Thermal Decomposition of Methyl Titanium Chlorides

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The thermal decomposition of CH_3TiCl_3 and $(CH_3)_2TiCl_2$ in C_2Cl_4 and C_6H_6 has been examined over the range 20 to 110 °C under a nitrogen atmosphere utilizing n.m.r. spectroscopy, mass spectroscopy, and elemental analysis. The reaction products are found to be the result of at least four separate, simultaneous, and competing reactions.

La décomposition thermique de CH_3TiCl_3 et de $(CH_3)_2TiCl_2$ dans C_2Cl_4 et C_6H_6 a été examinée sur une échelle de température allant de 20 à 110 °C, sous une atmosphère d'azote, et en utilisant la spectroscopie et RMN et de masse ainsi que l'analyse élémentaire. Les produits de la réaction sont le résultat d'au moins quatre réactions isolées, simultanées, et compétitives.

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Introduction

Studies of the decomposition of alkyl titanium chlorides have yielded a diversity of views on the mechanism involved. The proposition that decomposition involved a radical attack upon the solvent (1, 2) has been effectively disproven as a general theory by de Vries (3), although radical attack may occur under special conditions (4). However the theory of de Vries leads to awkward explanations for the decomposition of methyl titanium halides, particularly the postulated existence of either CH_2 or CH_2TiCl_3 without supporting evidence.

The present work was designed to inquire into the decomposition of methyl titanium chlorides, with a view to either producing evidence to support one of the existing theories or uncovering an alternative.

Experimental

(i) Use of Nuclear Magnetic Resonance Spectroscopy

The decomposition of both methyl titanium trichloride and dimethyl titanium dichloride and the corresponding production of soluble hydrogen-bearing products such as methane, were conveniently followed by n.m.r. spectroscopy. Samples were made up in n.m.r. tubes to known concentrations and component ratios. Spectra were obtained periodically as required on a Varian A-60 spectrometer equipped with a variable temperature probe.

Samples were prepared in a dry nitrogen atmosphere using syringes of from 0.1 ml to 1.0 ml capacity. Samples involving study of more than a few hours duration were made up in tubes having a constriction near the top at which a flame seal was made after filling. Liquid volumes were chosen to minimize vapor volume. This decreased the proportion of volatile products which was in the gaseous phase and which was, consequently, not in the n.m.r. sample region.

Samples were stored, between spectral measurements, in a rotating drum which ensured continuous mixing by turning the samples end over end in a period of about 1 min. The drum for ambient temperature was constructed by boring holes in a polyethylene block. A second mixing drum, constructed from aluminum, was mounted in a modified laboratory oven. Light was excluded totally in storage and as much as possible during handling. Just prior to each n.m.r. determination, any solids were centrifuged to the top of the tube so as not to interfere with the homogeneity of the liquid phase. The solid was redispersed before returning the sample to the mixer.

Peak positions, and quantitative measurements of the concentration of each species, were obtained by comparison of spectra and integrated peak heights with those of a reference material of known concentration. This reference was usually cyclohexane, but cyclopentane, benzene, and dichloromethane were used on occasions when a search for some special phenomenon was made. Integral values used were the average of five or more consecutive runs.

Studies were made of the path of decomposition at 20, 50, 80, and $110 \,^{\circ}$ C and in a variety of solvents. A few specialized experiments, such as continuous centrifuging to compact the solid or removal of the solid initially formed, were also performed.

(ii) Elemental Analyses

Elemental analyses were carried out by both chemical means (A. Bernhardt)³ and by neutron activation analysis (General Atomic).⁴ The first was used for carbon, hydrogen, and chlorine, and the second for zinc, chlorine, and titanium.

Solid decomposition products were isolated using fine porosity ground glass filter crucibles, dried by pumping to 10^{-4} Torr or better, sealed in glass and sent for analysis. A

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few samples were sent in a moist condition as a test for volatile products.

Analysis of solids initially precipitated on mixing dimethyl zinc with titanium tetrachloride in a solvent were also carried out by methods analogous to those above. In this case speed was important and tests were made to ensure that filter porosity did not effect either the weight or nature of the product.

