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THERMAL DECOMPOSITION OF DICYCLOPENTADIENYLTITANIUM(IV) DIARYL AND DIBENZYL COMPOUNDS

C.P. BOEKEL, J.H. TEUBEN and H.J. DE LIEFDE MEIJER

Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Zernikelaan, Groningen
(The Netherlands)

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Summary

The thermal decomposition of compounds of the type Cp_2TiR_2 (Cp = cyclopentadienyl, R = aryl or benzyl) in the solid state and in various solvents has been studied. In the solid state and in aromatic and aliphatic hydrocarbon solvents the compounds decompose with quantitative formation of R—H and a Ti-containing residue which has lost the Cp_2Ti structure. Experiments with deuterated compounds and solvents showed that decomposition proceeds via intramolecular abstraction of a hydrogen atom either from a cyclopentadienyl ring or from the other coordinated group R. Results of insertion reactions with tolane confirm these two reaction pathways. In tetrahydrofuran and tetrachloromethane, decomposition proceeds in a more complex way, with participation of the solvent.

Introduction

There have been several studies of the thermal decomposition of alkyl- and aryl-dicyclopentadienyltitanium compounds, but there still is uncertainty concerning the mechanism of the thermolysis. Razuvaev et al. [1] studied the thermal decomposition of Cp_2TiR_2 (R = alkyl, aryl) in various solvents. From consideration of the products (Cp_2Ti, RH, R—R), they propose a homolytic cleavage of the Ti—C σ-bond as the main decomposition pathway. Dvorak et al. [2] studied the thermal decomposition of $Cp_2Ti(C_6H_5)_2$ in benzene and found C_6H_6 as the main reaction product; no biphenyl formation was observed. They suggest that benzene is formed by abstracting a hydrogen atom from another phenyl group with simultaneous formation of a phenylenetitanium complex. The decomposition of the related compounds $Cp_2Ti(R)Cl$ was studied by Waters et al. [3], who found evidence for a non-ionic mechanism. The rate-determining step is the promotion of R to a non-ionic activated state in which R is still within the coordination sphere of titanium, but mobile enough to migrate from one titanium atom to another. Investigations in our laboratory on the thermal decomposition of Cp_2TiR [4] have indicated that the cyclopentadienyl groups serve as a hydrogen source in the formation of RH.

The results outlined above prompted us to investigate the thermal behaviour of the compounds Cp_2TiR_2 (R = aryl, benzyl) in detail. DTA measurements were used to establish the dependence of the stability on R. Decompositions were examined in solution (benzene, toluene, cyclohexane, THF and CCl_4) and in the solid state, using deuterated compounds and solvents in order to get insight in the thermal decomposition pathway.

Experimental

Procedures

All experiments were carried out under N_2 or in vacuum using Schlenk-type glassware. Gas chromatographic analyses were performed with a Hewlett—Packard 7620 A research chromatograph; for quantitative measurements an internal standard was used. Infrared spectra were recorded with a Hitachi EPI-G spectrophotometer; visible and ultraviolet spectra with a Perkin—Elmer EPS-3T spectrophotometer. The mass spectra were recorded by Mr. A. Kiewiet with an AEI-MS 9 instrument. Thermograms were obtained using a low-temperature DTA apparatus [5]; the decomposition points were found by an interpolation method [6]. Samples of about 20 mg of the pure compounds Cp_2TiR_2 were sealed in evacuated (0.1 mmHg) glass ampoules and heated at a rate of 2-3°/min. The temperature effect ΔT was measured as a function of the temperature T of the sample-holder block.

Starting materials

The aryl compounds Cp_2TiR_2 were prepared by a modification of the published method [7]. After reaction of Cp_2TiCl_2 with two equivalents of RLi, the solvent was removed; the residue was extracted with CH_2Cl_2 and the product recrystallized from ether. The benzyl compound was obtained by the method of Razuvaev et al. [8]. The compounds with deuterated cyclopentadienyl groups were prepared from the starting material Cp_2TiCl_2-d_{10} which was synthesized by the method of Martin et al. [9]; mass spectra showed a degree of deuteration over 90%. For all compounds satisfactory elementary analysis were obtained.

