

THERMOLYSIS OF DI- π -CYCLOPENTADIENYL- σ -ORGANOTITANIUM CHLORIDES

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SUMMARY

The thermolysis of a series of compounds $\text{Cp}_2(\text{R})\text{TiCl}$ (where $\text{Cp} = \pi$ -cyclopentadienyl and R is a σ -bonded hydrocarbon moiety) was studied. After an initial unsteady period, first-order loss of the R group was observed. The activation energy of bond breaking was approximately 25 kcal/mole for all compounds. The products and kinetics are explained by postulating that the rate-determining step is the promotion of the R group to a non-ionic activated state in which it is still within and influenced by the titanium coordination sphere but mobile enough to migrate from one titanium atom to another.

INTRODUCTION

As a continuation of a previous study¹ on the chemistry of di- π -cyclopentadienyl- σ -organotitanium chlorides [$\text{Cp}_2(\text{R})\text{TiCl}$, where $\text{Cp} = \pi$ -cyclopentadienyl and R is a wide range of hydrocarbon groups], a quantitative study was undertaken of the behavior of these compounds upon heating. This study adds a new facet to organotitanium chemistry. Not only is this apparently the first thermolysis study of these compounds, but previous studies of the thermal decomposition of pure tetravalent organotitanium compounds have been restricted mainly to methyl and phenyl compounds²⁻²⁶ with a recent product study being reported for a benzyl derivative²⁷.

This work also provides an insight into Ti-C bond strength concerning which there has been only one measurement reported in the literature²⁸.

It was a purpose of the present study to obtain information on the mechanism of thermal decomposition of compounds $\text{Cp}_2(\text{R})\text{TiCl}$. Ti^{III} has been seen by ESR spectroscopy after thermolysis of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ ³⁻⁵, and there is general agreement that Ti^{III} species are formed as products of the thermal cleavage of Ti-C σ -bonds in such compounds. However, one report of no valence change has been published²⁹. The exact mechanism by which Ti-C bonds cleave is very much unsettled.

Some authors have presented convincing evidence that free radicals are formed and therefore concluded that homolytic cleavage of the Ti-C bond occurs. For instance, solvent fragments have been isolated⁵⁻⁹, quantitative reaction with a solvent has been claimed⁵, radical trapping experiments have been described⁷, and the decomposition reaction has been reported to initiate polymerization of a vinyl monomer^{4,14}

Certain solvents, such as ethers and chlorinated hydrocarbons, can definitely be involved in the reaction and their role could be the promotion of homolytic bond cleavage^{8-10,13}. In fact, direct reaction between $(\text{CH}_3)_4\text{Ti}$ and CCl_4 has been reported¹⁵. However, reaction of lower-valent titanium species with solvents, especially chlorinated solvents, could generate solvent free radicals and could initiate polymerization^{2,3}. Numerous examples of radical generation from solvents by a host of lower-valent metal compounds have been reported in the last decade. Thus, it is not entirely clear whether the free radicals are formed in the thermolysis reaction itself or in a subsequent secondary reaction.

Some authors present convincing evidence that free radicals are not formed. Isotopic labeling experiments have shown that hydrocarbon solvents are not chemically involved, as they should be if free radicals were formed⁸⁻¹². These authors, therefore, favor a molecular mechanism for the thermal decomposition, although one report has claimed an ionic mechanism²⁶.

It is possible that the Ti-C σ -bond may be broken by more than one mechanism. In studies of the CH_3 -Ti bond, no CH_3Cl was formed in CCl_4 solvent unless ether was present⁸, and no CH_3D was formed in deuterotoluene solvent unless tetrahydrofuran was present¹³. A change in mechanisms in the presence of donor solvents would be one explanation for these results.

The present study represents a departure from the approaches of previous studies. All of the past studies have been carried out in the presence of a solvent. Kinetic studies have been reported only in the presence of donor- or acceptor-type molecules.

In the present study, most decompositions were carried out on neat pure compounds, although some comparison runs were made in a solvent. The reaction kinetics were followed both by thermogravimetric analysis (TGA) and by rate of appearance of volatile products. The volatile products were also isolated and identified. As a result of this somewhat different approach, some previously unreported aspects of the decomposition of organotitanium compounds were uncovered and a mechanism which explains essentially all of the experimental data is proposed.

