The Gas-Phase Chemistry of Chlorotitanium Ions with Oxygen-Containing Organic Compounds

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Abstract: The gas-phase reactions of the ions formed by electron impact on $TiCl_4$ with a series of ketones, aldehydes, ethers, esters, and water are reported. Ti^+ and $TiCl^+$ extract an oxygen atom from smaller carbonyl compounds and cyclic ethers forming TiO^+ and $TiClO^+$ but are not observed to react with carbonyl compounds with more than five carbons. $TiCl_2^+$ and $TiCl_3^+$ combine with smaller carbonyl compounds to eliminate HCl in a dissociative addition process. With carbonyl compounds containing four or more carbons, $TiCl_2^+$ and $TiCl_3^+$ undergo dissociative additions resulting in the elimination of various small olefins. The observed chemistry of species containing carbon-oxygen single bonds is dominated by cleavage of those bonds. Ionic products of processes involving such bond cleavages are typically of the type $TiCl_nOR^+$, but $(C_2H_5)_2O$ reacts with $TiCl_3^+$ to give predominantly $TiCl_3(H_2O)^+$. Mechanisms are proposed which rationalize relationships between reactant structure and observed product distributions. The observed chemistry is compared with the chemistry of a number of related systems. A number of limits on bond strengths are deduced from the reactions observed.

Introduction

Titanium compounds containing oxygen dominate the organometallic chemistry of this metal.[1,2] The first organic derivative of titanium was an alkoxytitanium compound prepared by Demarcay in 1875.[3] Such compounds have found use in paints and in the treatment of textiles and paper, and are important as polymerization catalysts.[1,2]

Reactions of $TiCl_4$ with most classes of oxygen-containing organic compounds have been reported in solution. Demarcay's alkoxide was prepared from $TiCl_4$ and ethanol, following the reaction[3]

$$TiCl_4 + 3ROH \rightarrow (RO)_2TiCl_2 \cdot ROH + 2HCl \quad (1)$$

Alkoxytitanium chlorides are also formed when $TiCl_4$ reacts with ethers.[4] Organic acids react with titanium tetrahalides to form carboxylates[5] as exemplified by the reaction[6]

$$TiCl_4 + 2CH_3COOH \rightarrow (CH_3COO)_2TiCl_2 + 2HCl \quad (2)$$
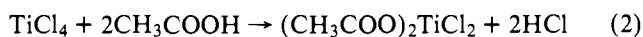
Stable $TiCl_4$-ester complexes can be formed, and thermally decompose by the reaction[7]

$$TiCl_4 \cdot RCOOR' \rightarrow (RCOO)TiCl_3 + R'Cl \quad (3)$$

$TiCl_4$ has also been used as a Lewis acid to catalyze a number of synthetic organic reactions. Recently, for example, it has been used to catalyze useful condensation reactions involving enol acetates, acetals, carbonyl compounds, and other oxygen-containing organic molecules.[8]

The simplest organic derivatives of lower valent titanium are addition compounds of the di- and trihalides. Ti(III) is mostly hexacoordinate, $TiX_3 \cdot 3L$.[1] $TiCl_2$ and $TiCl_3$ are polymeric[1] and have different reactivities than the tetrahalides. Recently, Ti(II) species formed by reaction of $TiCl_3$ and $LiAlH_4$ have been shown to be useful in organic synthesis. Such Ti(II) complexes efficiently induce reductive coupling of carbonyls[9] and deoxygenate epoxides.[10]

A number of other titanium-containing species have found use as synthetic reagents. Reactive titanocene species efficiently reduce aldehydes, esters, and epoxides to alkanes in solution.[11]

Here we present a study of the gas-phase ion-molecule reactions observed in mixtures of $TiCl_4$ with a series of ketones, and with small aldehydes, esters, alcohols, ethers, and water. Ionization is induced in these mixtures by electron impact. A number of ion-molecule processes are then observed which

may be elementary steps of reactions characteristic of condensed phase titanium organometallic chemistry. The general features of the chemistry of the ketones and aldehydes closely parallel the gaseous ionic chemistry observed in mixtures of $TiCl_4$ with olefins which we have recently described.[12]
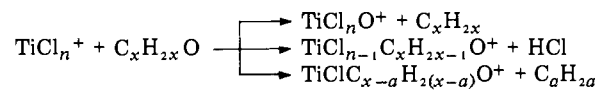
Experimental Section

All experiments were performed on an ion cyclotron resonance[13] instrument of conventional design described elsewhere.[14] Reaction pathways were identified by observing changes in reactant and product ion signal intensities as a function of pressure, and by the ion cyclotron double resonance technique.[13]

$TiCl_4$ was obtained from Alfa Products. Multiple freeze-pump-thaw cycles using an acetonitrile-CO_2 bath were used to minimize impurities. Commerical samples of organic compounds were used as supplied. Their purity was confirmed by mass spectral analysis. Acetone-d_6 was obtained from Merck Sharp and Dohme of Canada Ltd.
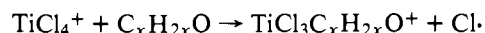
In a typical experiment, $TiCl_4$ was admitted to a pressure of approximately 10^{-6} Torr. Through a second inlet, the organic substrate was admitted and spectra taken until the $TiCl_4:C_aH_bO_c$ ratio was approximately 1:10. All experiments were performed at an ionizing energy of 70 eV. The 70-eV mass spectrum of $TiCl_4$ has been reported.[12]

Results

The general reaction scheme observed for the reactions of the electron impact fragment ions of $TiCl_4$ with aldehydes and ketones is

$$TiCl_n^+ + C_xH_{2x}O \quad \begin{cases} \rightarrow TiCl_nO^+ + C_xH_{2x} \\ \rightarrow TiCl_{n-1}C_xH_{2x-1}O^+ + HCl \\ \rightarrow TiClC_{x-a}H_{2(x-a)}O^+ + C_aH_{2a} \end{cases}$$

The parent ion of $TiCl_4$ generally reacts by

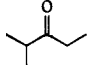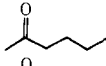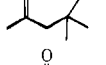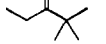$$TiCl_4^+ + C_xH_{2x}O \rightarrow TiCl_3C_xH_{2x}O^+ + Cl \cdot$$
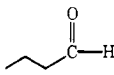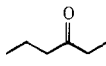
Ti^+ and $TiCl^+$ react with small aldehydes and ketones smaller than hexanone to form TiO^+ and $TiClO^+$. $TiCl_2^+$ and $TiCl_3^+$ complex with small aldehydes and acetone and lose HCl. With larger ketones, elimination of small alkenes becomes the predominant decomposition pathway.

