to 1.2 water molecules (cf. ref 4 and 6).

In the other type of two-correlation time model there is only one class of hydration water, i.e., this is a two-state model. Due to the influence of the protein surface, the reorientation of the hydration water is anisotropic; hence it must be described by two correlation times. This model is consistent with the magnitude of the two correlation times τ_f and τ_s and is also physically attractive in view of the similarity of the local environment near a protein surface and that in anisotropic lyotropic liquid crystals. Similar models have been used to interpret nuclear magnetic relaxation data in solutions of micelles[25] and biological macromolecules.[66,73] Recently a qualitative reinterpretation of previous[4,6] proton and deuteron dispersion data for protein solutions using this model has been published.[67] In that work, however, the contribution from the fast motion (eq 4a) was neglected.

The emerging picture of protein hydration is intermediate between the two extremes of polarized multilayers[68] on the one hand and a small number of irrotationally bound water molecules[4,6] on the other. Approximately two layers of water are, on the average, hindered in their reorientation by a factor of ca. 8. This rapid local motion has a small anisotropic component which is averaged out by protein reorientation. Charged residues, particularly carboxylate, are more extensively hydrated than other residues. This fact accounts for the variation in the extent of hydration between different proteins (Figure 9a).

Note Added in Proof: Since the completion of this work, it has been shown[79] that existing analytical expressions[80] for the relaxation rates, i.e., for the functions $f_i(\tau_s,\omega_0)$ in eq 4b, are accurate to better than 2% for the present data. The numerical diagonalizations of the relaxation matrices that were performed in this work, although correct, are thus unneccessary. Furthermore, a detailed derivation and discussion of the "two-step averaging" relaxation model (eq 3–5) will appear shortly (Wennerström, H.; Halle, B. *J. Chem. Phys.*, submitted).

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Gas-Phase Ion Chemistry of $TiCl_4$ and CH_3TiCl_3. Reaction of $CH_3TiCl_2^+$ with Ethylene

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Abstract: $TiCl_4^+$ and $TiCl_3^+$ are the principal ions produced by electron-impact ionization of $TiCl_4$. Both react with $TiCl_4$ to give $Ti_2Cl_7^+$. Reactions of this and other species of the form $TiCl_3$(ligand)$^+$ allow the determination of an order of relative ligand binding energies to $TiCl_3^+$ of MeF < $TiCl_4$ < MeCl < EtCl < benzene. MeI, propylene, and butenes are also found to be stronger ligands for $TiCl_3^+$ than $TiCl_4$. Study of halide-transfer and proton-transfer reactions leads to determination of the thermochemical results: $D(TiCl_3^+–Cl^-) = 217 \pm 11$ kcal/mol, $D(TiCl_3^+–F^-) = 254 \pm 4$ kcal/mol, and $PA(TiCl_4) \equiv D(TiCl_4–H^+) = 175 \pm 11$ kcal/mol. Chloride transfer from CH_3TiCl_3 to $TiCl_3^+$ yields $CH_3TiCl_2^+$ as the major ion at intermediate times in the ion chemistry of CH_3TiCl_3. $CH_3TiCl_2^+$ reacts with C_2H_4 to give $C_3H_5TiCl_2^+$ with H_2 elimination. $C_3H_5TiCl_2^+$ does not react further with ethylene. With C_2D_4, HD elimination predominates (>85%). A mechanism involving insertion of C_2D_4 into the Ti,C bond in $CH_3TiCl_2^+$ followed by 1,2-elimination of HD at the β- and γ-carbons is inferred. This demonstrates carbon–carbon bond formation and chain growth in a Ziegler–Natta catalyst site model system, but this gas-phase bimolecular process does not lead to continued polymerization because disposal of the excess internal energy of the complex results in chain termination by unimolecular decomposition.

