
Gas-Phase C–F Bond Cleavage in Perfluorohexane Using W-, Si-, P-, Br-, and I-containing Ions: Comparisons with Reactions at Fluorocarbon Surfaces

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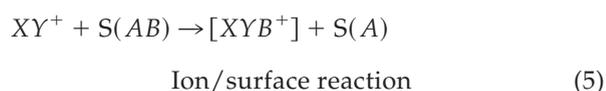
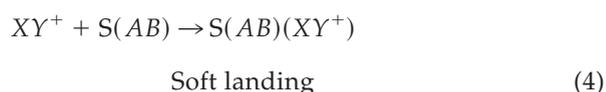
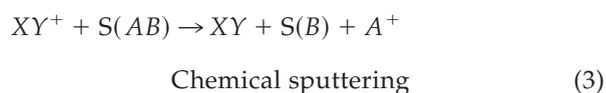
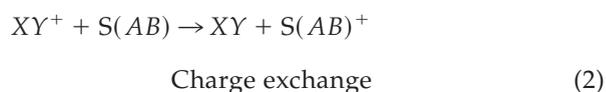
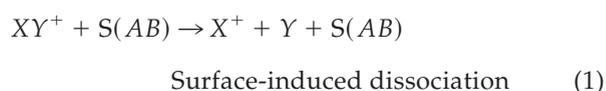
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Gas-phase reactions of W-, Si-, P-, Br-, and I-containing ions with the target molecule perfluorohexane at low collision energies (<15 eV) parallel known ion/surface reactions of the same projectile ions at fluorinated self-assembled monolayer surfaces. Charge exchange, dissociative charge exchange, and fluorine atom abstraction are observed and the majority of the projectile ions also undergo reactive charge exchange to produce specific fluorocarbon fragment ions of the target molecule in distinctive relative abundances. Abstraction of up to five fluorine atoms is observed upon collision of W^+ with gaseous perfluorohexane, while similar experiments with Cl^+ , $SiCl^+$, and PCl^+ show abstraction of one or two fluorine atoms. Other projectiles, including Si^+ , PCl_2^+ , Br^+ , CBr^+ , and I^+ , abstract only a single fluorine atom. These patterns of fluorine atom abstraction are similar to those observed in ion/surface collisions. Also paralleling the ion/surface reactions, halogen exchange (Cl-for-F) reactions occur between the Cl-containing projectile ions and perfluorohexane to produce $C_6F_{12}Cl^+$, a product of chemical modification of the target. Collisions of PCl^+ and PCl_2^+ also result in production of $C_6F_{12}^+$, indicating that the corresponding surface modification reaction involving molecular defluorination should be sought. Implications for previously proposed mechanisms, new ion/surface reactions, and for the use of gas-phase studies to guide investigations of the ion/surface reactions are discussed. (J Am Soc Mass Spectrom 1998, 9, 1158–1167) © 1998 American Society for Mass Spectrometry

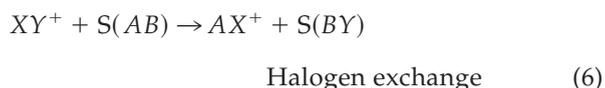
Collisions of low-energy (10–1000 eV) ions with surfaces are receiving attention owing to their potential utility in surface analysis and modification [1–5]. The processes that occur during ion/surface collisions include fragmentation of the projectile ion [surface-induced dissociation (SID), eq 1] [6–12], electron transfer from the surface to the projectile ion (charge exchange, eq 2), followed by ejection of an ionized species from the surface (chemical sputtering, eq 3) [13, 14], intact deposition of polyatomic ions at the surface (soft landing, eq 4) [15], and reactions between the projectile ion and the surface or molecules adsorbed at the surface (ion/surface reactions, eq 5) [16–28]:



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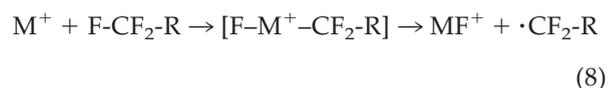
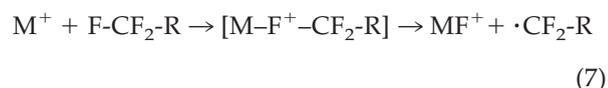
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In these equations $S(AB)$ represents a surface-bound molecule AB and XY^+ is the projectile ion. Note that the charge exchange process may be accompanied by dissociation, one form of which is the process known as chemical sputtering. In rare cases ion/surface reactions may occur but lead to products that do not include atoms from the projectile ion; this phenomenon is known as reactive sputtering [26]. A more typical example of an ion/surface reaction is halogen exchange [29] between a target and a projectile ion (eq 6). The halogen atom A on the surface is exchanged with another halogen, Y , in the projectile and both the gaseous and surface-bound products contain halogen:



Collisions of both organic and inorganic ions have been studied at low energy with a wide variety of surfaces and many different types of reactions have been observed. These reactions have been reviewed [1]. They include the abstraction of hydrogen atoms [21, 25, 30, 31], alkyl groups [6, 30–32], fluorine atoms [16, 23, 26–28], and other functional groups [24] from surfaces by the projectile ion. For those ion/surface reactions in which the projectile ion abstracts multiple surface atoms or groups, it is suggested that the projectile undergoes multiple interactions in a single collision event at a particular local site [1, 27]. The processes involving abstraction of multiple surface atoms are more complex, and it is considerably more difficult to investigate their mechanisms. For example, highly unsaturated ions, such as C_2HN^+ , abstract multiple hydrogen atoms from hydrocarbon surfaces, and in this case the hydrogen atoms are known to originate from the same surface chain by using an isotopically mixed self-assembled monolayer (SAM) surface [13, 26]. Some ion/surface reactions have been thoroughly studied, leading to some understanding of their mechanisms [1, 6, 19, 24]. In particular, mechanisms have been proposed for two well-studied types of ion/surface reactions [6]: (i) hydrogen and alkyl radical abstraction from alkyl groups on surfaces by radical cations and (ii) fluorine atom abstraction from fluoroalkyl groups on surfaces by metal or metal-containing cations. The first type of reaction is proposed to occur via electron transfer from the surface to the projectile ion as the first step, followed by fragmentation of the surface-bound ion and combination of an ionic fragment from the surface with the neutralized projectile [1] or by a closely related process in which an ion derived from the surface reacts with the neutralized projectile [19, 20]. Formation of $C_7H_7^+$ from the collision of a benzene molecule ion with a hydrocarbon-covered surface is similarly suggested to occur by association of a sputtered ion, such as $C_3H_5^+$, from the surface, with the neutralized projectile [19, 20]. The second type of reaction for which mechanistic information is available involves oxidative addition of the