The reactions of the $TiCl_4$ electron impact fragment ions with a series of aldehydes and ketones are summarized in Table I. All compounds in Table I were observed to displace a Cl⋅ atom from $TiCl_4^+$. No other reactions of $TiCl_4^+$ were observed.

A number of product ions undergo ligand substitution-type

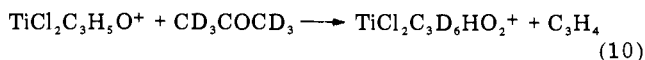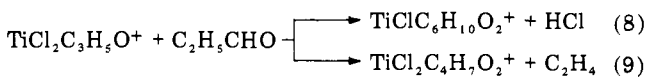**Table I.** Reactions of Aldehydes and Ketones with TiCl$_n{}^+$

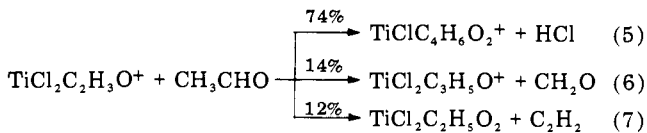| Reactant neutral	Reactant ion[b]			
	Ti$^+$	TiCl$^+$	TiCl$_2{}^+$	TiCl$_3{}^+$
CH$_3$CHO (acetaldehyde)	TiO$^+$ + C$_2$H$_4$	TiClO$^+$ + C$_2$H$_4$	TiClC$_2$H$_3$O$^+$ + HCl	TiCl$_2$C$_2$H$_3$O$^+$ + HCl
CH$_3$CH$_2$CHO (propionaldehyde)	TiO$^+$ + C$_3$H$_6$	TiClO$^+$ + C$_3$H$_6$	TiClC$_3$H$_5$O$^+$ + HCl	TiCl$_2$C$_3$H$_5$O$^+$ + HCl
CH$_3$CH$_2$CH$_2$CHO (butyraldehyde)	TiO$^+$ + C$_4$H$_8$	TiClO$^+$ + C$_4$H$_8$	TiCl$_2$CH$_2$O$^+$ + C$_3$H$_6$	TiCl$_3$CH$_2$O$^+$ + C$_3$H$_6$
(acetone)	TiO$^+$ + C$_3$H$_6$	TiClO$^+$ + C$_3$H$_6$	TiClC$_3$H$_5$O$^+$ + HCl	TiCl$_2$C$_3$H$_5$O$^+$ + HCl
(2-butanone)	TiO$^+$ + C$_4$H$_8$	TiClO$^+$ + C$_4$H$_8$	*a*	TiCl$_3$C$_4$H$_6{}^+$ + H$_2$O (0.38) TiCl$_3$H$_2$O$^+$ + C$_4$H$_6$ (0.38) TiCl$_2$C$_3$H$_5$O$^+$ + CH$_3$Cl (0.13) TiCl$_3$CH$_2$O$^+$ + C$_3$H$_6$ (0.11)
(2-pentanone)	TiO$^+$ + C$_5$H$_{10}$	TiClO$^+$ + C$_5$H$_{10}$	TiCl$_2$C$_2$H$_4$O$^+$ + C$_3$H$_6$	TiCl$_3$C$_2$H$_4$O$^+$ + C$_3$H$_6$ (0.83) TiCl$_3$CH$_2$O$^+$ + C$_4$H$_8$ (0.17)
(3-hexanone)	*a*	*a*	TiCl$_2$C$_3$H$_6$O$^+$ + C$_3$H$_6$ (0.66) TiCl$_2$C$_2$H$_4$O$^+$ + C$_4$H$_8$ (0.34)	TiCl$_3$C$_3$H$_6$O$^+$ + C$_3$H$_6$ (0.61) TiCl$_3$CH$_2$O$^+$ + C$_5$H$_{10}$ (0.21) TiCl$_3$C$_2$H$_4$O$^+$ + C$_4$H$_8$ (0.18)
(3-methyl-2-pentanone)	*a*	*a*	TiCl$_2$C$_2$H$_4$O$^+$ + C$_4$H$_8$	TiCl$_3$C$_2$H$_4$O$^+$ + C$_4$H$_8$ (0.79) TiCl$_3$C$_3$H$_6$O$^+$ + C$_3$H$_6$ (0.21)
(2-hexanone)	*a*	*a*	TiCl$_2$C$_2$H$_4$O$^+$ + C$_4$H$_8$	TiCl$_3$C$_2$H$_4$O$^+$ + C$_4$H$_8$ (0.91) TiCl$_3$C$_3$H$_6$O$^+$ + C$_3$H$_6$ (0.09)
(pinacolone type)	*a*	*a*	*a*	*a*
(ethyl tert-butyl ketone)	*a*	TiClC$_3$H$_4$O$^+$ + C$_4$H$_8$ + H$_2$	TiCl$_2$C$_3$H$_6$O$^+$ + C$_4$H$_8$ (0.70) TiCl$_2$C$_2$H$_4$O$^+$ + C$_5$H$_{10}$ (0.30)	TiCl$_3$C$_3$H$_6$O$^+$ + C$_4$H$_8$ (0.68) TiCl$_3$C$_2$H$_4$O$^+$ + C$_5$H$_{10}$ (0.32)

a No reaction observed. *b* As noted in the text all reactants listed in this table displace a Cl atom from TiCl$_4{}^+$.

processes of the type

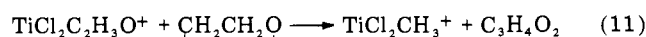$$\text{TiCl}_n\text{A}^+ + \text{B} \rightarrow \text{TiCl}_n\text{B}^+ + \text{A} \qquad (4)$$
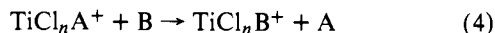
where TiCl$_n$A$^+$ is the product of reaction between TiCl$_n{}^+$ and B. Observed reactions of this type are listed in Table III. Other secondary reactions observed are reactions 5-7 in the CH$_3$CHO mixture, reactions 8 and 9 in the C$_2$H$_5$CHO mixture, and reaction 10 in the acetone mixture.