EXPERIMENTAL

Procedures

For the kinetic experiments, a du Pont 950 TGA instrument was employed with a standard gas flow rate of 1.0 l/min at atmospheric pressure. The sample size was approximately 5 mg. In order to determine the approximate stability of each compound, programmed decompositions at $5^\circ/\text{min}$ were made. The inability to obtain clean stages of decomposition prevented further analysis by dynamic thermogravimetry. Instead, isothermal thermogravimetry, in which there was a continuous recording of the weight change as a function of time, was used. In a few cases, the effluent gases were passed through a liquid-nitrogen trap and the condensable gases were identified by gas chromatography. The kinetic data are summarized in Table 1.

In order to obtain more product information, samples of the pure $\text{Cp}_2(\text{R})\text{TiCl}$ compounds (alone or with toluene) were sealed in glass tubes at high vacuum (10^{-4} mm) and placed in an oil bath at the temperatures and for the times indicated in Table 2. For the phenyl, benzyl, and phenethyl compounds, an inverted U-shaped tube was

TABLE 1

DECOMPOSITION DATA FOR COMPOUNDS OF STRUCTURE $\text{Cp}_2(\text{R})\text{TiCl}$

R	Temp. (°C)	$k \times 10^3$ (sec^{-1})	Wt. loss (% of theory)	ΔE^* (kcal/ mole)	Ambient atmosphere
CH_3 (does not melt)	110.	0.024			Vacuum
		0.066			N_2 380 mm
		0.066			Ar 380 mm
C_2H_5 (m.p. 88.7°)	110.9	1.0	115	27	Ar
	122.6	2.8	125		
	131.8	6.4	138		
	100.5	0.61	156	20	0.02% O_2 in Ar
	111.9	1.1	144		
	120.1	2.4	114		
	95.7	0.51	110	22	0.1% O_2 in Ar
	108.3	1.6	168		
	119.2	3.1	158		
	92.4	0.39	94	24	25% H_2 in Ar
	100.3	0.73	129		
	107.4	1.5	134		
	109.0	9.9	140	28	25% C_2H_4 in Ar 0.001% O_2 in N_2
	102.6	0.55	136		
	110.0	1.2	133		
122.7	3.8	152			
$(\text{CH}_3)_2\text{CHCH}_2$ (m.p. 70.5°)	75.2	0.65	91	25	Ar
	91.5	3.6	101		
	95.3	4.8	108		
	105.9	11.	109		
C_6H_5 (does not melt)	68.5	0.11	77	29	Ar
	78.7	0.27	80		
	88.9	0.80	74		
	98.5	4.2	52		
	109.3	7.3	69		
$\text{C}_6\text{H}_5\text{CH}_2$ (m.p. 107°)	62.2	4.0	77		Ar
	68.9	9.5	57		
	78.9	10.	68		
	87.6	7.8	57		
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$ (m.p. 139°)	99.1	0.07	66	52	Ar
	108.6	0.25	86		
	116.6	1.8	68	25	
	127.4	3.4	55		
	139.1	8.4	66		
	148.4	20.	60		

used, one leg of the tube being in the oil bath and the other immersed in liquid nitrogen. This promoted distillation and trapping of liquid products. The volatile products, identified by gas chromatography/mass spectrometry, are listed in Table 2. The non-volatile products were not examined except in one experiment with $\text{Cp}_2(\text{CH}_3)\text{-TiCl}$. In this one experiment, the infrared spectrum was recorded and the residues were hydrolyzed with methanolic HCl to determine the amount of hydrolyzable methyl groups remaining.

The product, mass balance, and kinetic studies were confirmed for the ethyl and methyl compounds using larger samples and a conventional laboratory hot-tube apparatus, following the kinetics by appearance of gaseous products rather than by weight loss.

Data treatment

Kinetic data were derived from the steady portion of the raw thermogravimetric curves by computer-assisted treatment. It will be recalled that eqn. (1) describes weight loss for any simple decomposition.

$$-dx/dt = k \cdot x^n \quad (1)$$

where x = weight fraction of undecomposed material; t = time; k = reaction rate constant; n = reaction order.

