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THERMAL DECOMPOSITION OF DICYCLOPENTADIENYLNIOBIUM(IV)DIPHENYL

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Summary

The thermal decomposition of dicyclopentadienylniobium(IV)diphenyl in the solid state and in hydrocarbon solvents has been studied. The compound decomposes with quantitative formation of C_6H_6 and a Nb-containing residue which has lost the Cp_2Nb structure. Experiments with deuterated compounds and solvents show that decomposition proceeds via intramolecular abstraction of a hydrogen atom from a cyclopentadienyl ring. The reaction is first-order with an activation energy of about 35 kcal/mol, both in the solid state and in toluene. Deuteration of the phenyl groups leads to a higher value of the activation energy (~39 kcal/mol), whereas deuteration of the Cp ligands does not. The decomposition mechanism is discussed and compared with that of the analogous titanium compound.

Introduction

Siegert and De Liefde Meijer [1] noted a close resemblance in chemical behaviour between $Cp_2Nb(C_6H_5)_2$ and the corresponding titanium complex; they also reported that $Cp_2Nb(C_6H_5)_2$ is thermally more stable (decomposition above 150°C) than $Cp_2Ti(C_6H_5)_2$ (dec. 120°C [2]).

Recently, we described the thermal decomposition of the compounds Cp_2TiR_2 [2,3,4] in some detail. In this paper we describe a study of the thermal behaviour of $Cp_2Nb(C_6H_5)_2$. DTA was used to establish the thermal stability. The mechanism of the decomposition reaction was studied in solution (toluene, cyclohexane) and in the solid state using deuterated compounds and solvents.

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Results and discussion

Thermolysis of the compound $Cp_2Nb(C_6H_5)_2$ in the solid state or in toluene or cyclohexane solution, results in quantitative formation of C_6H_6 and of a black-brown solid residue (Table 1, exp. 1—4). In experiments where the decomposition was incomplete, treatment of the residue with HCl (eq. 1 [1]) produced Cp_2NbCl_2 and C_6H_6 in a molar ratio of 1 : 2 (Table 1, exp. 2, 4), demonstrating the presence of a corresponding amount of undecomposed $Cp_2Nb(C_6H_5)_2$; the total amount of C_6H_6 corresponds to the original number of phenyl groups in the starting material $Cp_2Nb(C_6H_5)_2$.

$$Cp_2Nb(C_6H_5)_2 + 2\ HCl \rightarrow Cp_2NbCl_2 + 2\ C_6H_6 \tag{1}$$

The thermal decomposition of $Cp_2Nb(C_6H_5)_2$ in toluene-d_8 (Table 2, exp. 3), in which only C_6H_6 is produced, shows that the solvent does not act as a hydrogen source for the formation of C_6H_6. In all cases therefore, the hydrogen atoms are abstracted from the Cp groups, resulting in a destruction of the original Cp_2Nb structure. The decomposition may be represented by the overall eq. 2:

$$Cp_2Nb(C_6H_5)_2 \rightarrow \text{“}C_{10}H_8Nb\text{”} + 2\ C_6H_6 \tag{2}$$

For stoichiometric reasons, the solid niobium-containing residue is formulated as “$C_{10}H_8Nb$”. The IR spectrum of the residue shows relation with that of niobocene [5]. Treatment with HCl/ether in excess does not yield Cp_2NbCl_2.

Thermolysis experiments with an equimolar mixture of $Cp_2Nb(C_6H_5)_2$ and $Cp_2Nb(C_6D_5)_2$-d_{10} (Table 2, exp. 4, 5) in the solid state or in toluene show that the decomposition is an intramolecular process. Only C_6H_6 and C_6D_6 (1 : 1) are produced and no partly deuterated benzenes, which would be expected if the decomposition were an intermolecular process.