projectile ion, or its SID fragments, to the species on the surface [25–28]. Experimental data suggest that charge exchange is not a prerequisite for this type of ion/surface reaction. For some fluorine atom abstraction and transhalogenation reactions [23, 28, 29, 33], fluoronium ions may be key reaction intermediates. This is shown in eq 7, where M^+ is the projectile ion, and $F-CF_2-R$ represents a surface-bound fluorocarbon chain. However, a mechanism involving insertion into a C–F bond (eq 8) is also possible in some cases [36]. A mechanism involving a fluoride



intermediate may also operate when projectile ions with very low second ionization energies are used. Such a fluoride mechanism involves charge exchange so as to give, formally, a metal dication and a fluoride anion [34, 35]. On the other hand, the fluoronium mechanism involves electron donation from a fluorine atom to the projectile ion [23, 28, 29, 36]. Although studies have not yielded direct information on the time scale of ion/surface interactions, time-of-flight (TOF) data [21] place an upper limit of about 1 ns on the residence time in SID, and molecular dynamics simulations [1, 37, 38] suggest that the direct reactions involved proceed on a very short time scale (i.e., several picoseconds).

Implicit in the occurrence of any ion/surface reaction is the simultaneous chemical modification of the surface. In some instances modification of the fluorinated surface has been observed only indirectly, through characterization of the scattered ion products. In others, direct post-reaction analysis of the surface by secondary ion mass spectrometry (SIMS) or by chemical sputtering using Xe^+ [23, 29] has been used to reveal the nature of the modification. Therefore, additional interest in ion/surface reactions is warranted as a tool for the selective chemical modification of the outermost layers of surfaces. Ion/surface reactions obviously depend upon the nature of both the projectile and the surface at which it collides. This dependence of the course of reaction on the chemical nature of both the surface and the projectile potentially provides the basis for a new method of surface analysis. In order to develop these capabilities for surface modification and surface analysis, a more thorough understanding of ion/surface reactions and their mechanisms must be achieved. The goal of the present study is to further this objective through observations on gas-phase model systems.

Ion/molecule reactions have been investigated previously in seeking analogies with ion/surface reactions [19, 27, 28, 39]. For example, previous work [39] attempted to provide insights into ion/surface reactions

of tungsten-containing ions by examining their reactions with perfluorohexane and tetrafluoromethane in the chemical ionization source. In a tandem mass spectrometry study conducted at low collision energy, abstraction of multiple fluorine atoms [39] was observed when gas-phase W^+ projectiles were collided with perfluorohexane in the collision cell of a triple quadrupole instrument. Stable 1:1 complexes between tungsten hexacarbonyl cations and fluorocarbon radicals such as C_6F_{13} were observed, and subsequent collision-induced dissociation (CID) of these complexes produced ions corresponding to WF_n^+ ($n = 0-5$) [39], in analogy to the WF_n^+ ions observed in ion/surface reactions [28]. These gas phase results suggest that the WF_n^+ ions observed in ion/molecule reactions arise by a mechanism in which multiple fluorine atoms are abstracted from a complex comprised of the projectile ion and a single target molecule. These findings demonstrate that gas-phase ion/molecule reactions show similarities to those which occur in ion/surface collisions, and suggest they may indeed provide information relevant to the mechanisms involved in ion/surface reactions.

In the present investigation, the role of the ionic projectile in the surface modification and ion/surface abstraction reactions is investigated through studies of model ion/molecule reactions. Specifically, a variety of projectiles that have been demonstrated previously to abstract fluorine atoms and effect surface modification [26–28] are reacted in the gas phase with a model for a fluorinated SAM, perfluorohexane [29, 39]. Parallels with and extensions of previously observed ion/surface reactions are sought.

Experimental

Ion/molecule reactions were carried out in a Finnigan TSQ 700 triple quadrupole mass spectrometer (Finnigan MAT, San Jose, CA). Unless otherwise stated, 70-eV electron impact (EI) was used for ionization. The source temperature was maintained at 150°C and the vacuum manifold was maintained at 70°C. Solid samples were introduced using aluminum microvials from which evaporation occurred without additional heating of the solids probe. Vapors from liquid samples were admitted through a leak valve (Granville Phillips, Boulder, CO). Perfluorohexane (Lancaster, Windham, NH) was introduced into the differentially pumped collision cell through a needle valve after several cycles of freezing and thawing under vacuum. All other compounds were obtained from Aldrich (Aldrich Chemical, Milwaukee, WI) and were used without further purification.

Product ion mass spectra were recorded by selecting the desired ion using the first, mass-analyzing, quadrupole and passing the ion through the second, rf-only, quadrupole with laboratory kinetic energies between 0 (nominal) and 15 eV, then scanning the third quadrupole over the mass range of interest at a rate of 500 Th/s. [Note that the unit Thomson (Th) is one atomic mass unit per unit charge [40].] Only positive ion mass

spectra were acquired. Collision energies were calibrated using a retarding potential experiment and the reported energies, which have been corrected, are estimated to be accurate to within ± 3 eV. When specified, experiments were performed under single-collision conditions achieved by maintaining a parent ion attenuation of between 10% and 15%, which corresponded to indicated collision quadrupole pressures of about 0.4 mtorr. For multiple-collision conditions the pressure of perfluorohexane, the reagent gas, was maintained at ~ 1.5 mtorr.

