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The Thermal Decomposition of CH_3TiCl_3 in Ethyl Ether

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Modes of decomposition of σ-bonded alkyl and aryl transition metal compounds have been a subject of intense study in recent years [1–3]. Many of the earlier studies in the area of organotitanium compounds were initiated because of the importance of such species as olefin polymerization catalysts [4, 5]. However, as shown by one of us recently [6, 7], even as simple a compound as methyltitanium trichloride, CH_3TiCl_3 (**1**), decomposes in a number of ways.

A major factor in determining the relative importance of the various possible pathways is the solvent. In the specific case of **1**, Beerman and Bestian [4] discovered that the rate of decomposition in ethyl ether is much more rapid than in alkanes or carbon tetrachloride, the major product in all cases being methane. Radical processes were inferred, giving rise to subsequent studies involving deuterated solvents [5, 7, 8] which seemed to suggest that free radical pathways are probably generally of minor importance.

The decomposition reaction of **1** in ethyl ether seemed worthy of further study for two reasons. The unusually high rates suggested that the solvent may be participating in an unusual manner, and there are few precedences in the literature for reactions of organometallic compounds with ethers [9–11]. Secondly, a byproduct of the reaction is a green, crystalline material which has been identified as both a tris- [4] and a bis-ether [12] complex of titanium trichloride. The green crystals were known to us as being very unstable [13] and this fact, coupled with the above-mentioned disagreement in the literature, suggested that the green compound may have been identified incorrectly. A recurring theme in the literature on decomposition reactions of alkylmetal compounds is the possible presence of carbene, carbyne or carbide byproducts [1–3] and we wondered if, in fact, the green crystals might be something more exotic than a simple ether complex.

Experimental

CH_3TiCl_3 was prepared using $(CH_3)_2Zn$ and $TiCl_4$. Except for the use of bench-top vacuum equipment in place of glove box mounted equipment, and the use of pentane rather than $CFCl_3$, the preparation was as described earlier [7].

$(CH_3)_2Zn$ was prepared from CH_3I (Aldrich Chemicals) and Zn/Cu powder (91% zinc; Alfa Division, Ventron Corporation) using a method suggested by Dr. B. K. Hunter. In a typical preparation, 43.5 g of the metal powder and 3.65 cm^3 of CH_3I were sealed under vacuum in a heavy wall Carius tube. This was held at 373K for 20 hours, cooled to 77K, and finally opened to vacuum while still at 77K by cracking the neck open within a tight-fitting heavy wall rubber tube attached to vacuum. Great care must be exercised at all stages due to the high pressures within the tube. The $(CH_3)_2Zn$ was condensed into the vacuum system and purified by trap-to-trap distillation.

Both the pentane (Caledon Laboratories) used in the preparation of **1** and the ether used in the decomposition studies (deuteroether from Merck, Sharpe and Dohme; standard ether from Baker) were dried over sodium and then distilled under vacuum. $TiCl_4$ (Alfa Division, Ventron Corporation) was also distilled under vacuum before use.

All mass spectral measurements were obtained using an AEI MS-10 mass spectrometer. Mass changes during decomposition of crystalline products were measured using a Cahn RG-10 electrobalance. Chemical analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, N.Y., U.S.A.

Results and Discussion

Solutions of **1** in ethyl ether rapidly turn deep red-brown and evolve methane in a highly exothermic reaction. If the temperature of the reaction is maintained at or below 0 °C, the only other gaseous products are trace amounts of ethane and acetaldehyde, although allowing the reaction mixture to become warm results in the formation of small amounts of ethylene and both methyl and ethyl chloride, and the precipitation of a purple–brown material. On standing for an hour or more, large green crystals also form, but addition of triphenylphosphine to a fresh reaction mixture yields no recognizable compounds. No polymeric hydrocarbons were ever detected.

