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THERMAL DECOMPOSITION OF DICYCLOPENTADIENYLARYLVANADIUM COMPOUNDS

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Summary

The thermolysis of compounds of the type Cp_2VR (R = aryl) in the solid state has been studied. A distinct increase in thermal stability is observed upon substitution of the *ortho*-position of the aryl group. Thermal decomposition occurs with formation of RH, Cp_2V, a vanadocene homologue with the group R substituted in one of the Cp rings and, probably, a vanadocene homologue with two substituted Cp rings. It is shown that the abstraction of the hydrogen atom from the cyclopentadienyl ring, necessary for the formation of RH, is an intermolecular process, whereas the substitution of the aryl group in the Cp ring is intramolecular. A decomposition mechanism is proposed in which the group R is transferred from the vanadium atom to the C_5H_5 ring of the same molecule by interaction with an aryl group of another molecule. The thermal decomposition of Cp_2VR is compared with that of the analogous titanium compounds.

Introduction

Our investigations on Cp_2TiR (R = aryl) [1] led us to study the thermal behaviour of the corresponding vanadium complexes, which are thermally much more stable [2]. Previously, Razuvaev et al. [3] studied the thermal decomposition of $Cp_2VC_6H_5$ in the solid state and in benzene solution; they reported C_6H_6 (60—65%), $(C_6H_5)_2$ (10—13%) and Cp_2V (80—90%) as the main reaction products. These authors suggest a mechanism which involves, among other features, the disproportionation of $Cp_2VC_6H_5$ into $(C_5H_5)_3V$ and $C_5H_5V(C_6H_5)_2$ followed by formation of benzene from the latter compound by abstraction of a hydrogen atom from a Cp ring.

In this paper we describe our studies of the thermal decomposition of the compounds Cp_2VR (R = aryl). DTA was used to determine the relative thermal stabilities. The reaction was studied by thermolysis of Cp_2VR and deuterated compounds followed by analysis of the reaction products.

Experimental

All experiments were carried out under N_2. Elemental analyses were performed at the Analytical Department of the Chemical Laboratories of this University under supervision of Mr. A.F. Hamminga. Gas-chromatographic analyses were carried out with a Hewlett—Packard 7620-A Research Chromatograph. Infrared spectra were recorded with a Hitachi EPI-3G spectrophotometer. Magnetic susceptibilities were determined by Miss R. Haange with a vibrating-sample magnetometer (Par Magnetometer type 150 D). The mass spectra were recorded by Mr. A. Kiewiet with an AEI-MS 9 instrument. Thermograms were obtained using a low-temperature DTA-apparatus [4]; heating rate 2—3°/min.

Starting materials

The aryl compounds Cp_2VR were made by an established method [5]. The compounds with R = phenyl, *o*-tolyl, *m*-tolyl and *p*-tolyl were purified by crystallization from n-pentane; the compound with R = 2,6-xylyl by sublimation (140°C/0.5 mmHg) after extraction from the reaction mixture with n-pentane.

The compounds with deuterated cyclopentadienyl groups were prepared from Cp_2VCl-d_{10} which was made from cyclopentadiene-d_6, which was prepared by a published method [6]; mass spectra showed a degree of over 90% deuteration. The purity of all compounds was checked by elemental analyses.

Procedures and results

In general the procedures were as described for the thermal decomposition of Cp_2TiR_2 [7].

Differential thermal analysis. The thermograms in all cases showed a reversible endothermic effect, at higher temperatures followed by an irreversible exothermic peak. The first transition temperature is due to melting of Cp_2VR, and the second to its decomposition. The transition temperatures are listed in Table 1.

