

Halogen Exchange Reactions of Methyl Fluoride with Gaseous Group 4 Chlorocations and Solid Group 3 Chlorides. A Study of Parallels in the Chemistry of Isoelectronic Species[†]

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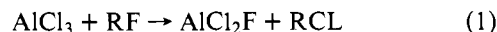
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Abstract: Halogen exchange reactions of CH₃F with SiCl₃⁺ and TiCl₃⁺ and several other halosilicon and halotitanium ions are described and reaction rates are reported. The halogen exchange reactions of CH₃F with AlCl₃ and ScCl₃ are described. The mechanism of the reaction is considered in view of kinetic data and observations of related processes. Periodic and isoelectronic effects are discussed. The order of chloride affinities of the group 4 trichlorocations are found to be TiCl₃⁺ > SiCl₃⁺ > GeCl₃⁺ > SnCl₃⁺ > CCl₃⁺. The three cations with the lowest chloride affinities are found to be unreactive toward CH₃F. Limits on the heats of formation of a number of halotitanium and halosilicon cations are deduced from reactions observed.

Introduction

Recently, we have shown that TiCl₃⁺, a powerful electron acceptor, has a rich chemistry with simple organic species in the gas phase.^{1,2} In an attempt to discover generalizations which might govern the reactions of such species we have begun to compare the chemistry of TiCl₃⁺ with that of CCl₃⁺, SiCl₃⁺, GeCl₃⁺, and SnCl₃⁺. We report here halogen exchange reactions of TiCl₃⁺ and SiCl₃⁺ with CH₃F. We also report halogen exchange reactions of CH₃F with the solid aluminum and scandium trichlorides and chloride affinities of the group 4 trichlorocations as determined by competitive chloride transfer reactions.

An introductory word about halogen transfer reactions of alkyl halides will be useful in discussing the results. The group 3A halides typically react with alkyl chlorides and bromides to exchange a heavier halogen for a lighter one.³ General features of these halogen exchange reactions which will be useful in discussing the present results are: (1) They seem to involve a one-to-one donor-acceptor adduct. Little kinetic data are available on such processes but those which are available support a mechanism involving a one-to-one adduct.³ Such adducts have been implicated as intermediates in Friedel-Crafts alkylation.⁴ (2) They occur as both homogeneous³ and heterogeneous processes.⁵⁻⁸ (3) Only AlCl₃ has been reported to react with aliphatic fluorides.⁵ The reaction



proceeds under very mild conditions where RF is any of several olefinic fluorides.⁵ BCl₃ does not similarly react.⁵ AlCl₃ also exchanges a chloride for a fluorine with a number of chlorofluoroalkanes.⁶⁻⁸

Experimental Section

The ion chemistry described below was examined using a conventional ion cyclotron resonance instrument described elsewhere.⁹ The reaction rate constants were determined by the method of Comisarow and Marshall.¹⁰ All the reported rate constants are the average of at least three determinations. Pressures of 2 × 10⁻⁵ Torr and higher were measured with an MKS Baratron capacitance manometer. Where necessary Baratron readings were extrapolated to lower pressures by monitoring the total ion current as pressure was decreased. With the normal configuration of fields ion collection efficiency does not depend on pressure so total ion current can be considered proportional to pressure. Reaction pathways were confirmed by ion cyclotron double resonance.¹¹ Where two reactants gave the same product the pro-

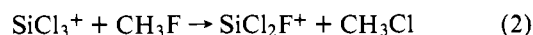
portion of product coming from a given reactant was determined by ejecting that reactant from the cell with the double resonance oscillator.¹² All reagents were obtained commercially with a stated purity greater than 99%. No significant impurities were detected in the mass spectra of the reagents. Liquid TiCl₄, SiCl₄, GeCl₄, and CCl₄ were subjected to freeze-pump-thaw cycles to remove dissolved gases. The CCl₂F⁺ ion was produced by electron impact on CCl₂F₂ (Freon 12) obtained from Du Pont.

In a typical experiment SiCl₄, for example, was admitted to the instrument through one inlet and maintained at constant pressure (~10⁻⁶ Torr). The energy of the ionizing electron beam was 70 eV. Methyl fluoride was admitted through a second inlet. Spectra from which rate constants were calculated were taken at several different CH₃F pressures (~5 × 10⁻⁶ to ~5 × 10⁻⁵ Torr).