Results and Discussion

Product ion spectra (Table 1) resulting from gas-phase collisions of a variety of ions with perfluorohexane were recorded to model collisions of these ions with fluorinated alkane self-assembled monolayer surfaces. In the following sections, the reactions of these projectile ions with perfluorohexane are discussed systematically and correlated with the corresponding ion/surface reactions [27, 29]. One consideration in understanding these reactions is the underlying thermochemistry, so pertinent thermochemical data for some of the projectile ions and their reactions are listed in Table 2.

Fluorine Atom Abstraction

Abstraction of fluorine atoms occurs for each of the projectile ions examined, with up to five fluorine atoms being abstracted by W^+ , two F atoms being abstracted in the case of Cl^+ and PCl^+ projectiles, and just one fluorine atom being abstracted by Si^+ , P^+ , I^+ , and Br-containing ions (see Table 1). The maximum numbers of atoms abstracted in ion/surface reactions are similar [26–29], although the product ion abundances are much greater than in the corresponding gas phase processes. As will be discussed further below for the charge exchange reactions, conversion of translational energy apparently assists in driving fluorine abstraction. Some of the observed reactions are endothermic but others, e.g. mono- and difluorine abstraction by P- and Si-projectile ions, are exothermic as is the formation of the WF_2^+ abstraction products by W^+ (see Table 2). The thermodynamics for double fluorine pickup are dependent upon whether one or two fluorocarbon chains are involved, and whether or not new carbon-carbon bonds are formed. However, most single-fluorine atom abstraction reactions must be endothermic. (See [6] for an analogous discussion of the thermochemistry of hydrogen atom pickup reactions.)

Figure 1A shows the product ion spectrum obtained upon collision of 6-eV, mass-selected W^+ ions with perfluorohexane under single collision conditions. Note the presence of the ions WF_n^+ ($n = 1-5$). In addition, the presence of WCF_4^+ is indicative of tungsten insertion into the C–C bond, a reaction that has been suggested to occur in ion/surface collisions [28]. Other ions in the

Table 1. Product ions formed upon low-energy collisions of mass-selected ions with perfluorohexane^a

Precursor	Ion	Product ions (% relative abundance)
CBr ₄	Br ⁺	CF(0.1); CF ₃ (8.8); C ₂ F ₄ (3.1); C ₂ F ₅ (3.1); C ₃ F ₅ (1.3); C ₃ F ₆ (5.4); C ₃ F ₇ (8.8); C ₄ F ₇ (1.0); C ₄ F ₉ (5.2); C ₅ F ₉ (7.2); C ₆ F ₁₃ (54.3); C ₆ F ₁₄ (0.5); BrF(1.0)
CBr ₄	CBr ⁺	CF(2.9); CF ₃ (3.7); C ₂ F ₄ (1.4); C ₂ F ₅ (5.8); C ₃ F ₅ (3.6); C ₃ F ₆ (1.4); C ₃ F ₇ (4.3); C ₄ F ₇ (3.5); C ₄ F ₉ (1.7); C ₅ F ₉ (5.2); C ₆ F ₁₃ (23.0); C ₆ F ₁₄ (0.3); CBrF(43.2)
CH ₃ I	I ⁺	CF(0.6); CF ₃ (8.8); C ₂ F ₄ (9.1); C ₂ F ₅ (5.7); C ₃ F ₅ (1.7); C ₃ F ₆ (10.1); C ₃ F ₇ (10.3); C ₄ F ₇ (1.0); C ₄ F ₉ (5.6); C ₅ F ₉ (2.0); C ₆ F ₁₃ (7.1); C ₆ F ₁₄ (4.1); IF(33.7)
CH ₃ I	Cl ⁺	CF(1.7); CF ₃ (6.2); C ₂ F ₅ (2.2); C ₃ F ₅ (5.3); C ₃ F ₇ (4.6); C ₄ F ₇ (3.8); C ₅ F ₉ (6.9); C ₆ F ₁₃ (11.7); C ₆ F ₁₄ (0.7); ClF(51); IF(3.8); ClF₂(1.6)
PCl ₃	P ⁺	CF ₃ (23.7); C ₂ F ₅ (14.3); C ₃ F ₅ (11.7); C ₃ F ₇ (10.8); C ₄ F ₇ (12.6); C ₅ F ₉ (14.3); C ₆ F ₁₃ (6.1); PF(6.9)
PCl ₃	PCl ⁺	CF(1.5); CF ₃ (8.6); C ₂ F ₄ (1.7); C ₂ F ₅ (3.6); C ₃ F ₅ (41.5); C ₃ F ₆ (1.7); C ₃ F ₇ (3.6); C ₄ F ₇ (3.0); C ₄ F ₉ (0.9); C ₅ F ₉ (4.7); C ₆ F ₁₂ (4.8); C ₆ F ₁₃ (6.5); C ₆ F ₁₄ (0.3); C₆F₁₂Cl(0.3); PCIF(14.3); PCIF₂(1.5)
PCl ₃	PCl ₂ ⁺	CF ₃ (23.3); C ₂ F ₅ (1.9); C ₃ F ₅ (1.0); C ₃ F ₇ (1.8); C ₄ F ₇ (0.1); C ₅ F ₉ (0.8); C ₆ F ₁₂ (0.3); C ₆ F ₁₃ (1.6); C ₆ F ₁₄ (0.3); PCl(67.6); C₆F₁₂Cl(0.1); PCIF(1.7); PCl₂F(0.1)
SiCl ₄	Si ⁺	CF ₃ (35.8); C ₂ F ₄ (0.34); C ₂ F ₅ (12.1); C ₃ F ₅ (11.4); C ₃ F ₆ (0.3); C ₃ F ₇ (17.2); C ₄ F ₇ (0.3); C ₄ F ₉ (0.3); C ₅ F ₉ (1.0); C ₆ F ₁₃ (3.1); SiF(0.2)
SiCl ₄	SiCl ⁺	CF ₃ (11.4); C ₂ F ₅ (3.4); C ₃ F ₅ (19.0); C ₃ F ₇ (2.7); C ₄ F ₇ (4.9); C ₅ F ₉ (5.4); C ₆ F ₁₃ (12.2); C₆F₁₂Cl(0.1); SiClF(10.5); SiF(30.5); SiClF₂(0.8)
W(CO) ₆	W ⁺	CF ₂ (0.4); CF ₃ (8.2); C ₂ F ₅ (2.0); C ₃ F ₅ (20.1); C ₃ F ₇ (1.4); C ₄ F ₇ (36.5); C ₅ F ₉ (12.5); C ₆ F ₁₂ (3.6); C ₆ F ₁₃ (3.6); C ₆ F ₁₄ (0.8); WF(3.0); WF₂(4.0); WF₃(3.0); WF₄(3.0); WF₅(4.0); WCF₄(3.0)

^aPerfluorohexane pressure was ~1.5 mtorr and collision energies between 6 and 8 eV in the laboratory frame.

