Gas-Phase Chemistry of Ti^+ with Halomethanes, Alkyl Chlorides, Chloroethylenes, and Chlorobenzene

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Abstract: Volatilization/ionization of titanium metal by a pulsed laser is utilized as a source of Ti^+ for studies of its ion chemistry by ion cyclotron resonance spectroscopy. Chloride transfer and oxidative halogen transfer to give TiX^+ are the most prevalent reactions of Ti^+ with the halomethanes and alkyl chlorides. New chloride affinity values of $D(Ti^+\text{-}Cl^-) = 185 \pm 5$ kcal/mol and $D(TiCl^+\text{-}Cl^-) = 202 \pm 6$ kcal/mol are inferred from the results. Homolytic Ti^+-halogen bond dissociation energies are also obtained: $D(Ti^+\text{-}F) = 118 \pm 9$ kcal/mol, $D(Ti^+\text{-}Cl) > 86$ kcal/mol, $D(Ti^+\text{-}Br) > 71$ kcal/mol, and $D(Ti^+\text{-}I) > 57$ kcal/mol. Observation of hydride transfer from CH_3F to TiF_2^+ implies a lower limit for the hydride affinity of TiF_2^+ of $D(TiF_2^+\text{-}H^-) \geq 288$ kcal/mol. Ti^+ dehydrochlorinates vinyl chloride and chlorobenzene, ultimately resulting in a complex of the form $TiCl_2(\text{ligand})^+$ in the case of vinyl chloride. Reactions with the chloroethylenes include oxidation to give $TiCl_2^+$. This charge transfers to several of the chloroethylene neutrals; an ionization potential for $TiCl_2$ of $IP(TiCl_2) = 9.76 \pm 0.11$ eV is inferred.

The role of titanium in catalysis of olefin polymerization and related processes makes studies of the gas-phase chemistry of titanium ion species of particular interest. Mechanistic insights and thermochemical data that are obtained from such studies can be applied to better understand the catalytic processes. Several studies of titanium ion chemistry have been carried out using ion cyclotron resonance (ICR) spectroscopy. Reactivity similar to that expected for Ziegler-Natta active sites has been observed in reactions of $CH_3TiCl_2^+$ with olefins.[1] Ion-molecule reactions of the parent and fragment ions of $TiCl_4$ with olefins,[2] oxygen-containing organic compounds,[3] and other organic molecules[4] have been examined. The chloride affinity of and ligand binding energies to $TiCl_3^+$ have been determined by observation of chloride-transfer[4,5] and ligand-exchange[4] reactions.

It has recently been discovered that a convenient source for production of metal cations for studies of their gas-phase ion chemistry by ICR is afforded by focusing a pulsed laser onto a piece of metal located inside the ICR cell.[6] Such a source has been utilized for extensive studies of copper ion chemistry in our laboratory.[7] We have also found that other atomic metal cations including Ti^+, Al^+, Mg^+, Fe^+, and Cr^+ can be reliably and conveniently produced using this source.[8] In the present paper we report initial studies of Ti^+ generated using this source including its ion chemistry with halomethanes, alkyl chlorides, chloroethylenes, and chlorobenzene. Mechanistic and thermochemical implications of the results are examined.

Experimental Section

All experiments were carried out using an ion cyclotron resonance spectrometer built at the Massachusetts Institute of Technology. Our instrument has a 12-in. pole piece electromagnet which can be operated to about 11.5 kG. The cell is similar to one described by McIver[9] and has stainless steel plates spaced 2.5 cm apart. It is 7.8 cm long with one end open.

A capacitance bridge circuit with the cell as one of the capacitors is used to detect the ions.[10] The signal from the balance point goes to a lock-in amplifer through a LM310 opamp. The lock-in reference output is gated to a pulse transformer which drives the bridge through LM310 opamps. The level on the balance capacitor side is adjusted to balance the bridge when there are no ions. Dc potentials for the cell plates are supplied through the transformer center tap and a 1-mΩ resistor to the balance point. Output from the lock-in is processed by a boxcar amplifier. Magnetic field is scanned to obtain a mass spectrum.

Titanium ions are produced by focusing the beam of a doubled Nd:YAG laser (λ 532 nm) through a sapphire window and the open end of the cell onto a 0.5-cm long, 3-mm diameter Ti rod target mounted on the far end of the cell. The laser is typically operated with 10-ns pulses of 30-50 mJ at 4-8 pps. The beam is focused to a 0.8-mm diameter spot at the target giving a power density of 600-1000 MW/cm². Volatization/ionization of solids by pulsed laser sources has been previously utilized analytically with quadrupole mass spectrometers; the thermal plasma formed by the laser pulse produces kinetically hot monatomic ions.[11] This is consistent with our observation that signal increases with trapping potential up to at least +5 V. Signal is independent of target potential below the drift plate potential but decreases with increasing target potential above the drift plate potential and is cut off above the trapping potential. With a +5-V trapping potential the Ti^+ signal is about 100 times larger than typical signals obtained with electron-beam ionization. Stability improves to about ±20% from pulse to pulse and signal level approaches a more normal range as trapping potential is reduced to +1 V. Signal level and stability also vary with laser pulse energy. Above a threshold, signal level increases slowly with laser pulse energy and stability improves greatly. We typically operate at 20% above threshold in laser energy and pulse the trapping plates to a lower value for 5 ms around the laser pulse to improve stability. The target potential is maintained below the drift plate potential.