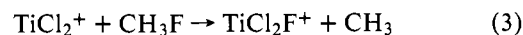
Reactions between CH₃F gas and solid ScCl₃ and AlCl₃ were observed as follows. A Schlenk tube containing 1.0 g of ScCl₃ (6.6 × 10⁻³ mol) was attached to one inlet of the ion cyclotron resonance spectrometer. A bulb containing 2.0 × 10⁻² mol of CH₃F gas was attached to the inlet also. The inlet was evacuated and the CH₃F bulb opened to expose the solid to this gas. The pressure created by the gas in the inlet was approximately 450 Torr. Mass spectra were taken of the gas over the solid at regular intervals. Relative amounts of CH₃F and CH₃Cl were determined from these spectra. The total pressure was determined at the end of the experiment to assure that it stayed constant (i.e., to assure that a significant amount of adsorption had not occurred). In an analogous fashion, the reaction between 0.5 g (3.8 × 10⁻³ mol) of AlCl₃ and 0.39 g (1.14 × 10⁻² mol) of CH₃F gas was studied. ScCl₃ was obtained from the Research Organic/Inorganic Chemical Corp., AlCl₃ from Matheson Coleman and Bell, and CH₃F from Matheson Gas Co.

Results and Discussion

Two different kinds of reactions occur between methyl fluoride and primary ions formed by electron impact on the group 4 chlorides. The first is a halogen exchange process typified by the reaction



The ions which react in this manner also include SiCl₂F⁺, TiCl₃⁺, TiCl₂F⁺, TiClF₂⁺, TiCl₂⁺, TiClF⁺, and TiCl⁺. Competitive with the halogen exchange reaction in some cases are halogen abstraction reactions such as the reaction



(see Table I). As noted in Table I the CCl₃⁺ analogue of reaction 2 is immeasurably slow in both forward and reverse directions under our experimental conditions. GeCl₃⁺ and SnCl₃⁺ are also unreactive.

There is a direct relationship between the reactivity of the

[†] Based in part on the Masters Thesis of R. D. Kinser, University of Delaware, 1976.

Table I. Halogen Exchange and Fluorine Transfer Reactions of CH₃F

Reactants	Products	$k \times 10^{10}, \text{cm}^3$ $\text{molecule}^{-1} \text{s}^{-1} \text{ }^a$	Thermochemical inference, ^b kcal/mol
Ti ⁺ + CH ₃ F	→ TiF ⁺ + CH ₃	1.2	$D(\text{Ti}^+-\text{F}) \geq 109$
TiF ⁺ + CH ₃ F	→ TiF ₂ ⁺ + CH ₃	1.6	$D(\text{TiF}^+-\text{F}) \geq 109$
TiCl ⁺ + CH ₃ F	→ TiClF ⁺ + CH ₃	0.2	$D(\text{TiCl}^+-\text{F}) \geq 109$
TiClF ⁺ + CH ₃ F	→ TiF ₂ ⁺ + CH ₃ Cl	1.0	$D(\text{TiF}^+-\text{F}) - D(\text{TiF}^+-\text{Cl}) \geq 27$
	→ TiClF ₂ ⁺ + CH ₃	0.4	$D(\text{TiClF}^+-\text{F}) \geq 109$
TiClF ₂ ⁺ + CH ₃ F	→ TiF ₃ ⁺ + CH ₃ Cl	0.5	$D(\text{TiF}_2^+-\text{F}) - D(\text{TiF}_2^+-\text{Cl}) \geq 27$
TiCl ₂ ⁺ + CH ₃ F	→ TiClF ⁺ + CH ₃ Cl	1.0	$D(\text{TiCl}^+-\text{F}) - D(\text{TiCl}^+-\text{Cl}) \geq 27$
	→ TiCl ₂ F ⁺ + CH ₃	0.5	$D(\text{TiCl}_2^+-\text{F}) \geq 109$
TiCl ₂ F ⁺ + CH ₃ F	→ TiClF ₂ ⁺ + CH ₃ Cl	0.9	$D(\text{TiClF}^+-\text{F}) - D(\text{TiClF}^+-\text{Cl}) \geq 27$
TiCl ₃ ⁺ + CH ₃ F	→ TiCl ₂ F ⁺ + CH ₃ Cl	0.7	$D(\text{TiCl}_2^+-\text{F}) - D(\text{TiCl}_2^+-\text{Cl}) \geq 27$
SiCl ₂ ⁺ + CH ₃ F	→ SiCl ₂ F ⁺ + CH ₃	2.0	$D(\text{SiCl}_2^+-\text{F}) \geq 109$
SiCl ₂ F ⁺ + CH ₃ F	→ SiClF ₂ ⁺ + CH ₃ Cl	0.5	$D(\text{SiClF}^+-\text{F}) - D(\text{SiClF}^+-\text{Cl}) \geq 27$
SiCl ₃ ⁺ + CH ₃ F	→ SiCl ₂ F ⁺ + CH ₃ Cl	1.0	$D(\text{SiCl}_2^+-\text{F}) - D(\text{SiCl}_2^+-\text{Cl}) \geq 27$
CCl ₃ ⁺ + CH ₃ F	→ CCl ₂ F ⁺ + CH ₃ Cl	<0.05	
CCl ₃ F ⁺ + CH ₃ Cl	→ CCl ₃ ⁺ + CH ₃ F	<0.05	
GeCl ₃ ⁺ + CH ₃ F	→ GeCl ₂ F ⁺ + CH ₃ Cl	<0.05	
SnCl ₃ ⁺ + CH ₃ F	→ SnCl ₂ F ⁺ + CH ₃ Cl	<0.05	