^bFluorine abstraction and halogen exchange reaction products are bold.

spectrum correspond to products of dissociative charge exchange, viz., charge exchange to give C₆F₁₄⁺ with enough internal energy to fragment to give the observed fluorocarbon fragment ions. Figure 1B shows the spectrum recorded for the projectile ion W(CO)₃⁺ under similar conditions. Ion/molecule reactions lead to abstraction of just one or two fluorine atoms in this case to produce W(CO)₃F⁺ and W(CO)₃F₂⁺, respectively. Collision-induced dissociation to give the CO loss products and charge exchange is also evident. This behavior is consistent with that observed in ion/surface reactions [28], where the similar reaction products are obtained with a W(CO)₃⁺ projectile ion that includes carbonyl-containing fluorine abstraction products. Most significantly, the abundant ion at 608 Th corresponds to a 1:1 complex of W(CO)₃⁺ and perfluorohexane (Figure

1B). The intensity of the complex as well as other abstraction products increases, as expected, with increases in perfluorohexane pressure (Figure 1C). At these higher pressures, the complex is formed with the accompanying loss of one or more carbonyls, consistent with an increased degree of accompanying collision-induced dissociation. Similar complexes are formed between perfluorohexane and other W-containing ions (data not shown), but the most reactive projectile ion in terms of complex formation was W(CO)₃⁺. It is likely that the carbonyls act as a sink for the release of excess internal energy, either through fragmentation or through transfer of energy to vibration modes, to stabilize the complex. However, the presence of more than three carbonyl groups may impose steric restrictions on the ability of the ion to interact with the target molecule.

Table 2. Some thermochemical data^a

E	RE (eV)	ΔH_f (ion) (kcal/mol)			ΔH_{rxn} (kcal/mol) ^b		
		E	EF	EF ₂	Single F abstraction	Double F abstraction	
					Single chain ^c	Two chains ^d	
Si	8.15	295	163	108	-24	29	-24
P	10.49	317	212	90	3	-11	-64
Br	11.81	299	257	—	66	—	—
I	10.45	267	222	—	63	—	—
W ^e	7.60	379	282	182	11	19	-34

^aE = element; RE = recombination energy; EF and EF₂ = mono- and difluorine abstraction products; thermochemical data taken from or calculated from [42].

^bData calculated for reaction between the projectile ion and C₃F₈.

^cAbstraction of two F atoms from a single fluoroalkane chain with formation of C=C double bond in the chain.

^dAbstraction of two F atoms from separate fluoroalkane chains with formation of C–C single bond between the chain.

^eValues for ΔH_f (ion) for WF₃⁺, WF₄⁺, and WF₅⁺ are 81, -18, and -103 kcal/mol, respectively.

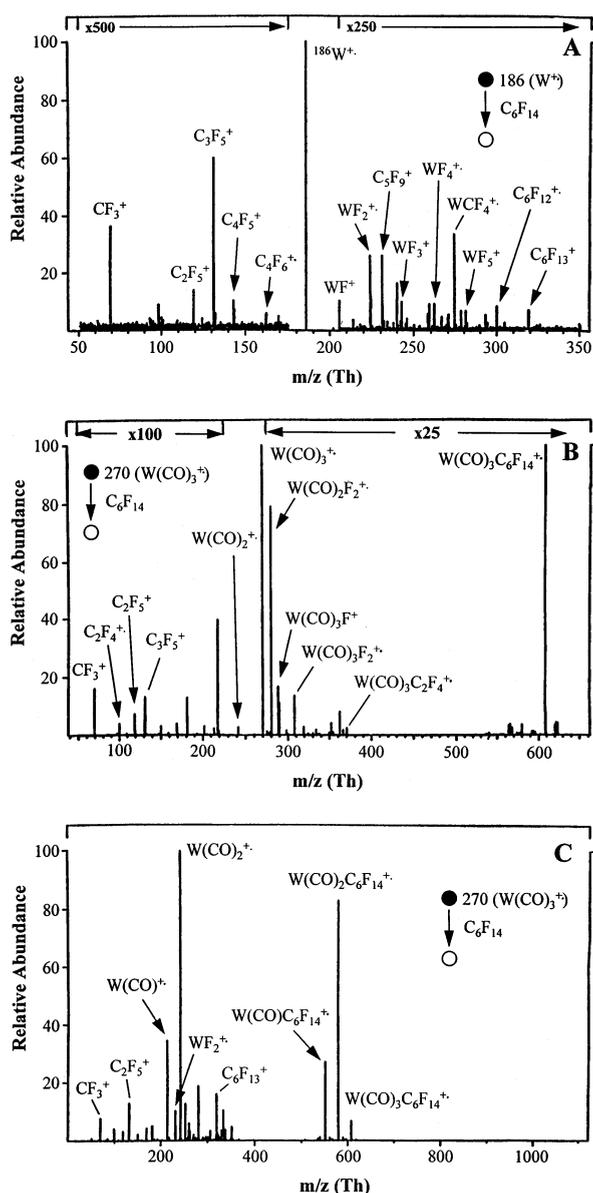


Figure 1. Product ion mass spectra obtained by collisions of 6-eV tungsten-containing projectile ions with perfluorohexane at 0.4 mtorr (single collision conditions). (A) $^{186}\text{W}^+$ projectile, (B) $^{186}\text{W}(\text{CO})_3^+$ projectile, (C) product ion spectrum resulting from 6-eV collisions of $\text{W}(\text{CO})_3^+$ with perfluorohexane at 2.2 mtorr (multiple collision conditions).