The active sites of certain Ziegler–Natta catalysts for the polymerization of ethylene are thought to involve a Ti(IV) species which likely has at least a partial positive charge.[1] In particular, the active catalyst system $CH_3TiCl_3 \cdot CH_3AlCl_2$ appears to involve the $[CH_3TiCl_2]^+[CH_3AlCl_3]^-$ ion pair which may be partly or wholly dissociated.[2] Studies of the gas-phase ion chemistry of Ti(IV) species can thus be expected to provide useful mechanistic and thermochemical data leading to improved understanding of the chemistry of the Ziegler–Natta class of catalysts.

Ridge has investigated the initial reactions of ions derived from electron-impact ionization of $TiCl_4$ with a variety of organic molecules using ion cyclotron resonance (ICR) drift techniques.[3-5] In this paper we report the results of studies using ICR trapping

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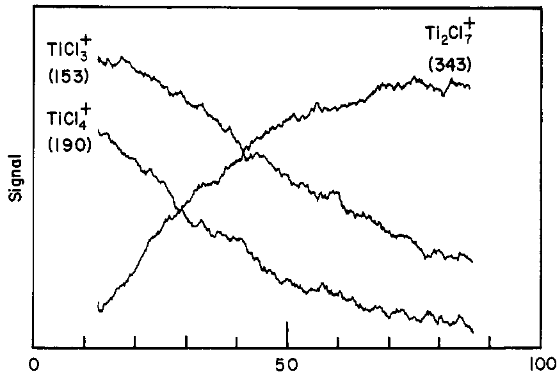

Figure 1. Variation of ion abundance with time following a 10-ms, 15-eV electron beam pulse in 3×10^{-6} torr $TiCl_4$. $Ti_2Cl_7^+$ is formed by reactions of $TiCl_3^+$ and $TiCl_4^+$ with $TiCl_4$. The *m/e* value for the isotopic peak which was followed for each species is indicated in parentheses.

techniques to study secondary and subsequent reactions in the ion chemistry of $TiCl_4$. This leads to determinations of the proton affinity of $TiCl_4$ and halide affinities and ligand binding energies for $TiCl_3^+$. Reactions of a gas-phase ion species, $CH_3TiCl_2^+$, containing a covalent carbon–titanium bond are reported for the first time.

Experimental Section

These studies were carried out by using an ICR spectrometer and techniques which have been previously described.[6,7] Relative accuracy of rate constants and product ratios is ±15% or better. Absolute accuracy of rate constants is limited to a factor of 2 by pressure measurements. All experiments were carried out at ambient temperature which is typically 25 °C in our laboratory.

Chemicals were obtained from commerical sources and used after degassing by repeated freeze–pump–thaw cycles. $TiCl_4$ was purified by vacuum distillation. CH_3TiCl_3 was prepared by reaction of $(CH_3)_3Al$ and $TiCl_4$ following a reported procedure[8] except that the addition of VCl_4 to bind excess $(CH_3)_3Al$ was omitted. The bulk CH_3TiCl_3 was stored at about 270 K in an evacuated bulb. A fresh sample of CH_3TiCl_3 was obtained each day by vacuum distillation from the bulk. At room temperature, the sample decomposed in a few hours as indicated by the appearance of $TiCl_4^+$ in the mass spectrum. When this occurred, either the sample was purified by pumping on the sample at a temperature just below its freezing point or a new sample was prepared.

Results

The electron-impact ICR spectrum of $TiCl_4$ at 15 eV consists of the parent ion $TiCl_4^+$ and the fragment ion $TiCl_3^+$ in a ratio of 3:4. This is in agreement with the previously reported mass spectrum.[3,9] Both ions react rapidly with $TiCl_4$ to give $Ti_2Cl_7^+$. Variation of ion abundance with time following a 10-ms, 15-eV electron beam pulse in 3×10^{-6} torr of $TiCl_4$ is shown in Figure 1. $TiCl_4^+$ displaces a Cl atom from $TiCl_4$ (reaction 1), $k = 3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. $TiCl_3^+$ condenses directly with $TiCl_4$ (reaction 2); at 3×10^{-6} torr the apparent rate constant is 2×10^{-10} cm^3 molecule^{-1} s^{-1}.