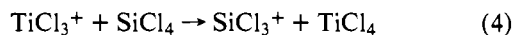
^a Estimated uncertainty in rate constant measurements is $\pm 30\%$. ^b Based on $D(\text{CH}_3-\text{F}) = 109$ kcal/mol and $D(\text{CH}_3-\text{Cl}) = 81.9$ kcal/mol from data in A. S. Rogers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **3**, 117 (1974).

Table II. Chloride Affinities of MCl₃⁺ Ions^a

M ^b	AP (MCl ₃ ⁺) ^c from MCl ₄ , eV	CA (MCl ₃ ⁺) ^d kcal/mol
Ti	13.3 \pm 0.3 ^e	223 \pm 7
Si	12.48 \pm 0.02 ^f	204.4 \pm 0.5
Ge		201 \pm 4 ^g
Sn	12.2 \pm 0.4 ^h	198 \pm 9
C	11.65 \pm 0.10 ⁱ	185 \pm 2 ⁱ

^a Chloride affinity of MCl₃⁺ is $D(\text{MCl}_3^+-\text{Cl}^-)$. ^b Listed in the order of decreasing MCl₃⁺ chloride affinity as determined in the present study. ^c AP (MCl₃⁺) from MCl₄ is the appearance potential of the MCl₃⁺ fragment from MCl₄ and is the minimum energy which must be imparted to an electron beam to produce MCl₃⁺ from MCl₄. It is assumed to be ΔH for the process $\text{MCl}_4 \rightarrow \text{MCl}_3^+ + \text{Cl}^- + e$. ^d Chloride affinities calculated from appearance potentials using the relationship $\text{CA}(\text{CCl}_3^+) = \text{AP}(\text{CCl}_3^+) - \text{EA}(\text{Cl}^-)$ where EA (Cl⁻) is the electron affinity of chlorine atom and is taken to be 3.613 eV (R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38**, 1540 (1963)). ^e R. W. Kiser, J. G. Dillard, and D. L. Dugger in "Mass Spectrometry in Inorganic Chemistry", *Adv. Chem. Ser.*, No. **72** (1968). ^f 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.*, **26**, (1969). ^g Present results. Based on the assumption that the chloride affinities listed for SiCl₃⁺ and SnCl₃⁺ are correct. ^h A. S. Buchanan, D. J. Knowles, and D. L. Swinger, *J. Phys. Chem.*, **73**, 4394 (1969). ⁱ May be as much as 15 kcal mol⁻¹ too high. See, for example, F. C. Fehsenfeld, P. Crutzen, A. O. Schmeltekopf, C. J. Howard, D. L. Abrisson, E. E. Ferguson, J. H. Davidson, and H. I. Schiff, *J. Geophys. Res.*, **81**, 4454 (1976).

various MCl₃⁺ ions and their chloride affinities. The relative chloride affinities of these species were determined by examining the ion chemistry in mixtures of two tetrachlorides. In a mixture of TiCl₄ and SiCl₄, double resonance indicates that the reaction

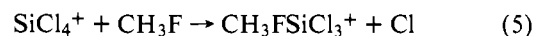


is observed. At higher pressures the TiCl₃⁺ disappears in favor of SiCl₃⁺. In this way the chloride affinities of the MCl₃⁺ ions are found to decrease in the order TiCl₃⁺ > SiCl₃⁺ > GeCl₃⁺ > SnCl₃⁺ > CCl₃⁺ (see Table II).

