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THE THERMAL DECOMPOSITION OF DICYCLOPENTADIENYL-DIMETHYLTITANIUM(IV)

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Summary

Thermal decomposition of $(C_5H_5)_2Ti(CH_3)_2$ in alkane or benzene solution yields primarily methane, with only traces of ethane. Methane is produced by hydrogen abstraction from both the cyclopentadienyl rings and from the methyl groups, but never from the alkanes or benzene. A scheme of decomposition is suggested involving two paths, each with a two stage formation of methanes. A very much slower ethane formation competes with the second stage. Strong evidence exists for slow hydrogen exchange between the cyclopentadienyl rings and the methyl groups prior to significant production of ethane. Decomposition in diethyl ether yields methane, much of it arising through hydrogen abstraction from the ether. Decomposition in CCl_4 and C_2Cl_4 yields mainly methane but also some methyl chloride and ethane. Both diethyl ether and C_2Cl_4 almost block methane formation through ring attack.

Introduction

Only brief references have appeared [1–3] to the thermal decomposition of dicyclopentadienyldimethyltitanium(IV) although there have been several studies of dicyclopentadienyldiphenyltitanium(IV) [1–7] and of dicyclopentadienyldibenzyltitanium(IV) [6–9]. This paper reports a preliminary study of the thermal decomposition of $(C_5H_5)_2Ti(CH_3)_2$ and compares the findings with those reported for related compounds. Emphasis is on the role of the solvent.

Experimental

(a) Preparation of materials

All stages of the preparation were carried out either within a glove box or within a vacuum rock as described previously [10], although the product com-

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compound is not air sensitive and was handled in the open atmosphere once prepared and purified. Starting materials were purchased in pure grades and purified as necessary. Solvents were dried, distilled under vacuum and stored in the dry box before nitrogen was admitted. $(C_5H_5)_2TiCl_2$ and solutions of the organolithium compound were used as purchased.

$(C_5D_5)_2TiCl_2$ was prepared by the method of Martin et al. [11,12] with some variations. 2-methylallylmagnesium chloride was used rather than the crotyl, ether was removed and cyclohexane added without filtering to remove magnesium chloride, and D_2 was used to generate the hydride. The cyclopentadienyl rings in the final product were 30% deuterated.

$(C_5H_5)_2Ti(CH_3)_2$ was prepared by a modification of the method of Clauss and Bestian [13]. Two dropping funnels were charged in the glove box, one with 25 ml of a 1.0 M solution of methyllithium in diethyl ether and the other with 50 ml of diethyl ether. A three neck, 150 ml flask containing a stirrer bar was charged outside the box with 2.87 g (0.115 mol) of $(C_5H_5)_2TiCl_2$. The dropping funnels were attached and the flask evacuated up to the funnel stopcock. The flask was maintained at 10°C and shielded from light while first the ether, then the methyllithium solution, were slowly added with stirring. The resulting orange-brown solution was allowed to stir for 20 min. Decomposition of excess methyllithium by adding ice/water created two liquid layers. The ether layer was separated and the orange product obtained by evaporating the solvent under vacuum. These crystals were then recrystallized from n-pentane. Orange needles in 80–85% yield were obtained. The material was stored in the dark at 255 K prior to use.

(b) Thermal decomposition studies

The standard vessel for decomposition studies in solution was a simple glass tube sealed by a stopcock and fitted with a taper joint. The solution in question was injected into the tube, and the tube evacuated while the solution was frozen at liquid nitrogen temperatures. The stopcock was closed, and the contents warmed to whatever temperature was required. For decomposition in the solid state, the same simple tube described above was used. Some studies were also conducted using break-seal tubes.

Gas-liquid chromatography and NMR spectrometry were used to identify products and mass spectrometry to determine deuterium content. For mass spectrometry, accurate determination of isotopic distribution for a given chemical species was enhanced by taking successive samples at approximately 80, 200 and 273 K. Instrumentation utilized involved a Bruker HX-60 for NMR spectrometry, A.E.I. MS-10 for mass spectrometry, Beckman IR-10 and Perkin-Elmer 180 for IR spectrometry and a Hewlett-Packard 5750 for gas-liquid chromatography.

Results and discussion

Data on the volatile products of thermal decomposition are summarized in Table 1.

(a) Decompositions in benzene and in alkanes

Experiments 11 to 16 demonstrate that hydrogen atoms originally present in

TABLE 1
VOLATILE PRODUCTS FROM THERMAL DECOMPOSITION OF DICYCLOPENTADIENYLDIMETHYLTITANIUM(IV)

