Journal of Organometallic Chemistry, 170 (1979) 51—61

HYDROGEN EXCHANGE DURING THE THERMAL DECOMPOSITION OF DICYCLOPENTADIENYLDIMETHYLTITANIUM(IV)

GORDON J. ERSKINE, JUDITH HARTGERINK, ERICA L. WEINBERG and JAMES D. McCOWAN *

Department of Chemistry, Queen's University, Kingston, Ontario (Canada)

(Received October 5th, 1978)

Summary

A previous suggestion that cyclopentadienyl rings exchange hydrogens with methyl groups during the thermal decomposition of $(C_5H_5)_2Ti(CH_3)_2$ is supported by additional studies. The thermal decomposition is found to proceed in two stages.The first involves an intramolecular α-elimination yielding methane and a black precipitate. In the second stage, this process is catalyzed, but in addition ring attack becomes important and slow exchange of ring and methyl hydrogens occurs. All stage two processes occur out of solution. Solid state decompositions appear to follow a closely similar path at comparable temperatures, as do photodecompositions.

Introduction

Although the thermal decomposition products of $(C_5H_5)_2Ti(CH_3)_2$ are capable of nitrogen fixation [1] and may also be active as catalysts for alkene polymerization [2,3], efforts to understand the thermal decomposition of this compound have been few [4—7]. Thermal decompositions in both the solid state [6] and in benzene solution [7] yield methane and very small amounts of ethane. At least above 373 K, solid state decompositions also yield ethene, cyclopentadiene and methyl cyclopentadiene. Methane is in both cases the most abundant volatile product. Selective deuteration shows that some methane arises from an α-elimination involving just methyl groups, while some incorporates hydrogens from the rings [6,7]. None arises from attack on the benzene [7]. The fact that the very small amounts of ethane also incorporate ring hydrogens [7] led to the suggestion that hydrogens could be exchanged between cyclopentadienyl rings and methyl carbons in the partially decomposed material. This study of that exchange permits revision and extension of our understanding of the decomposition mechanism.

Experimental

(a) Preparation of materials

Preparation and handling techniques have been described previously [7] but a superior method has been developed for making $(C_5D_5)_2TiCl_2$. Although the modifications are substantial, the method is based on that of Brintzinger et al. [8].

(i) Preparation of perdeuterodicyclopentadienyldichlorotitanium(IV), $(C_5D_5)_2TiCl_2$. Titanocene dichloride (5 g, 20 mmol) in a 250 ml, 3-neck flask was covered with 100 ml of sodium-dried diethyl ether, purged with argon, and cooled to about 273 to 280 K in an ice bath. Methyllithium (22 ml of a 2.0 mol l^{-1} solution in ether) was injected by syringe into the stirred suspension over a period of 2—3 minutes. The reaction mixture was stirred for half an hour at 273 to 280 K. Methanol, 1 ml, was added to remove excess methyllithium. The deep yellow solution over a white precipitate was evaporated to dryness at the pump, and the residue was extracted several times with dry hexane.

The resulting hexane solution was filtered into a 250 ml, 3-neck flask, concentrated by pumping and cooled under argon at 193 K for several hours. The supernatant liquid was decanted and the mass of crystalline $(C_5H_5)_2Ti(CH_3)_2$ was washed once with 60 ml of hexane at 193 K. Enough hexane was then added to give a thick slurry of crystals at 273 K.

Deuterium was introduced at one atmosphere. Within 5—10 minutes, formation of blue-black $[Cp_2TiD]_2$ began in the solid state and then spread smoothly until the entire reaction mixture was a very dark brown-black. A precipitate formed and the pressure in the flask slowly increased. The flask was purged periodically with fresh deuterium, and the reaction appeared to be complete within 5 h.

The solvent was removed at the pump and 60 ml of dry toluene was added by syringe at room temperature, producing a deep, green-black solution over a very dark solid. Note that the following deuterium/hydrogen ring exchange does not take place unless this change in solvent is made.