General features of the instrumentation and techniques of ICR have been described elsewhere.[9,12] Typically, studies of Ti^+ reactions were carried out by obtaining mass spectra and time plots at about 2×10^{-6} Torr of added gas. Calibrant gases were sometimes added to check mass assignments. All of the reactions reported in this study were confirmed by double-resonance spectra. A mass spectrum with the Ti^+ source and no added gases shows the five isotopes of titanium in relative abundances of 7, 5, 100, 5, and 5% for masses 46, 47, 48, 49, and 50, respectively, compared to the 10.8, 9.9, 100, 7.4, and 7.0% expected from their natural abundances. No Ti^{2+}, Ti_2^+, or TiO^+ was detected; the latter might arise from a surface oxide layer.

All chemicals were obtained from commercial sources and were used without further purification other than degassing by repeated freeze-pump-thaw cycles. Values for rate constants and product distributions for the reactions observed are included where possible as a guide to the practicing ion chemist. Absolute accuracies are limited to a factor of 2 by pressure measurements. Pressure was measured using a flange-mounted Bayard-Alpert ion gauge located 50 cm from the cell on the pump side. Relative accuracy of rate constants and product ratios is ±15% or better. All experiments were carried out at ambient temperature, which is typically 25 °C in our laboratory.

Results

Variation of ion abundance with time for the Ti^+ source in the presence of 2.6×10^{-6} Torr of methyl chloride (CH_3Cl) is shown in Figure 1. Ti^+ reacts with CH_3Cl by chlorine atom transfer to give $TiCl^+$, reaction 1, X = Cl. This is repeated to give $TiCl_2^+$, and again to give $TiCl_3^+$, reactions 2 and 3, X = Cl. These successive chlorine atom transfers result in the oxi-

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dation of Ti(I) to sequentially Ti(II), Ti(III), and finally Ti(IV). The $TiCl_3^+$ produced by reaction 3, X = Cl, is stable, undergoing no further reaction in this system. The rate constant for reaction 1, X = Cl, is $k = 2.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The subsequent reactions proceed at comparable rates.

$$Ti^+ + CH_3X \rightarrow TiX^+ + CH_3\cdot \qquad (1)$$

$$TiX^+ + CH_3X \rightarrow TiX_2^+ + CH_3\cdot \qquad (2)$$

$$TiX_2^+ + CH_3X \rightarrow TiX_3^+ + CH_3\cdot \qquad (3)$$

The ion chemistry of Ti^+ with methyl bromide and methyl iodide is identical with that with methyl chloride. Reactions 1, 2, and 3 with X = Br and I are observed. For methyl fluoride, reactions 1 and 2, X = F, are observed but reaction 3, X = F, is not. Instead, TiF_2^+ reacts with CH_3F by hydride transfer to give TiF_2H and CH_2F^+, reaction 4; the rate constant is 1.4×10^{-10} cm^3 molecule^{-1} s^{-1}. CH_4, CHF_3, and CF_4 are unreactive with Ti^+.

$$TiF_2^+ + CH_3F \rightarrow CH_2F^+ + TiF_2H \qquad (4)$$

The chloromethanes, CH_2Cl_2, $CDCl_3$, and CCl_4, all yield their respective chloride transfer products as the dominant ion at long times in reactions with Ti^+. For methylene chloride, chloride transfer occurs via a $TiCl^+$ intermediate, reactions 5 and 6. Direct chloride transfer does not appear to occur. $CDCl_3$ was studied rather than $CHCl_3$ so that the $CDCl_2^+$ ion (*m/e* 84) could be distinguished from the $TiCl^+$ ion (*m/e* 83). In $CDCl_3$ and CCl_4 chloride transfer is predominantly direct, reactions 7 and 10. Some $TiCl^+$ is also produced, reactions 8 and 11; this reacts further by chloride transfer, reactions 9 and 12. Double-resonance spectra for reactions 9 and 12 saturate at about 10% decrease in the product signal, indicating that about 90% of the product is produced by another process, the direct chloride transfer. The overall reaction rate for Ti^+ in these systems is 4×10^{-10} cm^3 molecule^{-1} s^{-1}.

$$Ti^+ + CH_2Cl_2 \rightarrow TiCl^+ + CH_2Cl\cdot \qquad (5)$$

$$TiCl^+ + CH_2Cl_2 \rightarrow CH_2Cl^+ + TiCl_2 \qquad (6)$$

$$Ti^+ + CDCl_3 \begin{cases} \rightarrow CDCl_2^+ + TiCl & (7) \\ \rightarrow TiCl^+ + CDCl_2\cdot & (8) \end{cases}$$

$$TiCl^+ + CDCl_3 \rightarrow CDCl_2^+ + TiCl_2 \qquad (9)$$

$$Ti^+ + CCl_4 \begin{cases} \rightarrow CCl_3^+ + TiCl & (10) \\ \rightarrow TiCl^+ + CCl_3\cdot & (11) \end{cases}$$

$$TiCl^+ + CCl_4 \rightarrow CCl_3^+ + TiCl_2 \qquad (12)$$

Several Freons were also examined. CF_3Cl reacts to give $TiCl^+$, reaction 13; this is followed by fluoride transfer, reaction 14. The chloride transfer product, CF_3^+, is not observed. CF_2Cl_2 shows fluoride transfer, reaction 15, in addition to producing $TiCl^+$, reaction 16. Some CCl_2^+ is also produced, reaction 17. The $TiCl^+$ reacts further by chloride transfer, reaction 18. Direct chloride transfer to Ti^+ does not appear to occur. In $CFCl_3$, direct chloride transfer to give $CFCl_2^+$ is the major reaction, reaction 19. Fluoride transfer and oxidation to give $TiCl^+$ are also observed, reactions 20 and 21. The latter is followed by a second oxidation to $TiCl_2^+$, and a smaller amount of reaction to give CCl_2^+, reactions 22 and 23. $TiCl_2^+$ reacts by fluoride transfer, reaction 24. Slow fluoride transfer from $CFCl_3$ to the major ion in this system, $CFCl_2^+$, to give CCl_3^+ has been reported[13] but was not observed to occur significantly on the time scale of our experiments.

