.

The various aspects of metallocene stability (quantum-chemical, thermodynamic, kinetic) [10], the mechanisms and some elementary steps on thermal decomposition of various types of organometal compounds [11] have been treated theoretically.

The kinetic data on thermodecomposition of metallocenes are practically absent from the literature, with the exception of a work devoted to ferrocene pyrolysis [12]. The limited number of publications on pyrolysis of these compounds impelled us to investigate systematically the kinetics and thermal decomposition products of cyclopentadienyl compounds of the first row transition metals.

Results and discussion

Formally-kinetic pyrolysis regularities

Thermal decomposition of vanadocene, chromocene, manganocene, ferrocene, cobaltocene and nickelocene in the vapour phase was investigated by a manometric method under static conditions in vacuum glass vessels. The apparent rate constants of the gross process were used to measure the reactivity of the thermal decomposition reaction. They are calculated graphically on the basis of kinetic curves. Ferrocene decomposes with a convenient rate for measurement above 550°C. The reaction vessel was repeatedly used (35—40 preliminary experiments) in order to obtain reproducible kinetic data. Poor reproduction of kinetic data prevented us from investigating the pyrolysis of ferrocene in glass vessels. Kinetic curves of ferrocene decomposition have an S-form in contrast to other metallocenes. In the interval of initial ferrocene pressures (50—300 mmHg) at 550°C, the time for decomposition of 25% ferrocene is constant. Therefore, the kinetic pyrolysis curve demonstrated a first order reaction up to 25% ferrocene decomposition. At 550°C the apparent value of rate constant was 1.6×10^{-5} s^{-1}.

The pyrolysis of vanadocene, chromocene, manganocene, cobaltocene and nickelocene is described by the first order rate expression. The obtained data are listed in Table 1.

TABLE 2

COMPARATIVE KINETIC METALLOCENE STABILITY

Compound	$\overline{D}$(M—Cp) (kcal mol^{-1})^a	$\Delta\overline{S}$(M—Cp) (cal mol^{-1} K^{-1})^a	$\Delta\overline{G}$(M—Cp) (kcal mol^{-1})^a	$k \times 10^3$ (s^{-1}) at 500°C
Cp_2V	88	47	74	0.14
Cp_2Cr	67	40	55	1.34
Cp_2Mn	51	35	40	7.20
Cp_2Fe	72	41	60	0.01
Cp_2Co	64	41	52	3.30
Cp_2Ni	60	37	49	29.5 [b]

[a] Refs. 13 and 14. [b] Calculated from Arrhenius equation, other values are experimental.

Ferrocene is the most thermally stable compound of all the metallocenes studied. The central metal atom influences greatly the thermal stability of these compounds. In π-complexes of metals which are to the left of iron in the Periodic System, the thermal stability decreases in the order: $Cp_2V > Cp_2Cr > Cp_2Mn$. Thermodynamic dissociation characteristics of the ring—metal bond, i.e., average Gibbs free energy ($\Delta\overline{G}$) and average dissociation energy ($\overline{D}$) change in the same order (Table 2).

Thermal stability of iron-triad metallocenes decreases in the order: $Cp_2Fe > Cp_2Co > Cp_2Ni$ in parallel to a decrease in $\overline{D}$ and $\Delta\overline{G}$ of the M—Cp bond. The experiments show that the rate constant of cobaltocene pyrolysis are to a power of two larger and the rate constant of nickelocene pyrolysis to a power of three larger than the rate constant of ferrocene decomposition. The difference in thermal decomposition rates for vanadium, chromium and manganese π-complexes is not larger than a power of one although characteristic thermodynamic values of ring—metal bond dissociation differ considerably more than $\overline{D}$, $\Delta\overline{S}$ and $\Delta\overline{G}$ values for iron-triad metallocenes. This indicates that on closer examination electronic structure factors (along with thermodynamic ones) play a significant role on the reactivity of metallocenes in thermal decomposition reactions.

Indeed, being to the left and to the right of iron in the Periodic System and having a lack and an excess of electrons, respectively, metal π-complexes are less stable than ferrocene (Tables 1 and 2). Ferrocene has unusual stability when compared with its analogues and holds a unique position among metallocenes.

A considerable decrease in the stability of cobaltocene and nickelocene when compared with ferrocene may be due to the presence of one electron on the anti-bonding cobaltocene orbital and two electrons on the anti-bonding nickelocene orbitals. Thus, the reactivity of iron, cobalt and nickel metallocenes in thermal decomposition reaction is due not only to the thermodynamic factors but to a greater extent to the electronic structure and conforms to Sidgwicks rule [10].