Deuterium was introduced at one atmosphere and the mixture was stirred at room temperature. Every fifteen minutes, the deuterium atmosphere was replaced to remove the HD and H_2 formed and maintain a high D_2 concentration. The progress of the reaction was followed using a mass spectrometer to monitor the gas phase. A slight overpressure developed in the flask and slow bubbling was noted for 19 h. The deuteration proceeded smoothly and rapidly in the initial stages, falling from a D_2/HD ratio of 12/1 to 3/1 in 15 minutes. After eight purges with D_2 the vessel was filled with D_2 (D_2/HD = 18.5/1) and left stirring overnight. After a 14 h interval, the D_2/HD ratio was 2/1. Purges with fresh D_2 were then carried out at 1 h intervals until D_2/HD ratios of about 18/1 were recorded after an hour at room temperature. The total elapsed time was three days.

The reaction flask was cooled to about 183 K and hydrogen chloride in diethyl ether (10 ml) was added, producing a vigorous reaction. The mixture was warmed to room temperature and stirred in air for 2 h. The red $(C_5D_5)_2TiCl_2$ was filtered, washed with toluene and dried in air. NMR and IR spectra were obtained. The yield was 2.94 g (57%). Deuteration was 97% as measured by both NMR and mass spectrometry.

(ii) Preparation of $(C_5H_5)_2Ti(CD_3)_2$ and $(C_5D_5)_2Ti(CD_3)_2$. CD_3Li in ether (prepared according to ref. 9) was added rapidly by syringe to a suspension of $(C_5H_5)_2TiCl_2$ in ether, under an atmosphere of argon and cooled by a dry ice/ methanol mixture. Warming to room temperature and working up in the usual way [7] produced some decomposition products and yellow $(C_5H_5)_2Ti(CD_3)_2$ (0.85 g, 30%). $(C_5D_5)_2Ti(CD_3)_2$ is prepared by an identical route using $(C_5D_5)_2$-$TiCl_2$.

(b) Thermal decomposition studies

The standard vessel for mass spectrometric determinations was a closed glass tube fitted with a vacuum stopcock and a taper joint. Samples were frozen, pumped free of air, thawed, frozen and pumped again. Each was then stored in a bath of appropriate temperature. From time to time the gaseous contents of this tube were transferred to a second vessel, the decomposition vessel being cooled to reduce solvent transfer. Mass spectrometry was used to analyze the contents of this latter vessel for deuterium content in the methane, and for indications of any other volatile products. The use of calibrated vessels, permitted measurement of the amount of methane produced. The ionizing electron energy was 70 eV (1.12×10^{-17} J). The cracking patterns of mixed methanes were analyzed by computer. Cracking pattern information for this program was obtained by calibration runs on pure samples of methane in the actual spectrometer.

Simultaneously NMR spectrometry was used to monitor the decomposition of portions of the same solution. Samples were flame-sealed in 5 mm tubes. Spectrometer temperatures were maintained at the temperature of decomposition (310 or 340 K). In many cases, spectra were obtained every 5 minutes but where intervals were much longer, samples were stored in constant temperature baths between measurements. Integrations were used to determine the concentration of the decomposing material as a function of time. Toluene was the usual internal reference but cyclohexane was used in some instances.

A Bruker HX-60 was used to monitor composition in the solution phase for selected samples. All methane mass spectra were obtained using an A.E.I. MS-10. Mass spectra required to measure the deuterium content of titanium compounds and for other analytical needs were obtained using a JEOLCO JMS-01 SC.

(c) Consideration of errors

Errors were minimized in the mass spectra by repeated measurements on the same sample, never less than three and usually five which were then used as the basis for an extrapolation to the time at which the instrument was first opened to the sample. The amount of gas was sufficiently large relative to the leak rate into the spectrometer that the correction to zero time was small. Tests of the mass spectral calibrations using known amounts of methane indicate that the maximum error limits on a given determination are ± 10%.

In NMR spectrometry tests using samples in which relative peak heights were unchanging indicated that the standard deviation of determinations of concentration using this method were ±5% in FT mode on the HX-60.

