

Journal of Organometallic Chemistry, 102 (1975) 161–165
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MECHANISTIC ASPECTS OF THE THERMAL DECOMPOSITION OF DICYCLOPENTADIENYL TITANIUM(IV)DIARYL COMPOUNDS

C.P. BOEKEL*, J.H. TEUBEN and H.J. de LIEFDE MEIJER

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

(Received June 11th, 1975)

Summary

The thermal decomposition of a number of compounds Cp_2TiR_2 ($\text{R} = \text{aryl}$) was studied in the solid state and in various solvents. A first-order reaction was observed and activation energies of 20–30 kcal mol^{-1} were found depending on the nature of R . The activation energy for $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2$ (20–22 kcal mol^{-1}) appeared to be independent of the reaction medium (solid state or dissolved in cyclohexane, benzene, THF, CCl_4 or in the presence of toluene). Deuteration of the phenyl groups results in a higher value of the activation energy ($\sim 29 \text{ kcal mol}^{-1}$), whereas deuteration of the Cp ligands does not.

A reaction mechanism is proposed in which the first and rate-determining step of the decomposition is the conversion of one of the σ -bonded ligands R to a π -bonded activated state.

Introduction

Kinetic data on thermal decomposition reactions of aryltitaniums are scarce. Waters et al. [1] when studying the thermolysis of $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)\text{Cl}$ found a first-order loss of the group R and an activation energy of 29 kcal mol^{-1} . These authors postulated the formation of a π -bonded phenyl radical in the transition state, and considered this process in relation to experiments by Dvorak et al. [2] on the thermolysis of $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2$.

Recently, we reported the thermal decomposition of the compounds Cp_2TiR_2 ($\text{R} = \text{aryl, benzyl}$) proceeds according to [3]:



In order to obtain a more detailed insight into the mechanism of this decomposition we have studied the kinetics.

Results

Samples of about 0.5 mmol Cp_2TiR_2 ($\text{R} = \text{aryl}$) were heated under vacuum at various thermostatted temperatures ($\pm 0.1^\circ\text{C}$). The volatile products were pumped off and the fraction of undecomposed material x/x_0 was calculated from the weight of the residue, using the observation that thermal decomposition proceeds with quantitative formation of R-H [3].

In solution (N_2 atmosphere, solvent: benzene, toluene, cyclohexane, THF and CCl_4 ; $c = \text{about } 3 \times 10^{-3} \text{ mmol/liter}$) the thermal decomposition was monitored spectrophotometrically (Perkin—Elmer EPS-3T) at various temperatures ($\pm 0.1^\circ\text{C}$). The fraction of undecomposed material x/x_0 was calculated from the absorption of Cp_2TiR_2 at 425 nm. The spectra showed an isobestic point at 380 nm.

In all cases the fraction of undecomposed material x/x_0 fits the equation: $-\ln x/x_0 = kt$ for a first-order reaction. Satisfactory Arrhenius plots were obtained. The experimental conditions, the rate constants, and the derived values of E_A are given in Table 1.

The partly and completely deuterated analogues of $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2$ were investigated in the same way; the results are presented in Table 2.

TABLE 1
KINETIC DATA FOR THE DECOMPOSITION OF Cp_2TiR_2 COMPOUNDS

	R	Medium	T ($^\circ\text{C}$)	$k \times 10^4$ (sec^{-1})	E_A (kcal mol^{-1})	Dec. temp. ^a ($^\circ\text{C}$)
1.	Phenyl	Vacuum	70	0.012	22	120
			80	0.025		
			90	0.076		
2.	Phenyl	Cyclohexane	47	0.063	20	
			61	0.23		
			74	0.75		
3.	Phenyl	Benzene	47	0.060	22	
			64	0.42		
			77	1.06		
4.	Phenyl	THF	42	0.014	20	
			50	0.048		
			61	0.12		
5.	Phenyl	CCl_4	41	0.138	22	
			50	0.435		
			60	1.33		
6.	Phenyl	Toluene, toluene	51	0.065	20	
			61	0.23		
			78	0.93		
7.	<i>m</i> -Tolyl	Vacuum	70	0.005	30	134
			80	0.022		
			90	0.071		
8.	<i>p</i> -Tolyl	Vacuum	70	0.010	23	125
			80	0.025		
			90	0.074		
9.	3,4-Xylyl	Vacuum	70	0.005	36	136
			80	0.022		
			90	0.070		

^aObtained from DTA measurements [3].

TABLE 2

KINETIC DATA FOR THE DECOMPOSITION OF DEUTERATED Cp_2TiR_2 COMPOUNDS IN THE SOLID STATE IN VACUUM

Compound	T ($^{\circ}\text{C}$)	$k \times 10^4$ (sec^{-1})	E_A (kcal mol^{-1})	Dec. temp. ^a ($^{\circ}\text{C}$)
$\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2$	70	0.012	22	120
	80	0.025		
	90	0.076		
$\text{Cp}_2\text{Ti}(\text{C}_6\text{D}_5)_2$	70	0.008	29	134
	80	0.020		
	90	0.072		
$\text{Cp}_2\text{Ti}(\text{C}_6\text{D}_5)_2\text{-}d_{10}$	70	0.008	30	136
	80	0.019		
	90	0.072		
$\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2\text{-}d_{10}$	70	0.011	22	121
	80	0.025		
	90	0.076		

^aObtained from DTA measurements.

The thermal decomposition of $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2$ in toluene was also studied in the presence of one mole of diphenylacetylene (Table 1, exp. 6), since the presence of this compound is known to lead to, among other products, an insertion product of the proposed intermediate phenylenetitanium complex [2,3].