$$\text{TiCl}_2\text{C}_2\text{H}_3\text{O}^+ + \text{CH}_3\text{CHO} \begin{cases} \xrightarrow{74\%} \text{TiClC}_4\text{H}_6\text{O}_2{}^+ + \text{HCl} & (5) \\ \xrightarrow{14\%} \text{TiCl}_2\text{C}_3\text{H}_5\text{O}^+ + \text{CH}_2\text{O} & (6) \\ \xrightarrow{12\%} \text{TiCl}_2\text{C}_2\text{H}_5\text{O}_2 + \text{C}_2\text{H}_2 & (7) \end{cases}$$

$$\text{TiCl}_2\text{C}_3\text{H}_5\text{O}^+ + \text{C}_2\text{H}_5\text{CHO} \begin{cases} \rightarrow \text{TiClC}_6\text{H}_{10}\text{O}_2{}^+ + \text{HCl} & (8) \\ \rightarrow \text{TiCl}_2\text{C}_4\text{H}_7\text{O}_2{}^+ + \text{C}_2\text{H}_4 & (9) \end{cases}$$

$$\text{TiCl}_2\text{C}_3\text{H}_5\text{O}^+ + \text{CD}_3\text{COCD}_3 \rightarrow \text{TiCl}_2\text{C}_3\text{D}_6\text{HO}_2{}^+ + \text{C}_3\text{H}_4 \qquad (10)$$
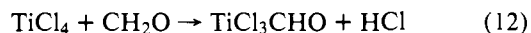
The chemistry of the electron-impact fragments of TiCl$_4$ with H$_2$O and with molecules containing carbon–oxygen single bonds is summarized in Table II. Again we observe in some cases the formation of TiO$^+$ and TiClO$^+$ from Ti$^+$ and TiCl$^+$, respectively. The titanium-containing ions also undergo dissociative additions similar to those observed with the ketones and aldehydes. The reaction complexes in these biomolecular processes generally lose alkyl radicals, alkyl chlorides, HCl, or small alkenes. All species in Table II react with TiCl$_4{}^+$ by displacing a chlorine atom.

As in the aldehydes and ketones, a number of product ions react further by ligand substitution-type processes which are

listed in Table III. In addition, in the ethylene oxide mixture, reaction 11 occurs.

$$\text{TiCl}_2\text{C}_2\text{H}_3\text{O}^+ + \underbrace{\text{CH}_2\text{CH}_2\text{O}} \longrightarrow \text{TiCl}_2\text{CH}_3{}^+ + \text{C}_3\text{H}_4\text{O}_2 \qquad (11)$$

With CH$_2$O, at a mixture pressure of approximately 2 × 10^{-6} Torr, ions such as TiO$^+$, TiClO$^+$, and TiCl$_2$CHO$^+$ appear. These ions might be expected as ion–molecule reaction products. Double resonance experiments indicate, however, that these ions have no ionic precursors. In addition the relative peak intensities in the single resonance spectra of the mixture do not change with drift voltages. If ion–molecule reactions were occurring, the ratio of reactant to product peak intensities should vary with drift voltages. The ions are apparently not products of ion–molecule reactions but electron impact fragments of a neutral compound or neutral compounds present in the system in addition to TiCl$_4$ and CH$_2$O. Another ion that appears with the oxytitanium ions is HCl$^+$. These observations suggest that some process such as the reaction

$$\text{TiCl}_4 + \text{CH}_2\text{O} \rightarrow \text{TiCl}_3\text{CHO} + \text{HCl} \qquad (12)$$

is occurring in our instrument. This may be a bimolecular gas-phase reaction, or may occur on the inner walls of the instrument. Since the electron impact fragment ions of this product are the same as expected ion–molecule reaction products, and since the formation of this product increases rapidly with increasing pressure, the occurrence of ion–molecule reactions in this system could not be established.
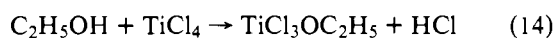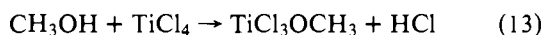
Neutral–neutral reactions similar to that observed with CH$_2$O were so rapid that they precluded observation of ion–molecule reactions with CH$_3$OH, C$_2$H$_5$OH, and CH$_3$COOH. Our observations in these systems are consistent with the re-

Table II. Reactions of Small Ethers, Esters, and Alcohols with $TiCl_n^+$

Reactant neutral	Ti^+	$TiCl^+$	$TiCl_2^+$	$TiCl_3^+$
H–O–H	a	a	a	$TiCl_2OH^+ + HCl$
H_3C–O–CH_3	a	$TiClOCH_3^+ + CH_3$	$TiCl_2OCH_3^+ + CH_3$	$TiCl_2OCH_3^+ + CH_3Cl$ (0.79) $TiCl_2CH_2OCH_3^+ + HCl$(0.21)
H_2C—CH_2 (epoxide)	TiO^+	$TiClO^+$	$TiClC_2H_5O^+ + HCl$	$TiCl_2C_2H_5O^+ + HCl$ (0.94) $TiCl_3CH_3^+ + HCl + CO$(0.06)
$\diagdown$O$\diagup$	a	$TiClC_2H_4O^+ + C_2H_6$	$TiClC_2H_5O^+ + C_2H_5Cl$ (0.71) $TiCl_2C_2H_4O^+ + C_2H_5$ (0.13) $TiCl_2H_2O^+ + C_4H_8$ (0.16)	$TiCl_3H_2O^+ + 2C_2H_4$ (0.41) $TiCl_2C_2H_5O^+ + C_2H_5Cl$(0.25) $TiCl_3C_2H_4^+ + C_2H_5OH$ (0.16) $TiCl_3C_2H_5O^+ + C_2H_5$ (0.18)
(tetrahydrofuran)	$TiO^+ + C_4H_8$	$TiClO^+ + C_4H_8$	$TiCl_2CH_2O^+ + C_3H_6$	$TiCl_3CH_2O^+ + C_3H_6$ (0.95) $TiCl_2C_3H_5O^+ + CH_3Cl$ (0.05)
(dihydrofuran)	$TiO^+ + C_4H_6$	$TiClO^+ + C_4H_6$	a	$TiCl_3CH_2O + C_3H_4$
CH_3COCH_3	a	a	a	a
$CH_3COC_2H_5$	a	$TiCH_3COO^+ + C_2H_5Cl$	$TiClCH_3COO^+ + C_2H_5Cl$	$TiCl_3C_2H_4O_2^+ + C_2H_4$

^{a} No product observed.

actions

$$CH_3OH + TiCl_4 \rightarrow TiCl_3OCH_3 + HCl \qquad (13)$$

$$C_2H_5OH + TiCl_4 \rightarrow TiCl_3OC_2H_5 + HCl \qquad (14)$$

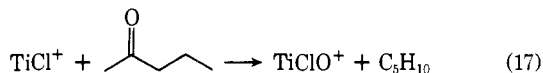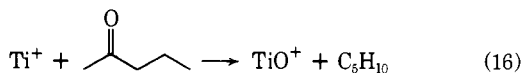$$CH_3COOH + TiCl_4 \rightarrow (CH_3COO)TiCl_3 + HCl \qquad (15)$$