TABLE 1

PRODUCTION OF METHANE BY THERMAL DECOMPOSITION OF $(C_5H_5)_2Ti(CH_3)_2$ AND ITS DEUTERATED ANALOGUES IN BENZENE AT 340 K

	$(C_5H_5)_2Ti(CH_3)_2$	$(C_5D_5)_2Ti(CH_3)_2$	$(C_5H_5)_2Ti(CD_3)_2$	$(C_5D_5)_2Ti(CD_3)_2$	$0.52(C_5H_5)_2Ti(CH_3)_2$ $+ 0.48(C_5D_5)_2Ti(CD_3)_2$
Deuteration (%)	0	97	99	rings 96, methyls 99	as with separate materials
Average duration of stage one (h)	2	2	60	60	2
Amount of methane formed during stage one per mol Ti	0.1	0.08	0.1 to 0.2	0.1 to 0.2	0.1 to 0.2
Composition of methane formed during stage one (%)	CH_4(100)	CH_4(>99)	CD_4(~50), CHD_3(~50)	CD_4(~50), CHD_3(~50)	CD_4(10), CHD_3(17) CH_4(73)
Amount of methane formed during stage two, per mol Ti	1.2	1.3	1.2	1.3	0.8+
Composition of methane formed during stage two (%)	CH_4(100)	CD_4(3), CHD_3(6), CH_2D_2(7), CH_3D(35), CH_4(49)	CD_4(26), CHD_3(56) CH_2D_2(16), CH_3D(1), CH_4(1)	CD_4(73) CHD_3(26), CH_2D_2(1)	CD_4(10), CHD_3(39), CH_2D_2(7), CH_3D(13), CH_4(31)

Results

(i) Decomposition in solution

The thermal decompositions of $(C_5H_5)_2Ti(CH_3)_2$ and its deuterated analogues have been studied in benzene solution at 340 K. Decompositions of $(C_5D_5)_2Ti(CH_3)_2$ at 310 K were also carried out and a few experiments were made with toluene and with hexane as the solvent. With these solvents as with benzene, no solvent hydrogen was ever found in the methane formed. Moreover, although the kinetic data are imprecise, the general pattern of decomposition, the appearance at each stage and the rates of methane formation are similar for the three solvents, so that all available evidence suggests that each provides a relatively inert medium in which thermal decomposition takes place.

Decomposition in solution occurs in two stages. In the first stage, there is perceptible darkening of the solution but no visible precipitate. NMR spectra show that 80 to 90% of the subject compound remains undecomposed and in solution at the end of this period. Mass spectral data, summarized in Tables 1 and 2, show particularly with $(C_5D_5)_2Ti(CH_3)_2$ that an α-elimination involving methyl/methyl attack is the major mechanism operative in this stage.

In the second stage, the "solution" becomes black and opaque. This is, at least partly, due to a finely divided precipitate, since black solid is sometimes seen on the glass walls. NMR spectra show that the parent compound disappears from solution within about twenty minutes of the onset of visible precipitation.

No broadening of other resonances is observed, as might be expected if this disappearance were caused by a soluble paramagnetic species. The methane which appears in this twenty minutes period, while produced at a much more rapid rate than during stage one, nevertheless represents decomposition of less than half the parent compound. The remaining $(C_5H_5)_2Ti(CH_3)_2$ must be removed from solution by complexing with the solid or by some other process, but not by decomposition. The rapidity of decomposition in stage two relative to that in stage one suggests autocatalysis involving the product solid. The methane produced in stage two includes a large amount produced by α-elimination, an almost equally large amount incorporating one ring hydrogen, and small but measurable amounts incorporating two or more ring hydrogens.

