Ethyl Titanium Trichloride

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A reliable synthesis using Schlenk techniques is described for the thermally unstable compound, ethyl titanium trichloride. The compound is shown to have properties very similar to those of the much better known methyl titanium trichloride except in their modes of thermal decomposition.

Introduction

Compounds of the type $RTiCl_3$, where R is an alkyl group, have been of interest for many years, not least as suspected intermediates in the formation of several Ziegler-Natta catalysts based on alkyl aluminum and titanium tetrachloride. Their study has been hampered, however, by their extreme reactivity with both oxygen and water, and by their thermal instability at ambient temperatures. This latter problem is most severe for those alkyls having a hydrogen on the carbon β to the metal, a basic distinction first identified and demonstrated by de Vries [1]. Thus although the most important catalytic systems are those based on higher alkyls, especially ethyl and isobutyl, most published work pertains to CH_3TiCl_3. Aside from some publications involving bimetallic systems, the major published work on $C_2H_5TiCl_3$ is a short but very valuable paper by Bawn and Gladstone [2].

The present work reports further studies of C_2H_5-$TiCl_3$, particularly its thermal decomposition, and compares the findings with those in ongoing studies of the decomposition of methyl titanium(IV) compounds.

Experimental

Preparation and Characterization

A variety of preparative techniques were attempted using several solvents and several reagent combinations. Preparations using $(C_2H_5)_2Zn$ and $TiCl_4$ led to low yields and rapid decomposition of the product. Preparations using $(C_2H_5)_3Al$ or $(C_2H_5)_2AlCl$ with $TiCl_4$ led to material which was contaminated with aluminum despite repeated trials and variations aimed at purifying the product. The only totally reliable syntheses were those based on the preparation of Bawn and Gladstone [2], using $(C_2H_5)_4Pb$ and $TiCl_4$.

Both $(C_2H_5)_4Pb$ (Ventron Corporation) and $TiCl_4$ (Fisher Scientific and Ventron Corporation) were distilled under vacuum. All solvents were dried and then vacuum distilled, the benzene (Caledon Laboratories) over sodium and the CCl_3F (Matheson of Canada), C_2Cl_4 and CCl_4 (Fisher Scientific spectrograde) over Linde 3A molecular sieves. Deuterated solvents (Merck, Sharpe and Dohme Canada) were handled in an analogous manner. Storage and handling of all materials and preparation of all solutions was in a glove box filled with dry nitrogen.

The simplest preparation utilized standard Schlenk techniques. A solution of 0.90 ml of $(C_2H_5)_4Pb$ (4.6 mmol) in 30 ml of $CFCl_3$ was added slowly (30 drops per minute) and with stirring to a solution of 1.20 ml of $TiCl_4$ (11.0 mmol) in 30 ml of $CFCl_3$ at −80 °C. The solution becomes yellow and a precipitate forms. Prompt separation is required at this point to minimize decomposition. The mixture is allowed to warm slowly while pumping the volatiles through a trap at about −25 °C. The $CFCl_3$ passes through the trap but most of the $C_2H_5TiCl_3$ is collected there in the form of blue-purple needle-like crystals. Dry solvent can then be added to the trap and the solution transferred at as low a temperature as the solvent permits to the appropriate reaction vessels. This method appears to yield very pure material (no other hydrogen bearing species whatsoever being observed by NMR) but additional trap-to-trap sublimations can easily be inserted, if desired, prior to the solvent addition. $C_2H_5TiBr_3$ was prepared by the same method.

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TABLE I. NMR Data.[a]

Compound	Solvent	δ_{CH_2}/ppm	δ_{CH_3}/ppm	J_{H-H}/Hz
$C_2H_5TiCl_3$	CCl_4	3.05	1.83	7.5
$C_2H_5TiCl_3$	C_2Cl_4	3.33	2.08	7.5
$C_2H_5TiBr_3$	CCl_4	2.87	1.98	7.5
$C_2H_5OTiCl_3$	CCl_4	4.73	1.50	

[a]All concentrations are 0.25 mol l^{-1}.

$C_2H_5OTiCl_3$ was prepared by the addition, with stirring, of 1.5 ml of C_2H_5OH (26 mmol) in 5 ml of $CHCl_3$ to 3.0 ml of $TiCl_4$ (27 mmol) in 20 ml of $CHCl_3$ at 0 °C. The resulting yellow solution was warmed to room temperature and the solvent removed by pumping. The pale yellow powder remaining was washed several times with C_2Cl_4, filtered and dried.