$$TiCl_4^+ + TiCl_4 \rightarrow Ti_2Cl_7^+ + Cl \qquad (1)$$

$$TiCl_3^+ + TiCl_4 \rightarrow Ti_2Cl_7^+ \qquad (2)$$

Protonated $TiCl_4$ is produced in a mixture of $TiCl_4$ and CH_4. The ion chemistry of CH_4 is well-known; the principal ions CH_4^+ and CH_3^+ react to give CH_5^+ and $C_2H_5^+$, respectively. These both react with $TiCl_4$ by proton transfer to give $TiCl_4H^+$ (reactions 3 and 4). $TiCl_4$ displaces HCl from $TiCl_4H^+$ to give $Ti_2Cl_7^+$ (reaction 5). Methyl cation, CH_3^+, also reacts directly with $TiCl_4$ by chloride transfer (reaction 6). Protonated benzene, $C_6H_7^+$, is unreactive with $TiCl_4$.

$$CH_5^+ + TiCl_4 \rightarrow TiCl_4H^+ + CH_4 \qquad (3)$$

$$C_2H_5^+ + TiCl_4 \rightarrow TiCl_4H^+ + C_2H_4 \qquad (4)$$

$$TiCl_4H^+ + TiCl_4 \rightarrow Ti_2Cl_7^+ + HCl \qquad (5)$$

$$CH_3^+ + TiCl_4 \rightarrow TiCl_3^+ + CH_3Cl \qquad (6)$$

Halide-transfer reactions dominate the chemistry of $TiCl_3^+$ with alkyl halides. Chloride transfer (reaction 7) is observed with RCl = $CHFCl_2$, CF_2Cl_2, C_6H_5Cl, C_2H_5Cl, *i*-C_3H_7Cl, *t*-C_4H_9Cl, CCl_4, CH_2Cl_2, and $CHCl_3$. Fluoride transfer (reaction 8) is observed with RF = CHF_2Cl, CHF_3, and CF_3Cl. $TiCl_3^+$ is unreactive with CH_3Cl and CF_4.

$$TiCl_3^+ + RCl \rightarrow R^+ + TiCl_4 \qquad (7)$$

$$TiCl_3^+ + RF \rightarrow R^+ + TiFCl_3 \qquad (8)$$

Some of the carbonium ions produced in reactions 7 and 8 react with $TiCl_4$ by halogen-exchange reactions; CHF_2^+ reacts with $TiCl_4$ to give $CHFCl^+$ which reacts further with $TiCl_4$ to produce $CHCl_2^+$ (reactions 9 and 10). Similarly CF_3^+ reacts to give CF_2Cl^+ (reaction 11), which reacts further to yield $CFCl_2^+$ (reaction 12).

$$CHF_2^+ + TiCl_4 \rightarrow CHFCl^+ + TiFCl_3 \qquad (9)$$

$$CHFCl^+ + TiCl_4 \rightarrow CHCl_2^+ + TiFCl_3 \qquad (10)$$

$$CF_3^+ + TiCl_4 \rightarrow CF_2Cl^+ + TiFCl_3 \qquad (11)$$

$$CF_2Cl^+ + TiCl_4 \rightarrow CFCl_2^+ + TiFCl_3 \qquad (12)$$

Halogen-exchange reactions also occur in the chemistry of $TiCl_3^+$ with CH_3F. Reactions 13 and 14 have been previously reported.[5] The products, $TiFCl_2^+$ and TiF_2Cl^+, react with $TiCl_4$ to regenerate $TiCl_3^+$ (reactions 15 and 16). This reaction sequence thus constitutes a chain reaction which converts CH_3F to CH_3Cl and $TiCl_4$ to $TiFCl_3$ and TiF_2Cl_2.