Integrating and solving eqn. (1) for k yields the following pair of equations:

$$k = -\frac{(x^{1-n} - 1)}{t \cdot (1-n)} \quad \text{if } n \neq 1$$

$$k = -\frac{\ln(x)}{t} \quad \text{if } n = 1$$

TABLE 2

VOLATILE PRODUCTS OF THERMAL DECOMPOSITION

R	Temp. (°C)	Time (min)	Volatile products
Methyl ^a	90	120	Methane
	110	90	Methane and traces of ethylene
	150	10	Methane, traces of ethane and ethylene
Ethyl ^a	110	90	Ethane and ethylene, traces of butane, hexane, and ethylcyclopentadiene
	125	10	Equal amounts of ethane and ethylene
Isobutyl	75	75	Equal amounts of isobutane and isobutylene, traces of an octane and isobutylcyclopentadiene
Phenyl	89	22	Biphenyl, somewhat less phenylcyclopentadiene, trace of benzene
Benzyl	91	38	Bibenzyl and toluene in about equal amounts, traces of benzylcyclopentadiene and benzyl alcohol
Phenethyl	117	24	Mostly ethylbenzene, some styrene ^b

^a Mass balance made to be sure there were no unidentified volatile products. ^b Styrene formed at this temperature could thermally polymerize, lowering the observed styrene yield.

Values of k for selected orders can be calculated by normalizing residual weights again total weight loss for a series of times. If these values of k are plotted against time for each order, a family of curves is obtained such as shown in Fig. 1. These curves have a common intercept at k since, when $t=0$, $x^n=1$ regardless of the value of n . The order of the reaction is numerically the value of n for which k becomes constant over the course of the reaction (i.e., that which gives a line with zero slope in a plot like Fig. 1). The reaction order, n , was unity for all compounds, and therefore k is given in sec^{-1} .

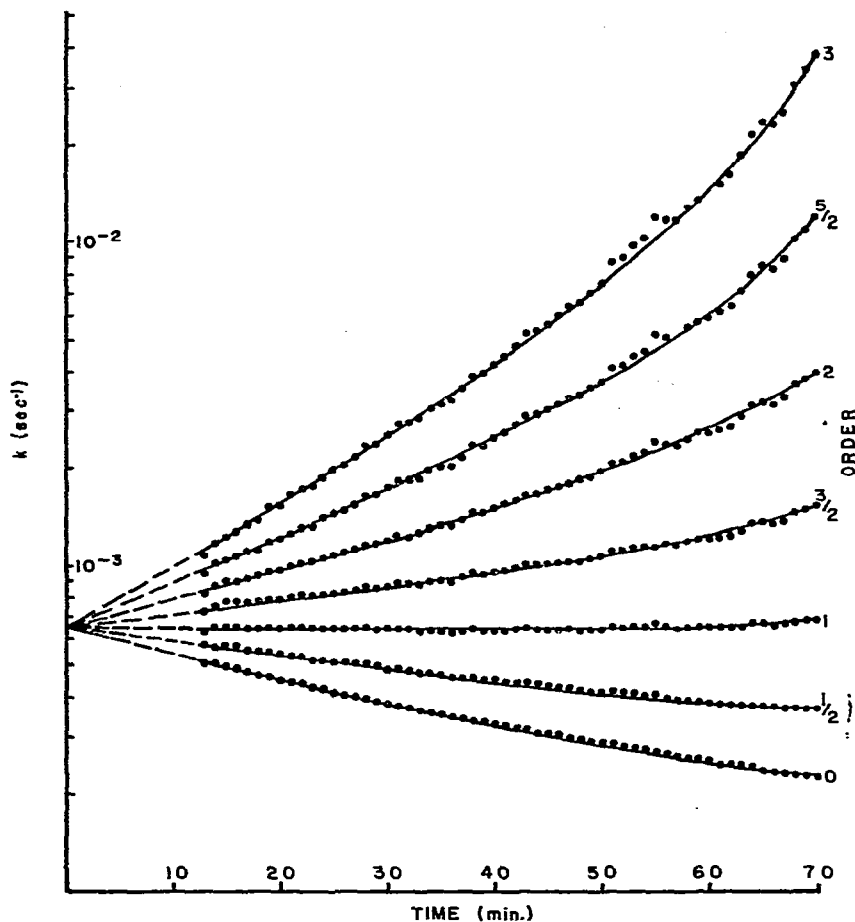


Fig. 1. Effect of reaction order on constancy of rate constant^c.

