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Dissociative charge transfer in reactions of CCl_4 and SF_6 with ions having recombination energies between 6.4 eV and 24.5 eV

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Abstract

Gas mixtures of CCl_4 and SF_6 with rare gases and simple diatomic gases in reactive plasmas are often used to etch insulating and semiconductor layers. However, much of the kinetic and product ion information for ion-molecule processes that occur in such plasmas is not known. To improve this situation, a selected ion flow tube (SIFT) study has been made of reactions of CCl_4 and SF_6 variously with D_3^+, H_3^+, D^+, N^+, D_2^+, N_2^+, Ar^+, Ne^+, He_2^+, and He^+ at 298 K. Because water is a common plasma impurity, the reactions of H_2O^+ and H_3O^+ have also been included. With this information, better models can be developed to predict plasma conditions that are optimal for etching. Reactions generally proceed by dissociative charge transfer with rate coefficients close to the collisional values. The degree of fragmentation (into Cl^+, CCl^+, CCl_2^+, CCl_3^+ and SF_3^+, SF_4^+, SF_5^+) and the energy thresholds at which products are observed are frequently consistent with a long-range mechanism in which the available energy goes into fragmentation. Notable exceptions to this are reactions of D_3^+ and H_3O^+ with CCl_4 and D^+, H_3^+, H_2O^+, and H_3O^+ with SF_6. Rate coefficients and product ion information are discussed in terms of photoelectron spectroscopy (PES) and photoionization (coincidence) data (e.g. threshold photoelectron-photoion coincidence (TPEPICO) and PEPICO techniques) available in the literature. From this comparison, a better fundamental understanding of the dynamics of charge transfer is obtained. In addition to the reactions of neutral CCl_4 and SF_6 gases, Cl_2^+, CCl_2^+, CCl_3^+ and SF^+, SF_2^+, SF_3^+, SF_4^+, SF_5^+ studies with H_2 have also been conducted. (Int J Mass Spectrom 185/186/187 (1999) 759–772) © 1999 Elsevier Science B.V.

Keywords: SIFT; Charge transfer; Sulfur hexafluoride; Carbon tetrachloride; Photoelectron spectroscopy

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1. Introduction

In the etching of/deposition on semiconductor chips and in high power electrical “switches”, plasmas containing mixtures of electron attaching gases, such as CCl_4 and SF_6, with rare and simple diatomic gases are often involved [1–6]. For example, the etching process relies on bombardment of the semiconductor surface by positive ions followed by the removal of semiconductor material by radicals created in the plasma (e.g. F and Cl). For many years, it has been possible to optimize the etch rate and shape and dimensions of the etch pits by trial-and-error methods. However, with the increasing density of elements required on semiconductor surfaces, this approach is no longer viable and the details of the discharge plasma and of the plasma/surface interaction have to be modeled [7–13]. As a contribution to this effort, we

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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have studied the reactions of a series of plasma and impurity ions with the rapidly electron attaching gases CCl_4 and SF_6. For the sequence of ions in this investigation (H_3O^+, D_3^+, H_3^+, H_2O^+, D^+, N^+, D_2^+, N_2^+, Ar^+, Ne^+, He_2^+, and He^+), a major overall reaction mechanism is dissociative charge transfer and, through interpretation of these data in terms of photoelectron spectroscopy (PES) and photoionization (coincidence) data, valuable insights about the charge transfer process have been gained. Charge transfer is one of the processes to which Mike Bowers has made crucial contributions and it is a pleasure to acknowledge this by contributing this article to a volume in his honor.

This investigation has also been critical in interpreting our studies of the infrared emissions from ionic reactions and ion recombination processes (electron–ion and ion–ion) [14]. Because of the reduced sensitivity of the infrared detection techniques, relative to those at shorter wavelengths, it has been necessary to use a flowing afterglow, which has a high ionization density, to give detectable emissions, and this introduces the possibility of emissions from contaminating reactions. Many of these have been eliminated and the contributions of the others assessed using the data presented here. In addition to the reactions of neutral CCl_4 and SF_6 with the above reactant ions, Cl_2^+, CCl_2^+, CCl_3^+ (Cl^+ and CCl^+ have been measured previously [15]) and SF^+, SF_2^+, SF_3^+, SF_4^+, SF_5^+ reactions with H_2 have also been studied. This has enabled our newly developed infrared technique to be characterized fully.