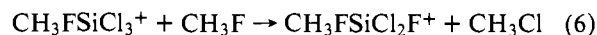
TiCl₃⁺ and SiCl₃⁺ have the highest chloride affinities and exchange halogens with CH₃F most rapidly. This correlation between chloride affinity and reactivity suggests that the mechanism of the exchange process involves ion-induced po-

larization of the C-F bond. It may be that GeCl₃⁺ and SnCl₃⁺ are not strong enough Lewis acids to polarize the C-F bond and initiate reaction. Alternatively the exchange reactions of GeCl₃⁺ and SnCl₃⁺ may be endothermic so that the impediment to their reactions is thermodynamic rather than mechanistic. Unfortunately insufficient data are available to provide even a rough estimate of the enthalpy changes of the GeCl₃⁺ and SnCl₃⁺ reactions. In the case of CCl₃⁺ we were able to determine that both forward and reverse reactions are slow. This suggests that at least in this case there is a mechanistic barrier to reaction.

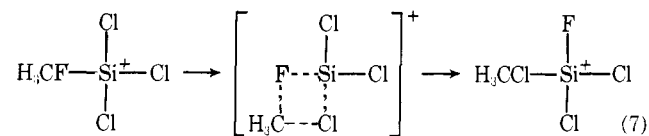
The complex formed in the Cl atom displacement reaction



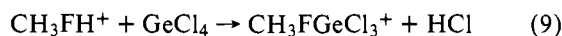
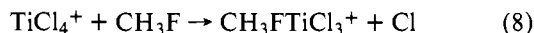
may be related to an intermediate in the halogen exchange process. In the subsequent reaction



CH₃F apparently displaces CH₃Cl from the CH₃FSiCl₃⁺ suggesting that the product of reaction 5 rearranges as indicated in eq 7. The mobility of the methyl group could arise



from the polarization of the C-F bond suggested above to be crucial to the halogen exchange reaction. Donor-acceptor complexes between CH₃F and TiCl₃⁺ and between CH₃F and GeCl₃⁺ are formed in the reactions



Further reactions of these complexes, however, are not observed.

The reactivity of SiCl₃⁺ toward CH₃F, the reactivity of AlCl₃ toward chloro-fluoroalkanes and fluoroolefins, and the effectiveness of AlCl₃ as a catalyst in Friedel-Crafts alkylations suggested that AlCl₃ might react with CH₃F. It was found that the reaction between gaseous CH₃F and solid AlCl₃ present initially in a 3:1 molar ratio goes smoothly to completion in accordance with the reaction

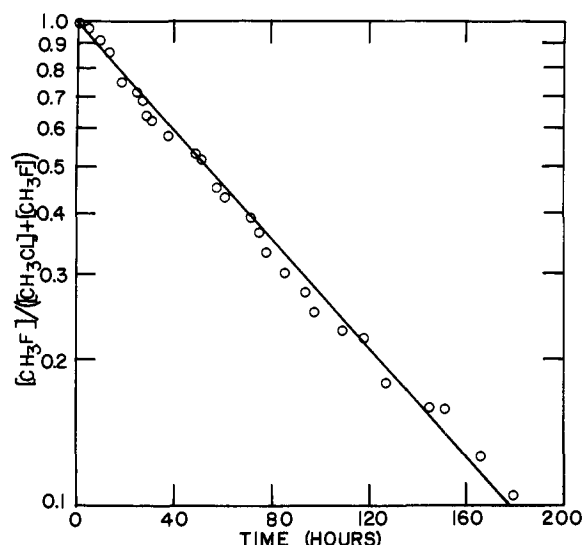
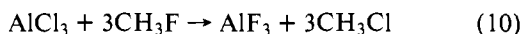


Figure 1. The variation of CH_3F concentration in a gas originally pure CH_3F as a function of the time the gas is exposed to solid ScCl_3 at 298 K. The initial molar amount of ScCl_3 present is one-third the initial molar amount of CH_3F present. The only gaseous product observed is CH_3Cl and the total pressure of gas does not change significantly. The solid line is a least-squares fit of the data ($R = 0.996$).