Results

The product data in Table 2 show that the σ -bonded ligand is lost, almost exclusively, as the first step in thermal decomposition. In no case was there a discrepancy between product data from sealed-tube and continuous-flow experiments. There is an indication from the data on the methyl compound that there can be a change in product distribution at different temperatures; ethylene was observed in both solid and solution experiments above 90° but not below. In six flow runs with the ethyl compound which were run to almost 90% theoretical loss of one ethyl group, the products isolated were $49.4 \pm 1.1\%$ ethane and $50.6 \pm 1.1\%$ ethylene. Beyond 90% loss of one ethyl group, a trace of cyclopentadiene was also found.

The results of the kinetic experiments were not clean-cut. When the ambient gas was essentially pure argon (less than 0.002% O₂), the decomposition (as judged by both weight loss and product evolution) began slowly and accelerated until perhaps 20% of the material had decomposed. Thereafter, the remainder of the reaction was quite cleanly first order in undecomposed material. The initial period was not reproducible between different compounds or even between runs at different tem-

peratures with the same compound. Moreover, it did not correlate with Ti^{III} concentration as might be expected for an autocatalyzed reaction. When other gases were added to the argon, the decomposition often had a different character: it began rapidly and decelerated to reach smooth first-order behavior. All k values in Table 1 are for the smooth first-order portion of the experimental curve. Except for the isobutyl compound, which is non-volatile itself and cleanly gave gaseous organic decomposition products, the observed weight losses in Table 1 were not quantitative, thus introducing some uncertainty into the k and ΔE^* values. The methyl compound was found to be so volatile that sublimation accounted for most of the weight loss in flow experiments. Therefore, the k value in Table 1 for this compound was derived from sealed tube studies. The high weight loss for the ethyl compound resulted from partial distillation of the undecomposed compound. The stability of the weight after decomposition indicates that Cp_2TiCl is not volatile. The organic products formed upon decomposition of the aromatic derivatives (Table 2) would not be expected to be completely vaporized under the conditions of the experiment, in agreement with the observed low weight loss percentages in Table 1. The mathematical technique of normalizing all data to observed weight loss implicitly assumes that the contribution