Results

Differential thermal analysis

In all cases the thermograms showed one irreversible exothermic effect, which was due to the heat of decomposition. The decomposition temperatures are listed in Table 1.

Thermolysis of the compounds

Samples of about 1 mmol of the solid compounds Cp_2TiR_2 were heated at a fixed temperature for a given time. Solutions of the compounds (1 mmol) in 10 ml of solvent were thermolyzed under N_2 at the boiling point of the solvent.

In a first series of experiments the volatile decomposition products were distilled into a cold trap and analyzed (GLC and mass spectrometry). The residue

TABLE 1

DATA FOR DIFFERENTIAL THERMAL ANALYSIS OF Cp_2TiR_2 COMPOUNDS

R	exothermic effect (°)
C_6H_5	120
m-$CH_3C_6H_4$	134
p-$CH_3C_6H_4$	125
$3,4$-$(CH_3)_2C_6H_3$	136
$CH_2C_6H_5$	95

was treated with an excess of HCl in ether at —78°C. The resulting ethereal solution was again analysed by GLC and mass spectrometry; Cp_2TiCl_2 was separated from the residue by extraction with $1,2$-$C_2H_4Cl_2$ and determined by UV-visible spectrometry. The results are shown in Table 2.

In a second series the decomposition of $Cp_2Ti(C_6H_5)_2$ was studied, experiments with deuterated $Cp_2Ti(C_6H_5)_2$ being included. The extent of deuteration of benzene formed in these experiments was determined by mass spectrometry. The results are presented in Table 3.

In one experiment $Cp_2Ti(C_6D_5)_2$ was thermolyzed in toluene at 80° in the presence of tolane (cf. Masai et al. [10]). A green product was obtained which, after purification, was characterized as dicyclopentadienyl-2,3-diphenyl-1-titana-5,6,7,8-tetradeuteroindene (yield 45%, based on Ti) (cf. Scheme 2). The volatile part of the reaction mixture was distilled into a cold trap and analyzed in the usual way (Table 3, exp. 7).

In separate experiments the solid decomposition products were investigated by IR, mass spectrometry, and magnetic measurements, and by reaction with HCl in excess.

Discussion

The DTA results show (Table 1) that the differences in thermal stabilities between the aryl compounds Cp_2TiR_2 ($R = C_6H_5$, m- and p-$CH_3C_6H_4$, $3,4$-$(CH_3)_2C_6H_3$) are small. Under the conditions used the complexes decompose rapidly at 120-136°. $Cp_2Ti(CH_2C_6H_5)_2$ (dec. 95°) is markedly less stable, in contrast with the findings of Razuvaev et al. [8].

All compounds behave quite similarly, giving quantitative formation of RH when heated in the solid state at the decomposition temperature for 1 h. (Table 2, exp. 1,11,14,16,19). No detectable amounts of radical coupling products were found. In these cases the Cp rings must act as hydrogen sources and destruction of the original Cp_2Ti structure is to be expected. Indeed no indication for the retention of the Cp_2Ti moiety is found in the solid black diamagnetic reaction product. No Cp_2TiCl_2 was obtained when the black product was exposed to HCl/ether in excess. Infrared spectra of the black residue show absorptions at 1050-1060 cm^{-1} indicating C_5H_4 groups as are present in $[Cp(C_5H_4)TiH]_2$ [11] and $[Cp(C_5H_4)TiCl]_2$ [11, 12]. Thermolysis in cyclohexane, benzene, or toluene solution gives the same products, only RH (quantitative) and a black solid residue