(iii) Mass Spectrometric Studies of the Nature of the Alkyl Content of the Solid Decomposition Products

Solid decomposition products were isolated as for elemental analysis, and sealed in a glass vessel designed for the purpose. D_2O was introduced and the resulting gaseous products analyzed by mass spectrometry.

(iv) Consideration of Errors

In the quantitative study of decomposition using n.m.r. spectroscopy, errors were introduced by syringe accuracy and handling, and by the reproducibility of the integrations by the spectrometer. Syringes of the most suitable size were used to minimize errors. Tests indicated that syringe errors are approximately 2 to 3% for any one measurement, giving a cumulative error of 5% from the double step of making the solution and drawing from it.

Errors in integration were minimized by running five integrals on each spectrum. Reproducibility of successive integrals was within 30%. This poor reproducibility arose since the spectra and integrals were obtained at low temperatures and the heater-sensor insert is subject to fluctuations in its position within the insert of the probe. Reproducibility



FIG. 1. Thermal decomposition at ambient temperature of initially 1.5 M CH₃TiCl₃ in C₂Cl₄. Symbols are: \bigcirc , CH₃TiCl₃; \triangle , CH₄; \blacktriangle , C₂H₆.

of the average of successive sets of five integrals was within 10% .

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(v) Materials

Trimethyl aluminum was used as obtained from Texas Alkyls.⁵ Dimethyl zinc was prepared by the method of Elston (6). Analysis indicated a high degree of purity in both cases. Dimethyl titanium dichloride and methyl titanium trichloride were prepared by the methods described previously (5).

Tetrachloroethylene, benzene, cyclohexane, and titanium tetrachloride were bought in the purest available grades and sparged with dry nitrogen. Batches of tetrachloroethylene, containing a non-volatile inhibitor (*t*-butyl phenol) which was not removed by sparging, were found to give anomalous results. Air distillation of tetrachloroethylene led to formation of traces of Cl₃CCOCl which likewise interfered. Care had to be taken in the storage of tetrachloroethylene from which the inhibitor had been removed in order to prevent formation of interfering oxidation products.

All light sensitive materials were stored in darkened storage bottles. Thermally unstable materials were stored at -195 °C in the short period before use. Air and water sensitive materials were stored in glass vessels with double ground-glass stoppers. The vessels were kept in a nitrogen atmosphere.

Results

Soluble Decomposition Products

Almost two hundred samples, mainly $(CH_3)_2Zn/TiCl_4$ systems, were studied. Table 1 summarizes the effect on decomposition product distribution of variations in solvent, temperature, and means of preparation of CH₃TiCl₃ and (CH₃)₂TiCl₂. The eight representative runs in Figs. 1 to 8 illustrate the rates under varying conditions, as well as showing exact values of product distribution for their particular cases. The amounts of each species are plotted as calculated from the n.m.r. integrals, except for a 6% addition for CH₄ corresponding to the amount of CH₄ in the vapor phase. This correction is based on known solubility data and is constant because the volumes of reagent solution were chosen always to total 95% of the 1.95 ml total volume of the sealed n.m.r. tube. Figure 9 illustrates the reproducibility to be expected and the hydrogen balance obtained. The latter assumes, for reasons to be discussed, that one CH_2 exists in the solid decomposition products for each CH_4 formed.

In all $(CH_3)_2Zn/TiCl_4$ systems (e.g. Figs. 5, 7, and 8), the observed initial concentrations of CH_3TiCl_3 and of $(CH_3)_2TiCl_2$ are less than

⁵Stauffer Chemical Company, 6910 Fannin St., Houston, Texas.

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IABLE I. Decomposition product