The similarities between condensed phase reaction 1 and reactions 13 and 14 and that between reaction 15 and condensed phase reaction 2 are obvious.
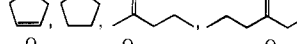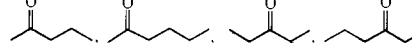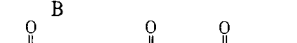
Discussion

Ti^+ and $TiCl^+$ with Ketones and Aldehydes. Typical of the reactions of Ti^+ and $TiCl^+$ with ketones and aldehydes are reactions 16 and 17 of those ions with 2-pentanone. Tita-

$$Ti^+ + \text{(2-pentanone)} \longrightarrow TiO^+ + C_5H_{10} \qquad (16)$$

$$TiCl^+ + \text{(2-pentanone)} \longrightarrow TiClO^+ + C_5H_{10} \qquad (17)$$

nium–oxygen bond strengths are very high so the propensity of Ti^+ and $TiCl^+$ to undergo oxidation is not surprising. The Ti^+-O bond strength has recently been measured to be 161 kcal/mol.[14] NO and O_2 are both known to readily oxidize Ti^+ to TiO^+ in the gas phase.[15] It is somewhat surprising that as indicated in Table I larger ketones oxidize the metal ions less readily than small carbonyl compounds. The thermodynamics of the oxidation does not change significantly with the length of the alkyl substituents on the carbonyl group. Competing processes do not appear to be important. It is possible that the energy released by formation of the ion–molecule complex is more effectively concentrated in the carbon–oxygen bond in the smaller compounds. In the case of the larger compounds more degrees of freedom are available to accept that energy and divert it from effecting the carbon–oxygen bond cleavage. The mechanism of the oxidation could involve a simple abstraction of the oxygen atom from the carbonyl leaving behind a carbene. The reactions of Ti^+ with NO and O_2 suggest that this is energetically possible. It seems more likely, however, that the oxygen atom abstraction is accompanied by a hydrogen atom shift so that the neutral product is a stable alkene.

Reactions 16 and 17 are reminiscent of the recently reported reductive coupling of ketones by low-valent titanium compounds exemplified by[9]

Table III. Ligand Substitution Processes^a

$TiCl_3A^+ \rightarrow$	$TiCl_3B^+ + A$
A	B
H_2O	$\diagdown$O$\diagup$
C_2H_4	$\diagdown$O$\diagup$
CH_2O	(tetrahydrofuran, dihydrofuran, ketones)
CH_3CHO	(ketones/aldehydes)
C_2H_5CHO	(ketones)

$TiCl_2A^+ + B \rightarrow$	$TiCl_2B^+ + B$
A	B
CH_3CHO	(ketones)

^{a} Observed in mixtures of $TiCl_4$ and B. In each case the $TiCl_3A^+$ and $TiCl_2A^+$ species are products of reaction between $TiCl_3^+$ and B or $TiCl_2^+$ and B.

$$2\ \text{(cycloheptanone)} \xrightarrow[\text{LiAlH}_4]{\text{TiCl}_3} \text{(bicycloheptylidene)}$$
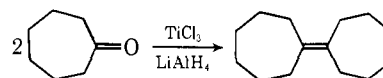
Whether or not there is a direct mechanistic relationship between the gas-phase ion–molecule process and the reductive coupling, they both reflect the remarkable reducing power of titanium in its lower oxidation states.

$TiCl_2^+$ and $TiCl_3^+$ with Small Carbonyl Compounds. The chemistry of $TiCl_2^+$ and $TiCl_3^+$ with the aldehydes and ketones differs sharply from that of Ti^+ and $TiCl^+$. Typical of the reactions of smaller compounds are those of acetone (18 and 19). Acetaldehyde and propionaldehyde react in a similar

$$TiCl_2^+ + \text{(acetone)} \longrightarrow TiClC_3H_5O^+ + HCl \qquad (18)$$

$$TiCl_3^+ + \text{(acetone)} \longrightarrow TiCl_2C_3H_5O^+ + HCl \qquad (19)$$

way. Propionaldehyde, for example, reacts with $TiCl_3^+$ according to eq 20. A possible mechanism for these processes is outlined in eq 21.

$$TiCl_3^+ + \quad \text{(allyl ether)} \quad \longrightarrow \quad TiCl_2C_3H_5O^+ + HCl \quad (20)$$

$$\text{(structure)} \quad \longrightarrow \quad \text{(structure)} \quad + HCl \quad (21)$$
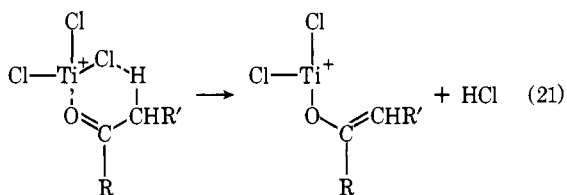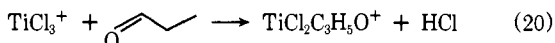
The product ions of eq 19 and 20 have the same empirical formula, but according to the mechanism postulated in eq 21 they should have different structures. That they have different structures is substantiated by their subsequent chemistry. The postulated structure of the product of eq 19 is **1** and that of the product of eq 20 is **2**. The product of eq 20 (structure **2**) reacts

1   **2**   **3**
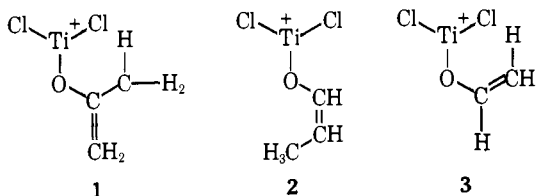
with propionaldehyde to lose HCl (reaction 8) probably by a mechanism analogous to eq 21. The product of eq 19 (structure **1**) reacts with acetone to lose the elements of allene (reaction 10). Structure **1** is represented in a configuration that could readily lose allene. A chlorine-assisted H atom shift from the methyl group to the oxygen of **1** either before or in concert with attack by an acetone molecule would result in the allene loss. The protons of the departing allene would all originate with the ion and none with attacking acetone which is consistent with the isotopic labeling results suggested in eq 10. Note that the analogous configuration **3** of the $TiCl_2(C_2H_3O)^+$ ion might lose acetylene by a similar mechanism. Such a process is actually observed in the reaction of that ion with acetaldehyde (reaction 7).
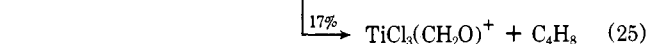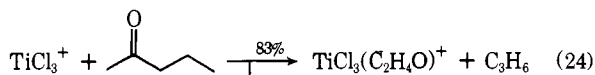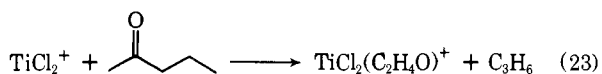
Minor reactions 6 and 9 of the enolate ions **3** and **2** seem to involve quite different mechanisms. It is difficult to account for the products observed in these reactions without postulating substantial modification of the attacking aldehyde. Reaction 11 between **2** and propionaldehyde to product $TiCl_2C_4H_7O_2^+$ could involve a mechanism similar to that postulated below for the elimination of olefins from larger ketones in $TiCl_2^+$ and $TiCl_3^+$ reactions. Since propionaldehyde does not react with $TiCl_3^+$ to lose ethylene we conclude that the alkenoxy substitute activates the metal center with regard to this type of process.