TABLE 2

SOLUTION PHASE THERMAL DECOMPOSITION OF $(C_5D_5)_2Ti(CH_3)_2$ AT 310 K

Deuteration (%)	97
Duration of stage one/h	80 ± 15
Amount of methane formed in stage one per mol of Ti	0.25
Composition of methane formed in stage one	CH_4(98), CH_3D(2)
Amount of methane formed during stage two per mol Ti	1.4
Composition of methane formed during stage two	CH_4(41), CH_3D(43), CH_2D_2(9), CHD_3(5), CD_4(2)

TABLE 3

DISTRIBUTION OF METHANES AS A FUNCTION OF TIME DURING THE THERMAL DECOMPOSITION OF $(C_5D_5)_2Ti(CH_3)_2$ AT 310 K. STAGE TWO BEGAN AT ABOUT 80 h.

Sample 77—21

Time (h)	Amounts/μmol and percentages (brackets)				
	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
0—19	14.6(99.7)	0.033(0.2)	0.018(0.1)		
19—45	11.3(93.7)	0.736(6.1)	0.026(0.2)		
45—99	57.2(48.2)	56.1(47.3)	4.71(4.0)	0.525(0.4)	0.089(0.1)
99—286	1.95(24.4)	2.47(31.0)	1.96(24.5)	1.21(15.2)	0.395(4.9)
286—624	0.989(7.2)	3.06(22.3)	4.13(30.2)	3.70(27.0)	1.82(13.3)
624—1008	0.403(6.5)	1.01(16.3)	1.95(31.5)	1.85(29.9)	0.974(15.7)

Traces of ethane incorporating ring hydrogens were always observed as stage two progressed.

Experimentally, small amounts of CD_4 and CD_3H can be measured with great accuracy in the presence of large amounts of CDH_3 and CH_4 whereas the converse is not true with our method. Large fragments from abundant CD_4 and CD_3H, combined with an overall accuracy of no better than 3% on any peak, make measurements of species present in the order of 1% almost impossible. The entries for CH_4 and CDH_3 formed from $(C_5H_5)_2Ti(CD_3)_2$ are very much less reliable than are the measurements of highly deuterated methanes formed from $(C_5D_5)_2Ti(CH_3)_2$.

In the decomposition of $(C_5D_5)_2Ti(CH_3)_2$, the trend toward more deuterated methanes in stage two is gradual and continuous. This is illustrated in Table 3 by data from a typical sample. The onset of stage two in this sample occurred at about 80 h. Note that CH_4 and CH_3D are the most abundant products of stage two, even although they are relatively unimportant in the final hours.

In the decomposition of $(C_5H_5)_2Ti(CD_3)_2$ and of $(C_5D_5)_2Ti(CD_3)_2$ in C_6D_6, CHD_3 is abundant during stage one but its relative abundance declines steadily up to the onset of stage two. In a typical run in which samples were taken at 1, 9 and 21 h, the ratios of CD_4/CHD_3 were, respectively, 34/66, 65/35 and 91/9. There was considerable variation, however, in the fraction of CHD_3 from one preparation to the next although internal consistency for a given batch was good, and the declining trend described above was invariably present.

A supplementary experiment involved dissolving approximately equal amounts of $(C_5H_5)_2Ti(CH_3)_2$ and $(C_5D_5)_2Ti(CD_3)_2$ in benzene. These data are also shown in Table 1. Decomposition at 340 K gave primarily CH_4, CD_4 and CD_3H during stage one but gave the full range of methanes in stage two.

(ii) Decomposition in the solid state

At 340 K, orange crystals turn dark and eventually black within 6—8 h if the methyls are deuterated and within less than an hour if they are not. Small amounts of methane are produced before the colour change, largely by α-elimination. Methane production is rapid during the period of the colour change and ring hydrogens are incorporated to an increasing degree as decomposition continues. Crystals produced by the coprecipitation of $(C_5D_5)_2Ti(CD_3)_2$ and $(C_5H_5)_2Ti(CH_3)_2$, when decomposed at 340 K, yield CH_4, CHD_3 and CD_4 before the colour change but a complete range of methanes thereafter. All of these observations are in general conformity with those of 0.2 mol l^{-1} solutions in benzene except that the induction times are shorter in the solid state.