Thermolysis. Thermolysis of the solid compounds (about 2 mmol) were carried out at the decomposition temperatures given in Table 1 and the products were separated and analyzed. The yields are given in Table 2. The volatile products were condensed in a cold trap and analyzed by GLC and mass spectrometry;

TABLE 1

DATA FOR DIFFERENTIAL THERMAL ANALYSIS OF Cp_2VR COMPOUNDS

R	Endothermic effect (°C)	Exothermic effect (°C)
Phenyl	83	158
o-Tolyl	78	204
m-Tolyl	77	138
p-Tolyl	82	148
2,6-Xylyl	208	246

TABLE 2

YIELDS OF PRODUCTS FROM THERMOLYSIS OF Cp_2VR COMPOUNDS IN THE SOLID STATE

R	Experimental conditions	Decomposition products (%)			
		RH	RR	Cp_2V	$Cp(C_5H_4R)V$
C_6H_5	1 h, 158°C, N_2	30	<1	50	17
m-$CH_3C_6H_4$	1 h, 138°C, N_2	36	<1	57	13
p-$CH_3C_6H_4$	1 h, 148°C, N_2	35	<1	55	15

in all cases this material consisted of RH only. Vanadocene was isolated from the residues by sublimation in vacuo (0.1 mmHg) at about 70°C. The yields were determined by weighing. Upon subsequent heating at about 120°C another product sublimed.

In the case of the phenyl and p-tolyl residues, dark-grey crystals were obtained, while the m-tolyl residue gave a dark-violet viscous oil; these products were identified as vanadocene derivatives in which the R groups are substituted in one of the Cp rings. The infrared spectra of these products show the frequencies of π-bonded cyclopentadienyl rings (absorptions at 3080—3070, 1420, 1105, 1000 and 800—775 cm^{-1}) and also the C—H and C—C frequencies of the group R (absorptions at 3020, 2910, 1600—1500 and 770—690 cm^{-1}). The products are paramagnetic; in the temperature range 90—300 K a moment of 3.74 BM was measured (corrected for induced diamagnetism). This corresponds with three unpaired electrons per molecule (μ_{eff} 3.90 BM calculated for spin only), as is also found for vanadocene. The mass spectra show the presence of the parent ions $C_{10}H_9RV^+$ while the fragment ions include $C_5H_4RV^+$, $C_5H_5R^+$ and $C_5H_4R^+$ (Table 3). Evidence for the assumption that the group R is substituted in the Cp rings, was also found in the mass spectrum of the compound with R $= C_6D_5$, where a parent ion was observed at m/e 262 ($Cp(C_5H_4C_6D_5)V^+$) and the fragment ions at 197 ($C_5H_4C_6D$ [illegible]), 147 ($C_5H_5C_6D_5^+$) and 146 ($C_5H_4C_6D_5^+$) (Table 3). The elemental analyses of the decomposition products, which are presented in Table 4, also agrees with the formula $Cp(C_5H_4R)V$.

Further proof for the proposed structure was found in the reaction with HCl in ether at —78°C (eq. 1). No RH was formed, indicating the absence of a V—R

$$Cp(C_5H_4R)V + HCl \rightarrow Cp(C_5H_4R)VCl + 1/2\ H_2 \qquad (1)$$

σ-bond in the starting material. The results of elemental analyses of the green products of reaction 1 are in agreement with the formula $Cp(C_5H_4R)VCl$ (Table 4). The infrared spectra of these products show the characteristic absorptions of the Cp and R groups; peaks at 3090—3075, 1420, 1120, 1000 and 840—800 cm^{-1} are attributed to frequencies of the π-bonded C_5H_5 rings and at 3020, 2910, 1600—1500 and 800—690 cm^{-1} to σ-bonded aryl groups. In the mass spectra parent ions were observed at m/e ratios which agree with $C_{10}H_9RVCl^+$ while the fragment ions include $C_{10}H_9RV^+$, $C_5H_4RVCl^+$, $CpVCl^+$, $C_5H_5C_6H_5^+$, $C_5H_4C_6H_5^+$ and VCl^+ (Table 5). Magnetic susceptibility measurements showed that the complexes are paramagnetic with a moment of 2.66 BM (corrected for induced diamagnetism), which corresponds with two unpaired electrons (μ_{eff}

TABLE 3

MASS SPECTRA OF $Cp(C_5H_4R)V$ COMPOUNDS

(a) $Cp(C_5H_4C_6H_5)V$

m/e	Relative intensity	Ion
257	100	$C_5H_5(C_5H_4C_6H_5)V^+$
192	12	$C_5H_4C_6H_5V^+$
142	100	$C_5H_5C_6H_5^+$
141	62	$C_5H_4C_6H_5^+$
116	67	$C_5H_5V^+$
115	25	$C_5H_4V^+$
78	1	$C_6H_6^+$
77	3	$C_6H_5^+$
66	12	$C_5H_6^+$
65	9	$C_5H_5^+$
51	15	V^+