$$TiCl_3^+ + CH_3F \rightarrow TiFCl_2^+ + CH_3Cl \qquad (13)$$

$$TiFCl_2^+ + CH_3F \rightarrow TiF_2Cl^+ + CH_3Cl \qquad (14)$$

$$TiFCl_2^+ + TiCl_4 \rightarrow TiCl_3^+ + TiFCl_3 \qquad (15)$$

$$TiF_2Cl^+ + TiCl_4 \rightarrow TiCl_3^+ + TiF_2Cl_2 \qquad (16)$$

Protonated parent ions, RXH^+, of the alkyl halides RX = CH_3F, CH_3Cl, and C_2H_5Cl react with $TiCl_4$ to give $TiCl_3(RX)^+$ with elimination of HX (reaction 17). The dialkylhalonium ions, R_2X^+, that are formed in these systems[10] are unreactive with $TiCl_4$.

$$RXH^+ + TiCl_4 \rightarrow TiCl_3(RX)^+ + HCl \qquad (17)$$

$TiCl_4$ is displaced from $Ti_2Cl_7^+ \equiv TiCl_3(TiCl_4)^+$ by a variety of ligands L = MeCl, EtCl, MeI, propylene, 1-butene, *cis*- and *trans*-2-butene, isobutene, and benzene (reaction 18). The reverse

$$Ti_2Cl_7^+ + L \rightleftarrows TiCl_3(L)^+ + TiCl_4 \qquad (18)$$

reaction is observed for L = CH_3F. In two-ligand mixtures with $TiCl_4$, the two ligands can compete for the binding site on $TiCl_3^+$ (reaction 19). Figure 2 shows the variation of ion abundance

$$TiCl_3(L_1)^+ + L_2 \rightleftarrows TiCl_3(L_2)^+ + L_1 \qquad (19)$$

with time for a 1:1:1 mixture of $TiCl_4$, CH_3Cl, and C_6H_6 at a total pressure of 6×10^{-6} torr. Benzene, C_6H_6, displaces CH_3Cl in $TiCl_3(CH_3Cl)^+$ to give $TiCl_3(C_6H_6)^+$ (reaction 20), which does

$$TiCl_3(CH_3Cl)^+ + C_6H_6 \rightarrow TiCl_3(C_6H_6)^+ + CH_3Cl \qquad (20)$$

not react further in this system. The variation of ion abundance with time and double-resonance spectra show that reaction 20 proceeds only in the forward direction, indicating that $D(TiCl_3^+–C_6H_6) > D(TiCl_3^+–CH_3Cl)$. Similar results for other

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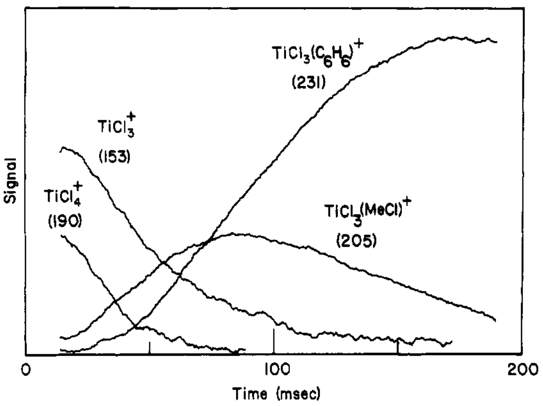


Figure 2. Variation of $TiCl_3(CH_3Cl)^+$ and $TiCl_3(C_6H_6)^+$ abundance with time in a 1:1:1 mixture of $TiCl_4$, CH_3Cl, and C_6H_6 at 6×10^{-6} torr following a 10-ms, 15-eV electron beam pulse. The abundance of $TiCl_3(CH_3Cl)^+$ decays due to the ligand-exchange reaction $TiCl_3(CH_3Cl)^+ + C_6H_6 \rightarrow TiCl_3(C_6H_6)^+ + CH_3Cl$. The *m/e* value for the isotopic peak which was followed for each species is indicated in parentheses.

ligand pairs indicate a relative ligand binding energy order for $TiCl_3^+$ of $CH_3F < TiCl_4 <$ MeCl < EtCl $< C_6H_6$.