Some solid material was decomposed at 400 K. Crystals turned black quickly five minutes after being placed in the oven. Five minutes represents only a limit, since the small samples in their heavy glass containers may have taken some time to reach 400 K. Almost all of the volatile product was methane, with less than 1% being ethane. No other volatile products were found. These samples were reexamined after storage at 400 K for 40 h. Only very small additional amounts of methane and even less ethane had been produced. The samples were then heated to 760 K over a period of 575 s. No large change was visible in the black solids but a metallic sheen appeared on a portion of the wall of the container. Mass spectrometric analysis of the volatile products showed the presence of small amounts of methane, ethene, ethane and cyclopentadiene.

Discussion

(i) Decomposition paths in solution

A previous analysis of the total volatile products of these materials [7] led to the suggestion that methane formation by methyl/methyl α-elimination and by ring attack were both of importance, much as had been reported previously for the phenyl analogues [10]. This work shows several additional features.

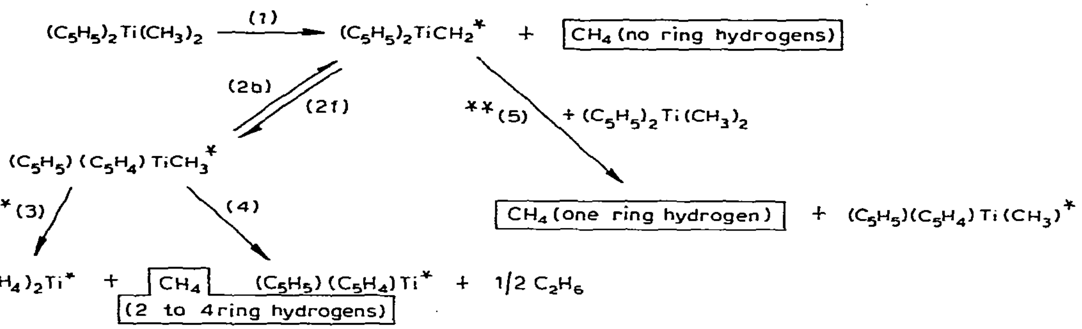
There is little doubt that the only significant mechanism during stage one is α-elimination involving methyl groups only. The data in Table 1 for $(C_5D_5)_2Ti(CH_3)_2$ are unambiguous. Those for $(C_5H_5)_2Ti(CD_3)_2$ are not without ambiguities but since the data for $(C_5D_5)_2Ti(CD_3)_2$ in C_6D_6 are nearly identical, we suggest that the high proportion of CHD_3 from this compound in stage one is due mainly to the preference for attack on the H impurity in the methyl. The difference in rates between CH_3 and CD_3 compounds is substantial, and the decline in CHD_3 during stage one is consistent with the steady and rapid reduction of this H impurity.

It is also believed that the decomposition in stage one is intramolecular. The absence of CH_2D_2 and CH_3D in the initial products from a mixture of $(C_5D_5)_2Ti(CD_3)_2$ and $(C_5H_5)_2Ti(CH_3)_2$ supports this but again, the presence of large amounts of CHD_3 introduces some doubt. However samples of $(C_5D_5)Ti(CD_3)_2$ alone in C_6D_6 showed CD_4/CHD_3 ratios in stage 1 ranging from 2/1 to 1/2 so it is reasonable to conclude that this effect, as in the paragraph above, arises from preferential attack on the H impurity. Note that, as expected on the basis of the induction times of the separate compounds, CH_4 is the most abundant product of stage one and most of the perdeutero compound is complexed into the solid.

This initial decomposition leads to a darkening of solution and eventually to the formation of a black suspension and precipitate. Parallel NMR observations show that the parent compound disappears from solution within about 20 minutes at this juncture. The total methane produced in this interval, while large, is still considerably less than one methane per titanium. In the case of $(C_5D_5)_2Ti(CH_3)_2$ where accurate determinations of isotope distribution can be made, this methane is mainly CH_4 and CH_3D indicating both catalysis of α-elimination and the advent of some new mechanism.