The similarity in reactivity between TiCl_3^+ and SiCl_3^+ suggested that ScCl_3 might react in the same way that AlCl_3 does. As indicated in Figure 1, the reaction between ScCl_3 and CH_3F goes smoothly to completion with reactants present initially in stoichiometric amounts. The time scale of the AlCl_3 reaction is essentially the same as that of the ScCl_3 reaction. Halogen exchange between scandium halides and alkyl halides has not been previously reported. The chemistry of scandium is generally rather different from that of aluminum. ScCl_3 is not a good catalyst for Friedel-Crafts alkylation, for example.¹³ Only the reactivity of TiCl_3^+ led us to look for the reaction between ScCl_3 and CH_3F . This is a novel feature of these results. Parallels between condensed-phase chemistry and ion-molecule reactions are usually discovered by looking for an ion-molecule reaction analogous to a known condensed-phase process.

Little is known about the mechanism of heterogeneous gas-solid or liquid-solid halogen exchange reactions.¹⁴ The present results suggest that the kinetics of eq 10 and its scandium analogue may depend on a potential surface similar to that governing the isoelectronic gas-phase ion-molecule reaction. This in turn suggests that the reactive site of the surface of the solid is a coordinatively unsaturated metal isoelectronic with gaseous SiCl_3^+ or TiCl_3^+ . It further suggests that a donor-acceptor adduct between the CH_3F and the metal is an intermediate in the reaction. We might expect that the reactive AlCl_3 and ScCl_3 would have higher chloride affinities than the nonreactive BCl_3 . The study of chloride transfer processes in nonaqueous solutions suggests, however, that BCl_3 has a higher chloride affinity than AlCl_3 .¹⁵ On the other hand, it has been suggested that BCl_3 does not effectively catalyze the alkylation of aromatics because BCl_4^- is relatively unstable compared to AlCl_4^- .¹⁶ Studies are underway in our laboratories to determine the relative chloride affinities of AlCl_3 and BCl_3 from competitive chloride transfer reactions in the gas phase.

The observed reactions have a number of thermochemical consequences with regard to bonds from silicon and titanium to halogens. The rates of the reactions in Table I are within one

or two orders of magnitude of the reactant collision frequencies which implies that the reactions are thermoneutral or exothermic. Reaction 2, for example, will be thermoneutral or exothermic if $D(\text{SiCl}_2^+-\text{F}) - D(\text{SiCl}_2^+-\text{Cl}) \geq D(\text{CH}_3-\text{F}) - D(\text{CH}_3-\text{Cl})$. The conclusions inferred in this manner are given in Table I.

Also of thermochemical consequence is the formation of stable ionic donor-acceptor complexes in these systems. Reactions analogous to reaction 8, for example, appear to be quite general between TiCl_4^+ and n -donor bases such as water, amines, phosphine, ketones, and ethers. In a number of cases n -donor bases will displace one another from the complexes formed in such reactions. Water will displace phosphine from a $\text{PH}_3\text{TiCl}_3^+$ complex, for example, which indicates that H_2O is a better base toward TiCl_3^+ than PH_3 . The opposite is true of the relative basicities of PH_3 and H_2O toward a proton in the gas phase. A complete study of such displacement reactions is underway in our laboratory.

Conclusions

- (1) Both SiCl_3^+ and its transition metal 4B congener TiCl_3^+ attack CH_3F to exchange a chloride for a fluoride in the gas phase. These reactions are bimolecular and so rapid that it can be concluded they have no activation energy.
- (2) Both solid AlCl_3 and its transition metal 3B congener solid ScCl_3 attack gaseous CH_3F to exchange a chloride for a fluoride. These reactions go to completion when the reactants are initially present in stoichiometric proportions. AlCl_3 and ScCl_3 are, of course, isoelectronic with SiCl_3^+ and TiCl_3^+ , respectively.
- (3) The other 4A trichlorocations, GeCl_3^+ , SnCl_3^+ , and CCl_3^+ , are not observed to react with CH_3F . These unreactive ions have lower chloride affinities than TiCl_3^+ and SiCl_3^+ , suggesting a relationship between reactivity and Lewis acidity.
- (4) The evidence indicates that the ion-molecule halogen exchange proceeds by formation of a 1:1 donor-acceptor adduct in which the C-F bond is polarized by the acceptor acid. This suggests that the heterogeneous exchange reactions of AlCl_3 and ScCl_3 proceed by a similar mechanism.
- (5) Information on the stability of species of the type MCl_nF_m^+ where $n + m \leq 3$ may be deduced from observed reactions. Information on the stability of species of the type MCl_3B^+ where B is an electron-donating base may also be deduced.

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