TABLE 2

YIELDS OF PRODUCTS AFTER THERMOLYSIS OF Cp_2TiR_2 COMPOUNDS AND REACTION OF THE RESIDUE WITH HCl

R	Thermal decomposition			Reaction with HCl	
	Exp. conditions	Volatile products		Volatile products	Cp_2TiCl_2
		RH (%)	other (%)	RH (%)	(%)
C_6H_5	1 1 h 120° vacuum	92		4	
	2 1 h 90° vacuum			99	94
	3 8 h 90° vacuum	27		77	71
	4 24 h 90° vacuum	90		6	4
	5 300 h 50° vacuum	20		79	75
	6 5 h 80° cyclohexane, N_2	85		4	2
	7 5 h 110° toluene, N_2	85		7	
	8 5 h 65° THF, N_2	61		30	25
	9 24 h 65° THF, N_2	88		11	
	10 24 h 75° CCl_4, N_2	60	31 C_6H_5Cl		
m-$CH_3C_6H_4$	11 1 h 134° vacuum	94			
	12 5 h 80° benzene, N_2	90		4	
	13 24 h 65° THF, N_2	87		6	
p-$CH_3C_6H_4$	14 1 h 125° vacuum	99			
	15 5 h 80° cyclohexane, N_2	90		3	4
3,4-$(CH_3)_2C_6H_3$	16 1 h 136° vacuum	96			
	17 5 h 110° toluene, N_2	92		2	
	18 5 h 80° cyclohexane, N_2	88		8	6
$CH_2C_6H_5$	19 1 h 95° vacuum	95			
	20 5 h 80° benzene, N_2	94			

TABLE 3

THERMAL DECOMPOSITION USING DEUTERATED COMPOUNDS AND SOLVENTS

Compound	Exp. conditions	Composition of RH (% relative [a])
$Cp_2Ti(C_6D_5)_2$	1 1 h 137° vacuum	C_6D_6 (90); C_6D_5H (100); $C_6D_4H_2$ (91)
	2 24 h 90° vacuum	C_6D_6 (84); C_6D_5H (100); $C_6D_4H_2$ (80)
	3 300 h 50° vacuum	C_6D_6 (95); C_6D_5H (100); $C_6D_4H_2$ (97)
	4 5 h 110° toluene, N_2	C_6D_6 (93); C_6D_5H (100); $C_6D_4H_2$ (95)
	5 24 h 65° THF, N_2	C_6D_6 (63); C_6D_5H (100); $C_6D_4H_2$ (58)
	6 24 h 75° CCl_4, N_2	C_6D_6 (70); C_6D_5H (100); $C_6D_4H_2$ (78)
	7 8 h 80° toluene, tolane, N_2	C_6D_6 (100); C_6D_5H (98); $C_6D_4H_2$ (—)
$Cp_2Ti(C_6H_5)_2$	8 5 h 110° d^8_8-toluene, N_2	C_6H_6 (100); C_6H_5D (—); $C_6H_4D_2$ (—)
	9 24 h 65° d^8-THF, N_2	C_6H_6 (100); C_6H_5D (55); $C_6H_4D_2$ (45)
$Cp_2TiC_6H_5)_2$ [b]	10 1 h 140° vacuum	C_6D_6 (100); C_6H_6 (100)
+	11 24 h 90° vacuum	C_6D_6 (100); C_6H_6 (95)
$Cp_2Ti(C_6D_5)_2$-d_{10}	12 5 h 110° toluene, N_2	C_6D_6 (100); C_6H_6 (93)
$Cp_2Ti(C_6H_5)_2$-d_{10}	13 1 h 140° vacuum	C_6H_6 (100); C_6H_5D (85); $C_6H_4D_2$ (80)
	14 5 h 110° toluene, N_2	C_6H_6 (100); C_6H_5D (83); $C_6H_4D_2$ (80)
$Cp_2Ti(C_6D_5)_2$-d_{10} [c]	15 1 h 137° vacuum	C_6D_6 (100); C_6D_5H (6); $C_6D_4H_2$ (—)
	16 5 h 110° toluene, N_2	C_6D_6 (100); C_6D_5H (8); $C_6D_4H_2$ (—)

[a] Relative amounts of volatile product from the peak intensities in the mass spectra. [b] Equimolar mixture of the two compounds. [c] Mass spectra showed a degree of deuteration of about 90% for the cyclopentadienyl groups.

being formed, and so participation of the solvent in the decomposition is unlikely. This is confirmed by the decomposition of $Cp_2Ti(C_6H_5)_2$ in toluene-d_8 (Table 3, exp. 8), where no deuterium is found in the product benzene. Also, the decomposition of $Cp_2Ti(C_6D_5)_2$-d_{10} in toluene produces only C_6D_6. In this case the small amount of C_6D_5H (8%) is due to incomplete deuteration of the Cp groups (Table 3, exp. 15).