$$Ti^+ + CF_3Cl \rightarrow TiCl^+ + CF_3\cdot \qquad (13)$$

$$TiCl^+ + CF_3Cl \rightarrow CF_2Cl^+ + TiFCl \qquad (14)$$

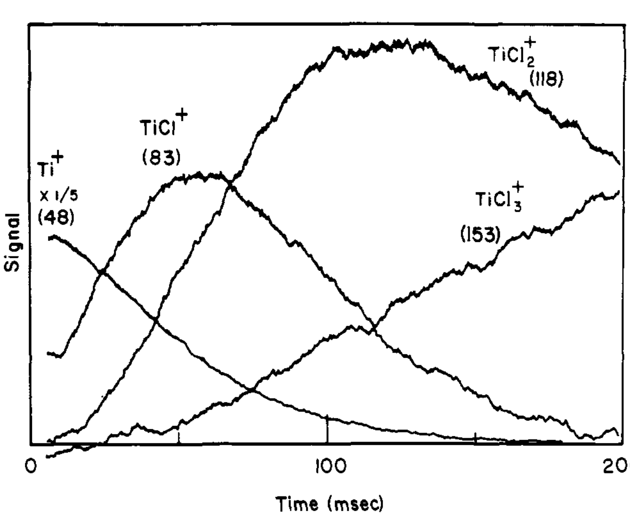

Figure 1. Variation of ion abundance with time following a 10-ns, 50-mJ laser pulse focused onto a titanium rod target in the presence of 2.6×10^{-6} Torr of methyl chloride (CH_3Cl). Ti(I) is oxidized to Ti(IV) by successive chlorine atom transfers from CH_3Cl. The *m/e* value for the isotopic peak which was followed for each ion species is given in parentheses.

$$Ti^+ + CF_2Cl_2 \begin{cases} \xrightarrow{39\%} CFCl_2^+ + TiF & (15) \\ \xrightarrow{51\%} TiCl^+ + CF_2Cl\cdot & (16) \\ \xrightarrow{10\%} CCl_2^+ + TiF_2 & (17) \end{cases}$$

$$TiCl^+ + CF_2Cl_2 \rightarrow CF_2Cl^+ + TiCl_2 \qquad (18)$$

$$Ti^+ + CFCl_3 \begin{cases} \rightarrow CFCl_2^+ + TiCl & (19) \\ \rightarrow CCl_3^+ + TiF & (20) \\ \rightarrow TiCl^+ + CFCl_2\cdot & (21) \end{cases}$$

$$TiCl^+ + CFCl_3 \begin{cases} \rightarrow TiCl_2^+ + CFCl_2\cdot & (22) \\ \rightarrow CCl_2^+ + TiFCl_2 & (23) \end{cases}$$

$$TiCl_2^+ + CFCl_3 \rightarrow CCl_3^+ + TiFCl_2 \qquad (24)$$

Ti^+ reacts with ethyl chloride (CH_3CH_2Cl) to give $TiCl^+$, reaction 25; this reacts further by chloride transfer, reaction 26. The strong double-resonance signal for reaction 26 and time dependence of the $TiCl^+$ and $C_2H_5^+$ signals suggest that direct chloride transfer does not occur in this system. With isopropyl chloride ($(CH_3)_2CHCl$) direct chloride transfer is the major reaction, reaction 27. Some $TiCl^+$ is also produced which reacts further by chloride transfer, reactions 28 and 29. 1,2-Dichloroethane (CH_2ClCH_2Cl) reacts with Ti^+ principally by chloride transfer to give $C_2H_4Cl^+$, reaction 30, but also produces some $C_2H_4^+$, $TiCl_2^+$, and $TiCl^+$, reactions 31-33.

$$Ti^+ + CH_3CH_2Cl \rightarrow TiCl^+ + C_2H_5\cdot \qquad (25)$$

$$TiCl^+ + CH_3CH_2Cl \rightarrow C_2H_5^+ + TiCl_2 \qquad (26)$$

$$Ti^+ + (CH_3)_2CHCl \begin{cases} \rightarrow (CH_3)_2CH^+ + TiCl & (27) \\ \rightarrow TiCl^+ + (CH_3)_2CH\cdot & (28) \end{cases}$$

$$TiCl^+ + (CH_3)_2CHCl \rightarrow (CH_3)_2CH^+ + TiCl_2 \qquad (29)$$

$$Ti^+ + CH_2ClCH_2Cl \begin{cases} \xrightarrow{69\%} C_2H_4Cl^+ + TiCl & (30) \\ \xrightarrow{18\%} C_2H_4^+ + TiCl_2 & (31) \\ \xrightarrow{10\%} TiCl_2^+ + C_2H_4 & (32) \\ \xrightarrow{3\%} TiCl^+ + C_2H_4Cl\cdot & (33) \end{cases}$$