The analysis of thermochemical data [13,14] indicates that the process according to scheme:

$$(C_5H_5)_2M(g) \rightarrow 2\ C_5H_5(g) + M(c)$$

is thermodynamically allowed for nickelocene at a temperature above 550 K and for vanadocene only at a temperature above 1100 K. For ferrocene ΔG_g of the

TABLE 3

THE INFLUENCE OF SURFACE UPON THE RATE CONSTANT (k 10^3 s^{-1}) OF METALLOCENE PYROLYSIS

Reaction vessel volume 60 ml

Compound	T (°C)	Vessel without packing (s/v 1.5 cm^{-1})			Vessel with packing (s/v 25 cm^{-1})
		Glass	Pyrolytical coating		Glass
			1[a]	2[b]	
Cp_2V	500	0.14	—	—	0.51
	520	0.31	0.32	0.26	1.20
	540	0.69	0.66	—	—
	550	1.03	—	—	1.44
Cp_2Cr	460	0.48	2.70	3.10	—
	500	1.34	—	—	1.70
Cp_2Mn	460	2.50	6.40	10.50	—
Cp_2Fe	550	0.01	29.44[c]	—	—
Cp_2Co	450	1.17	—	—	1.13
Cp_2Ni	360	1.55	—	—	1.33

[a] The inside walls of the vessel are coated with solid products. [b] Before the experiment, coating I was evacuated for some hours at 500—520°C. [c] Calculated from the equation $k = 2.15 \times 10^9 \, exp(-40900/RT) \, s^{-1}$ [12].

process becomes negative above 1073 K. Relative to the above listed process of decomposition, thermodynamic metallocene stability decreases in the order of metals: V > Fe > Cr > Mn > Co > Ni. Our experiments show that under real conditions the decomposition process occurs at lower temperatures and according to a more complex scheme. The more so, as the formation of the pure metal was observed in none of the cases.

On pyrolysis of metallocenes the regularities peculiar to homogeneous—heterogeneous processes were found. The influence of surface upon the rate of the metallocene pyrolysis is shown in Table 3. The dependence of the pyrolysis rate constant upon the surface value of the reaction vessel is seen vividly with vanadocene decomposition (Table 3). With an increase in temperature, the influence of surface value upon the pyrolysis rate decreases; this shows the predominant role of the vessel volume in the reaction.

Uncontrolled changes in the states of the vessel wall have a greater influence upon the rate of pyrolysis of cobaltocene, nickelocene and especially ferrocene than the surface value. The investigations showed that solid ferrocene products; obtained in preliminary experiments (containing iron and carbon) stimulated the decomposition of ferrocene itself. With each following experiment the decomposition rate increased further. The rate of decomposition increased to some limiting value after 20—30 experiments. With a further increase in the thickness of the iron—carbon coating the decomposition rate of ferrocene remained constant. Hereafter the vessel walls became suitable for kinetic measurements.

The catalytic effect of the iron—carbon coating is so great that it allows the kinetics of ferrocene decomposition to be studied at low temperatures, at which the decomposition in glass vessels does not occur at all. Ferrocene decomposi-

TABLE 4

PYROLYSIS PRODUCTS OF Cp_2M IN STATIC SYSTEM
p_0 = 100–200 mmHg

Compound	T(°C)	t (min)	α	mol per mol of compound decomposed										
				H_2	C_5H_6	C_5H_8	C_5H_{10}	CH_4	C_2H_6	C_6H_6	$C_6H_5CH_3$	C_2H_4	C_3H_8	C_3H_6
Cp_2V	550	4	0.30	0.892	0.488	0.057	0.001	0.073		0.013				
	550	60	1.00	1.590	0.045	0.012	0.002	0.205	0.086	0.028	0.004	0.013	0.010	0.020
C_5H_6 [a]	520	225	0.99	0.472	0.020	0.008	0.020	0.768	0.296	0.158	0.058	0.070	0.076	0.168
Cp_2Cr	500	10	0.21	0.437	1.100	0.064	traces	0.009		0.006	0.002			
	500	50	0.84	1.120	0.083	0.011	0.014	0.583		0.009	0.002			
Cp_2Mn	450	5	0.23	0.063	0.937									
	450	10	0.55	0.435	1.200	0.028								
	450	40	0.88	0.482	0.372	0.070	traces	0.690						
	390	10	0.24	0.075	0.771	0.008								
	390	180	0.75	0.553	0.670	0.045		0.018						
	450 [b]	45		0.321	0.003	0.001	traces	0.050	0.003	0.002				
Cp_2Fe [c]	570	60	0.08	3.900	n.d. [d]	n.d.	n.d.	0.370	0.035	n.d.	n.d.	0.043	n.d.	n.d.
	570	90	0.14	3.960	n.d.	n.d.	n.d.	0.590	0.072	n.d.	n.d.	0.057	n.d.	n.d.
	570	140	0.56	4.200	n.d.	n.d.	n.d.	0.293	—					
	570	180	1.00	4.400	n.d.	n.d.	n.d.	0.286	0.023	n.d.	n.d.		n.d.	n.d.
Cp_2Co	450	60	1.00	0.580	0.430	0.200	0.040	0.320	0.030	0.050	0.003			
Cp_2Ni	340	7	0.10	0.021	0.910	0.013		0.001		0.008				
	340	24	0.30	0.038	1.180	0.028		0.015		0.010	0.001			
	360	25	1.00	0.025	1.060	0.094	0.010	0.062		0.023				