A mechanism similar to eq 21 has been postulated to be important in the enolization of ketones by Grignard reagents.[16] This mechanism involves formation of an enolate as illustrated in eq 22 and is believed to be important in cases where the ketone is particularly inclined to form the enol.

$$R-Mg \quad \longrightarrow \quad R-Mg \quad + HX \quad (22)$$
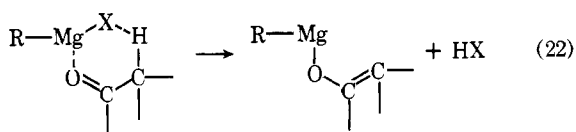
tone is particularly inclined to form the enol.

$TiCl_2^+$ and $TiCl_3^+$ with Larger Ketones and Aldehydes. It is evident from Table I that reactions of $TiCl_2^+$ and $TiCl_3^+$ with ketones and aldehydes having a secondary carbon β to the carbonyl group follow a distinctive pattern. Typical of these systems are the reactions of 2-pentanone, reactions 23, 24, and 25. The products of each of these reactions react with 2-pen-

$$TiCl_2^+ + \quad \text{(2-pentanone)} \quad \longrightarrow \quad TiCl_2(C_2H_4O)^+ + C_3H_6 \quad (23)$$

$$TiCl_3^+ + \quad \text{(2-pentanone)} \quad \xrightarrow{83\%} \quad TiCl_3(C_2H_4O)^+ + C_3H_6 \quad (24)$$

$$\xrightarrow{17\%} \quad TiCl_3(CH_2O)^+ + C_4H_8 \quad (25)$$

tanone in a ligand displacement sense, e.g., reaction 26. The

$$TiCl_3(C_2H_4O)^+ + \quad \text{(2-pentanone)} \quad \longrightarrow \quad TiCl_3(C_5H_{10}O)^+ + C_2H_4O \quad (26)$$
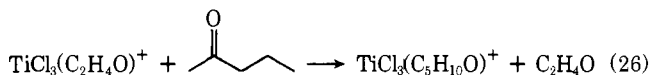
major products of reactions of both $TiCl_2^+$ and $TiCl_3^+$ with all the carbonyl compounds having a secondary β carbon are consistent with the mechanism suggested for the specific case of 2-pentanone in reaction 27. Several considerations lead us

4

$$\longrightarrow \quad \text{(structure)} \quad + \quad \text{(propene)} \quad (27)$$
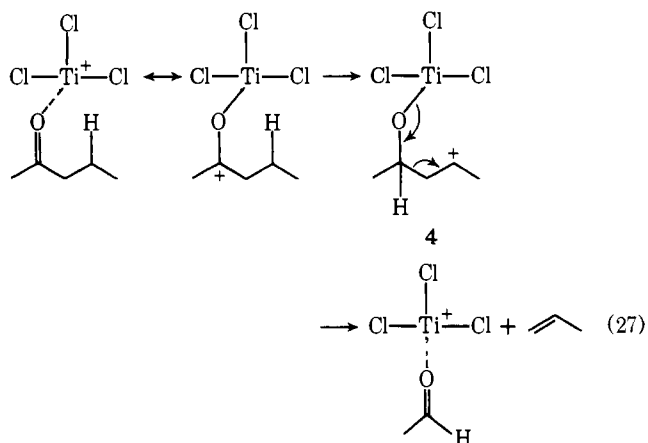
to suggest this as a general mechanism. A secondary β carbon atom seems to facilitate the reaction. If the carbonyl compound involved has only primary β carbons, the intermediate analogous to **4** would be a primary alkyl cation. We expect, then, that the process will be less important in this case than in the case of carbonyl compounds with secondary β carbons. As discussed below, this is what we observe. In addition, 4,4-dimethyl-2-pentanone, which has no hydrogen atom on its β carbon, is not observed to react at all:

$$TiCl_3^+, TiCl_2^+ + \quad \text{(4,4-dimethyl-2-pentanone)} \quad \longrightarrow \quad \text{no products}$$
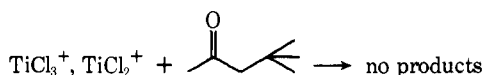
A strong interaction between titanium and oxygen is suggested by numerous observations including the formation of TiO^+ and $TiClO^+$ in the reactions of carbonyl compounds with Ti^+ and $TiCl^+$. The postulated product ion structure is consistently supported by displacement reactions such as reaction 26. The shift of positive charge into the hydrocarbon chain is a reasonable possibility since the ionization potential of $TiCl_3$ (9.76 eV[17]) is in the range of the ionization potentials of alkyl radicals. Other mechanisms are certainly possible but the above considerations and relative simplicity seem to commend this one. The detailed mechanism of the 1,3 hydrogen atom shift can only be speculated upon. The empty d orbitals on the titanium may well be involved.

Rearrangements of intermediates similar to **4** could lead to a number of the minor products of reactions between the carbonyl compounds and the $TiCl_3^+$ and $TiCl_2^+$ ions. The process outlined in eq 28, for example, leads to the formation of an