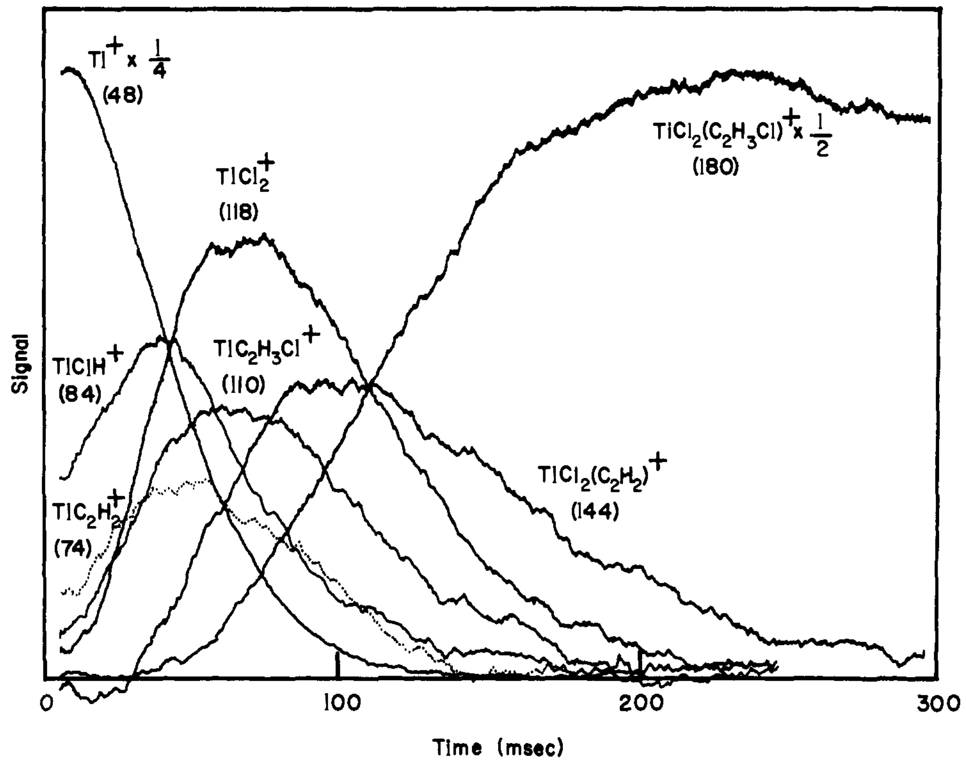

Figure 2. Variation of ion abundance with time for reaction of Ti^+ with vinyl chloride (CH_2CHCl) at 3.0×10^{-6} Torr. Initial dehydrochlorination is followed by displacement to give $Ti(CH_2CHCl)^+$. In the next step this is oxidized to $TiCl_2^+$. Another dehydrochlorination and displacement give $TiCl_2(CH_2CHCl)^+$ as the final, Ti(III) product. The proposed structure for this species is supported by the observation that acetontrile (MeCN) will readily displace CH_2CHCl^+ to give $TiCl_2(MeCN)^+$. The *m/e* value for the isotopic peak which was followed for each ion species is given in parentheses.

The ion chemistry of vinyl chloride and the chloroethylenes with Ti^+ is more complex than that of the halomethanes or alkyl chlorides. Variation of ion abundance with time for the Ti^+ source with vinyl chloride (CH_2CHCl) at 3.0×10^{-6} Torr is shown in Figure 2. The initial reaction is dehydrochlorination, reactions 34 and 35. Both of the possible product channels are observed: elimination of C_2H_2 with retention of HCl by Ti^+ and elimination of HCl with retention of C_2H_2 by Ti^+. The second reaction step appears[14] to be displacement of the HCl or C_2H_2 in these products to give $Ti(CH_2CHCl)^+$, reactions 36 and 38. The next step is oxidation to give $TiCl_2^+$, reaction 39. Relative strengths of the double-resonance spectra for $Ti(CH_2CHCl)^+$ and $TiCl_2^+$ suggest that there is also some direct reaction of $Ti(HCl)^+$ to $TiCl_2^+$, reaction 37. Another dehydrochlorination and displacement follow, reactions 40 and 41; only retention of C_2H_2 is observed in the dehydrochlorination. Vinyl chloride is inferred to be intact in the final product, $TiCl_2(CH_2CHCl)^+$, since addition of acetronitrile (MeCN) results in its displacement, reaction 41. A small amount (<5% of total ionization) of TiC_2HCl^+ is also produced in the vinyl chloride system. This appears to come directly from Ti^+ and reacts further to products which could not be unambiguously established. The overall rate constant for reaction of Ti^+ in vinyl chloride, reactions 34 and 35 together, is 3.3×10^{-10} cm^3 molecule^{-1} s^{-1}.

$$Ti^+ + CH_2CHCl \xrightarrow{72\%} Ti(HCl)^+ + C_2H_2 \quad (34)$$

$$Ti^+ + CH_2CHCl \xrightarrow{28\%} Ti(C_2H_2)^+ + HCl \quad (35)$$

$$Ti(HCl)^+ + CH_2CHCl \rightarrow Ti(CH_2CHCl)^+ + HCl \quad (36)$$

$$Ti(HCl)^+ + CH_2CHCl \rightarrow TiCl_2^+ + C_2H_4 \quad (37)$$

$$Ti(C_2H_2)^+ + CH_2CHCl \rightarrow Ti(CH_2CHCl)^+ + C_2H_2 \quad (38)$$

$$Ti(CH_2CHCl)^+ + CH_2CHCl \rightarrow TiCl_2^+ + C_4H_6\ (?) \quad (39)$$

$$TiCl_2^+ + CH_2CHCl \rightarrow TiCl_2(C_2H_2)^+ + HCl \quad (40)$$

$$TiCl_2(C_2H_2)^+ + CH_2CHCl \rightarrow TiCl_2(CH_2CHCl)^+ + C_2H_2 \quad (41)$$