The perfluorohexane pressure effects have also been studied for the projectile ion SiCl^+ . By increasing the pressure from 0.4 mtorr (single collision) to 1.5 mtorr (multiple collision), the relative intensities of the fluorine abstraction products, SiF^+ and SiClF^+ , increased from 1.5% and 0.25% to 10% and 0.8%, respectively (data not shown).

Although of different composition than the $\text{C}_6\text{F}_{13} \cdot \text{W}(\text{CO})_n^+$ complexes observed previously in ion source reactions [39], the intact $\text{C}_6\text{F}_{14} \cdot \text{W}(\text{CO})_3^+$ complex observed here between $\text{W}(\text{CO})_3^+$ and perfluorohexane is consistent with the proposed role of long-lived, ion/molecule complexes in fluorine atom abstraction reac-

tions. The differences between the complex observed here and those examined previously [i.e., $\text{C}_6\text{F}_{14}\text{W}(\text{CO})_3^+$ versus $\text{C}_6\text{F}_{13}\text{W}(\text{CO})_6^+$ [39]] may simply be the result of differences in energies produced by the very different time scales and pressures employed.

For W-containing ions, the effect of projectile preexcitation was examined by varying the electron energy across the range 25–200 eV. This showed little effect on the resulting product-ion spectra for collisions with perfluorohexane. However, variation of the collision energy showed that efficient fluorine abstraction occurred only within a narrow range of collision energies, nominally 2–10 eV, with no measurable abstraction product being produced above 15 eV. This behavior was observed under both single and multiple collision conditions and is consistent with the suggestion of an endothermic reaction progressing through a collision complex mechanism [41, 42]. This is consistent with the fact that the thermodynamically favored product WF_2^+ is generated from W^+ in greater abundance than the analogous WF_2^+ and WF_3^+ ions.

Although the extent of fluorine atom abstraction by Si^+ does not vary with electron impact energy, as is also the case for the W-containing ions mentioned above, the reaction of SiCl^+ is strongly dependent on this parameter (Figure 2). At an electron energy of 25 eV, no fluorine abstraction product ion is observed at a collision energy of 4 eV (Figure 2A) although fluorocarbon fragment ions are present in the spectrum. When the electron energy was raised from 25 to 28 eV (spectra not shown), the relative abundances of fluorocarbon fragments increased and both SiF^+ and SiClF^+ started to appear and the relative abundances of fluorocarbon ions increased. Coincidentally, SiClF_2^+ (101 Th) appears in the spectrum upon further increasing the electron energy to 40 eV (compare Fig. 2A and B). These data suggest that preexcitation of the projectile SiCl^+ may enhance fluorine atom abstraction, presumably via an easily accessible excited electronic state of SiCl^+ .

Charge Exchange and Dissociative Charge Exchange

Fluorocarbon fragment ions are observed in all the product-ion spectra acquired upon collisions of the projectile ion of interest with perfluorohexane (see Table 1). This is indicative of charge exchange and subsequent fragmentation of the ionized target molecule. The endothermicity of charge exchange is the difference between the ionization energy (IE) of the target molecule and the recombination energy of the projectile ion. If an IE of 13.6 eV (the value for perfluoroethane) [43] is assumed for perfluorohexane, then charge exchange is endothermic by from 1.8 to 6 eV for the atomic ions of Si, P, Br, I, and W (Table 2). Collision energies in the center-of-mass frame of reference range from approximately 4 to 6 eV, and represent the maximum amount of energy available for conversion from

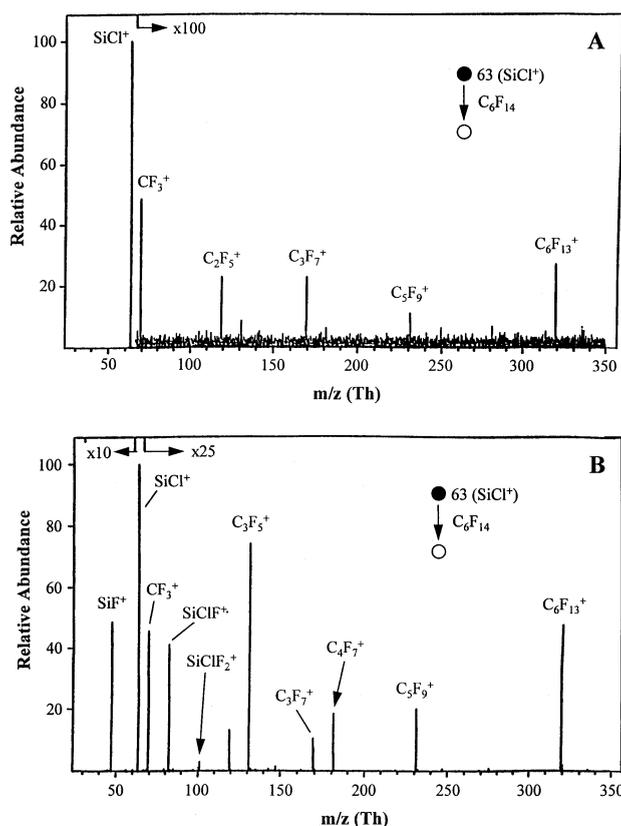


Figure 2. Product ion mass spectra due to 4-eV collisions of SiCl^+ (63 Th) with 0.8 mtorr of C_6F_{14} at different electron impact energies: (A) 25 and (B) 40 eV. Note the appearance of peaks at 47, 82, and 101 Th due to SiF^+ , SiClF^+ , and SiClF_2^+ at 40 eV ionization energy. Also note the presence of the weak ion at 335 Th that corresponds to $\text{C}_6\text{F}_{12}\text{Cl}^+$.

translational to internal energy in a single collision event. The deposition of this energy, along with any internal excitation energy of the projectile ion, must provide the energy needed to drive these endothermic charge exchange reactions, and to produce the fragmentation observed [41, 42]. The greatest amount of fluorocarbon fragmentation is observed for collisions of Br^+ with perfluorohexane. Approximately 70% of the scattered ions from the collisions are derived from ionization and fragmentation of the target molecule. This is consistent with Br^+ having the highest recombination energy among the projectile ions examined, viz., its IE (11.8 eV) is the closest to the IE (13.6 eV) of perfluorohexane (see Table 2). Collisions of W^+ with perfluorohexane show the least amount of fluorocarbon fragment ions (only 1% of the total scattered ions), which is consistent with W^+ having the lowest recombination energy (7.6 eV). Although the product-ion spectra show general trends that are in agreement with the thermochemical considerations, substantial abundance differences in the fluorocarbon fragment ions abundances are observed that are not predicted by thermochemistry. These differences suggest a gas-phase analog of the “reactive sputtering” [27] process, which is discussed in more detail below.