(b) $Cp(C_5H_4C_6D_5)V$

m/e	Relative intensity	Ion
262	16	$C_5H_5(C_5H_4C_6D_5)V^+$
197	10	$C_5H_4C_6D_5V^+$
147	100	$C_5H_5C_6D_5^+$
146	38	$C_5H_4C_6D_5^+$
116	20	$C_5H_5V^+$
115	8	$C_5H_4V^+$
83	1	$C_6D_5H^+$
82	2	$C_6D_5^+$
66	5	$C_5H_6^+$
65	5	$C_5H_5^+$
51	3	V^+

(c) $Cp(C_5H_4\text{-}m\text{-}CH_3C_6H_4)V$

m/e	Relative intensity	Ion
271	52	$C_5H_5(C_5H_4C_7H_7)V^+$
206	10	$C_5H_4C_7H_7V^+$
156	100	$C_5H_5C_7H_7^+$
155	10	$C_5H_4C_7H_7^+$
116	29	$C_5H_5V^+$
115	8	$C_5H_4V^+$
92	2	$C_7H_8^+$
91	4	$C_7H_7^+$
66	5	$C_5H_6^+$
65	3	$C_5H_5^+$
51	5	V^+

(d) $Cp(C_5H_4\text{-}p\text{-}CH_3C_6H_4)V$

m/e	Relative intensity	Ion
271	100	$C_5H_5(C_5H_4C_7H_7)V^+$
206	4	$C_5H_4C_7H_7V^+$
156	14	$C_5H_5C_7H_7^+$
155	3	$C_5H_4C_7H_7^+$
116	20	$C_5H_5V^+$
115	2	$C_5H_4V^+$
92	2	$C_7H_8^+$
91	3	$C_7H_7^+$
66	6	$C_5H_6^+$
65	5	$C_5H_5^+$
51	4	V^+

TABLE 4

ANALYTICAL DATA FOR THE COMPLEXES $Cp(C_5H_4R)V$ AND $Cp(C_5H_4R)VCl$

Compound	Analysis, found (calcd.) (%)		
	C	H	V
$Cp(C_5H_4C_6H_5)V$	74.58	5.58	19.67
	(74.70)	(5.44)	(19.80)
$Cp(C_5H_4\text{-}m\text{-}CH_3C_6H_4)V$	74.82	6.33	18.67
	(75.24)	(5.90)	(18.79)
$Cp(C_5H_4\text{-}p\text{-}CH_3C_6H_4)V$	74.50	6.12	18.66
	(75.24)	(5.90)	(18.79)
$Cp(C_5H_4C_6H_5)VCl$	65.59	4.86	17.38
	(65.74)	(4.79)	(17.46)
$Cp(C_5H_4\text{-}p\text{-}CH_3C_6H_4)VCl$	66.26	5.42	16.63
	(66.66)	(5.23)	(16.61)

TABLE 5

MASS SPECTRA OF $Cp(C_5H_4R)VCl$ COMPOUNDS [a]

(a) $Cp(C_5H_4C_6H_5)VCl$			(b) $Cp(C_5H_4\text{-}p\text{-}CH_3C_6H_4)VCl$		
m/e	Relative intensity	Ion	*m/e*	Relative intensity	Ion
292	28	$C_5H_5(C_5H_4C_6H_5)VCl^+$	306	40	$C_5H_5(C_5H_4C_7H_7)VCl^+$
257	17	$C_5H_5(C_5H_4C_6H_5)V^+$	271	5	$C_5H_5(C_5H_4C_7H_7)V^+$
227	17	$C_5H_4C_6H_5VCl^+$	241	29	$C_5H_4C_7H_7VCl^+$
192	14	$C_5H_4C_6H_5V^+$	206	11	$C_5H_4C_7H_7V^+$
151	100	$C_5H_5VCl^+$	156	17	$C_5H_5C_7H_7^+$
142	40	$C_5H_5C_6H_5^+$	155	100	$C_5H_4C_7H_7^+$
141	36	$C_5H_4C_6H_5^+$	151	33	$C_5H_5VCl^+$
116	51	$C_5H_5V^+$	116	12	$C_5H_5V^+$
115	32	$C_5H_4V^+$	115	11	$C_5H_4V^+$
86	36	VCl^+	86	26	VCl^+
66	24	$C_5H_6^+$	66	4	$C_5H_6^+$
65	23	$C_5H_5^+$	65	28	$C_5H_5^+$
51	20	V^+	51	16	V^+

[a] Only peaks corresponding to ^{35}Cl are listed.