$$Cl-Ti-Cl \quad \longrightarrow \quad Cl-Ti-Cl \quad \longrightarrow \quad Cl-Ti^+-Cl \quad (28)$$
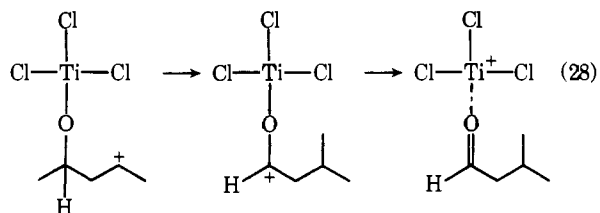
aldehyde complex from which $TiCl_3(CH_2O)^+$ may be formed by a mechanism analogous to reaction 27. This would account for the product formed in reaction 25 of 2-pentanone. We note in t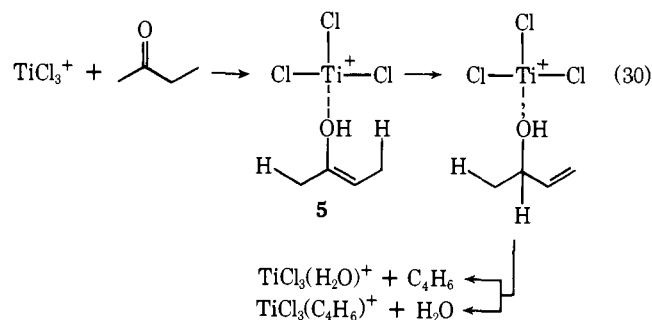his connection that $TiCl_3(CH_2O)^+$ is the only product of reaction between $TiCl_3^+$ and butyraldehyde. The $TiCl_3(CH_2O)^+$ products observed in 2-butanone, 2-pentanone, and 2-hexanone might be rationalized in terms of similar processes. We suggest a process in eq 29 which might be viewed
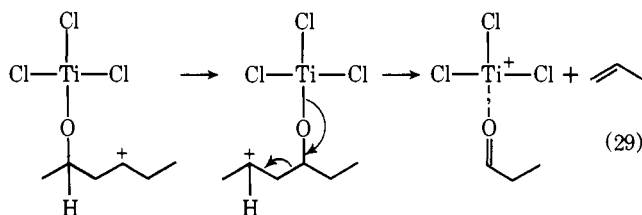

as a shift of the $TiCl_3O^-$ moiety to the center of positive charge producing an ion which might lose an olefin in the manner shown. The $TiCl_3(CH_2O)^+$, $TiCl_2(C_2H_4O)^+$, and $TiCl_3(C_2H_4O)^+$ products in 3-hexanone and the $TiCl_3(C_3H_6O)^+$ product in 2-hexanone may all be rationalized in terms of this process. Where the mechanisms of reactions 28 and 29 give the same products there is little basis for preferring one over the other. In fact, all the products that might be expected to result from processes analogous to reactions 28 and 29 are observed except in the cases of the reactions of 2-methyl-3-pentanone and 2,2-dimethyl-3-pentanone. The chemistry of these two compounds probably involves a different mechanism as discussed below.

Further support for the mechanism suggested in eq 27 is provided by the chemistry of neutral Lewis acids. The BF_3-catalyzed polymerization of aldehydes, for example, is believed to involve a BF_3-aldehyde complex in which positive charge is generated on the carbonyl carbon.[18] This is analogous to the interaction suggested in eq 27 between $TiCl_3^+$ and a ketone that leads to a β-hydride shift and elimination of an olefin.

Mechanisms analogous to reaction 27 account for some of the products of the reactions between $TiCl_3^+$ and carbonyl compounds with only primary β carbons. These products, however, are generally minor products. The major products seem to be the result of several different mechanisms. One important mechanism seems to involve the metal-induced enolization of the ketone. The major channel of reaction between $TiCl_3^+$ and 2-butanone involves the dehydration of the ketone and could proceed through intermediate **5** as indicated in reaction 30. The enolization which produces **5** could be fa-


cilitated by the attacking $TiCl_3^+$ ion. A metal ion induced enolization might be the initial step in the major channel of reaction between 2-methyl-3-pentanone and the two titanium ions. This major reaction channel involves elimination of butene from the ketone. A 1,3 methyl shift would convert the enol into 3,3-dimethyl-2-butanone (methyl *tert*-butyl ketone) as indicated in reaction 31. The product of reaction 31 could lose isobutene by a reaction 27 type of mechanism. It is relevant in this connection to note that 2,2 dimethyl-3-pentanone (ethyl *tert*-butyl ketone) reacts predominantly by butene loss. Two
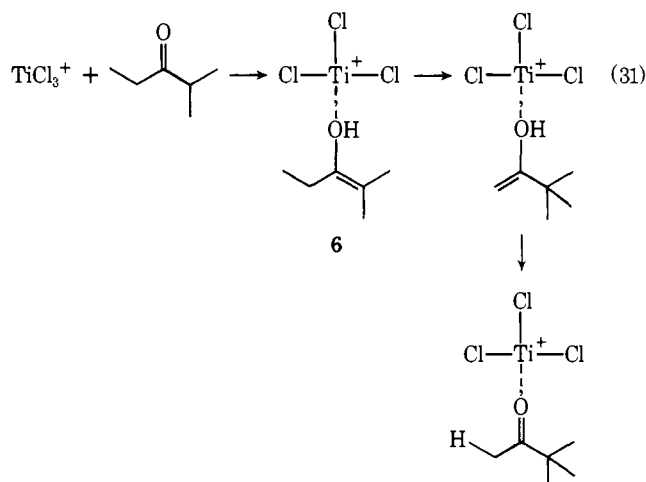

additional observations support the possibility of the enolization process. First, the expected products of analogous processes in other ketones are generally observed. Second, the process accounts for the major product only in the case of 2-methyl-3-pentanone. This molecule is, of course, particularly susceptible to enolization since it has a tertiary α carbon.

It is of interest to recall at this point the reactions of $TiCl_3^+$ and $TiCl_2^+$ with smaller ketones and aldehydes. These reactions involve the loss of HCl from the ion-ketone complex and presumably formation of an enolate structure as suggested in eq 21. This substantiates the possibility of metal-induced enolization playing the kind of role indicated in eq 30 and 31. It also suggests that hydrogen bonding of some kind between an α H atom and one of the chlorines is important in the enolization. It is also of interest to recall again that Grignard reagents interact with ketones to form enolates as discussed above (reaction 22).

Reactions of OR and OH Compounds. The chemistry of the chlorotitanium ions with compounds containing single carbon-oxygen bonds is dominated by the cleavage of those bonds. It appears that most of the reactions involve formation of titanium-oxygen bonds. In a number of cases formation of a carbon-chlorine bond accompanies formation of the titanium-oxygen bond. Typical is the case of dimethyl ether. Ti^+ is unreactive with dimethyl ether but $TiCl^+$, $TiCl_2^+$, and $TiCl_3^+$ react as indicated in eq 32 to form alkoxychlorotitanium ions.

$$TiCl_n^+ + CH_3OCH_3$$
$$\rightarrow TiCl_{n-1}OCH_3^+ + CH_3Cl \quad n = 1, 2, 3 \quad (32)$$
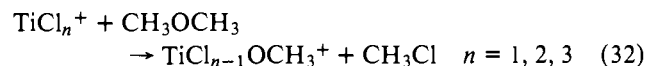
Such metathetical processes probably proceed through a short-lived addition complex as suggested in reaction 33. The
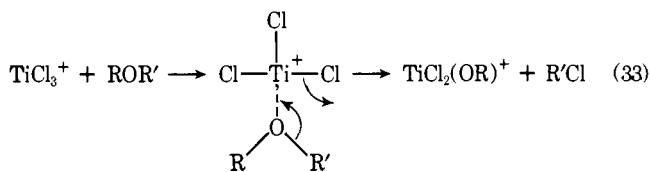
chlorotitanium ions undergo a similar metathesis in reacting with methyl fluoride.[19]