Reactive Charge Exchange

Reactive sputtering [27] is an ion/surface reaction that yields product ions originating entirely from the target. It is typically distinguished from simple chemical sputtering by unusual relative abundance ratios between these target fragment ions, which are characteristic of particular projectile ions [27]. The analogous gas-phase process, reactive charge exchange [41, 42], is sought here. If the fragmentation of the ionized target is controlled by the charge exchange process, differences in the relative abundances of the fragment ions would simply be the result of differences in the internal energy distribution of the charge exchange product. As such, the fragmentation behavior would in principle be predictable from standard unimolecular dissociation kinetics. On the other hand, if charge exchange were accompanied by a chemical reaction, then the parent ion that yields the observed fragments would not dissociate in the same way as that due to the ion produced by simple charge exchange. In the former case, even if the parent ion were not observed, its participation might be evident in the distinctive relative abundances of its fragment ions. This appears to be the case in the collisions of W^- , Si^- , P^- , Br^- , and I^- -containing ions with perfluorohexane. The relative abundances of the specific fluorocarbon fragments are dramatically different for projectile ions which have comparable recombination energies. Data are summarized in Table 3, where the projectiles are arranged for convenience in order of their estimated recombination energies. Note the following anomalies: (i) the high relative abundance of the fluorocarbon fragment ion CF_3^+ (69 Th) observed for P^+ and Si^+ ; (ii) the very high abundance of the fragment ion C_4F_7^+ (181 Th) observed for W^+ and P^+ ; and (iii) the high relative abundances of ions C_2F_5^+ (100 Th) and C_3F_7^+ (150 Th) observed for I^+ but not for the other projectiles, except Br^+ , which yields less than half of the relative abundances of these ions in the case of I^+ . Reactive sputtering of a fluorinated SAM surface by I^+ has been observed in ion/surface collisions [27]. It was proposed that the observed ions are produced from fragmentation of a complex formed between the projectile ion and the terminal group of the surface-bound fluorocarbon chain. A similar mechanism can be invoked to explain the fragmentation observed in the analogous gas-phase system, as will be apparent in the next section.

Halogen Exchange

The reaction product spectra of P^+ and P_2^+ with perfluorohexane (Figure 3B, C) show the presence of $\text{C}_6\text{F}_{12}\text{Cl}^+$ (335 Th), an ion not seen in the spectrum of the P^+ projectile ion (Figure 3A). The occurrence of this ion suggests that target modification has occurred as a result of or in the course of charge exchange between the projectile ion and the target molecule. The peak assignment was confirmed by mass-selecting projectile ions containing each of the two common chlorine iso-

Table 3. Relative abundances of selected fluorocarbon fragment ions produced by gas-phase reactions of mass-selected ions with perfluorohexane molecules

Projectile ^a	RE (eV) ^b	Relative abundances (% total fluorocarbon ions)				
		CF ₃ ⁺	C ₂ F ₄ ⁺	C ₃ F ₆ ⁺	C ₄ F ₇ ⁺	C ₄ F ₉ ⁺
Br ⁺	11.81	11	5	7	<2	7
P ⁺	10.49	25	0	0	20	0
I ⁺	10.45	14	17	17	<2	9
CBr ⁺	10.43	6	0	2	10	6
Cl ⁺	9.07 ^c	13	0	0	8	0
PCl ⁺⁺	8.98 ^d	13	<2	4	4	1
PCl ₂ ⁺	8.51 ^e	80	0	0	<1	0
Si ⁺⁺	8.15	42	1	1	1	<1
W ⁺	7.60	9	0	0	41	0
SiCl ⁺	7.33 ^f	16	<2	0	7	<2

^aIons are arranged in the decreasing order of their recombination energies (RE).

^bValues are taken from [43].

^cEstimated from the value of I⁺ and the difference between the recombination energies of Br⁺ and CBr⁺.

^dNguyen, M. T. *Mol. Phys.* **1986**, *59*, 547.

^eBrum, J. L.; Hudgens, J. W. *J. Phys. Chem.* **1994**, *98*, 5587.

^fMarijnis, A.; Meulen, J. J. *Chem. Phys. Lett.* **1996**, *263*, 803.

topes (i.e., ³⁵Cl, ³⁷Cl) and observing the corresponding shift of C₆F₁₂Cl⁺ from 335 to 337 Th. Similarly, the observation of such a halogen exchange process is consistent with results from collisions of SiCl_n⁺ or CH₂Br⁺ with fluorinated SAM surfaces that, upon ex situ examination, showed incorporation of Cl and Br into the surfaces, respectively [29]. In the case of PCl⁺⁺ and PCl₂⁺, the formation of C₆F₁₂Cl⁺ in the gas-phase collisions is accompanied by formation of C₆F₁₂⁺ (300 Th) (Figure 3B, C), suggesting a new form of target molecule modification through molecular defluorination.