	Solvent	Soluble products by proton n.m.r.					
System		At 25 °C	At 80 °C				
CH ₃ TiCl ₃	C ₂ Cl ₄	CH_4 , C_2H_6 both important, C_2H_6 being more abundant above initial CH_3 TiCl ₃ concentrations of ~1 <i>M</i> ; traces of 1,1,2-trichloropropene-1, especially for very low initial concentrations*; traces of CH_3Cl	CH_4 , C_2H_6 , CH_3Cl , and 1,1,2-trichloropropene-l are all abundant				
CH ₃ TiCl ₃	C ₆ H ₆	CH_4 , C_2H_6 both important, with abundance of C_2H_6 again favored by high initial concentrations of CH_3 TiCl ₃					
$\begin{array}{l} (CH_3)_2 Zn/TiCl_4 \\ (Zn/Ti < 0.5) \dagger \end{array}$	C ₂ Cl ₄	CH ₄ , C ₂ H ₆ , CH ₃ Cl all important. CH ₃ Cl abundance increases as Zn/Ti ratio decreases;‡ traces of 1,1,2-trichloropropene-1	CH ₄ , C ₂ H ₆ , 1,1,2-trichloropropene-1 all abundant, with relative amounts dependent on initial concentrations, and Zn/Ti ratio. CH ₃ Cl depends on Zn/Ti ratio as at 20 °C. 1,1,2-trichloropropene-1 favored by low initial concentrations of CH ₃ TiCl ₃				
$(CH_3)_2 Zn/TiCl_4$ $(Zn/Ti < 0.5)^{\dagger}$	C_6H_6	CH_4 and C_2H_6 are abundant. Traces of toluene are found	CH_4 , C_2H_6 , and toluene are all abundant				
(CH ₃) ₃ Al/TiCl ₄ (Al/Ti < 0.33)†	C2Cl4 or C6H6	Products closely parallel those in $(CH_3)_2Zn/TiCl_4$ systems of $Zn/Ti < 0.5$	1,1,2-trichloropropene-1 very abundant. CH_4 , C_2H_6 , and CH_3Cl all abundant, with CH_3Cl showing usual inverse dependence on ratio				
(CH ₃) ₂ TiCl ₂ /CH ₃ TiCl ₃	C_2Cl_4	CH ₄					
$\begin{array}{l} (CH_3)_2 Zn/TiCl_4 \\ (Zn/Ti > 0.5) \end{array}$	C_2Cl_4	CH_4 , $(CH_3)_2Zn$ §	CH ₄ , (CH ₃) ₂ Zn§ and considerable 1,1,2-trichloropropene-1				
$\begin{array}{l} (CH_3)_2 Zn/TiCl_4 \\ (Zn/Ti > 0.5) \end{array}$	C_6H_6	CH_4 , $(CH_3)_2Zn$ §	CH_4 , $(CH_3)_2 Zn$ and traces of toluene, particularly at ratios near 0.5				
$(CH_3)_3Al/TiCl_4$ (0.33 < Al/Ti < 1.0)	C_2Cl_4	CH_4 , considerable 1,1,2-trichloropropene-1, and traces of C_2H_6					
(CH ₃) ₂ TiCl ₂	C_2Cl_4	CH ₄					
$\begin{array}{l} (CH_3)_3 Al/TiCl_4 \\ (Al/Ti > 1.0) \end{array}$	C_2Cl_4	CH_4 and traces of 1,1,2-trichloropropene-1 and C_2H_6					

*No sign of products of further exchange, such as 1,1-dichloro-2-methylpropene-1 or 2,2-dichlorobutene-2 were observed in any of this work.

†At these ratios, CH₃TiCl₃ is observed and (CH₃)₂TiCl₂ is not. ‡For three samples all of identical initial CH₃TiCl₃ concentration but of Zn/Ti ratios of 0.15, 0.30, and 0.45, the CH₃Cl produced corresponded to 32, 15, and 5%, respectively, of the total soluble products observable by proton n.m.r.

§See Figs. 7 and 8.

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At these ratios, both CH₃TiCl₃ and (CH₃)₂TiCl₂ are present, at least during part of the decomposition.

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FIG. 2. Thermal decomposition at ambient temperature of initially 0.22 *M* CH₃TiCl₃ in C₆H₆. Symbols are: \bigcirc , CH₃TiCl₃; \triangle , CH₄; \blacktriangle , C₂H₆.



FIG. 4. Thermal decomposition at ambient temperature of initially 0.11 M CH₃TiCl₃ and 0.051 M (CH₃)₂TiCl₂ in C₂Cl₄. Symbols are: \bigcirc , CH₃TiCl₃; \bigcirc , (CH₃)₂TiCl₂; \triangle , CH₄.