α-elimination should lead to some carbene-like species (see Scheme 1) and

SCHEME 1



such a species is a likely precursor for CH_2D_2 and, with the exchange considered later, for CHD_3 and CD_4. However the high proportion of CH_3D cannot be convincingly explained on the basis of methylene groups. To do so would require that the methylene group acquire hydrogens from other methylene groups, since the highly deuterated rings do not contain enough hydrogen to provide the third hydrogen for so much CH_3D. Rather, the CH_3D seems likely to arise from direct methyl attack on a ring hydrogen. This is, of course, the second pathway identified earlier [7], but the present work reveals that it operates to any significant degree only after stage two has begun and significant amounts of undecomposed parent compound have been removed from solution. This pathway, then, is associated with some complex of the parent rather than with the parent itself. The data in Table 1 for the mixed samples suggest that it is intermolecular. Again, a strong preference for abstracting H is shown with CHD_3/CD_4 being about 4/1 and CH_4/CH_3D being about 2.4/1.

The production of CH_2D_2 during stage two of the decomposition of $(C_5D_5)_2$-$Ti(CH_3)_2$ could be explained by an extension of the α-elimination, with a carbene product abstracting two deuterium atoms from the rings. The production of comparable amounts of CHD_3 and CD_4 require a further explanation, however, which we propose to be hydrogen exchange between the carbene and the rings.

(ii) Hydrogen exchange

The appearance of traces of ethane containing ring hydrogens [7] was attributed to hydrogen exchange between rings and methyl groups, and better understanding of that process was the main focus of the present work.

These experiments provide strong support for the concept that hydrogens are slowly exchanged between a ring and a methylene group or other product of α-elimination. The formation of CD_4 and other deuterated species in the

---

* Incorporated in solid.

** At least some methane formed in processes 3 and 5 includes hydrogens from rings and methyls not previously attached to the same titanium.

decomposition of $(C_5D_5)_2Ti(CH_3)_2$ is in itself strong evidence, but even more compelling is the gradually increasing proportion of these deuterated methanes as a function of time. This trend is exemplified by the data in Table 3. The exchange, in the context of the decomposition, is shown in Scheme 1.

The reversibility of process 2 is all that is required. If process 2 proceeds via a metal hydride intermediate, it constitutes a combination of two processes frequently suggested in work with related compounds. One is the formation of a carbene and a hydride from a methyl group, which has frequently been invoked in explaining the thermal decomposition of several methyl transition metal compounds [7,11—15], with methane being eliminated whenever a methyl and a hydride occur on the same centre. Green, Rooney and their coworkers have recently discussed much wider implications for this same process [16]. In the other direction, process 2 involves formation of C_5H_4 and a hydride from a cyclopentadienyl ring. Calderazzo [17] has reviewed the various configurations postulated for several situations in which such a process is known. Although the present work offers no direct evidence as to structure, hydrogen exchange is perhaps more likely with the (η^5, η^1 C_5H_4) structure than with the more restricted fulvalene structure. Hydrogen exchange has been observed with compounds containing (η^5, η^1 C_5H_4), including a particularly rapid exchange on zirconium and hafnium tetrahydroborates [18]. Although other schemes can easily be suggested for the present work, the formation of hydride intermediates is consistent with explaining both methane elimination and hydrogen exchange. Note that it is implicit in the data that C_5H_5 cannot yield the hydride/C_5H_4 form in undecomposed $(C_5H_5)_2Ti(CH_3)_2$, since ring hydrogens are rare in the methane formed during stage one.

It is of interest that the best authenticated case of an unsubstituted methylene transition metal complex appears not to be accessible by a process similar to 1. Schrock and Sharp [19] prepared $Ta(\eta^5\text{-}C_5H_5)_2(CH_2)(CH_3)$ by base deprotonation of $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)_2{}^+BF_4{}^-$ but failed to produce it by thermal decomposition of $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)_3$. Thermal decomposition of the last compound proceeds mainly by ring attack and, moreover, no scrambling is observed in $Ta(\eta^5\text{-}C_5H_5)_2(CH_2)(CD_3)$. Both findings suggest that formation of a carbene and hydride from a methyl is not a significant process with the Ta compound.