The 70-eV mass spectrum of CH_3TiCl_3 contains the parent ion, $CH_3TiCl_3^+$ (9), and fragment ions $TiCl_3^+$ (100), $CH_3TiCl_2^+$ (29), $TiCl_2^+$ (37), and $TiCl^+$ (15), where relative abundances are given in parentheses. A small (<10%) variable amount of $TiCl_4^+$ is also observed due to $TiCl_4$ impurity. This impurity increases with the decomposition of CH_3TiCl_3 and is periodically removed by pumping on the sample at a temperature just below its freezing point. $TiCl_3^+$ reacts with CH_3TiCl_3 by chloride transfer (reaction 21) to give $CH_3TiCl_2^+$ as the major ion (up to two-thirds of the total ionization) at intermediate times. $CH_3TiCl_2^+$ slowly reacts further with CH_3TiCl_3 to produce ions containing two titanium atoms which were not studied.

$$TiCl_3^+ + CH_3TiCl_3 \rightarrow CH_3TiCl_2^+ + TiCl_4 \qquad (21)$$

Ethylene reacts with $CH_3TiCl_2^+$ to give $C_3H_5TiCl_2^+$ and H_2 (reaction 22). The product ion does not react further with ethylene. In order to clarify the mechanism of reaction 22, we

$$CH_3TiCl_2^+ + C_2H_4 \rightarrow C_3H_5TiCl_2^+ + H_2 \qquad (22)$$

studied it by using C_2D_4 (Figure 3). $C_2H_2D_3TiCl_2^+$ is the predominant (>85%) reaction product as shown by comparison of its predicted and observed isotope pattern (Figure 4). With C_2D_4 reaction 22 thus gives mainly HD elimination with only small amounts of H_2 (<10%) and D_2 (<5%) elimination due to scrambling.

Propylene reacts with $CH_3TiCl_2^+$ by elimination of H_2 (reaction 23), paralleling the chemistry with ethylene. The product $C_4H_7TiCl_2^+$ does not react further with propylene. Studies of the ion chemistry of propylene and higher alkenes with $CH_3TiCl_2^+$ are hindered by reactions of these alkenes with the $TiCl_3^+$ present in the CH_3TiCl_3 system. For example, propylene reacts with $TiCl_3^+$ to give $C_3H_5TiCl_2^+$ (reaction 24). This prevents buildup of $CH_3TiCl_2^+$ by consuming the precursor $TiCl_3^+$. Similar condensations with elimination of HCl occur for $TiCl_3^+$ with the butenes as has been previously reported.[3]

$$CH_3TiCl_2^+ + C_3H_6 \rightarrow C_4H_7TiCl_2^+ + H_2 \qquad (23)$$

$$TiCl_3^+ + C_3H_6 \rightarrow C_3H_5TiCl_2^+ + HCl \qquad (24)$$

Discussion

Chloride and Fluoride Affinities of $TiCl_3^+$. Occurrence of the chloride-transfer reaction 7 establishes a lower limit on the chloride affinity of $TiCl_3^+$. The observed results imply $D(TiCl_3^+–Cl^-) > D(R^+–Cl^-)$ for RCl = t-C_4H_9Cl (155), CCl_4 (165), i-C_3H_7Cl (169), $CHCl_3$ (180), C_2H_5Cl (190), $CHFCl_2$ (191), CF_2Cl_2 (192), CH_2Cl_2 (195), and C_6H_5Cl (207); chloride affinities for the corresponding cations R^+ are given in parentheses; see Table I.