The formation of C₆F₁₂⁺ (300 Th) and C₆F₁₂Cl⁺ (335 Th) upon collision of PCl_n⁺ (*n* = 1–2) with perfluorohexane can be explained by the reaction sequence shown in Scheme I. The incident projectile ion attaches to the fluorocarbon through a fluorine atom (i.e., P–F–C bonding) creating a fluoronium ion (eq 7), similar to the halonium ions proposed previously [44–46] in reactions of metal ions with halogenated methanes. Subsequently, the fluorine atom from the adjacent carbon atom migrates to P and the C–F–P bond breaks on either side of the fluorine atom, resulting in C₆F₁₂⁺ or PClF⁺. In the intermediate, it is possible for the chlorine atom to transfer to the carbon chain, and subsequent heterolytic cleavage (c or d in Scheme I) on either side of the fluoronium results in the formation of a modified neutral target RC₂F₄Cl or the ion C₆F₁₂Cl⁺, respectively. The reaction exothermicity can be transferred to internal energy of the modified target molecule or to the resulting ions and causes further fragmentation. All the final product ions (PFC⁺, C₆H₁₂⁺, PClF₂⁺, and C₆F₁₂Cl⁺) were observed in the product mass spectrum due to collisions of PCl⁺⁺ upon the C₆F₁₄ target molecule (see Table 1).

Generalizations and Comparisons with Ion/Surface Reactions

Many similarities between ion/surface and ion/molecule reactions using W-, Si-, P-, Br-, and I-containing

projectile ions and the perfluorinated target have been observed and already commented upon. The various reactions observed in the gas-phase experiments are summarized in Table 4. The gas-phase analogs to chemical [14] and reactive [27] sputtering are observed to varying degrees in a manner that is dependent upon the characteristics of the particular projectiles. All the projectile ions studied have been found to undergo fluorine abstraction reactions in the gas phase, which parallel those observed in ion/surface studies [27]. Although single-fluorine abstraction is endothermic for most of the projectile ions investigated, it occurs efficiently at relatively low-energy collisions, suggesting that transfer of translational to internal energy must be efficient. Very little is known regarding the translational to internal energy conversion efficiency in ion/surface reactions, but there is some evidence [47] that it may be comparable to that which accompanies inelastic collisions, which lead to surface-induced dissociation. If so, then this is a further point of similarity between ion/molecule and ion/surface reactive scattering.

The ion/molecule reactions are accompanied by increased fluorocarbon fragmentation as the collision energy is increased. When the Cl-containing projectile ions SiCl⁺, PCl⁺, and PCl₂⁺ are used, the presence of C₆F₁₂Cl⁺ (335 Th) suggests that fluorine abstraction may involve ligand exchange and result in the formation of a chemically modified target molecule. Ions corresponding to the modified target can be directly observed in the gas-phase experiments just as modified surfaces are often identified by Xe⁺ chemical sputtering or by static SIMS analysis after ion/surface reactions [29]. This type of target modification has been used particularly for attempts at controlled surface modification. One notes here that the halogen exchange mechanism may also be operating when Br- and I-containing projectile ions are selected for target modification.

The direct observation of intact ion/molecule complexes (see Figure 1B, C) suggests that fluorine atom

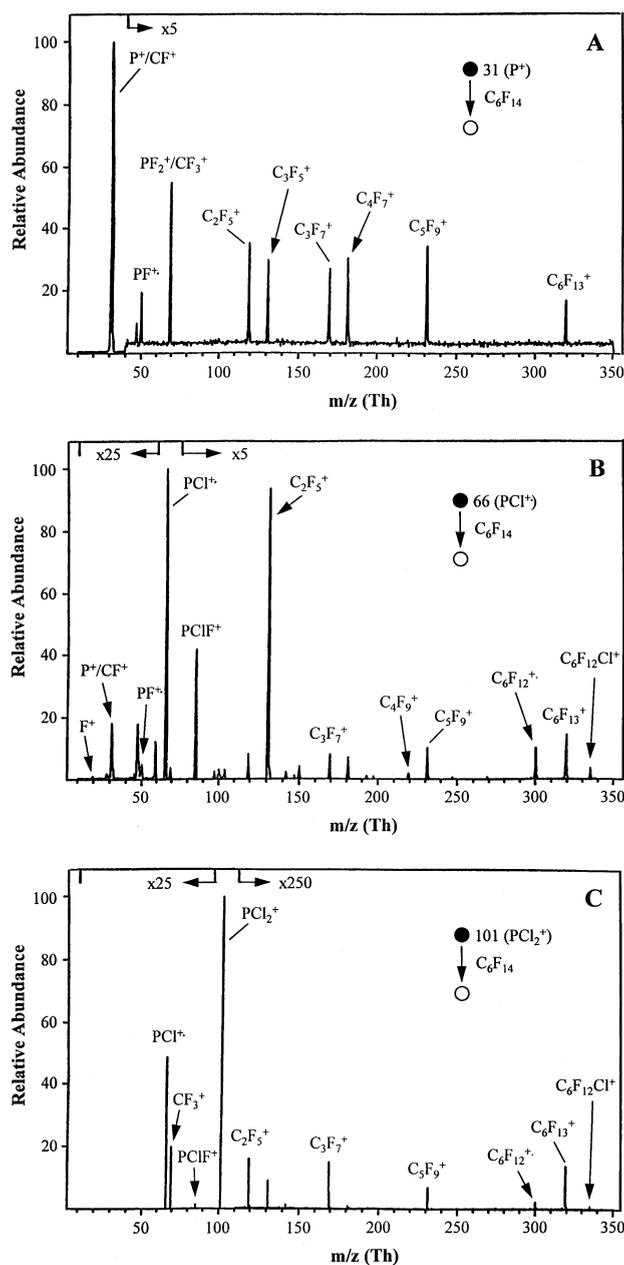
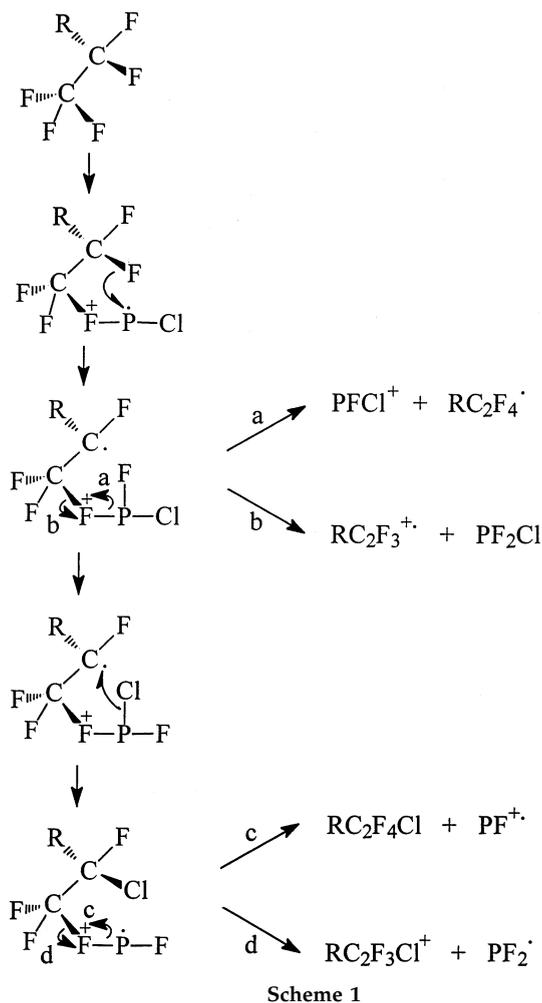