$$TiCl_2(CH_2CHCl)^+ + MeCN \rightarrow TiCl_2(MeCN)^+ + CH_2CHCl \quad (42)$$

The ion chemistry of *trans*-1,2-dichloroethylene with Ti^+ is similar to that of vinyl chloride. Variation of ion abundance with time for reaction of Ti^+ with *trans*-1,2-dichloroethylene (*trans*-CHClCHCl) at 4.1×10^{-6} Torr is shown in Figure 3. Oxidation of Ti^+ to $TiCl_2^+$ is direct, reaction 43. $TiCl_2^+$ charge transfers to *trans*-CHClCHCl, reaction 44, but also reacts to produce $TiCl_3(C_2H_2)^+$, another oxidation, reaction 45. Acetylene is displaced from this product in a final step to give $TiCl_3(C_2H_2Cl_2)^+$, reaction 46. Addition of acetonitrile (MeCN) also results in acetylene displacement from $TiCl_3(C_2H_2)^+$ to give $TiCl_3(MeCN)^+$, reaction 47. Displacement of $C_2H_2Cl_2$ from $TiCl_3(C_2H_2Cl_2)^+$ by MeCN could not be confirmed because of the long reaction sequence and high mass of this product. The rate constant for reaction of Ti^+ in this system is 4.8×10^{-10} cm^3 molecule^{-1} s^{-1}.

$$Ti^+ + trans\text{-}CHClCHCl \rightarrow TiCl_2^+ + C_2H_2 \quad (43)$$

$$TiCl_2^+ + trans\text{-}CHClCHCl \rightarrow CHClCHCl^+ + TiCl_2 \quad (44)$$

$$TiCl_2^+ + trans\text{-}CHClCHCl \rightarrow TiCl_3(C_2H_2)^+ + Cl\cdot \quad (45)$$

$$TiCl_3(C_2H_2)^+ + trans\text{-}CHClCHCl \rightarrow TiCl_3(C_2H_2Cl_2)^+ + C_2H_2 \quad (46)$$

$$TiCl_3(C_2H_2)^+ + MeCN \rightarrow TiCl_3(MeCN)^+ + C_2H_2 \quad (47)$$

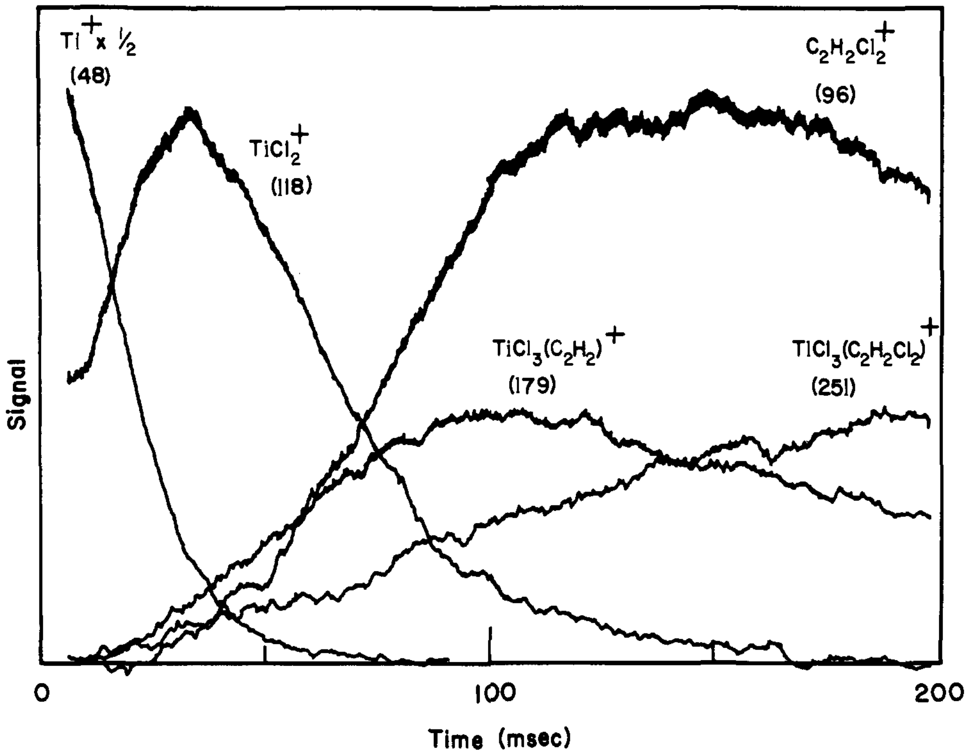

Figure 3. Variation of ion abundance with time for reaction of Ti^+ with *trans*-1,2-dichloroethylene (*trans*-CHClCHCl) at 4.1×10^{-6} Torr. Initial oxidation to form $TiCl_2^+$ is followed by charge transfer, giving $C_2H_2Cl_2^+$, or condensation with loss of Cl, another oxidation, giving $TiCl_3(C_2H_2)^+$. This is followed by displacement to produce the final, Ti(IV) product $TiCl_3(C_2H_2Cl_2)^+$. The proposed structure for the $TiCl_3(C_2H_2)^+$ species is supported by the observation that acetonitrile (MeCN) will readily displace C_2H_2 to give $TiCl_3(MeCN)^+$. The *m/e* value for the isotopic peak which was followed for each ion species is given in parentheses.