Number of experiment	Physical state or solvent	Initial concentration (mol l ⁻¹)	Atmosphere	Temperature ° (K)	Time (h)	Volatile products
<i>(a) (C₅H₅)₂Ti(CH₃)₂</i>						
1	Solid	—	Vacuum	340	290	CH ₄ ; trace of C ₂ H ₆
2	C ₆ H ₆	0.20	Solvent vapour	340	290	CH ₄ ; very small amount of C ₂ H ₆
3	C ₆ D ₆	0.20	Solvent vapour	340	50	CH ₄ ; very small amount of C ₂ H ₆
4 ^a	C ₆ H ₁₄	0.17	Solvent vapour	363	5	CH ₄ (CH ₄ /Ti = 1.6)
5	C ₆ D ₁₄	<0.1	Solvent vapour	340	290	CH ₄ ; trace of C ₂ H ₆
6 ^b	C ₆ H ₁₂	?	?	?	?	CH ₄ (CH ₄ : Ti = 1.5)
7	(C ₂ D ₅) ₂ O	0.15	Solvent vapour	310	70	Methane (CH ₄ /CH ₃ D 100 : 87)
8 ^a	C ₄ H ₈ O	0.18	Solvent vapour	363	5	CH ₄ (CH ₄ /Ti = 1.6)
9	C ₂ Cl ₄	0.20	Solvent vapour	340	290	CH ₄ ; ethane and methyl chloride not determined
10	CCl ₄	0.20	Solvent vapour	340	290	CH ₄ ; small amounts of CH ₃ Cl and C ₂ H ₆
<i>(b) (C₅D₅)₂Ti(CH₃)₂^c</i>						
11	Solid	—	Vacuum	340	50	Methane (CH ₄ /CH ₃ D/CH ₂ D ₂ 100 : 34 : 3); ethane not determined.
12	C ₆ H ₆	0.20	Solvent vapour	340	50	Methane; very small amounts of ethane (CH ₄ /CH ₃ D/CH ₂ D ₂ /CHD ₃ 100 : 23 : 2 : trace)
13	C ₆ D ₆	0.20	Solvent vapour	340	50	(C ₂ H ₆ /C ₂ H ₅ D/C ₂ H ₄ D ₂ /C ₂ H ₃ D ₃ 100 : 90 : 80 : 20)
14	C ₆ H ₁₄	<0.1	Solvent vapour	340	50	Methane; very small amounts of ethane (CH ₄ /CH ₃ D/CH ₂ D ₂ /CHD ₃ 100 : 25 : 1 : trace)
15	(C ₂ H ₅) ₂ O	0.20	Solvent vapour	310	70	(C ₂ H ₆ /C ₂ H ₅ D/C ₂ H ₄ D ₂ /C ₂ H ₃ D ₃ 100 : 70 : 50 : 20)
16	C ₂ Cl ₄	0.20	Solvent vapour	340	50	Methane; trace of ethane (CH ₄ /CH ₃ D/CH ₂ D ₂ /CHD ₃ 100 : 23 : 1 : trace)
						Methane; trace of ethane (CH ₄ /CH ₃ D 100 : 1)
						Methane; very small amounts of ethane and methyl chloride (CH ₄ /CH ₃ D 100 : 2)

^a Ref. 2, ^b Ref. 3, ^c Cyclopentadienyl rings were 30% deuterated.

TABLE 2

DISTRIBUTION OF ISOTOPES IN PRODUCTS OF EQUATIONS 1 TO 5 (SCHEMES 1 AND 2) FOR MATERIAL USED

Reaction product distribution

(a) First step processes

1	Methane	$\text{CH}_4/\text{CH}_3\text{D}$ 100 : 43
3	Methane	CH_4 100

(b) Second step processes assuming no scrambling

2a	Methane	$\text{CH}_4/\text{CH}_3\text{D}$ 100 : 43
2b	Ethane	C_2H_6 100
5a	Methane	$\text{CH}_4/\text{CH}_3\text{D}/\text{CH}_2\text{D}_2$ 100 : 85 : 18
5b	Ethane	$\text{C}_2\text{H}_6/\text{C}_2\text{H}_5\text{D}/\text{C}_2\text{H}_4\text{D}_2$ 100 : 85 : 18

(c) Second step processes assuming total scrambling after initial process

2a'	Methane	$\text{CH}_4/\text{CH}_3\text{D}/\text{CH}_2\text{D}_2/\text{CHD}_3$ 58 : 100 : 35 : 2
2b'	Ethane	$\text{C}_2\text{H}_6/\text{C}_2\text{H}_5\text{D}/\text{C}_2\text{H}_4\text{D}_2/\text{C}_2\text{H}_3\text{D}_3$ 45 : 100 : 76 : 23
5a'	Methane	$\text{CH}_4/\text{CH}_3\text{D}/\text{CH}_2\text{D}_2/\text{CHD}_3$ 50 : 100 : 43 : 4
5b'	Ethane	$\text{C}_2\text{H}_6/\text{C}_2\text{H}_5\text{D}/\text{C}_2\text{H}_4\text{D}_2/\text{C}_2\text{H}_3\text{D}_3$ 39 : 100 : 89 : 33

groups and cyclopentadienyl rings. Exchange between ring hydrogens and hydride hydrogens has already been established for the species $(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{TiH}$ [14], which also exchanges hydrogens with D_2 .