2. Experimental

These studies were made using a selected ion flow tube (SIFT) of a configuration that has been discussed in the literature previously [16,17]. Thus only the features salient to the present study will be presented here. The reactant ions were generated in a series of ion sources, microwave discharge (μW), low-pressure electron impact (LPEI) and high-pressure electron impact (HPEI), using a variety of source gases. He^+, Ne^+, Ar^+, N_2^+ and N^+ were produced respectively from He, Ne, Ar and N_2 in the μW source, D^+, D_2 and H_2O^+ from D_2 and H_2O in the LPEI source, and D_3^+ from D_2 in the HPEI source. (D^+ was studied rather than H^+ because of difficulties in separating the H^+ reactant ion from the total ion signal in the mass filters). The ion of interest was extracted from the ion source, focused into the quadrupole mass filter, mass selected and focused through a 1 mm diam. orifice into the flow tube. The ions were then entrained in a helium carrier gas at ~0.5 Torr, except in the case of He_2^+ which was produced by the tertiary association reaction [18]

$$He^+ + 2\,He \rightarrow He_2^+ + He \tag{1}$$

by selectively injecting He^+ and increasing the flow tube pressure to ~0.85 Torr. Only a small amount of He^+ (~ 20% of He_2^+ signal) remained to complicate the analysis. However, because the reaction of He^+ was studied with each reactant neutral, it was possible to account for this. D^+ was created by injecting D_2^+ at large injection energies (~25 eV in the center-of-mass frame) to cause a high degree of fragmentation (~98%). Note that for D_2^+ studies, injection energies of about 2 eV in the center-of-mass frame were used to minimize fragmentation (only about 16% D^+ was produced). In the CCl_n^+ and SF_n^+ reaction studies with H_2, reactant ions were generated from CCl_4 and SF_6 in the LPEI ion source and individually injected into the flow tube in sequential studies. For the Cl_2^+ reaction with H_2, Cl_2^+ was generated from the reaction [18]

$$Ar^+ + Cl_2 \rightarrow Cl_2^+ + Ar \quad (57\%) \tag{2a}$$

$$\rightarrow Cl^+ + Cl + Ar \qquad (43\%)$$

$$k = 1.5(-10)\ \text{cm}^3\ \text{s}^{-1} \tag{2b}$$

where Ar^+ was produced from Ar in the μW source and selectively injected into the flow tube and Cl_2 was added downstream. Note all rate coefficients are written in the form $a(-b)$ denoting $a \times 10^{-b}$ cm^3 s^{-1}.

The reactant and product ions were detected, after sampling through a nose cone orifice (0.3 mm diam), by a downstream quadrupole mass spectrometer followed by ion counting. Reactant gases and vapors were added at various ring ports (injection holes facing upstream) positioned along the flow tube and rate coefficients and product ion distributions were obtained in the usual way [19,20]. The SF_6 reactant gas ($\geq$99.8%) was used directly as obtained from Matheson whilst the CCl_4 reactant vapor was taken from a HPLC grade sample (99.97%) from Aldrich that had been freeze-pump-thawed several times before use. All measurements were made at 298 ± 2 K. Rate coefficients are accurate to ±20% for CCl_4 and ±15% for SF_6. Product ion distributions are accurate to within ±5 in the percentage value.

A sample of the data is shown in Figs. 1(a) and (b) where the primary ion decay can be seen to be extremely linear (approximately two orders of magnitude reduction). The product ion plot clearly shows that in this case the product ion distribution is 50% CCl_2^+ and 50% CCl_3^+.