2.89 BM calculated for spin only), as is found in Cp_2VCl.

After sublimation of the residue of thermolysis of the Cp_2VR compounds, a grey-black solid remained, which probably contains vanadocenes with two aryl groups substituted in the Cp rings. IR and mass spectrometry showed the presence of $(C_5H_4R)_2V$. Unfortunately, we could not isolate these compounds pure.

In other experiments deuterated Cp_2VR compounds were decomposed and the composition of the volatile and solid decomposition products examined by mass spectrometry.

Discussion

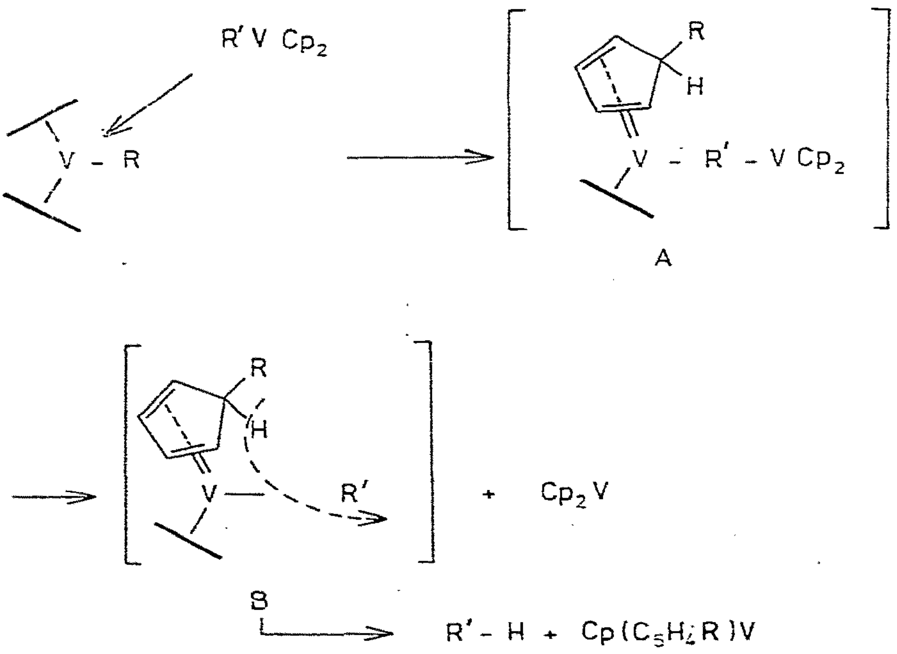
The DTA experiments (Table 1) show that the sequence of thermal stability for the Cp_2VR compounds is R = *m*-tolyl ~ *p*-tolyl ~ phenyl << *o*-tolyl < 2,6-xylyl. The compounds with *ortho*-substituted aryl groups are markedly more stable than the other aryl compounds. This effect, which was also observed for the series of compounds Cp_2TiR [1] is probably due to the shielding of empty coordination sites of the metal by the methyl group in the *ortho* position [8]. The higher thermal stability of the vanadium compounds compared to the corresponding titanium compounds is not unexpected since these two compounds differ in two respects. First, for Cp_2VR the two essentially non-bonding metal orbitals are each occupied by one electron (Cp_2VR is a 16-electron system), whereas for Cp_2TiR one of the non-bonding metal orbitals is empty (Cp_2TiR is a 15-electron system). Furthermore, the atomic radius of titanium is about 0.1 Å larger than that of vanadium, which is expected to lead to more space between the planes of the Cp rings. These two effects may result in an increase in reactivity of the Cp_2TiR molecule relative to Cp_2VR and so in a decrease in thermal stability. For example, several complexes Cp_2TiR react with N_2 [9], while the corresponding vanadium complexes do not.