FIG. 5. Thermal decomposition at 80 °C of materials formed from 0.17 *M* (CH₃)₂Zn and 0.56 *M* TiCl₄ in C₂Cl₄. Symbols are: \bigcirc , CH₃TiCl₃; \triangle , CH₄; \blacktriangle , C₂H₆; \bigtriangledown , CH₃Cl; \blacktriangledown , CH₃ClC=CCl₂.

Comp	opento as a	ided		Solid composition by Cl		y analysis		Liquid phase by difference		
Cl	Zn Zn	Ti	G.A.	A.B.	Ave	Zn	Ti	Cl	Zn	Ti
1.82	0.72	0.46	1.69	1.77	1.72	0.33	0.42	0.10	0.39	0.04
1.82	0.72	0.46	1.83	1.84	1.84	0.37	0.48	-0.02	0.35	-0.02
1.82	2.16	0.46	1.55	1.47	1.52	0.15	0.31	0.30	2.01	0.15
1.82	2.16	0.46	1.55	1.48	1.52	0.17	0.53	0.30	1.99	-0.07
1.82	0.72	0.46	1.62	1.66	1.64	0.28	0.37	0.18	0.44	0.09
3.64	0.72	0.91	3.56	3.60	3.58	0.57	0.92	0.06	0.15	-0.01

TABLE 2. Elemental analyses of solid decomposition products*

*All elements are given in equivalents $\times 10^2$. Total volume of solvent was 60 ml. No carbon and hydrogen measurements were made. Original components were measured by analysis. The number of equivalents of each element remaining in solution is determined by the difference of the component and product solid measurements.

would be expected from the stoichiometry. This is attributed to CH_3TiCl_3 complexing with solid $ZnCl_2$.

The role of the precipitated $ZnCl_2$ in realkylation of zinc (Figs. 7, 8) was explored by preparation of two identical n.m.r. samples, each containing 2.14×10^{-4} mol of $(CH_3)_2Zn$ and 1.45×10^{-4} mol of TiCl₄ in 1.85 ml of C₂Cl₄. One was mixed constantly so as to maintain a distribution of finely divided ZnCl₂ throughout the solution. The other was centrifuged constantly, to compact the $ZnCl_2$ and reduce its available surface area. In the latter, titanium chlorides formed by decomposition were deposited on the $ZnCl_2$ as they formed, further reducing the available area of ZnCl₂. In the mixed tube, 4.5×10^{-5} mol of $(CH_3)_2$ Zn and 7.2×10^{-5} mol of CH₄ were formed. In the centrifuged tube, 2.8×10^{-5} mol of (CH₃)₂Zn and $1.12 \times$ 10^{-4} mol of CH₄ were produced. In both cases, the quoted amount of $(CH_3)_2$ Zn is that formed in addition to the residual $(CH_3)_2$ Zn observed immediately after the formation of $(CH_3)_2$ TiCl₂.

Rates of Decomposition

The shape of the n.m.r. tubes precluded good mixing. Coagulation and disintegration of solid products periodically occurred. Consequently, kinetic data obtained from these experiments are too unreliable to permit unequivocal assignment of particular rate laws. Nevertheless, as Fig. 9 illustrates, accuracy and reproducibility are sufficient to yield considerable information.

 CH_3TiCl_3 in solution, even in $(CH_3)_2Zn/TiCl_4$ systems, decomposes unexpectedly slowly. Much more rapid is the decomposition of $(CH_3)_2TiCl_2$ and of CH_3TiCl_3 in the presence of $(CH_3)_2TiCl_2$. See Figs. 1–8. An induction time exists for the decomposition of CH₃TiCl₃ at 20 °C, the formation of CH₄ and of C₂H₆ being associated with autocatalysis (Figs. 1, 2, 4).

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Rates of formation of CH₃Cl, of 1,1,2-trichloropropene-1, and of toluene increase more rapidly with temperature than do those of CH₄ and C₂H₆.

Insoluble Decomposition Products

Elemental analyses of the solid decomposition products were obtained by both chemical methods and neutron activation analysis. Results obtained from both techniques had failings. Chemical methods indicated hydrogen contents in hydrogen-free test samples almost as great as those in the study samples. Chlorine analyses proved very accurate by chemical methods, but were more erratic in neutron activation data.