As discussed previously [2,3], the thermal decomposition of dicyclopentadienyltitaniumdiaryl compounds proceeds by intramolecular hydrogen abstraction via two routes, either directly from a Cp ring (Scheme 1, route 2) or from the other coordinated group R with formation of the intermediate phenylene-

TABLE 1

YIELDS OF PRODUCTS AFTER THERMOLYSIS OF $Cp_2Nb(C_6H_5)_2$ AND TREATMENT OF THE RESIDUE WITH HCl

Thermal decomposition		Reaction of residue with HCl	
Exp. conditions	Volatile products RH (%)	Volatile products RH (%)	Cp_2NbCl_2 (%)
1. 1 h, 159°C, vacuum	89	8	10
2. 16 h, 125°C, vacuum	45	47	40
3. 124 h, 110°C, toluene, N_2	90.	—	4
4. 60 h, 80°C, cyclohexane, N_2	46	48	46
5. 124 h, 110°C, toluene, tolane, N_2	89	—	—

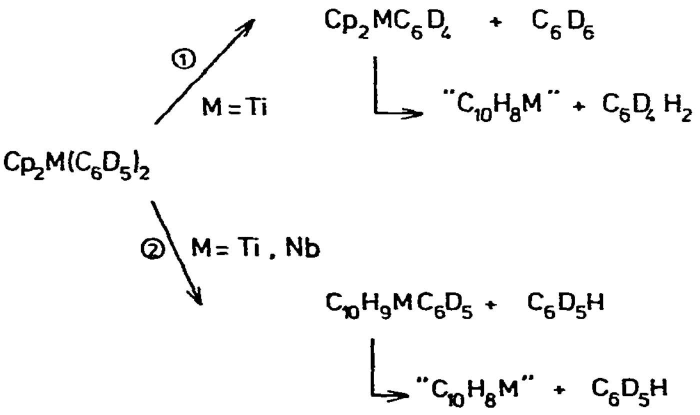
TABLE 2

THERMAL DECOMPOSITION USING DEUTERATED COMPOUNDS AND SOLVENTS

Compound	Exp. conditions	Composition of RH (% relative [a])
1. $Cp_2Nb(C_6D_5)_2$	1 h, 168°C, vacuum	C_6D_6(-): C_6D_5H(100): $C_6D_4H_2$(-)
2. $Cp_2Nb(C_6D_5)_2$	124 h, 110°C, toluene, N_2	C_6D_6(-): C_6D_5H(100): $C_6D_4H_2$(-)
3. $Cp_2Nb(C_6H_5)_2$	124 h, 110°C, d^8-toluene, N_2	C_6H_6(100): C_6H_5D(-)
4. $Cp_2Nb(C_6H_5)_2$ + $Cp_2Nb(C_6D_5)_2$-d_{10} [b]	1 h, 168°C, vacuum	C_6D_6(100): C_6D_5H(-): C_6H_6(100): C_6H_5D(-)
5. $Cp_2Nb(C_6H_5)_2$ + $Cp_2Nb(C_6D_5)_2$-d_{10} [b]	124 h, 110°C, toluene, N_2	C_6D_6(100): C_6D_5H(-): C_6H_6(100): C_6H_5D(-)

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

Scheme 1



titanium complex (Scheme 1, route 1). However, the experiments with $Cp_2Nb(C_6D_5)_2$ (Table 2, exp. 1, 2) show that in this case the volatile decomposition product is exclusively C_6D_5H with no C_6D_6 (Scheme 1). Thus benzene is formed only by direct abstraction of hydrogen from the Cp rings and no hydrogen is abstracted from the second phenyl group.

In the case of $Cp_2Ti(C_6H_5)_2$ the existence of route 1 was confirmed by performing the thermal decomposition in the presence of tolane. This led to an insertion product of the acetylene with the intermediate phenylenetitanium complex, formed during thermal decomposition via route 1, [6,7]. In a similar experiment with the niobium compound (Table 1, exp. 5), unchanged tolane was recovered almost quantitatively, along with a quantitative yield of C_6H_6, again indicating that the decomposition proceeds completely via route 2.