Separate experiments indicate that such exchange does not occur in $(\text{C}_5\text{H}_5)_2\text{-Ti}(\text{CH}_3)_2$ prior to decomposition. Material with partially deuterated rings was stored at 255 K for four weeks and at ambient temperature (both as a solid and in a benzene solution) for an hour before being treated with aqueous HCl. The resulting methane contained no deuterium. Similarly infrared spectra of material stored over even longer periods show no evidence of deuterium in the methyl groups. It is therefore believed that exchange occurs subsequent to decomposition beginning (i.e. subsequent to processes 1 and/or 3). This evidence also implies that no ethane is formed in a process simultaneous with reactions 1 or 3. Since there is no hydrogen exchange in the undecomposed material, such a process could produce C_2H_6 only. The high proportion of deuterium in the ethane shows that most, and probably all, must be formed subsequent to exchange and therefore subsequent to processes 1 and 3. On the other hand, most of the methane formed in the second stage (processes 2a and/or 5a) must be formed prior to exchange. Table 3, lines 2, 4 and 6, show that a much higher level of CH_2D_2 would otherwise be observed.

TABLE 3

DISTRIBUTION OF ISOTOPES IN METHANE ARISING FROM VARIOUS POSSIBILITIES

$\text{CH}_4/\text{CH}_3\text{D}/\text{CH}_2\text{D}_2/\text{CHD}_3$

Process 1 complete, process 2a to 50% completion, 100 : 43 : 0 : 0
Process 1 complete, process 2a' to 50% completion, 100 : 66 : 11 : 1
Process 3 complete, process 5a to 50% completion, 100 : 17 : 3
Process 3 complete, process 5a' to 50% completion, 100 : 22 : 10 : 1
First and third above proceeding equally, 100 : 29 : 2
Second and fourth above proceeding equally, 100 : 41 : 10 : 1

(b) Decomposition in diethyl ether

Whereas there is no evidence of direct participation of alkanes or benzene in the decomposition processes, experiment 7 shows that almost half the methane produced involves abstraction of a hydrogen from the solvent. Moreover experiment 15 shows that with ether present, little methane is produced by attack on the cyclopentadienyl rings.

(c) Decomposition in CCl₄ and C₂Cl₄

Brief examination of decomposition in these solvents showed that they exhibit similar behaviour. Methane is by far the most abundant volatile product but methyl chloride and ethane appear in small amounts. Whereas in alkanes or benzene, the resulting solution is green (when viewed against strong light) and the product solid a green-grey precipitate as described by Bercaw et al. [14], (C₅H₅)₂TiCl₂ and (C₅H₅)TiCl₃ are the major products in these solvents. Experiment 16 shows that C₂Cl₄, like ether, blocks abstraction of hydrogen from the rings. This is consistent with the observed nature of the product solid.

Comparison with related systems

Thermal decomposition of alkyl-transition metal compounds has been explained, for alkyls having a hydrogen on a carbon β to the metal, in terms of an olefin/hydride intermediate arising from the abstraction of a "β-hydrogen" as established by De Vries [15]. Such an intermediate has been proven convincingly in only a few cases, such as di-n-butylbis(triphenylphosphine)platinum(II) [16] but there is considerable consistent evidence for many compounds. A somewhat analogous intermediate, involving an *ortho*-phenyl position, has been put forward for (C₅H₅)₂Ti(C₆H₅)₂ [17].

For methyl compounds, α-elimination via a carbene/hydride intermediate has been proposed for methylchromium(III) compounds [18,19], (CH₃)₂TiCl₂ [20] and (C₅H₅)₂W(PR₃)(CH₃) [21]. For (C₅H₅)₂Ti(CH₃)₂, it can only be said that the evidence is not inconsistent with an intermediate hydride arising either from the rings (Scheme 1) or from a methyl (Scheme 2). Conditions which favour hydride formation lead to rapid alkane elimination. Introduction of hydrogen gas results in the facile and quantitative elimination of 2 CH₄.

If reversible hydride formation occurs in (C₅H₅)₂Ti(CH₃)₂, involving the formation of C₅H₄ (Scheme 1) or CH₂ (Scheme 2), it can be seen that this process would lead to hydrogen exchange in the reduced compound resulting from processes 1 or 3, since the other potential hydrogen accepting group would be present in each case. This would account for the highly deuterated ethane obtained. The results imply, however, that the exchange process is slow compared to processes 2a and 5a but rapid compared to processes 2b and 5b.

The attack on ethers has been observed for both CH₃TiCl₃ [20] and (C₅H₅)₂Ti(C₆H₅)₂ [7]. For both, it has been suggested [20,23] that abstraction follows coordination, with the additional suggestion, in the latter case, that coordination occurs only to a reduced species formed through an analogue of either Scheme 1 or Scheme 2. In the case of (C₅H₅)₂Ti(CH₃)₂, however, the absence of CH₃D indicates that ether blocks processes 1 and 4. This suggests that ether is coordinated from the beginning, blocking the necessary rearrangement of the ring.

Decomposition in CCl_4 and C_2Cl_4 produced some CH_3Cl . Although this is analogous to the production of $\text{C}_6\text{H}_5\text{Cl}$ from $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$ in CCl_4 [7], and of CH_3Cl from CH_3TiCl_3 in both solvents [20,22], the proportion of RCl to RH is very much lower in the case of $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$.

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