Figure 3. Product ion mass spectra due to 8-eV collisions of (A) P^+ , (B) PCl^+ , and (C) PCl_2^+ with 1 torr of C_6F_{14} . Note the appearance of signal at 300 and 335 Th due to $C_6F_{12}^{+}$ and $C_6F_{12}Cl^+$ and (B) and (C). Projectile ions were generated by 70-eV electron impact ionization of PCl_3 .

abstraction and the target modification processes involve long-lived ion/molecule complexes. Formation of this type of complex has been reported previously for reactions of a variety of halogenated benzene [48–50], and fluorinated aromatics [51] with metal ions in the gas phase. The most important consequence for formation of complexes between a target molecule and the projectile ion is in the production of a chemically modified target. In addition to intact ion/molecule complexes, clusters composed of target fragments [e.g., $W(CO)_3C_2F_4^+$, seen in Figure 1B] were also observed, suggesting alkene formation and the cleavage of C–C



bonds in the target molecule. The formation of an ionized alkene from the fluoroalkane target is also suggested by the observation of the ion $C_6F_{12}^{+}$ (300 Th) (see Table 1), which results from the elimination of two F atoms from perfluorohexane. The observation of double fluorine abstraction product ions (e.g., WF_2^+) under single collision conditions (Figure 1) is a complementary phenomenon. Multiple abstraction of halogens from a perhalogenated target molecule has been observed previously in the gas phase for reaction of Ti^+ with polychlorinated methanes [51, 52]. In a more general case, the abstraction of one or more halogen atoms by elemental ionic projectiles has been observed in numerous gas-phase reactions [45, 46], and these reactions have been proposed to involve halonium ion intermediates, similar to those proposed above. Our observation of multiple fluorine atom abstraction under single collision conditions also finds analogy in isotope exchange studies that demonstrated the exchange of multiple deuterium atoms through ion/molecule complex formation [53].

The present findings are consistent with previous results [27] on gas-phase F-atom abstraction and on ion/molecule reactions of perfluorohexane in the ion

Table 4. Summary of reactions observed for ion/molecule reactions with perfluorohexane target

Projectile ion	Comments on reaction products
Br ⁺	Charge exchange and dissociative charge exchange; reactive sputtering; single fluorine atom abstraction
CBr ⁺	Same as Br ⁺ , lower general yield of fluorocarbon fragment ions; similar F-atom abstraction yield
I ⁺	Lower fluorocarbon fragment ion yield; similar to Br ⁺ with comparable F-abstraction yields; substantial reactive sputtering (ions at 100 and 150 Th)
Cl ⁺	Same as I ⁺ except several ions absent in fluorocarbon fragments observed
Si ⁺⁺	Single F-atom abstraction; no likely charge exchange due to thermochemical considerations; reactive sputtering; very abundant ion at 69 Th
SiCl ⁺	Up to two F atoms abstracted; process is strongly dependent upon ionizing energy; small abundance of halogen exchange is observed (335 Th); diminished ion at 69 Th
P ⁺	Single, possibly double F-atom abstraction; reactive sputtering
PCI ⁺⁺	Single and double F-atom abstraction; halogen exchange; like P ⁺ ; suppressed 69 Th and enhanced 131 Th; perfluoroalkene product
PCI ₂ ⁺	Similar to PCI ⁺⁺ ; lower F-atom abstraction yields and sputter yields
W ⁺⁺	Up to five fluorine atoms abstracted; complex formed equivalent to WCF ₄ ⁺ ; some charge exchange
W(CO) ₃ ⁺⁺	Up to two fluorine atoms abstracted; abundant 1:1 complexes of W(CO) ₃ ⁺ and perfluorohexane formed

source [39]. Based upon these and other results it appears that the reaction of ions at surfaces involves the formation of a complex between the ion and adsorbed molecules. Energy is transferred from the projectile to the surface molecules, both impulsively in the form of translational energy through the collision process and as chemical energy through bond formation or charge exchange. After the deposition of this energy, the projectile, or a fragment thereof, may be liberated from the surface following a very brief period of residence [54–58]. Alternatively, after deposition of energy into the surface, the projectile may form a bond directly with a species at the surface.

Conclusions

The results of this study demonstrate several key points regarding parallels between ion/surface collisions and gas-phase reactions. First, nearly every ion investigated abstracted fluorine atom(s) from the perfluorinated target molecule. There is ample precedence for this, both in the analogous ion/surface reactions and in reactions of Al⁺, Ti⁺, and other ions [49, 53–56] previously found to abstract up to two chlorine atoms in the course of reactions with gaseous di-, tri-, or tetrachloromethane. Second, halogen exchange, observed previously in ion/surface reactions [27], also occurs in the gas phase. Here, it is seen to be accompanied by alkene formation, suggesting that the occurrence of the corresponding surface modification process be sought. Third, the presence of ion/molecule complexes in the product-ion spectra from reactions of W-containing ions supports the expectation of modification of the target surface through alkene formation. The presence of unusual relative abundances of fluorocarbon ions indicates that a process analogous to reactive sputtering occurs in the gas phase [27].

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