Preliminary kinetics studies, based on the rate of evolution of methane, showed that the reaction was essentially second order in **1** for 30–50% of its course, although it slowed down in the later stages. The

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volume of gas evolved when the reaction seems essentially complete was consistent with the following stoichiometry:

$$\underset{\mathbf{1}}{2CH_3TiCl_3} \longrightarrow CH_4 + \text{“}[CH_2(TiCl_3)_2]\text{”} \qquad (1)$$

Decomposition of **1** in ethyl ether-d_{10} at 0 °C yielded methane which contained about 5% each of CH_2D_2 and CH_3D, while reactions at higher temperatures yielded methane which contained up to 30–40% CH_3D. The course of the reaction at 0 °C was followed using ^1H n.m.r. spectroscopy. The methyl resonance of **1** at δ2.45 disappeared over a period of two to three hours, giving way to a CH_4 singlet at δ0.23 ppm. At the end of the reaction, the solution was somewhat paramagnetic, leading to some broadening of all resonances, but weak, rather broad resonances at δ3.00 and δ2.59 could also be observed.

The brown precipitate, mentioned above as a product of uncooled ether decomposition reactions, is probably $TiCl_3$, as is observed in decomposition reactions of **1** in hydrocarbon solvents [6]. Only small amounts of methane were evolved on treatment with sulfuric acid, and the material was not investigated further. Air oxidation of the supernatant liquid, followed by hydrolysis, yielded small amounts of ethanol.

The green crystalline compound was found to retain its colour and crystallinity only in the presence of ether. Although slightly soluble in ether, giving a pale green solution, solutions in benzene, for instance, were brown. Hydrolysis of solutions of the green compound in benzene, chloroform, trichloroethylene and dichloromethane yielded only ether in the organic phase, the aqueous phase assuming the violet–red colouration of the $[Ti(H_2O)_6]^{3+}$ ion [14]. Treatment of an ether solution with bromine yielded no new organic products.

Although the great lability of the green crystals made analyses difficult, a Cahn electrobalance was used to follow the evaporative process at ambient temperatures under a low pressure. Following a rapid initial loss of surface ether, about 55% of the weight was lost over sixty hours; the formulation, by Beerman and Bestian [4], of the compound as $TiCl_3(Et_2O)_3$ would result in a loss of 59.9% if all the ether were to be liberated. On the other hand, crystals which had been dried *in vacuo* at room temperature for a few hours (and which were visibly darkened) yielded a chemical analysis of 31.06% C, 6.48% H and 34.30% Cl. These data compare well with the calculated values of 31.76% C, 6.62% H and 35.19% Cl for $TiCl_3(Et_2O)_2$, verifying the conclusions of Thiele and Zdunneck [12].

Thus the dried, dark green, crystalline compound is almost certainly to be formulated as $TiCl_3(Et_2O)_2$, either as a trigonal bipyramidal monomer or as an octahedral dimer with chloride bridges. The far infrared spectrum exhibits bands at 360 cm^{-1} (s) and ~280 cm^{-1} (sh), attributable to titanium–chlorine modes [15]. Those bands at higher frequencies, attributed by Thiele and Zdunneck to ν_{Ti-Cl}, are probably better attributed to ether modes [16].

Most of the information presented above, the small amounts of ethane, ethylene, acetaldehyde, methyl chloride and ethyl chloride formed, the small amounts of deuterated methanes formed in ethyl ether-d_{10} (and other deuterated solvents [5, 7, 8]) and the rather inconclusive kinetics studies, which may imply a change in mechanism as the reaction proceeds, suggest that the decomposition of **1** in ethyl ether can proceed by several paths, as it does in other solvents [6]. The second order kinetics and the fact that the major product here and in other solvents, both perhydro and perdeutero, is CH_4 is consistent with previous suggestions [7] that the major process basically involves a combination of a hydrogen from the methyl group of one molecule of 1 with the methyl group of a second molecule of **1** (in this sense, the reaction in ethyl ether seems similar to that in hydrocarbon solvents).

Further data seem to indicate that the ratio of **1** consumed to CH_4 produced is about 2:1, that the reaction solution exhibits a low degree of paramagnetism throughout most of the reaction, and that solvated $TiCl_3$ is formed *slowly* after most or all of the methane has evolved. The latter conclusion is based on observations that the green crystals of $TiCl_3(Et_2O)_{2,3}$ appear after substantial decomposition has taken place and are often quite large ($\geqslant$8 mm^3), suggesting slow growth and, presumably, slow formation of $TiCl_3$ in solution.