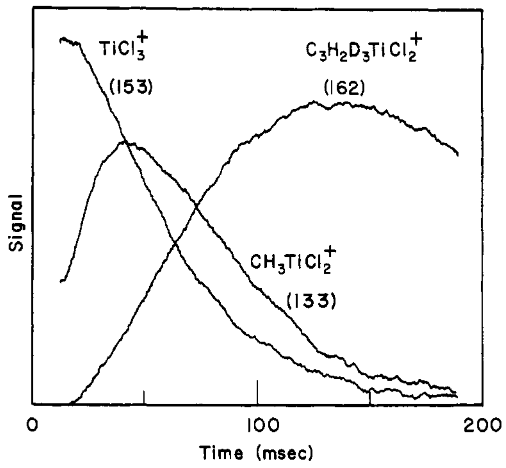


Figure 3. Variation of ion abundance with time for the major ions of interest in 1:1 mixture of CH_3TiCl_3 and C_2D_4 at 6×10^{-6} torr total pressure following a 10-ms, 70-eV electron beam pulse. $CH_3TiCl_2^+$ reacts with C_2D_4 predominantly by eliminating HD to give $C_3H_2D_3TiCl_2^+$. The *m/e* value for the isotopic peak which was followed for each species is indicated in parentheses.

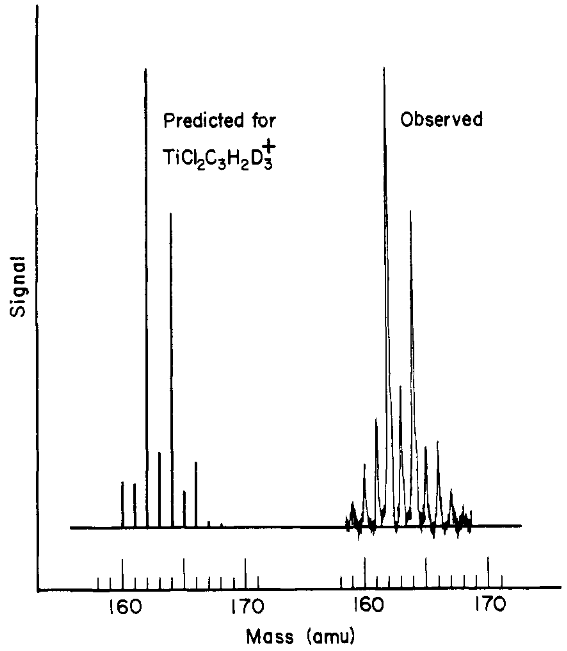


Figure 4. Predicted and observed isotope patterns for the reaction product of $CH_3TiCl_2^+$ with C_2D_4, indicating at least 85% elimination of HD. Discrepanices in the peaks at *m/e* 161, 163, and 165 can be accounted for by a small amount of scrambling to give H_2 and D_2 elimination. The major features of the isotope patterns result from the combination of Ti and Cl isotopes in the species.

The reverse of reaction 7 is observed for RCl = CH_3Cl; $TiCl_3^+$ is produced by chloride transfer from $TiCl_4$ to CH_3^+ (228) (reaction 6). This establishes an upper limit on the chloride affinity of $TiCl_3^+$ so that $D(TiCl_3^+–Cl^-)$ is bracketed in the range 217 ± 11 kcal/mol. This is consistent with a previous result of 223 ± 7 kcal/mol based on the appearance potential of $TiCl_3^+$.[5]

Lower limits for the fluoride affinity of $TiCl_3^+$ are established by observation of reaction 8 for RF = CHF_2Cl (236), CF_3Cl (241), and CHF_3 (250); fluoride affinities for the corresponding cations R^+ are given in parentheses; see Table I. Reaction 8 is not observed with RF = CF_4 (257) or CH_3F (260). We infer that fluoride transfer is endothermic for these cases since reaction 8 goes rapidly to completion with other fluoromethanes. This establishes an upper limit on the fluoride affinity of $TiCl_3^+$ so that $D(TiCl_3^+–F^-)$ is bracketed in the range 254 ± 4 kcal/mol.