3. Results and discussion

The rate coefficients and product-ion distributions for all the reactions of CCl_4 and SF_6, including that illustrated in Fig. 1, are given in Tables 1 and 2. These data show that almost all of the reactions proceed close to the gas kinetic rate (exceptions are the Ar^+ and N_2^+ reactions with CCl_4 and Ne^+ and H_2O^+ with SF_6, with no reaction for H_3O^+ with SF_6). Dissociative charge transfer is the predominant mechanism, with the degree of fragmentation increasing with increasing energy dissipated in the reaction (i.e. with increasing recombination energy of the reactant ion). Note that nondissociative charge transfer was never seen and thus a direct charge transfer would have to be followed by decomposition of the excited CCl_4^+ and SF_6^+ (denoted by CCl_4^{+*} and SF_6^{+*}). This is consistent with CCl_4^+ and SF_6^+ only being previously observed experimentally at very low levels [21,22] and with conclusions from TPEPICO (threshold photoelectron-photoion coincidence) and PEPICO data, that CCl_4^{+*} and SF_6^{+*} are unstable and fully dissociate [23–28]. SF_6^{+*} has also been shown to have an ionization onset, measured by photoelectron spectroscopy (PES), which is almost identical to the appearance energy of SF_5^+ from SF_6 as measured by photoionization mass spectrometry (PIMS) [29]. For the D^+ and D_2^+ reactions, the major contaminant primary ions HeD^+ and NeD^+ (from Ne impurity in the He) were also present in the flow tube. In addition, D^+ and D_2^+ react very rapidly with impurity species [15,18]. These effects were accounted for; nonetheless, uncertainty in product ion distribution is increased to ± 10 in the percentage value for D^+ with CCl_4 and SF_6. Unlike the reaction of D_2^+ with SF_6 in which only one product ion was observed (despite the presence of impurity ions) and thus reliable product ion information could be obtained, several product ions were observed for the D_2^+ reaction with CCl_4. Because of this, and because D_2^+ reacts rapidly with impurity species, only major product ions are reported with no percentage information given.

3.1. CCl_4 reactions

Rate coefficients are close to the collisional values except for N_2^+ (which is a factor of 6 smaller) and Ar^+ (a factor of 2 smaller). The Ar^+ reaction has been studied previously [30,31] and the rate coefficients are in agreement with the present value, although the distributions of the product ions differ, with CCl_2^+ being dominant in our case. This may be as a result of the presence of the Ar^+ $^2P_{3/2,\ 1/2}$ spin states which could react somewhat differently. There was some evidence for this in that the primary ion decay curve was less linear than is normally obtained. Fitting of the experimental data to the sum of two exponentials gave values of 1.3(−9) and 5.9(−10) $cm^3\ s^{-1}$ for the separate states (the relative magnitudes of the pre-exponential factors of 1.8 is consistent with the ratio of the statistical weights if the larger rate is associated with the 3/2 state). If reaction proceeds by long-range charge transfer then one might expect reactivity to be controlled by Franck-Condon overlap between the neutral CCl_4 and the specific state of CCl_4^+ that is being accessed. Such detailed information is not available, however, photoelectron spectra have previously been obtained for both CCl_4 [32] and SF_6 [33] and these are illustrated in Fig. 2. It should be noted