A methylene transition metal complex which is closely related to this work but which is not a carbene is $(C_5H_5)_2TiCH_2Al(CH_3)_3$ [20]. Here the methylene bridges the two metal atoms. This complex arises during the decomposition of $(C_5H_5)_2Ti(CH_3)_2$ in solutions containing $(CH_3)_3Al$. While its existence does lend a little support to our postulated carbene as a product of process 1, there is as yet no evidence on which to determine at what stage the $(CH_3)_3Al$ enters the process, nor how many of the processes subsequent to 1 are retarded or blocked.

Several effects of isotope on rate are observable. The α-elimination process in stage one and the timing of the onset of stage two both depend on the hydrogen isotope in the methyl groups. These two are, in fact, likely to be two aspects of the same effect. In stage two the incorporation of ring hydrogens in the methane formed during that stage is greater for $(C_5D_5)_2Ti(CH_3)_2$ than for $(C_5H_5)_2Ti(CD_3)_2$. Elimination of the second methane involves a competition between processes 3 and 2b. With H on the rings and a preponderance of D on the methyls, the ratio k_3/k_{2b} will be greater than for the converse case with D on the rings and H on the methyls. Thus with $(C_5D_5)_2Ti(CH_3)_2$, more exchange will occur before elimination of the second methane finally terminates the exchange process. Complications such as the presence of some H impurity on the deuterated rings of the presence of transferred hydrogens as exchange proceeds make kinetic calculations difficult, and with the present data, impossible, but they do not alter the above analysis.

(iii) Decomposition in the solid state

It can be seen in the results reported that solid state decomposition at 340 K does not differ markedly from decomposition in benzene solution at the same temperature. The duration of stage one is shorter for the solid state, and the extent of exchange appears to be less. Otherwise, the same pattern applies. Since NMR observations show that all $(C_5H_5)_2Ti(CH_3)_2$ is removed from solution at the onset of stage two, decomposition during stage two of "solution" decomposition in fact a solid state decomposition.

Some decompositions were carried out at higher temperatures in order to relate this work to that of Rausch and his coworkers [6]. Except for the faster rate, results at 400 K were essentially unchanged from those at 340 K. Methane and small amounts of ethane were the only volatile products. Only when the samples were taken to much higher temperatures were cyclopentadiene and other products observed.

Rausch [6] obtained thermograms of the solid state decompositions of $(C_5H_5)_2Ti(CH_3)_2$ and $(C_5H_5)_2Ti(CD_3)_2$ over the range 200 to 820 K at a heating rate of 40 K per minute. Rapid evolution of gas, accompanied by a colour change to black, occurred at between 393 and 398 K. Slow decomposition with very much smaller gas evolution occurred beyond this at higher temperatures. The most important volatile product was methane (60% with the ratio $CHD_3/CD_4 = 3/1$). A further peak of unreported but apparently small intensity at m/e 18 almost certainly arises from CH_2D_2. Cyclopentadiene (30%) and ethylene (10%) contained only ring hydrogens. Ethane (1%) on the other hand contained a mixture of H and D when formed from $(C_5H_5)_2Ti(CD_3)_2$.

The present work indicates that virtually all of the gas produced in the sharp "spike" just below 400 K in the thermogram is methane. The deuterium content of both the methane and ethane is fully explained although [6] implies a rather lower production of CH_2D_2 than is observed here. Cyclopentadiene, ethene and other products are clearly associated with the higher temperature portion of the thermogram and the absence of any deuterium in the ethene is consistent with it being produced by ring degradation.