Discussion

Our previous results on the thermal decomposition of Cp_2TiR_2 compounds ($\text{R} = \text{aryl}$) [3] suggested a strong similarity in decomposition routes for all the compounds, in the solid state and in hydrocarbon solvents, and indicated that the decomposition is intramolecular. This is confirmed in the present study which has revealed a first-order character for the decomposition in all cases. The activation energies, E_A which vary in the range of 20-30 kcal mol^{-1} , correlate with the observed decomposition temperatures (DTA) and correspond to a stability sequence $\text{R} = \text{phenyl-}d_5 \sim 3,4\text{-xylyl} \sim m\text{-tolyl} > p\text{-tolyl} > \text{phenyl}$. The values are comparable with that reported for $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)\text{Cl}$ ($= 29 \text{ kcal mol}^{-1}$) [1].

The energy of activation does not depend on the medium (solid state or in hydrocarbons, ethers or chlorine-containing solvents) (Table 1, exp. 1-5). This is strong evidence that the rate-determining step in all cases is the same unimolecular process, which occurs in the early stage of the decomposition. This rate-determining step clearly involves the R groups, as indicated by the E_A values found for the various deuterated compounds $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2$. Whereas deuteration of the Cp ligands does not influence the activation energy, deuteration of the aryl groups leads to a distinct higher value (Table 2).

The decomposition in the solid state and in hydrocarbon solution has been shown to be intramolecular [3]. A free-radical mechanism as proposed by Razuvaev et al. [4] is unlikely since radical-type products (for example the coupling product $\text{R}-\text{R}$) were found only in trace amounts, and no radical termination reactions, such as hydrogen abstraction from hydrocarbon solvents, were observed. It is unlikely therefore that the σ -bonded ligands are diffusing away as free

radicals from the original molecules as proposed for the decomposition of $\text{Cp}_2\text{-Ti}(\text{C}_6\text{H}_5)\text{Cl}$ [1].

We suggest a mechanism for the decomposition of Cp_2TiR_2 ($\text{R} = \text{aryl}$) in which the first and rate-determining step is the raising of one of the σ -bonded ligands R to a π -bonded "activated" state, probably by intramolecular coordination of the π -electron system of the aryl group with an unoccupied metal orbital (Cp_2TiR_2 is a 16 electron system). In the original molecule this vacant orbital is probably sterically shielded by the ligands R and the cyclopentadienyl groups, so that no other electron-donating groups can coordinate with the metal and take part in the first step. As a consequence of the reorientation of the R group, one of the π -bonded cyclopentadienyl groups may be pushed into a h^3 , h^2 or even h^1 bonded state. The activated ligand R is then converted into R-H by abstraction of a hydrogen atom from a Cp group or from the other coordinated ligand R , leaving a coordinatively and sterically unsaturated titanium species. This species is then able to coordinate donor molecules, which may participate in the further decomposition, e.g. the abstraction of a hydrogen atom from THF or of a chlorine atom from CCl_4 by the second ligand R . This mechanism explains the previously observed dependence of products on the solvent [3] even though the activation energy is independent of the medium (Table 1).

In the decomposition of $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2$ in the presence of toluene, coordination of the latter with the proposed intermediate phenylenetitanium complex leads to an insertion product [2,3,5] although the activation energy is unchanged (Table 1, exp. 6). This reaction is probably related to those described by Vol'pin et al. [6] and by Shur et al. [7], who observed insertion products with CO_2 and N_2 , respectively, in the decomposition of $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2$.

In our opinion the rate-determining step in the decomposition of $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)\text{Cl}$ [1], for which Waters et al. [1] in contrast, suggested the initial formation of a phenyl radical species in the intermolecular decomposition.

Dicyclopentadienyltitanium(IV)dibenzyl also decomposes with quantitative formation of R-H [3] but the decomposition is intermolecular, in contrast with that of the diaryl compounds. Studies of this decomposition are in progress.

Preliminary studies of the decomposition of Cp_2NbR_2 ($\text{R} = \text{aryl}$) (with quantitative formation of R-H via abstraction of a hydrogen atom from the cyclopentadienyl groups only) and Cp_2VR ($\text{R} = \text{aryl}$) (with formation of R-H , Cp_2V and a vanadocene derivative with the group R substituted in one of the cyclopentadienyl rings), and also the evidence that the decomposition of Cp_2TiR ($\text{R} = \text{aryl}$) [8] is different in type from that of Cp_2TiR_2 , indicate that one single mechanism cannot be assumed even for these related compounds. The stability of the compounds and the mechanism of their thermal decomposition depend strongly on the nature and oxidation state of the metal and the nature of the ligands.

Acknowledgement

The authors are much indebted to Prof. Dr. F. Jellinek for his most stimulating interest.

References

- 1 J.A. Waters, V.V. Vickroy and G.A. Mortimer, *J. Organometal. Chem.*, **33** (1971) 41.
- 2 J. Dvorak, R.J. O'Brien and W. Santo, *J. Chem. Soc. D, Chem. Commun.*, (1970) 411.
- 3 C.P. Boekel, J.H. Teuben and H.J. de Liefde Meijer, *J. Organometal. Chem.*, **81** (1974) 371.
- 4 G.A. Razuvaev, V.N. Latyaeva and L.I. Vishinskaya, *Dokl. Akad. Nauk SSSR*, **159** (1964) 383.
- 5 H. Masai, K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jap.*, **41** (1968) 750.
- 6 M.E. Vol'pin, V.A. Dubovitskii and O.V. Nogina, *Dokl. Akad. Nauk SSSR*, **151** (1963) 1100.
- 7 V.B. Shur, E.G. Berkovitch, L.B. Vasiljeva, R.V. Kudryavtsev and M.E. Vol'pin, *J. Organometal. Chem.*, **78** (1974) 127.
- 8 J.H. Teuben, *J. Organometal. Chem.*, **69** (1974) 241.