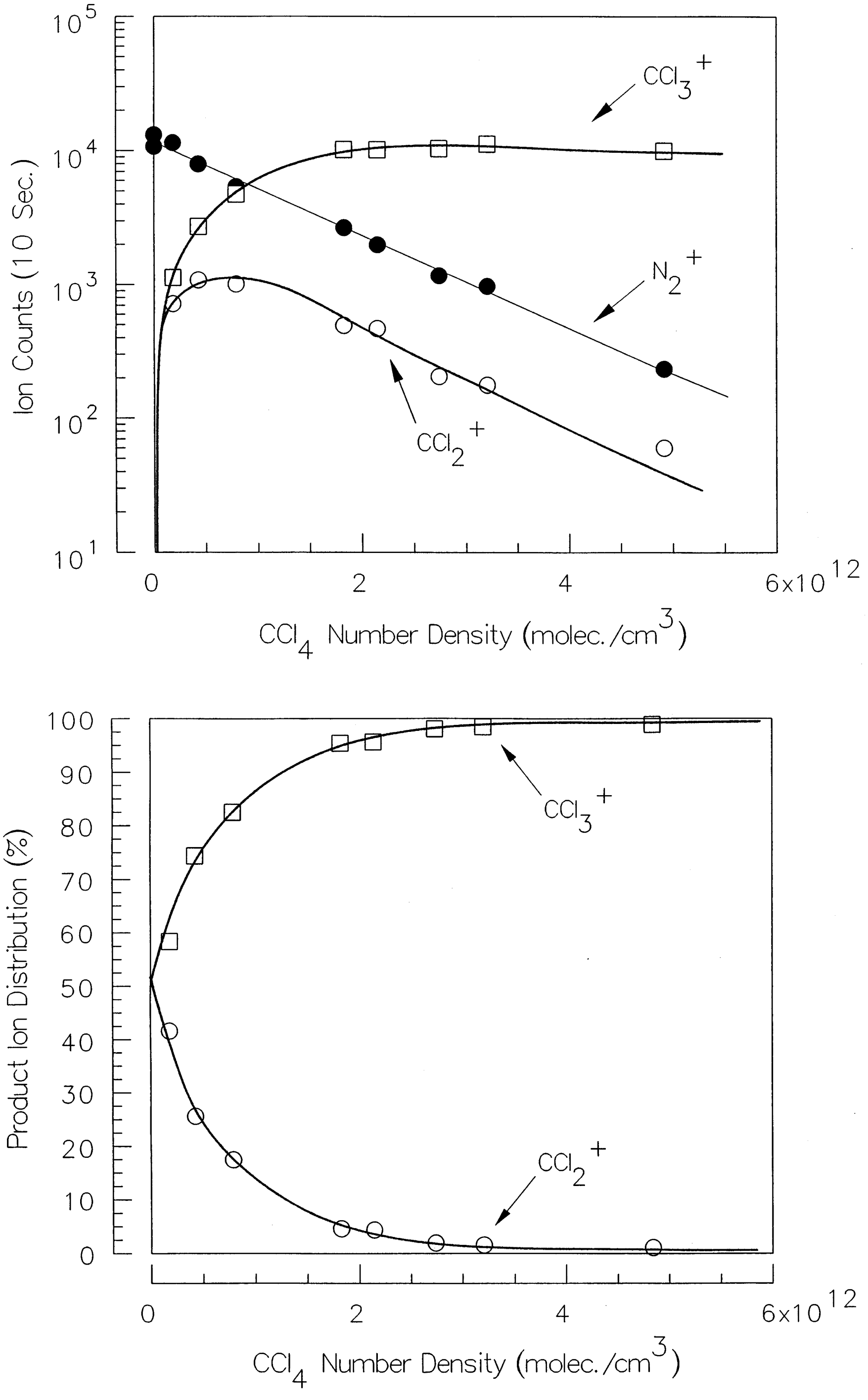

Fig. 1. (a) Decay of the N_2^+ count rate and increase in the primary product ions, CCl_2^+ and CCl_3^+, as a function of CCl_4 number density for the dissociative charge transfer reaction. CCl_2^+ reacts further. (b) Percentage product ion plot for the N_2^+ reaction with CCl_4. Note that the CCl_3^+ and CCl_2^+ count rates have been corrected for isotopic abundances and mass discrimination.