With 1,1-dichloroethylene (CH_2CCl_2), oxidation of Ti^+ to $TiCl_2^+$ is direct, reaction 48. Charge transfer to CH_2CCl_2 is not observed for $TiCl_2^+$ in this system. Instead, $TiCl_2^+$ reacts by chloride transfer, reaction 49, to give $C_2H_2Cl^+$, which reacts further. Trichloroethylene ($CHClCCl_2$) initially oxidizes Ti^+ to $TiCl_2^+$, but some $CHCCl^+$ is also generated, reactions 50 and 51. Both of these products rapidly charge transfer to $CHClCCl_2$, reactions 52 and 53. $TiCl_2^+$ also reacts by chloride transfer to produce some $C_2HCl_2^+$, reaction 54. The overall rate constant for reaction of Ti^+ in this system is 3.3×10^{-10} cm^3 molecule^{-1} s^{-1}. In tetrachloroethylene (C_2Cl_4), Ti^+ reacts to give $TiCl_2^+$, reaction 55. This charge transfers to C_2Cl_4, reaction 56, and also gives some $C_2Cl_2^+$, reaction 57. $C_2Cl_2^+$ charge transfers to C_2Cl_4, reaction 58.

$$Ti^+ + CH_2CCl_2 \rightarrow TiCl_2^+ + C_2H_2 \qquad (48)$$

$$TiCl_2^+ + CH_2CCl_2 \rightarrow C_2H_2Cl^+ + TiCl_3 \qquad (49)$$

$$Ti^+ + CHClCCl_2 \xrightarrow{78\%} TiCl_2^+ + C_2HCl \qquad (50)$$

$$Ti^+ + CHClCCl_2 \xrightarrow{22\%} C_2HCl^+ + TiCl_2 \qquad (51)$$

$$C_2HCl^+ + CHClCCl_2 \rightarrow CHClCCl_2^+ + C_2HCl \qquad (52)$$

$$TiCl_2^+ + CHClCCl_2 \rightarrow CHClCCl_2^+ + TiCl_2 \qquad (53)$$

$$TiCl_2^+ + CHClCCl_2 \rightarrow C_2HCl_2^+ + TiCl_3 \qquad (54)$$

$$Ti^+ + C_2Cl_4 \rightarrow TiCl_2^+ + C_2Cl_2 \qquad (55)$$

$$TiCl_2^+ + C_2Cl_4 \rightarrow C_2Cl_4^+ + TiCl_2 \qquad (56)$$

$$TiCl_2^+ + C_2Cl_4 \rightarrow C_2Cl_2^+ + TiCl_4 \qquad (57)$$

$$C_2Cl_2^+ + C_2Cl_4 \rightarrow C_2Cl_4^+ + C_2Cl_2 \qquad (58)$$

Ti^+ dehydrochlorinates chlorobenzene eliminating exclusively HCl. This occurs at least three times in succession, reactions 59, 60, and 61. $TiC_6H_4^+$, $TiC_{12}H_8^+$, and $TiC_{18}H_{12}^+$ all react further with chlorobenzene to give products which were not fully investigated. Similar chemistry has been reported by Ridge and co-workers for reaction of Fe^+ with phenyl halides.[15]

$$Ti^+ + C_6H_5Cl \rightarrow TiC_6H_4^+ + HCl \qquad (59)$$

$$TiC_6H_4^+ + C_6H_5Cl \rightarrow TiC_{12}H_8^+ + HCl \qquad (60)$$

$$TiC_{12}H_8^+ + C_6H_5Cl \rightarrow TiC_{18}H_{12}^+ + HCl \qquad (61)$$

Discussion

Oxidative halogen transfer reactions of Ti^+ with organic halides, reaction 62, are important in much of the chemistry

$$Ti^+ + RX \rightarrow TiX^+ + R\cdot \qquad (62)$$

studied in this work. Observation that reaction 62 proceeds exothermically to the right implies that $D(Ti^+\text{-}X) > D(R\text{-}X)$; i.e., the homolytic Ti^+-halogen bond dissociation energy is greater than the homolytic bond dissociation energy for the organic halide, RX. Observation of reaction 1, X = Cl, Br, and I, for reaction of Ti^+ with the methyl halides thus implies that $D(Ti^+\text{-}Cl) > 83$ kcal/mol, $D(Ti^+\text{-}Br) > 71$ kcal/mol, and $D(Ti^+\text{-}I) > 57$ kcal/mol; see Table I. Similarly, from reactions 2 and 3, X = Cl, Br, and I, we infer the same limits for $D(TiX^+\text{-}X)$ and $D(TiX_2^+\text{-}X)$, X = Cl, Br, and I, respectively. The methyl halides generally provide the best values for these lower limits since other organic halides for which $D(R\text{-}X)$ is known give the same or lower limits, for example, $D(Et\text{-}Cl) = 82$ kcal/mol and $D(CCl_3\text{-}Cl) = 70$ kcal/mol. Only for CF_3Cl is a higher value obtained, $D(CF_3\text{-}Cl) = 86$ kcal/mol. Thus, the observation that reaction 13 proceeds exothermically to the right provides a slightly better lower limit for $D(Ti^+\text{-}Cl)$, $D(Ti^+\text{-}Cl) > 86$ kcal/mol.

Observation of reactions 1 and 2 for X = F implies $D(CH_3\text{-}F) = 108$ kcal/mol $< D(Ti^+\text{-}F)$ and $D(TiF^+\text{-}F)$; see Table I. Since all of the observed halogen transfers are fast and

Table I. Homolytic R-X Bond Dissocation Energies, *D*(R-X), for Some Organic Halides Studied in This Work[a]

R-X	ΔH_f(RX)	ΔH_f(R)	ΔH_f(X)	*D*(R-X)
CH_3-Cl	−20.0[b]	34.8	28.9	84
CH_3-Br	−9.5[c]	34.8	26.7	71
CH_3-I	3.3[c]	34.8	25.5	57
C_2H_5-Cl	−26.7[c]	26.5[c]	28.9	82
CCl_3-Cl	−22.9	19 ± 2	28.9	71
CF_3-Cl	−169.2	−112.4	28.9	86
CH_3-F	−55 ± 2[c]	34.8	18.9	109
CHF_2-F	−166.6	−59.2[d]	18.9	126
CF_3-F	−223.0	−112.4	18.9	130

[a] All data are given in kcal/mol for 298 K and are from ref 16 except as noted. [b] Reference 17. [c] Reference 18. [d] J. A. Kerr and D. M. Timlin, *Int. J. Chem. Kinet.*, **3,** 427-441 (1971).