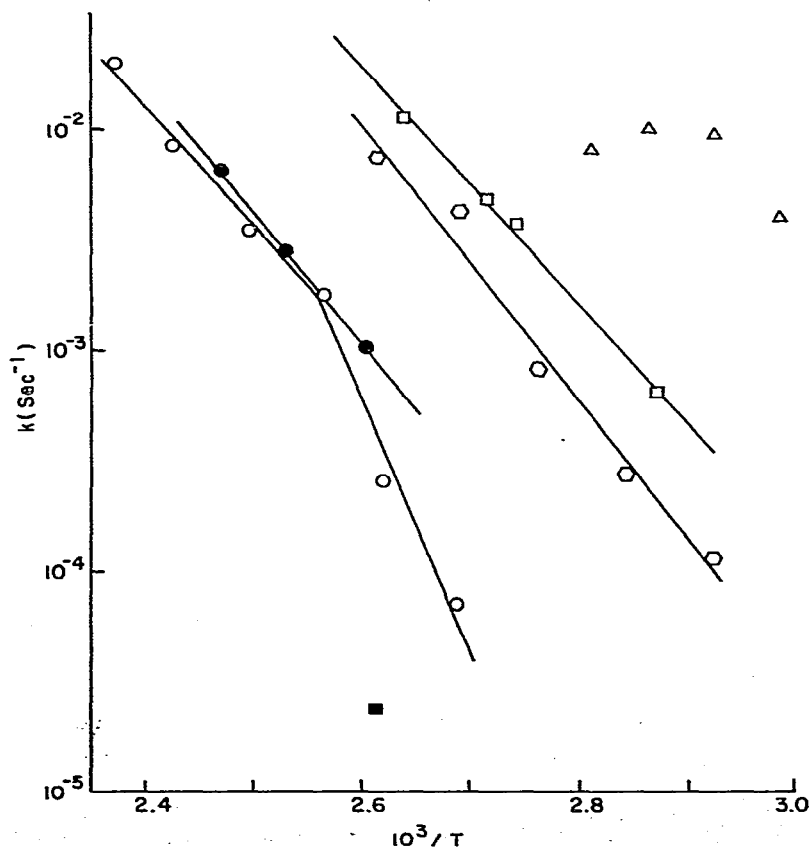


Fig. 2. Arrhenius plot of rate constants for compounds of structure $Cp_2(R)TiCl$ where $R = \blacksquare$, methyl; \bullet , ethyl; \square , isobutyl; \circ , phenyl; \triangle , benzyl; \circ , phenylethyl.

of all complications is proportional to the amount of decomposition, a convenient, but undoubtedly over-simplified, assumption. Nevertheless, where good Arrhenius plots resulted from the data, ΔE^* values were calculated. The data obtained under argon are displayed in Fig. 2.

It can be seen that the data obtained for the benzyl and phenethyl compounds did not yield a linear Arrhenius plot. For this reason, it is felt that comment on these data should be made. It can be seen from its position on the Arrhenius plot in Fig. 2 that the benzyl compound is extremely unstable. It also reacts readily with air¹. The non-linearity of the data is probably a reflection of a loss of purity in the time scale of the determination. Oxidation is indicated by the presence of benzyl alcohol in the products, and was detectable in this unstable compound during sample preparation for kinetic studies.

The phenethyl compound represented a somewhat different anomaly. It was one of the more stable compounds tested and at high temperatures behaved normally. At relatively lower temperatures, some 25° below the first-order transition (melting point), a break in the Arrhenius plot occurred with an approximate doubling of the slope.

The effects of various gases other than argon are seen in Fig. 3, where the solid line is that from Fig. 2 for the ethyl compound under argon. All of the gases tested

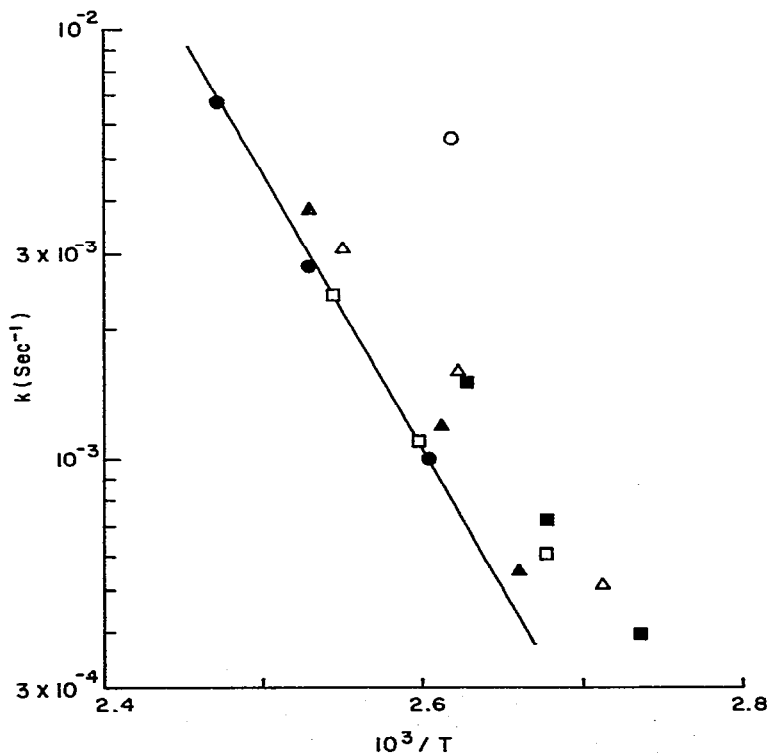


Fig. 3. Rate constants for thermal decomposition of $Cp_2(C_2H_5)TiCl$ under various gases. ●, ϵ line, argon containing 0.001% O_2 from Fig. 2; □, 0.02% O_2 in argon; Δ, 0.1% O_2 in argon; ■, 25% H_2 in argon; ○, 25% C_2H_4 in argon; ▲, pure N_2 containing 0.001% O_2 .