Where the organic reagent contains larger alkyl groups elimination of olefins becomes possible. Typical are the major reactions of diethyl ether and ethyl acetate with $TiCl_3^+$:

$$TiCl_3^+ + (C_2H_5)_2O \rightarrow TiCl_3(H_2O)^+ + 2C_2H_4 \quad (34)$$

$$TiCl_3^+ + CH_3COOC_2H_5$$
$$\rightarrow TiCl_3(C_2H_5COOH)^+ + C_2H_4 \quad (35)$$
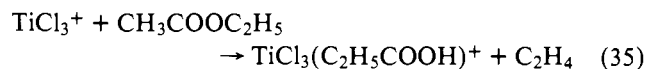
A possible mechanism for eq 34 is suggested in eq 36. The

Table IV. Units of Binding Energies between Various Substrates and $TiCl_n^+$

| Reaction	Implication[a]
$Ti^+ + \text{tetrahydrofuran} \rightarrow TiO^+ + C_4H_8$ [b]	$D(^+Ti\text{-}O) > 117.9$ [c]
$TiCl^+ + \text{tetrahydrofuran} \rightarrow TiClO^+ + C_4H_8$ [b]	$D(^+TiCl\text{-}O) > 117.9$ [c]
$TiCl_n^+ + \text{tetrahydrofuran} \rightarrow TiCl_nCH_2O^+ + C_3H_6$	$D(^+TiCl_2\text{-}CH_2O) > 20.0$ $n = 2, 3$
$TiCl_3^+ + \text{2-butanone} \rightarrow TiCl_3CH_2O^+ + C_3H_6$	$D(TiCl_3^+\text{-}CH_2O) > 35.3$
$TiCl_3^+ + \text{2-hexanone} \rightarrow TiCl_3CH_3COCH_3^+ + C_3H_6$	$D(^+TiCl_3\text{-}CH_3COCH_3) > 19.7$
$TiCl_3^+ + C_2H_5OC_2H_5 \rightarrow TiCl_3H_2O^+ + 2C_2H_4$	$D(TiCl_3^+\text{-}H_2O) > 27.5$
$ \rightarrow TiCl_3C_2H_4^+ + C_2H_5OH$	$D(^+TiCl_3\text{-}C_2H_4) > 16.6$
$TiCl_n^+ + CH_3OCH_3 \rightarrow TiCl_nOCH_3^+ + CH_3$	$D(^+TiCl_n\text{-}OCH_3) > 76.7$ $n = 1, 2$
$TiCl_2^+ + C_2H_5OC_2H_5 \rightarrow TiClOC_2H_5^+ + C_2H_5Cl$	$D(^+TiCl\text{-}OC_2H_5) > 86.0$
$TiCl_3^+ + C_2H_5OC_2H_5 \rightarrow TiCl_2OC_2H_5^+ + C_2H_5Cl$	$D(^+TiCl_2\text{-}OC_2H_5) > 74.0$
$TiCl_3^+ + CH_3OCH_3 \rightarrow TiCl_2OCH_3^+ + CH_3Cl$	$D(^+TiCl_2\text{-}OCH_3) > 73.2$
$TiCl_4^+ + A \rightarrow TiCl_3A^+ + Cl$	$D(TiCl_3^+\text{-}A) > 38.1$

[a] Binding energies based on heats of formation found in J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 26 (1969). [b] C_4H_8 assumed to be *cis*-2-butene. [c] $D(Ti^+\text{-}O)$ has been measured and found to be 161 kcal/mol (ref 14).
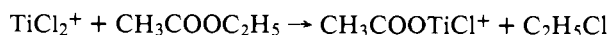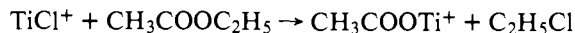

$$(36)$$
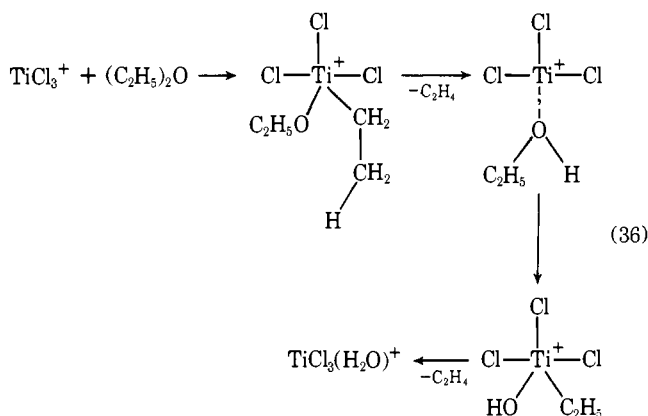
formation of $TiCl_3(C_2H_4)^+$ as a minor product in the ether reaction (Table II) supports the stepwise elimination of two molecules of ethylene. A rather similar mechanism might account for the ethyl acetate reaction where the $TiCl_3^+$ attacks the alkyl-oxygen bond and eliminates ethylene as shown in eq 37. Such a mechanism for the ethyl acetate reaction is con-


$$(37)$$
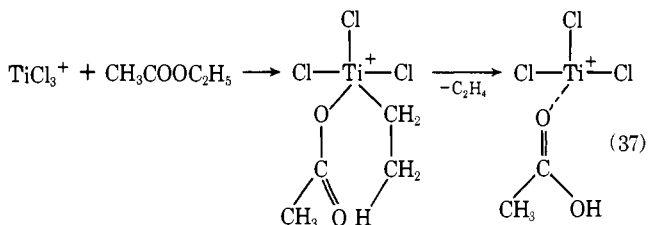
sistent with the inertness of methyl acetate toward $TiCl_3^+$. Attack at the alkyl-oxygen bond of the methyl ester, of course, cannot lead to elimination of an olefin.

Ethyl acetate reacts with $TiCl^+$ and $TiCl_2^+$ to form titanium acetate ions and ethyl chloride:

$$TiCl^+ + CH_3COOC_2H_5 \rightarrow CH_3COOTi^+ + C_2H_5Cl$$

$$TiCl_2^+ + CH_3COOC_2H_5 \rightarrow CH_3COOTiCl^+ + C_2H_5Cl$$

We suggest a mechanism involving a six-membered ring intermediate in eq 38. This mechanism is consistent with the inertness of methyl acetate to these two ions. The charge localization on the ethyl carbon suggested in eq 38 would be much less favorable for a methyl carbon.