(iv) Photochemical decomposition

$(C_5H_5)_2Ti(CH_3)_2$ is photosensitive and samples were kept dark except during the short periods in which gas was removed. Decomposition was therefore totally thermal in nature. Comparison with data obtained from photodecomposition of the same species in benzene [21,22] shows that the two have marked similarities. An induction period during which the solution darkens followed by rapid evolution of gas and formation of a black precipitate [21] is common to both. Although ESR data are interpreted as indicating homolytic cleavage of the methyl titanium bond [22], there is no incorporation of benzene hydrogen in the methane produced [21].

It is likely that the two decompositions differ only in the method of triggering stage two. The hydrogen exchange is not detected in the photodecomposition of $(C_5D_5)_2Ti(CH_3)_2$ but since the sample was taken after only 20—22 h at room temperature, none would be expected. The isotope effect in 88% deuterated rings would also serve to conceal it. In all respects save the length of the induction time, which in any event depends on temperature in thermal decomposition (Tables 1 and 2) and on intensity in photodecomposition [21], the photochemical observations parallel ours. Indeed, the opacity of the system once stage two begins is such that any process from that point on must be primarily thermal.

Acknowledgements

The authors gratefully acknowledge the assistance of Dr. Brian Hunter, the provision of the MS-10 spectrometer by Dr. John Stone and the financial support of the National Research Council.

References

1 M.E. Vol'pin, V.B. Shur, V.N. Latyaeva, L.I. Vyshinskaya and L.A. Shul'gaitser, Izv. Akad. Nauk. SSSR, Ser. Khim., (1966) 385.
2 K. Azuma, K. Shikata, S. Oba, K. Nishino and T. Matsumura, Kogyo Kagaku Zasshi, 68 (1965) 347.
3 K. Shikata, K. Nishino and K. Azuma, Kogyo Kagaku Zasshi, 68 (1965) 352.
4 G.A. Razuvaev, V.N. Latyaeva and L.I. Vyshinskaya, Dokl. Akad. Nauk SSSR, 159 (1964) 383.
5 G.A. Razuvaev, V.N. Latyaeva, L.I. Vyshinskaya and G.A. Kilyakova, Zh. Obshch. Khim., 36 (1966) 1491.
6 H.G. Alt, F.P. di Sanzo, M.D. Rausch and P.C. Uden, J. Organometal. Chem., 107 (1976) 257.
7 G.J. Erskine, D.A. Wilson and J.D. McCowan, J. Organometal. Chem., 114 (1976) 119.
8 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, J. Amer. Chem. Soc., 94 (1972) 1219.
9 H. Gilman, E.A. Zoellner and W.M. Selby, J. Amer. Chem. Soc., 55 (1933) 1252.
10 C.P. Boekel, J.H. Teuben and H.J. deLiefde Meijer, J. Organometal. Chem., 81 (1974) 371.
11 M. Michmann and H.H. Zeiss, J. Organometal. Chem., 13 (1968) P23.
12 J.R.C. Light and H.H. Zeiss, J. Organometal. Chem., 21 (1970) 391.
13 J.D. McCowan, Canad. J. Chem., 51 (1973) 1083.
14 L.S. Pu and A. Yamamoto, Chem. Commun., (1974) 9.
15 N.J. Cooper and M.L.H. Green, Chem. Commun., (1974) 761.
16 K.J. Ivin, J.J. Rooney, C.D. Stewart, M.L.H. Green and R. Mahtab, Chem. Commun., (1978) 604.
17 F. Calderazzo, J. Organometal. Chem., 53 (1973) 179.
18 T.J. Marks and J.R. Kolb, J. Amer. Chem. Soc., 97 (1975) 3397.
19 R.R. Schrock and P.R. Sharp, J. Amer. Chem. Soc., 100 (1978) 2389.
20 F.N. Tebbe, G.W. Parshall and G.S. Reddy, J. Amer. Chem. Soc., 100 (1978) 3611.
21 M.D. Rausch, W.H. Boon and H.G. Alt, J. Organometal. Chem., 141 (1977) 299.
22 E. Samuel, P. Maillard and C. Giannotti, J. Organometal. Chem., 142 (1977) 289.