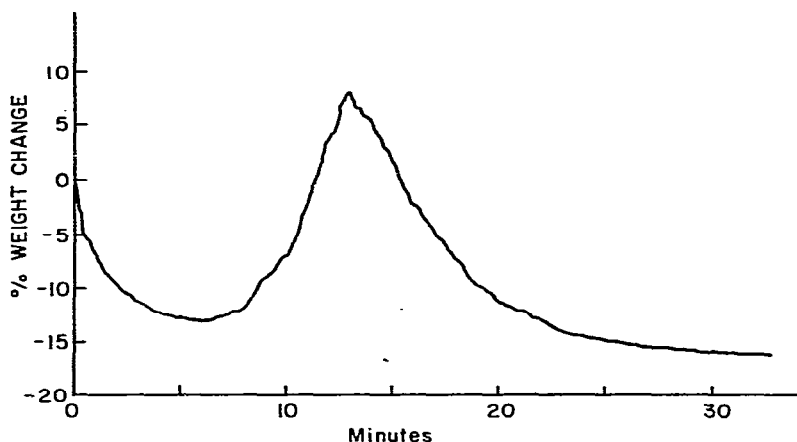


Fig. 4. Thermogravimetric recorder trace for thermolysis of $\text{Cp}_2(\text{C}_2\text{H}_5)\text{TiCl}$ in the presence of 25% C_2H_4 .

increased the rate of decomposition with the observed order being $\text{N}_2 < 0.1\% \text{O}_2 \approx 25\% \text{H}_2 < 25\% \text{C}_2\text{H}_4$. This suggests that the actual order of sensitivities of the compounds to these gases would be $\text{N}_2 < \text{H}_2 < \text{C}_2\text{H}_4 < \text{O}_2$. There is an indication of a decrease in activation energy also.

A strange behavior was observed in the presence of ethylene (see Fig. 4). After a short initial fast reaction (1 min) a smooth first-order weight loss took place for 4 min. The value for k in Table 1 and Fig. 3 was obtained from this portion of the plot. At 5 min, the sample began to increase in weight until a maximum was reached at 12.5 min. The maximum weight gain was equivalent to roughly 1.5 ethylene molecules per titanium. Weight was then lost until 30 min and no further weight change took place up to 50 min. The final weight was equivalent to 140% loss of the original ethyl group. The weight gain could be due either to a reversible adsorption of ethylene or to telomerization. If telomerization took place, the bulk of the telomers must have been in the C_4 – C_8 range, otherwise the weight loss would have been less than theoretical as was seen for the other compounds which gave heavy organic products. Thus, a substantial proportion of the titanium must have been involved in whatever mechanism caused the weight gain.

These results were corroborated by sealed tube experiments on $\text{Cp}_2(\text{C}_2\text{H}_5)\text{-TiCl}$. The normal products in a flow system are ethylene and ethane in equal amounts, as mentioned earlier. However, when the evolved gases were held in the presence of the decomposing compound, as they must be in sealed tube experiments, the ethane/ethylene ratio became 3/2 rather than 1/1. Moreover, small amounts of C_4 and C_6 hydrocarbons (not further identified) were detected by gas chromatography, indicative of ethylene being converted to telomers.

Careful mass balance checks were made with both methyl and ethyl derivatives to be sure that all products were accounted for. The solid residues generally were not studied although the characteristic greenish color of Cp_2TiCl was clearly evident in a number of runs before the residues were exposed to air.

One run was made with $\text{Cp}_2(\text{CH}_3)\text{TiCl}$ in which the residue after partial decomposition was analyzed for hydrolyzable methyl groups. It was found that 12% of the methyl groups were evolved as methane during heating, and 69% were evolved

as methane due to the subsequent hydrolysis. By difference, 19% were not recoverable as methane after heating. No C_2 or higher hydrocarbons were found.