The observation of reactions 15 and 21 shows the effect of substituents on the stabilities of titanium ion species as measured

Table I. Chloride and Fluoride Affinities of Carbonium Ions[a]

R^+	$\Delta H_f(R^+)$	$D(R^+–Cl^-)$[h,i]	$D(R^+–F^-)$[i,k]
CH_3^+	264[b]	228[j]	260[j]
CF_3^+	93.8 ± 2[c]	207	257[j]
$C_6H_5^+$	275[d]	207	
CH_2F^+	199.5 ± 6[c]	206	248[j]
CHF_2^+	142 ± 5[c]	201	250[j]
CH_2Cl^+	228.5 ± 0.4[e]	195	233
CF_2Cl^+	130 ± 2[f]	192	241
$CHFCl^+$	179 ± 5[c]	191	236
$C_2H_5^+$	219[b]	190	222[j]
$CHCl_2^+$	211.2 ± 0.4[e,g]	180	220
i-$C_3H_7^+$	191[b]	169	202
$CFCl_2^+$	155 ± 5[c]	168	214
CCl_3^+	198 ± 7[c]	165	208
t-$C_4H_9^+$	167[b]	155	

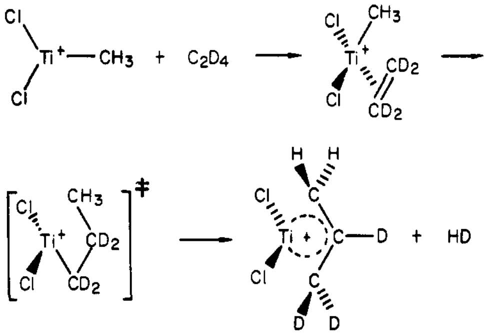
[a] All data in kcal/mol for the gas phase at 298 K. [b] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* 1977, *6*, Suppl. 1. [c] Lias, S. G.; Ausloos, P. *Int. J. Mass Spectrom. Ion Phys.* 1977, *23*, 273. [d] Johnstone, R. A. W.; Mellon, F. A. *J. Chem. Soc., Faraday Trans. 2* 1972, *68*, 1209. [e] Werner, A. S.; Tsai, B. P.; Baer, T. *J. Chem. Phys.* 1974, *60*, 3650. [f] Ajello, J. M.; Huntress, W. T.; Rayerman, P. *J. Chem. Phys.* 1976, *64*, 4746. [g] Lossing, F. P. *Bull. Soc. Chim. Belg.* 1972, *81*, 125. [h] $\Delta H_f(Cl^-) = -55.9$ kcal/mol from: Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* 1971, *NSRDS-NBS 37.* [i] $\Delta H_f(RX)$ except as noted from: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. [j] $\Delta H_f(RX)$ from: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976. [k] $\Delta H_f(F^-) = -58.5$ kcal/mol, ref b.

by their chloride affinities. Reaction 15 implies $D(TiFCl_2^+–Cl^-) > D(CH_3TiCl_2^+–Cl^-)$ and reaction 21 $D(TiCl_3^+–Cl^-) > D(CH_3TiCl_2^+–Cl^-)$, establishing a relative order of ion stabilities of $F–TiCl_2^+ < Cl–TiCl_2^+ < CH_3TiCl_2^+$. This reflects changes in polarizability and inductive effects for these substituents which have been previously noted in other series. For example, ion stability as measured by chloride affinity increases in the same order with substitution for the series $F–CH_2^+$ (206); $Cl–CH_2^+$ (195), $CH_3–CH_2^+$ (190). Chloride affinities for these ions are given in parentheses; see Table I.

Proton Affinity of $TiCl_4$. CH_5^+ and $C_2H_5^+$ proton transfer to $TiCl_4$ (reactions 3 and 4), indicating that $PA(TiCl_4) > PA(CH_4) = 126$ kcal/mol[11] and $PA(TiCl_4) > PA(C_2H_4) = 163.5$ kcal/mol,[12] where $PA(B) \equiv D(B–H^+)$ is the proton affinity of a base B. Protonated benzene, $C_6H_7^+$, is unreactive with $TiCl_4$, indicating that $PA(TiCl_4) < PA(C_6H_6) = 185.8$ kcal/mol.[12] This brackets $PA(TiCl_4)$ in the range 175 ± 11 kcal/mol. This value is similar to proton affinities of organic chlorides, e.g., PA(MeCl) = 160 kcal/mol and PA(EtCl) = 167 kcal/mol.[11]

