

MECHANISTIC ASPECTS OF THE THERMAL DECOMPOSITION OF DICYCLOPENTADIENYL TITANIUM(IV) DIBENZYL

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Summary

The thermal decomposition of dicyclopentadienyltitanium(IV) dibenzyl in the solid state and in hydrocarbon solvents has been investigated. The compound decomposes via intermolecular abstraction of hydrogen atoms from the cyclopentadienyl rings with quantitative formation of toluene. The reaction was found to be of first-order with an activation energy of about 16 kcal mol⁻¹. Deuteration of the benzyl groups leads to a higher activation energy (19 kcal mol⁻¹), whereas deuteration of the Cp ligands does not. A reaction mechanism is proposed in which the rate-determining step is the conversion of one of the σ -bonded benzyl ligands into a π -allylic state.

Introduction

Fachinetti and Floriani [1] observed the quantitative formation of toluene on heating of $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$ in benzene. The thermal decomposition of the related compound $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}$ in the solid state was studied by Waters et al. [2], who found bibenzyl, toluene and traces of benzylcyclopentadiene. A mechanism was proposed with a first-order rate-determining step in which the benzyl ligand is promoted to a π -allylic intermediate.

Our investigations on Cp_2TiR_2 (R = aryl, benzyl) showed the exclusive formation of RH on heating the compounds in the solid state and in hydrocarbon solution [3]. A more detailed investigation of the aryl compounds showed the decomposition to occur via an intramolecular pathway: the promotion of an aryl group to a π -bonded state was proposed as the rate-determining step [4]. Since the benzyl differs from the aryl ligands in a number of aspects (e.g. the absence of β -hydrogen atoms), the thermolysis of $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$ was also studied in more detail.

Results and discussion

As previously reported [1,3], the thermal decomposition of $\text{Cp}_2\text{Ti}(\text{CH}_2\text{-C}_6\text{H}_5)_2$ in the solid state and in hydrocarbon solvents proceeds with quantitative formation of toluene. In contrast to the decomposition of Cp_2Ti diaryl compounds the thermolysis of Cp_2Ti dibenzyl probably is an intermolecular process because equimolar mixtures of $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$ and $\text{Cp}_2\text{Ti}(\text{CD}_2\text{C}_6\text{D}_5)_2$ - d_{10} produce C_7H_8 , C_7D_8 , $\text{C}_7\text{H}_7\text{D}$ and $\text{C}_7\text{D}_7\text{H}$ in about equal amounts (Table 1, exp. 4,5,6).

The presence of the partly deuterated toluenes in the decomposition products cannot be ascribed to an exchange of cyclopentadienyl or benzyl ligands preceding the decomposition; analysis of the residue after partial thermolysis (50%) by mass spectrometry revealed the presence of $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$ and $\text{Cp}_2\text{Ti}(\text{CD}_2\text{C}_6\text{D}_5)_2$ - d_{10} and the absence of partly deuterated compounds.

The experiments with $\text{Cp}_2\text{Ti}(\text{CD}_2\text{C}_6\text{D}_5)_2$ (Table 1, exp. 1, 2, 3) show that only $\text{C}_7\text{D}_7\text{H}$ is formed. This indicates that in the solid state and in hydrocarbons only abstraction of hydrogen atoms from Cp groups takes place, which is in contrast with the diaryl compounds [3] where hydrogen abstraction from other groups R was also observed. This may be due to the absence of β -hydrogen atoms on the benzyl ligand. Participation of the solvent is unlikely; when $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$ is decomposed in benzene- d_6 (Table 1, exp. 7) no deuterium is found in the product toluene.

Kinetic measurements showed in all cases a first-order reaction. The activation energy E_A for $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$ was established as 16 kcal mol⁻¹, both in the solid state and in benzene solution (Table 2, exp. 1, 2). This value of E_A correlates with the stability sequence for the aryl and benzyl compounds as derived from the decomposition temperatures [3,4]; the benzyl complex being the least stable one. As is apparent from the results listed in Table 2, deuteration of the benzyl ligands results in a higher value of the activation energy (19 kcal mol⁻¹), whereas deuteration of the Cp groups does not affect E_A , proving that only the benzyl group is involved in the rate-determining step.