DISCUSSION

The rate-determining step in the thermal decomposition of compounds of structure $Cp_2(R)TiCl$ is clearly unimolecular. The kinetics for all compounds are clearly first-order after an initial unsteady period. The similarity in activation energy for all compounds regardless of physical state and the absence of a break at the melting point in the Arrhenius plot for the phenethyl compound are strong evidence that the same unimolecular process is occurring for all compounds and that mobility is not a requirement for decomposition.

In contrast to the rate-determining step, the product-determining step appears to be bimolecular. The products were principally those of disproportionation (if there was a hydrogen atom β to titanium), hydrogen abstraction (if there was an α - but no β -hydrogen) and ligand combination (if there were no α - or β -hydrogens). The experiment with the methyl compound in which the residues were hydrolyzed strongly suggests that the abstracted hydrogen comes from σ -bonded ligands which have not yet been split off. Thus, all three product-forming possibilities require interaction of two ligands.

In light of the foregoing, the decomposition mechanism of these compounds appears to involve two separate steps. First, in a slow, unimolecular reaction, the σ -bonded organic ligand is converted into an active species of some sort. This species must be sufficiently mobile that it can encounter other σ -bonded ligands even in a powdery solid. In the second and rapid step of the reaction, this active species attacks a molecule of undecomposed starting compound, reacting with the organic ligand and generating the final products of the reaction.

The nature of this active species is suggested by the present data. It is noteworthy that, with the exception of the phenyl compound, the stabilities of the various $Cp_2(R)TiCl$ compounds correlate roughly with the difficulty of forming either a free radical or a carbonium ion from the respective R groups. This suggests that the active species has either radical or cationic character. However, the product studies indicate that the active species cannot be a true free radical since radical-radical combination would predominate for all radicals at the conditions of these experiments. A carbonium ion intermediate is even more unlikely. A charged ligand would have difficulty diffusing away from its counter ion in a solid matrix and should not be very mobile. Ti^{IV} cations have been reported, but a Ti^{IV} anion has not, to our knowledge. Furthermore, dimerization of cations seems unlikely. Finally, donor molecules would contribute electron density to titanium and would resist, not assist, the departure of a positive species.

Considering all these facts, we postulate that the active species is neutral and therefore has radical character. However, we suggest that it is not formed by complete homolytic cleavage of a $Ti-C$ σ -bond, but by activation of the σ -bond, perhaps by promotion of one electron out of the bonding orbital. In essence, we postulate a radical modified by and bound within the titanium coordination sphere. In the case of the benzyl compound, the active species could easily be a true π -allyl intermediate, as observed for some benzyl derivatives of transition metals, formed by a true $\sigma-\pi$

rearrangement.

As is indicated in Table 1, the activation energy for decomposition of all compounds studied is 20–29 kcal/mole, which value should approach the Ti–C bond strength for the mechanism suggested. This is consistent with the only published value of the Ti–C bond strength, which places it at 31 kcal/mole²⁸.

It is noteworthy that these compounds have an absorption band at 1.1 to 1.2 μ , corresponding to about 25 kcal/mole energy, which is absent in the parent Cp_2TiCl_2 . This band could be due to titanium *d*-electron promotion in these compounds, but the band is weak and the assignment uncertain.

The instability of the benzyl derivative does not accord with the relative stability of the recently reported dibenzyl compound²⁷ $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_2$ or the stability of tetrabenzyltitanium relative to that of the tetramethyl derivative³⁰. The lack of stability of $\text{Cp}_2(\text{C}_6\text{H}_5\text{CH}_2)\text{TiCl}$ may denote an easy access of coordinating species. Alternatively it may indicate a lack of steric restriction for forming a complexed allyl-type intermediate the likes of which have been seen for a benzyl derivative of molybdenum (the molybdenum also being σ -bonded to cyclopentadienyl, incidentally)³¹. Assuming that the formation of such a π -allyl complex determines the decomposition rate, then the stability of the multi benzyl derivatives would be explained by a sterically enforced σ -bonded configuration about the metal atom and hindrance of formation of the π -bonded species.