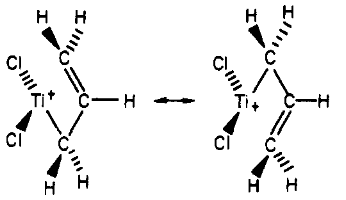
Ligand Binding Energies. Reaction of $TiCl_4$ with $TiCl_4^+$, $TiCl_3^+$, $MeClH^+$, $EtClH^+$, and $MeFH^+$ results in an ion species of the form $TiCl_3(ligand)^+$ (reactions 1, 2, and 17). Observation of ligand-exchange reactions (reaction 19) establishes a relative order of ligand binding energies to $TiCl_3^+$ of MeF < $TiCl_4$ < MeCl < EtCl < C_6H_6. Also, MeI, propylene, 1-butene, *cis*- and *trans*-2-butene, and isobutene are found to bind more strongly to $TiCl_3^+$ than does $TiCl_4$. This basicity order is very similar to that which is found with respect to the proton except that here $TiCl_4$ is below the organic chlorides MeCl and EtCl; uncertainities in the proton affinity values for $TiCl_4$, MeCl, and EtCl are so large, however, that their relative order could be reversed.[11] The $TiCl_3^+$ basicity order is *not* similar to that with respect to Li^+: propylene < MeCl < EtCl < isobutene < MeF < benzene.[13] The basicity order for the transition-metal complex $(\eta^5\text{-}C_5H_5)Ni^+$ has also been found to be similar to that for the proton but unlike that for Li^+.[14] The data for $TiCl_3^+$ basicities is not sufficiently extensive to warrant further analysis, but extensive data sets for basicities with respect to a variety of transition-metal cations will be forthcoming shortly from results obtained by using laser sources of atomic transition-metal cations.[6,7]

Scheme I



(25)

Reactions with Olefins. The role of titanium species in the catalysis of olefin polymerization has prompted this and other studies[3-5] of the gas-phase chemistry of titanium ion species. The key step in olefin polymerization catalysis is carbon–carbon bond formation, but this has not previously been demonstrated in these studies. $TiCl_3^+$ reacts with propylene by eliminating HCl to give $C_3H_5TiCl_2^+$ (reaction 23). This is probably a resonance stabilized allyl-$TiCl_2$ cation (structure I). It does not react further with propylene. HCl is also eliminated in reactions of butenes and higher olefins[3] with $TiCl_3^+$, presumably giving alkyl-substituted versions of I. $TiCl_3^+$ does not react with ethylene.



I

$CH_3TiCl_2^+$ reacts with C_2H_4 to form $C_3H_5TiCl_2^+$ eliminating H_2 (reaction 22). This alone does not demonstrate carbon–carbon bond formation since the reaction could be a simple dehydrogenation of C_2H_4 as has been observed with Ti^+.[7,15] However, with C_2D_4, at least 85% of the reaction proceeds by HD elimination. These results suggest a mechanism (Scheme I), in which after association with the Ti(IV) cation center, the C_2D_4 inserts into the Ti–C bond of $CH_3TiCl_2^+$ as would occur in polymerization of ethylene. The resulting species undergoes unimolecular decomposition because it is unable to dispose of its excess internal energy in any other way in this gas-phase bimolecular process; 1,2-elimination of HD across the β- and γ-carbons gives the resonance-stabilized allyl-$TiCl_2$ cation I. This does not react further with ethylene.

The initial steps of Scheme I are clearly consistent with addition of ethylene to a growing alkyl chain (here represented by $-CH_3$) as would be expected for an active Ziegler–Natta polymerization site. The *final* product in Scheme I does not react further with ethylene, however. Reaction 25 may thus be viewed as a possible termination mechanism for Ziegler–Natta polymerization. The naked $CH_3TiCl_2^+$ appears to be too reactive to be an effective site for long-chain polyethylene growth under these bimolecular gas-phase conditions. Mediation of its reactivity by solvent, the nearby presence of a counterion, or some other device is apparently necessary to control the reactivity of such a site for sustained alkene polymerization.

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