$C_2H_5TiCl_3$ melts at 283 K ± 5 K yielding a wine-red liquid. The melt can be refrozen but decomposition is rapid, especially in the neat liquid. The compound has a significant vapour pressure at ambient temperature and can be readily sublimed from crystals or distilled from solution. The vapour is red.

It is readily soluble in alkanes, aromatics, CH_2Cl_2, CCl_4, $CFCl_3$ and C_2Cl_4. It decomposes immediately in diethyl ether but reacts with both dioxane and tetrahydrofuran to form royal blue solids which change slowly to lime green and release ethane.

Reaction with dry air produces $C_2H_5OTiCl_3$, which was identified by NMR and confirmed by the superposition of the spectrum of $C_2H_5OTiCl_3$ prepared separately as described above. Reaction with water produces C_2H_6, HCl and TiO_2. Reaction with iodine in benzene solution yields C_2H_5I and $ITiCl_3$.

Bubbling ethylene through a dilute solution of $C_2H_5TiCl_3$ in C_2Cl_4 at ambient temperature results in rapid formation of brown $TiCl_3$ as a decomposition product. Considerable polymerization of ethylene occurs.

Chemical shifts and coupling constants for NMR spectra are listed in Table I.

Thermal Decomposition

Thermal decomposition studies were carried out for solid material just below its melting point and for solutions in C_2Cl_4, CCl_4 and alkanes. NMR was used to monitor the concentration of the solution phase species and mass spectrometry to characterize the volatile products.

For decompositions of the solid, ethane is by far the most abundant volatile product but butane (5% relative to ethane) and hexane (2% relative

to ethane) were both produced in significant quantities. Ethene and butene were present in trace amounts.

In solution decompositions in all solvents, ethane is again the most abundant volatile product. Butane and hexane were relatively less abundant than in the solid state cases, and ethene and butene were not observed at all. NMR spectra of the solution phase showed the gradual formation, as decomposition progressed, of a broad peak in the polyethylene region.

Rates of decomposition were measured for solutions in C_2Cl_4 and in CCl_4. Tetrachloroethylene was chosen because it is inert (at room temperature, although not at 80 °C), because it has no interfering resonances in the ^1H NMR spectrum, and because it is a solvent employed in related catalytic studies. Moreover, these same factors led to its use in an earlier study of decomposition of CH_3TiCl_3 [3] and the use of C_2Cl_4 here permitted some direct comparisons between the ethyl and methyl cases.

Samples were prepared in flame-sealed NMR tubes. A carefully measured amount of a reference material, cyclohexane or benzene, was added to each tube as an internal standard by which concentrations could be measured using NMR integration. Since solids are produced, the samples were stirred in a slowly rotating drum to ensure homogeneity. Details of these procedures have been published elsewhere [3].

Concentrations were measured twice daily for a week and once daily thereafter using a Bruker HX-60 NMR spectrometer. Ten to twelve integrals of the complete spectrum were averaged to obtain each set of points. A Fortran program was written to process the data and to test the results against various rate laws. Calculations were based on the methyl triplet, with the methylene quartet used as an independent check.

With either C_2Cl_4 or CCl_4 as solvent, the data were consistent with a second order rate law

$$-\frac{d[C_2H_5TiCl_3]}{dt} = k_{obs}[C_2H_5TiCl_3]^2$$

TABLE II. Decomposition Data.

Solvent	Initial Concentration of $C_2H_5TiCl_3$ mol l^{-1}	Initial Concentration of $TiCl_4$ mol l^{-1}	k_{obs} l mol^{-1} s^{-1}
C_2Cl_4	0.139	0	1.8×10^{-5}
C_2Cl_4	0.094	0	1.6×10^{-5}
C_2Cl_4	0.081	0	1.7×10^{-5}
C_2Cl_4	0.080	0	1.4×10^{-5}
C_2Cl_4	0.078	0.50	0.83×10^{-5}
CCl_4	0.255	0	1.0×10^{-5}
CCl_4	0.142	0	1.1×10^{-5}
CCl_4	0.170	0.50	0.75×10^{-5}

The value of k_{obs} at 295 K was found to be 1.1×10^{-5} l mol^{-1} s^{-1} for solutions in CCl_4 and 1.6×10^{-5} l mol^{-1} s^{-1} for solutions in C_2Cl_4.