In the case of the phenyl compound, the active species could be a π -bonded phenyl radical, formed by a sort of σ - π rearrangement, with the π electrons of the benzene ring contributing to the overall stabilization of the transition state. This would account for the phenyl compound being unusually reactive compared with compounds bearing aliphatic ligands. In support of this postulate, some authors have shown recently that the phenyl radical does not readily become free when homolytically cleaved from titanium and suggest that a coordinated benzyne molecule may also be formed²⁶. Sterically, two π -bonded cyclopentadienyl ligands and a π -bonded phenyl are crowded. With the radical site being adjacent to cyclopentadienyl ligand in this activated form, intramolecular attack to give the observed unusually large amount of phenylcyclopentadiene is then understandable also.

In order for the kinetics to be first order, it is necessary that the energy involved in this activation or σ - π -type rearrangement be conserved in the molecule. This requires that the activated state be sufficiently stabilized to be long-lived in comparison with the time required to form products. In order to account for the mobility of the active species, we postulate that, with low additional activation energy, the active species can transfer from the coordination sphere of one titanium to an adjacent one*. Thus, this species could move through a liquid or solid matrix, without ever

* An alternate mechanism which has been suggested is that the monoalkylated Cp_2RTiCl is converted into $\text{Cp}_2\text{R}_2\text{Ti}$ by a series of rapid redistribution reactions. The rate-determining decomposition step, then, would be the monomolecular simultaneous loss of both R groups to yield the observed products with Cp_2Ti formed as an intermediate. This suggestion was considered and rejected. In unpublished work, attempts to prepare $\text{Cp}_2(\text{C}_2\text{H}_5)_2\text{Ti}$, the assumed intermediate in the decomposition of the ethyl compound, failed. The formation of ethane and ethylene was seen as low as -70° , and essentially complete decomposition occurred at -40° . Thus the decomposition of $\text{Cp}_2\text{R}_2\text{Ti}$ could not be the slow step under the conditions of the thermolysis. The redistribution reaction would then have to be the slow step, but this would require second-order kinetics rather than the observed first order kinetics.

being truly free to react with the surrounding environment. When it contacted a titanium atom bearing an unchanged σ -bonded ligand, it could react with that ligand to generate products.

This formulation of the mechanism can also be invoked to explain some otherwise rather puzzling observations. Donor molecules should coordinate with titanium. It is possible that the neutral active species could then be expelled from the coordination sphere as a true free radical. It is also possible that it could react directly with the donor within the coordination sphere of the same titanium atom. In either case, the products of free-radical reactions, as observed by other workers, could be explained.

The active gases studied in this work all have some donor character, and it may be that the initial unsteady period prior to clean first-order kinetics is merely an indication of an equilibrium level of coordinated donor molecules being achieved. If so, the reaction rate should increase and activation energy decrease with increasing concentration of donor gas, as observed.

The short-lived oligomerization reaction of ethylene can also be explained by postulating a coordinated radical as the active species. Ethylene, as a donor molecule, would be expected to π -bond with the d -orbitals of titanium. If, within the same coordination sphere, a radical-like species were present, radical addition to the ethylene double bond could take place. However, radical addition should not be highly favored over the other possible reactions of the active species, and therefore high polymer would not be formed. Thus, slow oligomerization would take place until the active species moved into the coordination sphere of a titanium atom bearing an unchanged ligand, at which time the oligomer and the ligand would be expelled as products. The peculiar TGA results would then be rationalized as follows. In the initial stages of the thermolysis, active species would readily react with surrounding unchanged ligands, and weight would be lost. As such ligands became more scarce, the active species would have longer lifetimes during which they could add several molecules of ethylene, and weight would be gained. Upon their contact with unchanged ligands, these oligomeric species would react to form volatile products and decrease the number of active species. As the number of active species diminished, weight would be irreversibly lost.

The concept of a donor-assisted activation or σ - π -type rearrangement which converts a σ -bonded ligand into a titanium-coordinated neutral species bearing a loosely coordinated unpaired electron is thus seen to be useful in accounting for the reaction kinetics, products, and several unusual features of the thermolysis of compounds of structure $Cp_2(R)TiCl$. Moreover, it appears to us that the decompositions of many other organometallic compounds which are said to be free radical could possibly proceed by such a mechanism.

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