In experiments in which the thermal decomposition was not taken to completion, treatment of the residue with HCl in ether produced Cp_2TiCl_2 and RH (1/2), indicating a corresponding amount of undecomposed Cp_2TiR_2, which reacts quantitatively according to eqn. 1. The amounts of RH formed in the ther-

$$Cp_2TiR_2 + 2\ HCl \rightarrow Cp_2TiCl_2 + 2\ RH \qquad (1)$$

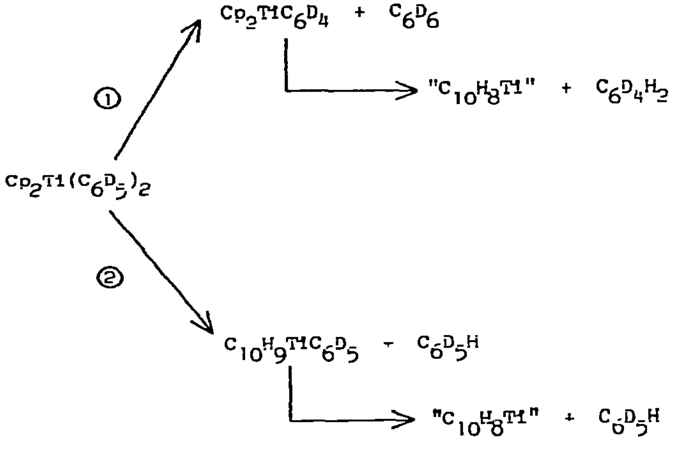
mal decomposition and of RH formed after treatment of the residue with HCl, together correspond to the amount of groups R in the original sample. From these results a step-wise degradation via stable intermediates with a Ti/R ratio of about 1/1 can be excluded. Evidently, both aryl groups attached to Ti are virtually simultaneously liberated as R—H, and the decomposition can be formulated as in eqn. 2. The decomposition is probably an intramolecular process. This is

$$Cp_2TiR_2 \rightarrow \text{“}C_{10}H_8Ti\text{”} + 2\ RH \qquad (2)$$

shown by experiments 10, 11, 12 in Table 3, in which decomposition of an equimolar mixture of $Cp_2Ti(C_6H_5)_2$ and $Cp_2Ti(C_6D_5)_2$-d_{10} in the solid state or in toluene produces only C_6H_6 and C_6D_6 (1/1) and no partially deuterated benzenes.

The results discussed so far are not consistent with a simple decomposition involving formation of free radicals, as suggested by Razuvaev et al. [1] or with the migration of a group R from a Ti atom to another as proposed for the decomposition of $Cp_2Ti(R)Cl$ [3]. The fact that the hydrogen atoms for the formation of RH are abstracted from ligands attached to the same Ti atom agrees with the view of Dvorak et al. [2] that benzene is formed by abstraction of hydrogen from the second phenyl group with simultaneous formation of an (instable) phenylenetitanium complex. This scheme is attractive, but our experiments (Table 3, exp. 1-4, 13, 14) lead us to conclude that another decomposition route is also operative, viz. an intramolecular decomposition with formation of C_6H_6 by direct abstraction of a hydrogen atom from the Cp rings. In the case of $Cp_2Ti(C_6D_5)_2$ this leads to the various deuterobenzenes as shown in Scheme 1. Route 1 leads via the intermediate formation of a phenylenetitanium complex to equimolar amounts of C_6D_6 and $C_6D_4H_2$. Route 2 only produces C_6D_5H by direct abstraction of hydrogen of the Cp rings. According to our experiments (Table 3, exp. 1-4) about 1/3 of the molecules decompose according to route 2. Experiments with $Cp_2Ti(C_6H_5)_2$-d_{10} (Table 3, exp. 13, 14) confirm these conclusions. Here equimolar amounts of C_6H_6 and $C_6H_4D_2$ (route 1) and of C_6H_5D (route 2) are found. Evidently, isotope effects do not play an important role; deviations from the expected values are mainly due to the fact that the degree of deuteration of the Cp rings is about 90%. Further proof for the proposed reaction scheme via two routes is found in the thermal decomposition of $Cp_2Ti(C_6D_5)_2$ in the presence of tolane (Table 3, exp. 7). The formation of $C_6D_4H_2$ via route 1 is blocked by the presence of tolane which is inserted in