Table II. Chloride Affinities of Ions Studied in This Work[a]

R^+	$\Delta H_f(R^+)$	ΔH_f(RCl)	$D(R^+\text{-}Cl^-)$[m]
CH_3^+	264[b]	−20.0 ± 0.5[h]	228
$C_2H_3^+$	271[b]	5.0[j]	210
$C_6H_5^+$	275[c]	12.2 ± 0.2[k]	207
CF_3^+	94 ± 2[d]	−169.2 ± 0.8[h]	207
CH_2Cl^+	228.8 ± 0.4[e]	−22.8 ± 0.2[h]	196
CF_2Cl^+	130 ± 2[f]	−117.5 ± 2[h]	192
$C_2H_5^+$	219[b]	−26.7[j]	190
$CHCl_2^+$	211.2 ± 0.4[e,g]	−24.6 ± 0.2[l]	180
Ti^+	271.8[h]	36.9 ± 10[h]	179
$(CH_3)_2CH^+$	191[b]	−33.6 ± 1.0[k]	169
$CFCl_2^+$	155 ± 5[i]	−69.0 ± 1.5[h]	168
CCl_3^+	192[i]	−22.9 ± 0.5	159

[a] All data are given in kcal/mol for 298 K. [b] Reference 19. [c] R. A. W. Johnstone and F. A. Mellon, *J. Chem. Soc., Faraday Trans. 2,* **68,** 1209 (1972). [d] Reference 17. [e] A. S. Werner, B. P. Tsai, and T. Baer, *J. Chem. Phys.*, **60,** 3650 (1974). [f] J. M. Ajello, W. T. Huntress, and P. Rayerman, *ibid.*, **64,** 4746 (1976). [g] F. P. Lossing, *Bull. Soc. Chim. Belg.*, **81,** 125 (1972). [h] Reference 16. [i] S. G. Lais and P. Ausloos, *Int. J. Mass Spectrom. Ion Phys.*, **23,** 273 (1977). [j] Reference 18. [k] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970. [l] A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **3,** 117 (1974). [m] $\Delta H_f(Cl^-) = -55.9 \pm 0.5$ kcal/mol from ref 16.

comparable in rate, we infer that the lack of reaction of Ti^+ with CHF_3 and CF_4 implies that reaction 62 for CHF_3 and CF_4 is endothermic. This establishes an upper limit for $D(Ti^+\text{-}F)$ of $D(CHF_2\text{-}F)$ = 126 kcal/mol. Thus, $D(Ti^+\text{-}F)$ = 118 ± 9 kcal/mol.

The reaction of TiF_2^+ with CH_3F, reaction 4, to give CH_2F^+ is the only hydride-transfer reaction observed in this study. It is interesting that hydride transfer from carbon to titanium is possible at all. This may have implications for possible mechanisms of reaction of organometallic titanium species and catalysts. The observation of reaction 4 implies that the hydride affinity of TiF_2^+, $D(TiF_2^+\text{-}H^-)$, is greater than the hydride affinity of CH_2F^+, $D(CH_2F^+\text{-}H^-)$. Using heats of formation values of 200 kcal/mol[19] for CH_2F^+, 33.2 kcal/mol[16] for H^-, and −55 ± 2 kcal/mol[18] for CH_3F, we calculate $D(CH_2F^+\text{-}H^-)$ = 288 kcal/mol. Therefore, $D(TiF_2^+\text{-}H^-) \geq 288 \pm 2$ kcal/mol.

Chloride transfer, reaction 63, is also prevalent in the

$$Ti^+ + RX \rightarrow R^+ + TiCl \qquad (63)$$

chemistry of Ti^+ with organic halides. Chloride transfer to Ti^+ is seen for CCl_4 (159), $CFCl_3$ (168), $(CH_3)_2CHCl$ (169), and $CHCl_3$ (180) but not for C_2H_5Cl (190), CF_2Cl_2 (192), CH_2Cl_2 (196), CF_3Cl (207), C_6H_5Cl (207), C_2H_3Cl (210), or CH_3Cl (228); chloride affinities, $D(R^+\text{-}Cl^-)$, are given in parentheses (see Table II). These results are consistent with a chloride affinity for Ti^+ between 180 and 190 kcal/mol or $D(Ti^+\text{-}Cl^-)$ = 185 ± 5 kcal/mol. This is somewhat higher than the literature value, Table II, of $D(Ti^+\text{-}Cl^-)$ = 179 ± 11 kcal/mol, but well within the reported range of uncertainty. Using our new value for $D(Ti^+\text{-}Cl^-)$ = 185 ± 5 kcal/mol we calculate a heat of formation for TiCl of ΔH_f(TiCl) = 36 ± 6 kcal/mol.

Chloride transfer from CH_2ClCH_2Cl to Ti^+ was also observed in our work, reaction 30. The chloride affinity of $C_2H_4Cl^+$ is not well established. We have observed, however, that CH_2ClCH_2Cl chloride transfers to $CHCl_2^+$.[8] The chloride affinity of $C_2H_4Cl^+$ is thus below 180 kcal/mol. Observation of reaction 30 is therefore consistent with the other chloride-transfer results obtained in this work.