Our kinetic measurements are also in agreement with the observed unimolecular character of the decomposition, since in all cases a first-order reaction was

TABLE 3

DIFFERENTIAL THERMAL ANALYSIS DATA AND ACTIVATION ENERGIES FOR Cp_2NbR_2 COMPOUNDS

Compound	Medium	Decomp. temperature (°C)	E_A (kcal/mol)
1. $Cp_2Nb(C_6H_5)_2$	vacuum	159	35
2. $Cp_2Nb(C_6H_5)_2$	toluene		34
3. $Cp_2Nb(C_6D_5)_2$	vacuum	169	39
4. $Cp_2Nb(C_6D_5)_2$-d_{10}	vacuum	168	38
5. $Cp_2Nb(C_6H_5)_2$-d_{10}	vacuum	158	34

found. An activation energy of about 35 kcal/mol was found for $Cp_2Nb(C_6H_5)_2$, both in the solid state and in toluene solution (Table 3, exp. 1, 2). This higher value of E_A is consistent with the higher thermal stability (Table 3) in comparison with that of the analogous titanium compound, for which an activation of 22 kcal/mol was found [2,3]. Deuteration of the phenyl groups leads to a higher value of the activation energy (39 kcal/mol), whereas deuteration of the Cp ligands does not affect E_A. A similar trend is also observed in the DTA data. This effect, which has also been observed for the corresponding titanium complexes, strongly indicates that σ-bonded phenyl groups are primarily involved in the rate-determining step of the decomposition reaction. The results indicate that the decomposition mechanisms of Cp_2NbR_2 and Cp_2TiR_2 are closely related. Therefore, a similar first and rate-determining step is suggested for $Cp_2Nb(C_6H_5)_2$ as for the analogous titanium compound: the conversion of an originally σ-bonded phenyl group to a π-bonded state, initiated by interaction of the π-electron system of the phenyl ring with the non-bonding metal orbital. Since the atomic radii of titanium and niobium are almost the same [1], one may assume that the titanium and niobium complexes sterically are very similar. However, for Cp_2NbR_2 (17-electron system) the non-bonding orbital is occupied by one electron, in contrast with Cp_2TiR_2 (16-electron system) where the non-bonding hybrid orbital is empty. This is probably the reason for the observed increase in thermal stability of Cp_2NbR_2 and also for the absence of the decomposition route via abstraction of a hydrogen atom from the other phenyl group (route 1), which was found for the corresponding titanium compound.

In further decomposition steps, the activated phenyl group of Cp_2NbR_2 abstracts a hydrogen atom from a Cp ring with formation of C_6H_6. This is immediately followed by abstraction of another hydrogen atom from the Cp rings by the second phenyl group, again with formation of benzene.

Experimental

The $Cp_2Nb(C_6H_5)_2$ compounds were synthesized by a modification of the method described previously [1]. After reaction of Cp_2NbCl_2 with two equivalents of phenyllithium in ether, the solvent was removed under vacuum. Washing with n-hexane and extraction of the residue with benzene gave the pure compound. The compounds with deuterated cyclopentadienyl groups were prepared from cyclopentadiene-d_6, which was made by a published procedure [8]. In all cases, mass spectra showed a degree of deuteration over 90%. The purity of all compounds was checked by element analyses.

Decomposition reactions were carried out as described for the Cp_2TiR_2 compounds [2]. However, after treatment of the solid decomposition residue with an excess of HCl, Cp_2NbCl_2 was separated from the reaction mixture by sublimation (260° C/0.1 mmHg) and quantitatively determined by weighing. In a separate experiment $Cp_2Nb(C_6H_5)_2$ was refluxed in toluene in the presence of diphenylacetylene. After 124 h. the volatiles were distilled off and analyzed (Table 1, exp. 5). Extraction of the residue with benzene gave a white product which was shown by IR and mass spectrometry to be unchanged tolane (recovered 86%).

The kinetic measurements on solid samples and on solutions were carried out as described for the titanium analogues [3]. In solution the decomposition was followed spectrometrically at 497 nm. An isobestic point was observed at 440 nm.

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