Despite these errors, some characteristics of the solids emerged clearly. The solids produced in CH_3TiCl_3 systems and in $(CH_3)_2Zn/TiCl_4$ systems of Zn/Ti < 0.5, have a Cl/Ti ratio very close to three, with virtually no non-volatile hydrocarbon content.

Solids produced by the thermal decomposition of $(CH_3)_2 TiCl_2$ alone in solution have a Cl/Ti ratio close to 2, and a large hydrocarbon content, the nature of which is described subsequently. Solids produced by $(CH_3)_2 Zn/TiCl_4$ systems of Zn/Ti > 0.5 have a Cl/Ti ratio intermediate between 2 and 3, and a moderate hydrocarbon content. Table 2 shows the results of the most self consistent set of analyses carried out on $(CH_3)_2 Zn/TiCl_4$ systems.

A preliminary study of the nature of the hydrocarbon content of the solid was made by mass 760

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FIG. 6. Thermal decomposition at 80 °C of materials formed from 0.17 *M* (CH₃)₃Al and 0.56 *M* TiCl₄ in C₂Cl₄. Symbols are: \bigcirc , CH₃TiCl₃; \triangle , CH₄; \blacktriangle , C₂H₆; \bigtriangledown , CH₃Cl; \blacktriangledown , CH₃ClC=CCl₂.

FIG. 7. Thermal decomposition at ambient temperature of materials formed from 0.11 M (CH₃)₂Zn and 0.15 M TiCl₄ in C₂Cl₄. Symbols are: \bigcirc , CH₃TiCl₃; \bigcirc , (CH₃)₂TiCl₂; \triangle , CH₄; \bigtriangledown , CH₃Cl.

spectrometric analysis of the gases produced on adding D_2O or H_2O to the solids. Solids obtained from the thermal decomposition of *n*-hexane or C_2Cl_4 solutions of $(CH_3)_2TiCl_2$, and from *n*-hexane solutions of $(CH_3)_2Zn/TiCl_4$ systems were studied.

In deuterated systems, the relative abundance of the products observed decreased as CH_3D , CH_4 , $C_2H_4D_2$, and C_2H_5D . Small amounts of higher alkyls observed in some samples appeared to arise from residual *n*-hexane. Slight amounts of more highly deuterated ethanes were observed. In the case of products from $(CH_3)_2TiCl_2$ solutions, the amounts of methane were from two to six times the amounts of ethanes. In the case of products of $(CH_3)_2Zn/TiCl_4$ systems of Zn/Ti ratios greater than one, the methanes to ethanes ratio was ten or more.

Discussion

The complexity of these reactions can lead to false conclusions if data from different systems are compared without knowledge of, or consideration of, the effects of different solvents, different temperatures, or different means of preparation. The experiments in this paper were carried out to provide a background of such knowledge against which more detailed and specific experiments could be judged. As such, they permit, when considered with the data of others (3, 4), postulation of a set of reactions which, while not entirely proven, provides a consistent explanation of both kinetic and polymerization observations.

(i) $(CH_3)_2 TiCl_2$

It is our hypothesis that some unknown, otherwise unimportant mechanism produces traces of $TiCl_2$ in $(CH_3)_2 TiCl_2$ systems. Reaction 1 then occurs on the crystal surface.⁶

[1]
$$(CH_3)_2 TiCl_2 + TiCl_2(s) \rightarrow 2CH_3 - TiCl_2(s)$$

The solid so formed would have a valency intermediate between 2 and 3, depending on the extent to which reaction 1 occurs. Such an intermediate and variable valency explains the

⁶The notation R—TiCl_n(s) implies a surface R group on a titanium chloride lattice. It does not imply stoichiometric replacement of 1/(n + 1) of the chlorines by alkyls.

1.0

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range of valencies reported for related systems (7, 8, 9, 10). A speculation that further alkylation of the surface may occur by the exchange reaction 2 is reasonable but unsupported.

[2] $(CH_3)_2 TiCl_2 + Cl - TiCl_x(s) \rightarrow CH_3 - TiCl_x(s)$

+ CH₃TiCl₃

Since CH_4 is formed without hydrogen contribution by the solvent, a minimum of two methyl groups in near proximity on the surface are therefore required. Reactions 1 and 2 continuously regenerate the required methyl population on the surface.