Heating of the compounds Cp_2VR in the solid state at the decomposition temperature determined by DTA gives RH, Cp_2V and vanadocenes with a group R substituted in the Cp ring.

The experiments with $Cp_2VC_6D_5$ show the formation of C_6D_5H, Cp_2V and $Cp(C_5H_4C_6D_5)V$. This indicates that a hydrogen atom is abstracted from a Cp ring with formation of RH and that the group R is indeed substituted in a Cp ring. The formation of large amounts of Cp_2V suggests that the decomposition occurs via an intermolecular pathway, because a unimolecular reaction would lead to destruction of the vanadocene group. Indeed, thermolysis of an equimolar mixture of $Cp_2VC_6H_5$ and $Cp_2VC_6D_5$-d_{10} produces C_6D_6, C_6D_5H, C_6H_6 and C_6H_5D. The sublimation products consisted of Cp_2V, Cp_2V-d_{10}, $Cp(C_5H_4C_6H_5)V$ and $Cp(C_5D_4C_6D_5)V$-d_5. These results indicate that the substitution of the aryl group in the Cp ring is an intramolecular process, whereas the abstraction of a hydrogen atom from a Cp ring is intermolecular.

Although we were not able to isolate all the decomposition products quantitatively, the results prove that the compounds Cp_2VR (R = aryl) decompose by a route different from that proposed by Razuvaev et al. [3]. A free-radical decomposition is unlikely because radical reaction products such as R—R were found only in trace amounts. More likely is a mechanism in which the first step is the interaction of a non-bonding metal orbital of the molecule Cp_2VR with the aryl group (in Scheme 1) indicated by R′) of another molecule. Simultaneously,

SCHEME 1



the group R migrates to one of the C_5H_5 rings (Scheme 1, A). The dimer A then decomposes into Cp_2V and species B, which in turn decomposes by intramolecular abstraction of a hydrogen atom from the cyclopentadiene ligand by group R′ with formation of R′H and a vanadocene species with the group R substituted in the Cp ring. Thus, the stoichiometry of the decomposition is:

$$2Cp_2VR \rightarrow Cp_2V + RH + Cp(C_5H_4R)V \qquad (2)$$

The large yield of Cp_2V in the decomposition (Table 2), the small yield of $Cp(C_5H_4R)V$, and the appearance of some disubstituted species in the final residues can be explained by a partial disproportionation of $Cp(C_5H_4R)V$ into $(C_5H_4R)_2V$ and $(C_5H_5)_2V$ under the reaction conditions (eq. 3). Some evidence

$$2Cp(C_5H_4R)V \rightarrow Cp_2V + (C_5H_4R)_2V \qquad (3)$$

for this disproportionation reaction was found in the observation that resublimation of $Cp(C_5H_4R)V$ always yields some Cp_2V.

Scheme 1 explains the formation of the large amount of Cp_2V (more than 50%), the intermolecular abstraction of hydrogen from the Cp rings with formation of RH and the intramolecular substitution of the group R in the Cp rings.

We have assumed that the migration of the aryl group to a C_5H_5 ring of the same molecule is induced by the incoming group R of another molecule Cp_2VR. Steric effects may play a role in this process. It has been suggested that two aryl groups and two Cp rings around a vanadium atom would lead to large steric hindrance. Indeed no Cp_2VR_2 (R = aryl) complexes have been isolated [10].

It seems possible that the first step of the decomposition reaction (Scheme 1) involves a species with a η^1-C_5H_5 ligand. Some evidence for this type of migration of the aryl group was obtained from the reaction of $Cp_2VC_6H_5$ with LiC_6H_5; the mass spectrum of the reaction product showed the presence of $Cp(C_5H_4C_6H_5)VC_6H_5$. The migration of an aryl group from the metal atom to a Cp ring is also found in the reaction of $Cp_2VC_6H_5$ with CO described by Fachinetti and Floriani [11]. In this case, migration is induced by CO. Green and Lindsell [12] found substitution of a C_6F_5 group in the C_5H_5 ring in the reaction of Cp_2MCl_2 (M = Mo, W) with C_6F_5Li. Probably a similar migration occurs in this reaction.

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