In the case of decomposition of **1** in hydrocarbon solvents, precipitated $TiCl_3$ acts as a catalyst [4]. Although the mechanism of the catalytic process is not understood, it apparently involves adsorption of **1** onto a crystalline surface of $TiCl_3$, with perhaps methyl–chloride exchange between **1** (in solution) and solid $TiCl_3$ [6]. The rate of such a process would be subject to the usual limitations of heterogeneous catalytic reactions [17], and it is interesting to speculate on the possibility that the high rates of decomposition of **1** in ethyl ether are a result of the solubilization of catalytic amounts of $TiCl_3$, leading to homogeneous catalysis and the concomitant possible utilization of all catalyst sites.

Although our results suggest that $TiCl_3$ is probably only a minor product initially in an ethyl ether reaction mixture, it may well account for the paramagnetism observed, and could be generated in the initial stages of the decomposition as in (2)

$$\underset{\mathbf{1}}{2CH_3TiCl_3} \longrightarrow C_2H_6 + 2TiCl_3 \qquad (2)$$

The $TiCl_3$ so formed could then reaction with **1** to yield two products, as in (3) and (4)

$$\underset{\mathbf{1}}{CH_3TiCl_3} + TiCl_3 \longrightarrow \underset{\mathbf{2}}{CH_3TiCl_2} + TiCl_4 \qquad (3)$$

$$\underset{\mathbf{1}}{CH_3TiCl_3} + CH_3TiCl_2 \longrightarrow \underset{\mathbf{3}}{(CH_3)_2TiCl_2} + TiCl_3 \qquad (4)$$

Reaction (3) is analogous to the exchange reaction of **1** with solid $TiCl_3$ postulated above for decompositions in hydrocarbon solvents. The product, **2**, has been mentioned only briefly in the literature [18]; although poorly characterized, it decomposes rapidly at –40 °C, liberating methane. If $TiCl_2$ is also formed, it could react with the $TiCl_4$ produced in (3) to generate $TiCl_3$, thus making a catalytic cycle possible.

Compounds **1** and **2** could also react as in (4), to yield **3**, which is also very unstable with respect to loss of methane at the temperatures used here [6]. Again $TiCl_3$ would be formed, possibly maintaining a catalytic cycle.

Although, because of the complexity of the system, we do not have firm evidence for (2) or (3), and we certainly are not in a position to discuss the nature of the methane-forming step(s), it is clear that reactions (2), (3) and (4) do accommodate most our data, including the unusually high rates in ethyl ether, the diamagnetism of the reaction solutions and the dominance of methane in the gaseous products.

Other, as yet unidentified, organotitanium species must also be present, however, perhaps that suggested in (1). As mentioned above, only half the carbons of **1** appear as methane; the remainder are not liberated even on hydrolysis of the reaction solution [19]. The broad resonances observed at δ = 3.00 ppm and δ = 2.54 ppm in the ^1H n.m.r. spectrum of the reaction solution may well be indicative of carbene or carbyne species, at least one of which must decompose slowly to liberate the $TiCl_3$ which is eventually observed as $TiCl_3(Et_2O)_2$.

The apparently unique position of ethyl ether as a medium for the decomposition of **1** – decomposition is slower in both solvents which lack ligand properties (alkanes) and in the presence of good ligands [2] – is probably a result of its poor donor properties. Good ligands form reasonably stable complexes with both **1** and with $TiCl_3$ [1–3], presumably preventing the as-yet unidentified aggregative processes which must occur if methane formation is to be rationalized on the basis of a concerted reaction [7]. Ether complexes could well be too labile to prevent aggregation, but stable enough that catalytic amounts of $TiCl_3$ would remain in solution.

The formation of deuterated methanes during reactions in ethyl ether-d_{10} is a relatively minor process, supporting the conclusion that the ether does not interact with **1** in any special or unusual way. The deuterated methanes may indicate homolysis [7], or may indicate some type of combination of the methyl group of **1** with a hydrogen atom of a coordinated solvent molecule. The compounds $CH_3Ti(NR_2)_3$ (R = CH_3, C_2H_5), for instance, decompose to methane via a process in which the methyl group combines with a hydrogen from R [21].

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