$TiCl^+$ is formed in a number of the systems studied and chloride transfer, reaction 64, is observed with CCl_4 (159),

$$TiCl^+ + TX \rightarrow R^+ + TiCl_2 \qquad (64)$$

$CFCl_3$ (168), $(CH_3)_2CHCl$ (169), $CHCl_3$ (180), C_2H_5Cl (190), CF_2Cl_2 (192), and CH_2Cl_2 (196) but not CF_3Cl (207) or CH_3Cl (228). $TiCl^+$ is not formed in the C_6H_5Cl or C_2H_3Cl systems. These results are consistent with a chloride affinity for $TiCl^+$ between 196 and 207 kcal/mol or $D(TiCl^+\text{-}Cl^-)$ = 202 ± 6 kcal/mol.

Another interesting thermochemical result is provided by examination of the ion chemistry of Ti^+ with the chloroethylenes. $TiCl_2^+$ is produced in all of these systems but charge transfers to the neutral chloroethylene only in certain cases: with C_2Cl_4 (9.32 ± 0.01), C_2HCl_3 (9.46 ± 0.01), and *trans*-CHClCHCl (9.65 ± 0.02) but not CH_2CCl_2 (9.86 ± 0.02) and CH_2CHCl (10.00 ± 0.01); ionization potentials are given in parentheses (eV).[19] These results suggest that $IP(TiCl_2)$ falls between 9.65 and 9.86 eV or $IP(TiCl_2)$ = 9.76 ± 0.11 eV.

The dehydrochlorination reactions seen in the vinyl chloride and *trans*-1,2-dichloroethylene systems are similar to those observed for reaction of alkyl halides and alcohols with Li^+, Na^+, Fe^+, Co^+, Ni^+, and Cu^+.[7,20,21] Interestingly, with Ti^+ the dehydrochlorination-displacement sequence is combined with oxidation so that for vinyl chloride the final product is a $TiCl_2(\text{ligand})^+$ complex and for *trans*-1,2-dichloroethylene a $TiCl_3\,(\text{ligand})^+$ complex. Vinyl chloride and *trans*-1,2-dichloroethylene could thus serve as initiation reagents for ligand exchange studies to obtain relative ligand binding energies to $TiCl_2^+$ and $TiCl_3^+$. Reactions of alkyl halides with atomic metal cations have been used with success in such studies to obtain ligand binding energies to Li^+ and Cu^+.[7,20] However, unlike Li^+ and Cu^+, Ti^+ undergoes direct reactions with many likely ligand molecules.[8] Ti^+ may thus not prove to be a particularly convenient source for initiating ligand exchange studies of titanium ion complexes. Studies of $TiCl_3^+$-ligand binding energies are readily carried out using as an initiator $TiCl_4^+$ ions obtained by electron impact ionization of $TiCl_4$.[4]

The ion chemistry of Ti^+ with organic halides shows several instances of reaction of Ti^+ to give two product channels in which there are two species, one species carrying the charge in one channel and the other species carrying the charge in the other channel. In particular, this occurs for $CDCl_3$, CCl_4, $CFCl_3$, $(CH_3)_2CHCl$, and CH_2ClCH_2Cl, where the two channels are exothermic chloride transfer, reaction 65, and chlorine transfer to give $TiCl^+$, reaction 66.

$$Ti^+ + RCl \begin{cases} \rightarrow R^+ + TiCl & (65) \\ \rightarrow TiCl^+ + R\cdot & (66) \end{cases}$$

The second channel appears to be relatively small in all of these systems. Its appearance at all, however, is inconsistent with the expectation that the collision complex $[TiCl\text{-}R]^+$ should always dissociate to leave the charge on the species with the lowest ionization potential assuming that the difference in ionization potentials for the two species is substantial. A likely explanation is that reaction 66 may actually be reaction 67, where an electron is ejected at some stage in the reaction

$$Ti^+ + RCl \rightarrow R^+ + TiCl^+ + e^- \qquad (67)$$

process, giving two ionic products. Collisional ionization processes were also observed in the ion chemistry of some molecules with Cu^+ produced using the pulsed laser source.[7] It is not apparent with Ti^+ whether these processes result because of excess kinetic or internal energy of the laser-produced Ti^+. Variation of the trapping potential during the laser pulse, which affects the amount of Ti^+ retained in the cell, does not affect the product distribution of reactions 65 and 66.

The possibility that hot Ti^+ may be inducing significant amounts of endothermic reaction channels to occur is cause for caution in interpreting the thermochemical results obtained from this study. Results from quadrupole mass spectrometer studies indicate that ions produced with a pulsed laser source are kinetically hot with a spread of translational energies up to several electronvolts.[11] The physical behavior of the ion population in the ICR cell provides further evidence that some of the primary atomic ions have high kinetic energies: the number of ions trapped increases with increasing trapping potential through the highest value we have tried, 5 V. However, ICR spectra of the variation of ion abdundance with time and double-resonance spectra appear identical with those obtained with electron-impact ionization. In some systems up to about 10% of anomalous reaction products may be attributed to "hot" primary ions as discussed above. In these and other systems, the observed chemistry was not affected by variation of the trapping potential either during or after the laser pulse even though this should vary the fraction of "hot" ions in the cell. The thermochemical results obtained here are internally consistent and in reasonable agreement with the previously reported literature values. While results to date thus appear to warrant a cautiously positive attitude toward the validity of results obtained with the laser ion source, continued scrutiny of this question will be necessary until experience with a larger number of systems or some more definitive experiments lead to a final judgment.

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