The preliminary mass spectrometric data do not unequivocally determine the nature of that portion of the carbon and hydrogen which is incorporated in the solid. The large amount of CH₃D produced on adding D₂O implies the existence of methyl groups attached to the metal atoms in the solid in keeping with the equation postulated. As did Rodriguez et al. (15, 16), we found small amounts of more highly deuterated methanes. Unlike Rodriguez et al., we are reluctant to interpret these as other than the products of deuterium-hydrogen exchange either on the solid or on the inlet of the mass spectrometer. The former possibility would in itself be of interest. Isotopic exchange is well known for heavier transition metals (11, 12) and can occur quite rapidly for temperatures at least as low as 80 °C (13).

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Small amounts of low molecular weight alkanes were observed in solution and rather larger amounts were produced by deuterolysis of the solid. The latter was principally $C_2H_4D_2$,



(CH₃) ₂ TiCl₂

FIG. 8. Thermal decomposition at ambient temperature of materials formed from 0.11 M (CH₃)₂Zn and 0.077 MTiCl₄ in C₂Cl₄. Symbols are: \bullet , (CH₃)TiCl₂; \triangle , CH₄; \bigtriangledown , CH₃Cl.

with significant amounts of C_2H_5D (14). Although no careful measurements of quantities were made, such material is not sufficient to complete the mass balance.

The configuration of the important solid state precursor of $C_2H_4D_2$ is uncertain. It is geometrically possible for a dimethylene group to "bridge" two adjacent titanium atoms along the



FIG. 9. Reproducibility test showing (a) amounts measured in two identical runs, one designated by open symbols and one by black symbols and (b) comparison of amounts of carbon and hydrogen in the products, assuming that one methylene exists as polymer or in the solid for each methane, with the amounts in the initial material.

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[4]

c-axis of a β -TiCl₃ structure. The C—C axis would be skewed relative to the *c*-axis if the carbons occupied Cl vacancies and considerable strain would be expected. However, such a species would explain the origin of both the C₂H₄D₂ and the small amounts of low molecular weight alkanes, since it could be released as ethylene and subsequently incorporated in polymer at some Ziegler site.

 $(CH_3)_2Zn$ is regenerated where $(CH_3)_2TiCl_2$ is formed *in situ* in $(CH_3)_2Zn/TiCl_4$ systems. While this phenomenon is not essential to thermal decomposition, it is associated with it and must be explained concurrently. We believe that soluble CH_3ZnCl reacts with surface methyls according to reaction 3

[3] $CH_3ZnCl + CH_3 - TiCl_x(s) \rightarrow (CH_3)_2Zn$

 $+ Cl - TiCl_{x}(s)$

and that both CH_3ZnCl and $(CH_3)_2Zn$ are absorbed, to some extent, on the solid titanium chloride. $(CH_3)_2Zn$ formed by reaction 3 can then react with precipitated $ZnCl_2$ to generate more CH_3ZnCl . This is consistent with our experimental evidence that increasing the area of $ZnCl_2$ both retards CH_4 formation (by reducing the surface concentration of methyl groups through reaction 3) and accelerates $(CH_3)_2Zn$ formation (through permitting more rapid regeneration of CH_3ZnCl). This is consistent with n.m.r. mass balance data and with the high CH_3D content in the deuterolysis of $(CH_3)_2Zn/TiCl_4$ systems.

By contrast, $(CH_3)_3Al_2Cl_3$ produced in $(CH_3)_6Al_2/TiCl_4$ and $(CH_3)_4Al_2Cl_2/TiCl_4$ systems continues to methylate the solid, although slowly, and CH_4 continues to form (Fig. 6). Aluminum based systems therefore have a high surface concentration of methyl groups whereas with zinc based systems it is very low. If, as in Cossee's model (17), an active Ziegler site requires an alkyl bonded to a transition metal atom, such observations suggest an alternative to the explanation offered by Rodriguez and van Looy (18) for the difference in catalytic activity between $(CH_3)_3Al/TiCl_4$ systems and $(CH_3)_2Zn/TiCl_4$ systems.