[a] The inner walls of the reaction ampoule are coated with *solid products* of vanadocene pyrolysis. The pyrolytic coating was preliminary heated in vacuum to above 500°C. [b] The solid products of Cp_2Mn thermodecomposition, formed at 390°C after 180 nm, had undergone pyrolysis. Volatile products, contained in the pyrolytic coating, were preliminary distilled off. [c] Gas-chromatographic analysis. [d] n.d. not detected.

tion on the iron—carbon coating was investigated at 400—470°C and under initial pressures of 97—182 mmHg. Up to 60% decomposition the reaction can be described by the first order rate expression $k = 2.15 \times 10^9 exp(-40900/RT)$ s^{-1}.

The solid pyrolysis products which uniformly coated the walls of the vessel proved to be catalytically active in the case of chromocene and manganocene pyrolysis. Catalytic activity of the coating was increased on removing adsorbed products from the coating by prolonged heating with permanent evacuation, but it did not depend upon the thickness of coating at all (Table 3). The solid coating obtained on vanadocene pyrolysis had no influence upon the rate constant of the organovanadium compound (Table 3). Nevertheless, the initiating action of the vanadium coating was found and proved by special experiments. Vanadocene was firstly decomposed in a reaction vessel at 540°C for some minutes. After this time the compound had decomposed to some extent (up to 10%) and the walls of the vessel were coated with a dark transparent film of solid products. The reaction temperature was then raised to 400°C. The kinetic curve of this experiment demonstrated a first order reaction only up to 25% decomposition ($k = 0.8 \times 10^{-3}$ s^{-1}), after which time the reaction slowed down. It should be noted that in pure glass vessels pyrolysis of vanadocene at 400°C does not occur at all. A similar experiment was conducted at 500°C, when the kinetic curve 3 showed first order reaction up to 30% decomposition ($k = 0.7 \times 10^{-3}$ d^{-1}) and then slowed to the conventional rate at these temperatures ($k = 0.18 \times 10^{-3}$ s^{-1}). This latter value is practically equal to a rate constant value of vanadocene pyrolysis at 500°C in pure glass vessels.

At 400°C chromocene pyrolysis on a vanadium coating (primarily heated with permanent evacuation) leads to an increase of decomposition rate constant 17 times that of decomposition rate constant in pure glass vessels. This effect of acceleration is observed up to 22% decomposition after which time the reaction proceeds with the rate equal to that of chromocene pyrolysis in vessels without any coating

The pyrolysis coating obtained on manganocene decomposition at 400 and 240°C followed by heating at these temperatures for an hour with permanent evacuation, has still a greater catalytic effect. The rate constant of vanadocene decomposition at 450°C on such a coating is to the power two larger than that in the pure glass vessel. At 400°C, as in the above mentioned experiments, the kinetic curve of vanadocene pyrolysis on manganese coating was first order only to 25% decomposition ($k = 1.1 \times 10^{-3}$) after which the reaction slowed down. This indicates that the metallocene thermodecomposition is facilitated at the expence of the catalytic reaction on the surface of the solid phase, the activity of which may be suppressed during one experiment as a result of the absorbtion of other pyrolysis products on active centres.

The incommensurably great catalytic effect of solid products of ferrocene pyrolysis should be noted in comparison with other pyrolytic coatings.

Investigation of metallocene pyrolysis products

We examined the products of metallocene pyrolysis conducted in a closed vacuum system (static system) and the system where metallocenes were sublimated into a reaction zone and decomposition products were frozen out into a trap (quasi-flow system). The composition of the gaseous products of metallocene pyrolysis (Table 4) at low and high degrees of decomposition (α) were obtained by mass spectrometry. Table 4 shows that ferrocene differs from other metallocenes not only in the kinetic aspects but also in gaseous phase composition. Chromatographic analysis shows that the main products of ferrocene decomposition, even at low degrees of destruction is hydrogen. Its amount is substantial and increases with the extent of decomposition.