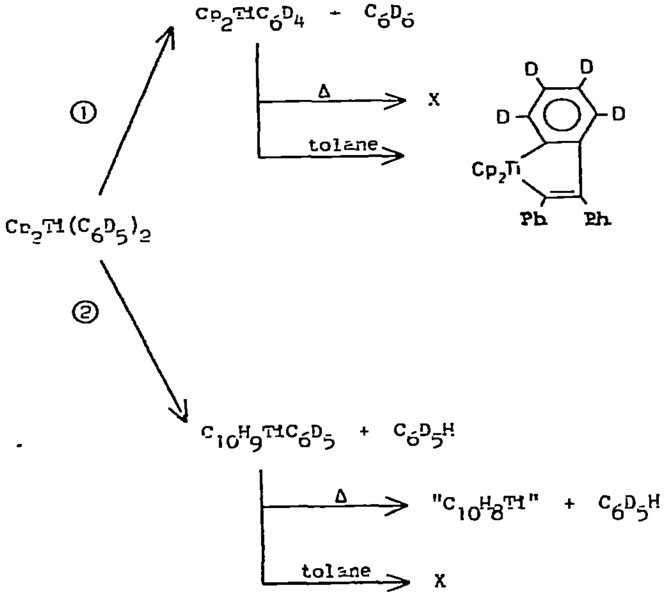
Scheme 1.



the phenylenetitanium complex under the formation of dicyclopentadienyl-2,3-di-phenyl-1-titana-5,6,7,8-tetradeuteroindene (Scheme 2). Indeed, this compound has been isolated from the reaction mixture (yield 45%). Analysis of the volatile decomposition products revealed the presence of C_6D_6 and the absence of $C_6D_4H_2$. However, the presence of C_6D_6 and C_6D_5H in equimolar amounts again shows that about 1/3 of the original $Cp_2Ti(C_6D_5)_2$ decomposes by route 2. Dvorak et al. [2] have suggested that the formation of dicyclopentadienyl-2,3-di-phenyl-1-titanaindene from $Cp_2Ti(C_6H_5)_2$ and tolane in refluxing benzene results from the insertion of the acetylene. Our results strongly support this view.

In contrast to the decomposition in hydrocarbon solvents, in which the solvent is not involved in the reaction, participation of the solvents THF and

Scheme 2



CCl_4 is evident. Decomposition of $Cp_2Ti(C_6H_5)_2$ in THF-d_8 (Table 3, exp. 9) gave C_6H_6, but also considerable amounts of C_6H_5D and $C_6H_4D_2$, showing the participation of the solvent. Although complete decomposition of Cp_2TiR_2 compounds in THF again proceeds with a quantitative formation of RH, the Ti-containing residue is different from that of the decomposition reactions in hydrocarbons. Its IR spectrum shows relation with that of dimeric titanocene $(C_{10}H_9TiH)_2$ [11] (absorption bands at 3100-3090, 1440, 1020, 800-790 characteristic for C_5H_5 and at 1060 cm^{-1} for C_5H_4 groups). Mass spectra indicate the presence of O-containing groups probably from cleavage of THF *. Treatment with HCl in excess gave a green product; no Cp_2TiCl_2 was formed. The IR spectrum of the green complex was identical with that of $(C_{10}H_9TiCl_2)_n$, the reaction product of titanocene $(C_{10}H_9TiH)_2$ with HCl in excess, reported by Salzmann and Mosimann [12].

Decomposition in carbon tetrachloride proceeds with formation of RH (60%) and RCl (31%) (Table 2, exp. 10). Sublimation of the yellow-brown residue yielded Cp_2TiCl_2 (24%) and $CpTiCl_3$ (58%). The participation of THF and CCl_4 in the decomposition is probably due to the donor properties of these solvents which can coordinate at the titanium atom.

The kinetics of the thermal decomposition reaction of dicyclopentadienyltitaniumdiaryl and dibenzyl compounds will be described in a forthcoming paper.

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* It has been reported that titanocene is able to coordinate ether molecules with formation of thermally unstable complexes which decompose by ether cleavage with formation of alkoxides [13].