(ii) CH_3TiCl_3

It is apparent from the diversity of products that the decomposition of CH_3TiCl_3 is more complicated than that of $(CH_3)_2TiCl_2$.

In C_2Cl_4 , one obtains CH_4 , C_2H_6 , 1,1,2-trichloropropene-1, and CH_3Cl . In C_6H_6 , the last two products are missing. In alkanes, CH_4 , C_2H_6 , and CH_3Cl occur (3, 4).

It is suggested that CH_4 formation is, at least in part, the product of $(CH_3)_2TiCl_2$ which has been formed through the equilibrium [4].

Such a route is supported by the slight reduction in CH_4 production observed at low Zn/Tiratios (where $TiCl_4$ is present in excess) and by the observation (3) that CH_4 is reduced relative to C_2H_6 and CH_3Cl by addition of $TiCl_4$ to CH_3TiCl_3 in *n*-heptane. Formation of $TiCl_2$ by decomposition can be expected to constantly increase the formation of $(CH_3)_2TiCl_2$ through removal of $TiCl_4$ according to reaction 5

[5]
$$TiCl_2(s) + TiCl_4 \rightarrow 2TiCl_3(s)$$

and contributes to the observed autocatalysis.

In contrast to the high alkyl content in the solid produced in $(CH_3)_2TiCl_2$ systems through the operation of reactions 1 and 2, CH_3TiCl_3 systems show low alkyl contents. This is to be expected on the basis of the unimportance of reaction 1 (due to low $(CH_3)_2TiCl_2$ concentrations) relative to reactions 5 and 6.

6]
$$TiCl_2(s) + CH_3TiCl_3 \rightarrow CH_3TiCl_2 \cdot TiCl_3(s)$$

The highly methylated solid produced by reaction 1 leads to CH_4 formation, reduction of titanium and residual hydrocarbon in the solid. The solid produced by reactions 5 and 6 is trivalent with a small methyl content.

Ethane formation is also autocatalytic. Unlike de Vries (3), we did not observe that the decrease in CH_4 associated with excess $TiCl_4$ was paralleled by an increase in C_2H_6 . However, excess $TiCl_4$ was present only in our $(CH_3)_2Zn/TiCl_4$ and $(CH_3)_3Al/TiCl_4$ systems, so the data are not strictly comparable.

The autocatalysis suggests that adsorption of CH_3TiCl_3 is a necessary step in C_2H_6 formation. It is reasonable to suppose that adsorbed CH_3TiCl_3 has a configuration and energy quite different from the solution species. Chlorine and titanium atoms are likely to enter lattice positions appropriate to the underlying β -TiCl_3 lattice. Such epitaxially induced changes are consistent with the observed increase in Ziegler

catalytic activity (3, 4) when TiCl₃ is introduced into a CH₃TiCl₃ solution.

 CH_3Cl is believed to form according to reaction 7

[7]
$$CH_3TiCl_3 + TiCl_4 \rightarrow CH_3Cl + 2TiCl_3(s)$$

Whether this reaction is influenced by the solid is not certain from the reaction rates. CH_3Cl is abundant only where $TiCl_4$ is present in excess. The low yields of CH_3Cl in CH_3TiCl_3 systems are attributed to the low $TiCl_4$ concentrations resulting from reactions 4 and 5. Direct reaction of two CH_3TiCl_3 to give CH_3Cl cannot be excluded.

Although in the work reported, CH_3Cl is produced in C_2Cl_4 and not in C_6H_6 , reaction with the solvent is not believed to be important. Both de Vries (3) and Beermann and Bestian (4) have shown it to be produced in alkanes where no solvent chlorine atoms are available. The lack of CH_3Cl in C_6H_6 is attributed to solvation of CH_3TiCl_3 by benzene inhibiting the reaction. Benzene solvation is supported by n.m.r. data on the pre-exchange lifetime of methyl groups on titaniums in the two solvents.

As to the formation of 1,1,2-trichloropropene, it is known from separate studies that this product forms by simple ligand exchange for other alkyl metal/halogenated solvent systems, such as those shown in reactions 8 and 9.