The chemistry of the cyclic ethers with the chlorotitanium ions resembles that of isomeric aldehydes. The products observed with ethylene oxide and tetrahydrofuran are nearly identical with those observed with acetaldehyde and butanal, respectively. This suggests that the chlorotitanium ions facilitate the rapid isomerization of the cyclic ethers to aldehydes.

$$(38)$$
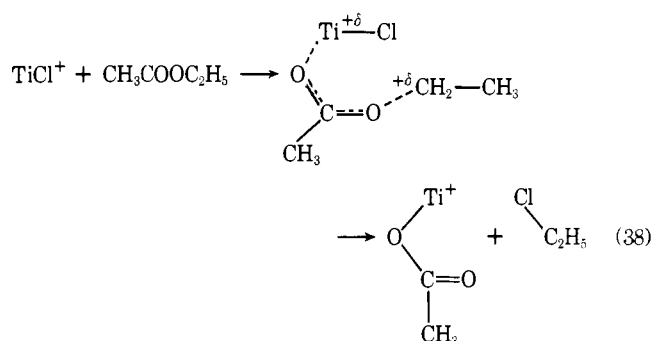
Since the aldehydes are thermodynamically more stable than the cyclic ethers, the isomerization makes more energy available for the decomposition of the bimolecular reaction complex. Thus it is not surprising that minor products appear in the reactions of the cyclic ethers which are not observed in the aldehyde reactions ($TiCl_2(C_3H_5O)^+$ and $TiCl_2(CH_3)^+$ in the reactions of $TiCl_3^+$ with ethylene oxide and tetrahydrofuran, respectively). Although no unsaturated aldehydes were studied, the products of the 2,5-dihydrofuran reactions are consistent with what might be expected from an isomeric unsaturated aldehyde.

The chemistry of compounds containing carbon-oxygen single bonds with the chlorotitanium ions resembles that with condensed phase titanium tetrachloride. As pointed out in the Introduction, $TiCl_4$ reacts with alcohols and acids to form titanium alkoxides and carboxylates, respectively. Indeed such reactions are so fast that we see evidence of them even at the very low pressures (10^{-6}-10^{-3} Torr) in our experimental system. These neutral-neutral reactions have precluded our observation of ion-molecule reactions of alcohols with the chlorotitanium ions. Water and ethers, however, react with the chlorotitanium ions to form titanium hydroxide and titanium alkoxide ions, respectively. In addition ethyl acetate reacts with $TiCl^+$ and $TiCl_2^+$ to form titanium carboxylate ions.

Of particular interest is the recent observation of the deoxygenation of epoxides by metal atom cocondensation. It is reported that Ti, V, Cr, Co, and Ni metal atoms react efficiently with epoxides to form the corresponding olefin and metal oxide (reaction 39).[20] The parallel with the reaction of Ti^+ and $TiCl^+$

$$(39)$$
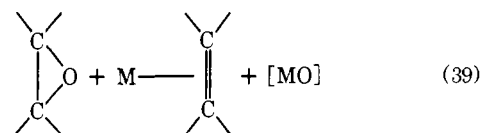
with ethylene oxide is intriguing.

Thermochemical Consequences. The time available to the ions for reaction in our apparatus is too short for us to observe

very slow reactions. The fact that we observe the reaction indicates that it is within at least two orders of magnitude of the collision frequency of the reactants. This sets an upper limit of ~ 1 kcal mol^{-1} on the activation energy and on the exothermicity of the observed reactions. A number of consequences of such limits are summarized in Table IV. Of particular interest is the evidence that $D(TiCl_n^+-OR)$ is greater than 75-80 kcal/mol. Little information is available on such bond strengths.

Also of thermochemical importance are the ligand exchange reactions listed in Table III. We may conclude that for the reactions tabulated $D(TiCl_3^+-B) \geqslant D(TiCl_3^+-A)$. The trend that emerges is that $D(TiCl_3^+-B)$ increases with the size of the alkyl groups on B. A thorough study of competitive ligand substitutions of this type with a series of bases is underway in our laboratory.

Summary and Conclusions

Several generalizations emerge from the chemistry of the aldehydes and ketones with the chlorotitanium ions.

1. Ti^+ and $TiCl^+$ react with smaller ketones and aldehydes to form TiO^+ and $TiClO^+$.

2. $TiCl_2^+$ and $TiCl_3^+$ react with smaller ketones and aldehydes to eliminate HCl, apparently forming enolate ions.

3. Two generalizations can be made regarding the reactions to $TiCl_2^+$ and $TiCl_3^+$ with larger ketones and aldehydes: (a) If a ketone has a secondary β carbon, the major product of its reaction with $TiCl_2^+$ and $TiCl_3^+$ will be that given by the β hydride shift mechanism exemplified by reaction 27. That is, a ketone R^1COR^2 will react with $TiCl_3^+$ to give $TiCl_3(R^1CHO)^+$ if there is a secondary β carbon in R^2. If both R^1 and R^2 have secondary β carbons and R^1 is smaller than R^2, then the major product will be $TiCl_3(R^1CHO)^+$. (b) If a ketone has only primary β carbons, the major products are more difficult to predict, but it appears that a metal-induced enolization plays an important role in these reactions.

These generalizations resemble the generalizations that emerge from the chemistry of olefins with the chlorotitanium ions. With both groups of compounds we find that Ti^+ and $TiCl^+$ react differently than $TiCl_2^+$ and $TiCl_3^+$. Ti^+ and $TiCl^+$ combine with olefins and eliminate one or more molecules of hydrogen. The result is an electron-rich donor which occupies one or more of the vacancies in the coordination shell of the metal. Ti^+ and $TiCl^+$ react with the carbonyl compounds to extract an oxygen atom which also helps fill the coordination shell of the metal. $TiCl_2^+$ and $TiCl_3^+$ combine with smaller olefins and smaller carbonyl compounds and lose HCl. $TiCl_2^+$ and $TiCl_3^+$ combine with larger olefins and carbonyl com-

pounds and eliminate smaller olefins. The chlorotitanium ions thus seem to interact with a carbon-oxygen double bond in a way similar to the way it interacts with a carbon-carbon double bond.

Several generalizations also emerge from the chemistry of the species containing carbon-oxygen single bonds:

1. The chlorotitanium ions tend to form alkoxychlorotitanium ions. This is accomplished either by simply extracting an alkoxy group from the substrate or exchanging a chlorine atom for an alkoxy group.

2. If the substrate contains ethyl groups attached to an oxygen atom the chlorotitanium ions tend to eliminate ethylene from the substrate molecule.

3. Cyclic ethers react similarly to isomeric aldehydes.

One final generalization is that all the oxygen-containing species examined react with $TiCl_4^+$ to displace a Cl atom forming a complex with $TiCl_3^+$.

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