Additional measurements were made using solutions that were originally 0.50 M in $TiCl_4$. The decomposition remained second order in ethyltitanium trichloride concentration, but proceeded with a slightly slower rate. Data are listed in Table II.

A series of qualitative tests established the effect of various materials on the decomposition rate. Powdered $ZnCl_2$, $AlCl_3$, $CdCl_2$ and $NaCl$ had no effect. However $(C_2H_5)_4Pb$, $(C_2H_5)_2AlCl$, C_2H_5Li and $(C_2H_5)_2Zn$ all increased the decomposition rate by several orders of magnitude.
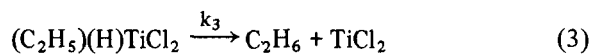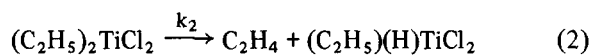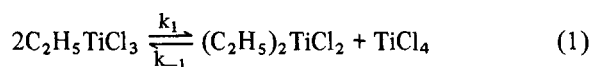
Discussion

It is clear that $C_2H_5TiCl_3$, in all properties reported above except those related to thermal decomposition, is very similar to its better known methyl analogue. These include appearance, melting point, solubility in several solvents, reaction with water to give the alkane, reaction with dry oxygen to give the alkoxy titanium trichloride and reaction with iodine to give RI and $ITiCl_3$. Both decompose rapidly in diethyl ether [4, 5]. Both form complexes with dioxane and tetrahydrofuran although those of the methyl compound are violet to pink and thermally stable at room temperature whereas those of the ethyl are royal blue and decompose.

In relatively inert solvents, the decomposition of the ethyl compound is rapid, follows a second order rate law, and results in volatile products which are 90 to 95% ethane. In contrast, the decomposition of the methyl compound is very slow, markedly autocatalytic and produces a number of volatile products, especially methane,

ethane and methyl chloride [3, 4]. Neither compound shows significant solvent attack on alkanes, benzene or C_2Cl_4 at room temperature or below.

The results show that most ethyl groups end up as ethane or polyethylene. There is insufficient information on which to do more then speculate as to how this comes about. β-Elimination of an ethylene (subsequently polymerized) to yield a metal hydride, followed by reductive elimination of ethane from an ethyl and that hydride, is a possibility consistent with earlier methyl work [3]. Although such ethane formation is clearly intermolecular in one sense, since the sixth hydrogen is drawn from a different ethyl group, this may be achieved by an intramolecular step. Differentiation of all of these possibilities is not easy and requires much information, a point made generally recently [7] for reductive eliminations.

Nevertheless, the speculative suggestion of a mechanism noted above is not without evidence. In outline, it would be as follows.

$$2C_2H_5TiCl_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C_2H_5)_2TiCl_2 + TiCl_4 \qquad (1)$$

$$(C_2H_5)_2TiCl_2 \overset{k_2}{\longrightarrow} C_2H_4 + (C_2H_5)(H)TiCl_2 \qquad (2)$$

$$(C_2H_5)(H)TiCl_2 \overset{k_3}{\longrightarrow} C_2H_6 + TiCl_2 \qquad (3)$$

Such a mechanism is consistent with the products observed, can easily fit the observed rate law, and is consistent with the slower rates observed in the presence of $TiCl_4$. There is further support in the enhanced decomposition rates observed where other metal alkyls are present, again a feature of methyl [3] as well as ethyl systems. It was noted earlier that rapid separation of alkyllead by-products was important in increasing yield. Such species would lead to further

alkylation of titanium and higher concentrations of the diethyl compound.

CH_3TiCl_3, as noted earlier, produces a range of products of which the alkane is only one. Moreover alkane formation is autocatalytic in the methyl case. While the initial step in decomposition may be the same for both ethyl and methyl, as suggested by earlier work [3], the slower α-elimination makes subsequent steps necessarily different. Rather than a hydride, it would produce a titanium carbene, formed in and stabilized by the solid. The existence of a carbene in the black solid produced in decomposition of the related $(C_5H_5)_2Ti(CH_3)_2$ has been inferred [8].

Acknowledgements

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