- $[8] \quad (CH_3)_2Zn + 2C_2Cl_4 \rightarrow ZnCl_2 + 2CH_3C_2Cl_3$
- $[9] \quad 2(CH_3)_3AI + 2C_2CI_4 \rightarrow (CH_3)_4AI_2CI_2 + 2CH_3C_2CI_3$

Production of $CH_3C_2Cl_3$ in CH_3TiCl_3 systems is presumably by a similar route [10]. Toluene production in benzene systems may be analogous.

[10] $CH_3TiCl_3 + C_2Cl_4 \rightarrow TiCl_4 + CH_3C_2Cl_3$

It should be noted that $CH_3C_2Cl_3$ is produced much more abundantly in $(CH_3)_2Zn/TiCl_4$ systems than in CH_3TiCl_3 systems, presumably through the action of residual CH_3ZnCl or $(CH_3)_2Zn$ in the solid according to reaction 8.

(iii) Solutions Containing both $(CH_3)_2TiCl_2$ and CH_3TiCl_3

The case of the decomposition of mixtures of CH_3TiCl_3 and $(CH_3)_2TiCl_2$ in solution is of special interest because of the abrupt change in decomposition rate and product distribution that occurs. Addition of a trace of $(CH_3)_2TiCl_2$

to a solution of CH_3TiCl_3 , or elevation of the Zn/Ti ratio to 0.55 from 0.45 in a $(CH_3)_2Zn/-TiCl_4/C_2Cl_4$ system, results in relatively rapid decomposition of the methyl titanium trichloride and virtual disappearance of ethane and 1,1,2-trichloropropene-1 from among the products.

Figure 4 illustrates the extraordinary autocatalysis exhibited by CH_3TiCl_3 systems. It is invariably found that, notwithstanding the much greater thermal "stability" of CH_3TiCl_3 , it is the first to disappear when mixed in solution with $(CH_3)_2TiCl_2$.

The rapid decomposition of CH_3TiCl_3 in these mixtures could be explained for $(CH_3)_2Zn/TiCl_4$ systems by reactions 4 and 11.

$$[11] \qquad (CH_3)_2 Zn + ZnCl_2 \rightleftharpoons 2CH_3 ZnCl$$

11a]
$$(CH_3)_2Zn + ZnCl_2 \rightleftharpoons (CH_3)_2Zn : ZnCl_2$$

 $(CH_3)_2Zn$ thus formed would in turn alkylate the CH_3TiCl_3 to yield more $(CH_3)_2TiCl_2$. Such a system is illustrated in Fig. 7. However, Fig. 4 illustrates the decomposition of a $CH_3TiCl_3/(CH_3)_2TiCl_2$ system containing no zinc chloride, and consequently the rapid decomposition of the CH_3TiCl_3 in this case cannot be explained by introducing an alkyl zinc intermediate.

Moreover, the data shown in Figs. 1–3 indicate that the equilibrium constant for reaction 4 is very small. Consequently, the rapid decline in CH₃TiCl₃ concentration cannot be explained on the basis of the equilibrium [4] operating to replace decomposed $(CH_3)_2$ TiCl₂, since the latter is at all times in much greater concentration than in the cases shown in Figs. 1–3. It is therefore concluded that CH₃TiCl₃ reacts directly with adsorbed $(CH_3)_2$ TiCl₂ to form CH₄ or with a product of $(CH_3)_2$ TiCl₂ decomposition, perhaps simply as in reaction 6.

Summary

CH₃TiCl₃ decomposes by several routes, including a free radical route in polar solvents (4, 20) not observed in our systems. In addition, alkyl analogues having a hydrogen on a carbon β to the metal may decompose by the path proposed by de Vries (3). Other alkyl titanium systems offer additional possibilities, such as intramolecular formation of CH₄ by abstrac-

tion of hydrogen from the amino group in $[(C_2H_5)_2N]_3TiCH_3$ (21).

For σ -bonded alkyl transition metal compounds, comparisons of "relative stabilities" are actually comparisons of "relative rates of decomposition" (19). Where there are many paths of decomposition, each affected differently by various parameters, predictions of "relative stabilities" based on data from different conditions are of dubious value. Moreover, any general explanation of thermal instability of σ -bonded organotransition metal compounds is likely to be more complex than those so far put forward (3, 22) if it is to account for all paths of decomposition.

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