In the static system the main gaseous decomposition products of other investigated metallocenes are cyclopentadiene, hydrogen and methane. The composition of products depends upon the temperature and duration of metallocene decomposition. Thus, a substantial cyclopentadiene formation is observed at low temperatures and short reaction times. With an increase in temperature and reaction time the cyclopentadiene yield decreases and the main products of complete pyrolysis are hydrogen and methane.

The increase in hydrogen yield with the extent of decomposition shows that it is also formed in secondary reactions. One of them may be cyclopentadiene pyrolysis, catalyzed by formation of the solid phase. Cyclopentadiene has been shown to decompose on solid products of vanadocene pyrolysis to give, in this case, the main pyrolysis products H_2 and CH_4 (Table 4) [15].

The formation of substantial amounts of CH_4 at high degrees of decomposition of metallocenes is due to pyrolysis of C_5H_6 as well as to hydrogen interaction with carbon of the pyrolytic coating. Especially conducted experiments showed that more than 10% CH_4 of the overall gas volume is formed when hydrogen is in contact with pyrolytic coating at 550°C in an ampoule for an hour.

Besides gaseous products, metallocene decomposition gives the solid products which cover the inner walls of the reaction vessel. These consist of condensation products of 5-member rings (from dimer to pentamer of cyclopentadiene), naphthalene, anthracene, phenantrene, pyrene, pyrylene and a pyrolytic coating, containing metals, carbon and hydrogen in the solid phase of metallocene pyrolysis (except ferrocene pyrolysis).

The decomposition in quasi-flow system was conducted in order to diminish the secondary influences on the reaction and to isolate the initial stage of prolysis. In such a system the main decomposition product of Cp_2M (M = V, Cr, Mn, Ni) is C_5H_6 (Table 5). The amount of hydrogen in decomposition products is negligible for Cp_2Mn and increases to Cp_2V.

TABLE 5

PRODUCTS OF METALLOCENE PYROLYSIS IN QUASI-FLOW SYSTEM

Compound	T (°C)	Mol ratio (%)				
		H_2	C_5H_6	C_5H_8	CH_4	C_6H_6
Cp_2V	550	25.2	74.8	traces	—	—
Cp_2Cr [a]	510	10.4	86.2	1.2	—	—
Cp_2Mn [b]	390	5.3	94.0	0.5	—	—
Cp_2Ni	360	11.1	83.5	0.7	3.7	1.0

[a] 2.2 of unidentified products. [b] 0.2 of unidentified products.

The comparison of the thermal decomposition products of metallocenes in quasi-flow system and in the static system at low degrees of decomposition shows that the main reactions of metallocene decomposition are due to M—Cp bond cleavage and dehydrogenation of the metallocene molecule.

The relative extent of these reactions depends upon the nature of the central atom. The metallocene decomposition products show that the dehydrogenation reaction increases in the series from Cp_2Ni to Cp_2Fe and from Cp_2Mn to Cp_2V. The increase of metallocene dehydrogenation reaction in these series may be due to M—Cp bond strenghth, if we take into consideration that the average C—H bond energy of dissociation in Cp rings does not depend essentially on the nature of the central atom.

Thus, the parallel change of properties takes place in the series of electron-deficient complexes (Cp_2V, Cp_2Cr, Cp_2Mn) and iron-triad complexes (Cp_2Fe, Cp_2Co, Cp_2Ni): the decrease in average dissociation energy of M—Cp bond, the increase in decomposition rate constant (the decrease in kinetic stability) and the decrease in dehydrogenation reaction of metallocene upon decomposition.

The investigation of kinetics and decomposition products allows us to draw the conclusion that pyrolysis of metallocenes is a complex process of homogeneous—heterogeneous nature consisting of a series of consecutive, parallel and catalytic reactions. All studied compounds have analogous mechanisms and products of decomposition and their reactivities are determined both by thermodynamic characteristics of cyclopentadienyl molecule ring—metal bond dissociation, by electronic structure of the as well as by catalytic activity of the solid phase formed.

Experimental

The investigated metallocenes were prepared as previously described by other workers [16,17], and were purified by repeated sublimation in vacuo. Mass spectrometric analysis of the metallocenes has shown that the total content of impurities did not exceed 0.30 mol % (the major impurity in all cases was $C_5H_5MC_5H_4CH_3$, where M is the same metal as in the parent compound). Because of the sensitivity to oxygen, the samples of metallocene were sublimated into the reactor through a special vacuum sluice system.

Gas-phase pyrolysis kinetics of metallocenes were investigated under static conditions by a manometric method. The progress of the reaction was followed by measuring the total pressure. Analysis of gaseous and liquid products was conducted by mass spectrometry on a MI-1305 model at accelerating voltage 2 kV, electron energy 70 eV and emission current 1.5 mA. The solid products were analyzed by placing them directly into the ion source of the mass spectrometer and by elemental analysis.

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