Although the decomposition of the dibenzyl complex deviates from that of the Cp_2Ti -diaryl compounds, the rate-determining step of the reaction is a

TABLE 1
THERMAL DECOMPOSITION USING DEUTERATED COMPOUNDS AND SOLVENTS

Compound	exp. conditions	Composition of R-H (% relative ^a)
$\text{Cp}_2\text{Ti}(\text{CD}_2\text{C}_6\text{D}_5)_2$	1. 1 h, 120° C, vacuum	C_7D_8 (-); $\text{C}_7\text{D}_7\text{H}$ (100)
	2. 5 h, 80° C, benzene	C_7D_8 (-); $\text{C}_7\text{D}_7\text{H}$ (100)
	3. 5 h, 80° C, cyclohexane	C_7D_8 (-); $\text{C}_7\text{D}_7\text{H}$ (100)
$\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$ ^b	4. 1 h, 120° C, vacuum	C_7D_8 (100); $\text{C}_7\text{D}_7\text{H}$ (86); C_7H_8 (100); $\text{C}_7\text{H}_7\text{D}$ (88)
	5. 5 h, 80° C, benzene	C_7D_8 (100); $\text{C}_7\text{D}_7\text{H}$ (93); C_7H_8 (100); $\text{C}_7\text{H}_7\text{D}$ (89)
$\text{Cp}_2\text{Ti}(\text{CD}_2\text{C}_6\text{D}_5)_2$ - d_{10}	6. 5 h, 80° C, cyclohexane	C_7D_8 (98); $\text{C}_7\text{D}_7\text{H}$ (94); C_7H_8 (100); $\text{C}_7\text{H}_7\text{D}$ (91)
$\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$	7. 5 h, 80° C, benzene- d_6 , N ₂	C_7H_8 (100); $\text{C}_7\text{H}_7\text{D}$ (-)

^a Relative amounts of volatile product from the peak intensities in the mass spectra. ^b Equimolar mixture of the two compounds.

TABLE 2
KINETIC DATA FOR THE DECOMPOSITION OF Cp_2TiR_2 COMPOUNDS

Compound	Medium	Temp. (°C)	$k \times 10^4$ (sec^{-1})	E_A (kcal mol^{-1})	Dec. temp. ^a (°C)
1. $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$	Vacuum	70	0.145	16	95
		80	0.269		
		90	0.471		
2. $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$	Benzene	41	0.011	16	
		52	0.025		
		61	0.045		
3. $\text{Cp}_2\text{Ti}(\text{CD}_2\text{C}_6\text{D}_5)_2$	Vacuum	70	0.094	18	110
		80	0.192		
		90	0.387		
4. $\text{Cp}_2\text{Ti}(\text{CD}_2\text{C}_6\text{D}_5)_2-d_{10}$	Vacuum	70	0.093	19	112
		80	0.192		
		90	0.405		
5. $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2-d_{10}$	Vacuum	70	0.146	15	95
		80	0.258		
		90	0.448		

^a Obtained from DTA measurements.

comparable step. In this step, one of the originally σ -bonded benzyl ligands may be promoted to a π -allylic transition state by interaction of the π -electron system of the benzyl group with a vacant metal orbital. This type of σ - π rearrangement has been reported for other transition-metal benzyl derivatives [5,6]. Probably, this activated benzyl group can move from one titanium atom to another, as proposed for the thermal decomposition of the related complex $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}$ [2]. A free-radical mechanism is unlikely, because reaction products like bibenzyl were found only in trace amounts and no radical termination reactions like the abstraction of hydrogen from solvents were observed. The activated benzyl group abstracts a hydrogen atom from a Cp ring; the second benzyl group is activated and abstracts a hydrogen from a Cp ligand in a similar way.

Experimental

The benzyl compounds Cp_2TiR_2 were prepared by the following modification of the published method [7]: the reaction of Cp_2TiCl_2 with two equivalents of RMgBr was carried out in the presence of two equivalents of dioxane; the product was crystallized from ether. The starting material $\text{Cp}_2\text{TiCl}_2-d_{10}$ was prepared by the method of Martin et al. [8]. The purity of all compounds was checked by elemental analysis and mass spectrometry.

The thermolysis experiments were carried out as described previously for the aryl compounds [3]. The degree of deuteration of toluene was determined by mass spectrometry. The results are presented in Table 1.

The kinetic measurements were performed as previously described [4]. In solution, the decomposition was followed spectrophotometrically from the absorption at 491 nm; an isobestic point in the spectra was observed at 438 nm.

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