Table 1
Rate coefficients and product ion distributions for the reactions of CCl_4 with common plasma ions

Reactant ion	Product channels[a]	Product ion distribution (%)		Rate coefficient ($cm^3\ s^{-1}$)			ΔH° (kcal mol^{-1})
		Present	Previous	Present	Previous	Langevin	
H_3O^+	$CCl_3^+ + HCl + H_2O$	100	. . .	1.8(−9)	. . .	1.9(−9)	1.3
D_3^+	$CCl_3^+ + DCl + D_2$	100	. . .	3.2(−9)	. . .	3.2(−9)	−64.4
H_2O^+	$CCl_3^+ + Cl + H_2O$	100	. . .	2.1(−9)	. . .	1.9(−9)	−39.6
D^+	$CCl^+ + Cl_2 + DCl$	10[b]	. . .	4.9(−9)	. . .	5.5(−9)	−68.7
	$CCl_2^+ + Cl + DCl$	10					−58.7
	$CCl_3^+ + DCl$	80					−166.7
N^+	$CCl_2^+ + Cl_2 + N$	10	. . .	2.1(−9)	. . .	2.2(−9)	−34.0
	$CCl_3^+ + Cl + N$	90					−84.0
D_2^+	$CCl^+ + Cl + 2\ DCl$	CCl^+[c]	. . .	3.7(−9)	. . .	3.9(−9)	−52.1
	$CCl_2^+ + 2\ DCl$	CCl_2^+	. . .		. . .		−52.1
	$CCl_3^+ + DCl + D$	CCl_3^+					−103.8
N_2^+	$CCl_2^+ + Cl_2 + N_2$	50	. . .	2.8(−10)	. . .	1.6(−9)	−58.1
	$CCl_3^+ + Cl + N_2$	50					−108.1
Ar^+	$CCl_2^+ + Cl_2 + Ar$	74[d]	39[e]	7.1(−10)[d]	8.1(−10)[f]	1.4(−9)	−62.2
	$CCl_3^+ + Cl + Ar$	26	61		5.4(−10)[e]		−112.2
Ne^+	$Cl^+ + CCl_3 + Ne$	9[g]	. . .	1.9(−9)	. . .	1.9(−9)	−127.1
	$CCl^+ + Cl_2 + Cl + Ne$	88					−148.1
	$CCl_2^+ + Cl_2 + Ne$	≤3[g]					−196.1
He_2^+	$Cl^+ + CCl_3 + 2\ He$	18	. . .	2.7(−9)	. . .	2.8(−9)	−142.2
	$CCl^+ + Cl_2 + Cl + 2\ He$	70					−163.2
	$CCl_2^+ + Cl_2 + 2\ He$	12					−211.2
He^+	$Cl^+ + CCl_3 + He$	22	. . .	3.3(−9)	. . .	4.0(−9)	−196.8
	$CCl^+ + Cl_2 + Cl + He$	78					−217.8

The enthalpy changes, ΔH°, in the reactions were calculated using thermochemical data from [45].

[a] Only the less fragmented neutral products are reported.

[b] Uncertainty in product ion distribution is increased to ± 10 in the percentage value because account had to be taken of the presence of primary impurity ion HeD^+ and NeD^+.

[c] All products observed (see text).

[d] Rate coefficient and product ion distribution for Ar^+ ($^2P_{3/2,\ 1/2}$) + CCl_4 (see text).

[e] See [30].

[f] See [31].

[g] Product ion could be a result of reactions of CCl_4 with $HeNe^+$ and Ne_2^+ contaminant ions (from a Ne impurity in the He) which could result in a maximum 10% combined contribution.

that in PES and PEPICO an additional ionization mechanism is possible, that of autoionization. Here the initial photoexcitation is to a highly excited state of the neutral which then autoionizes resonantly giving a threshold electron or autoionizes to a lower energy state of the ion with the energy released being taken up as electron kinetic energy. Autoionization is more common in threshold electron studies because the photon energy is varied and therefore can become resonant with excited neutral states (see [34,35] for details). Such a process is not possible in the present studies because there is no free electron. From the PES spectrum of CCl_4, it can be seen that the recombination energies of Ar^+ and N_2^+, are in a region where there are apparently no resonances in the spectrum and thus no available excited states of CCl_4^+. Therefore, if the reactions occur by long-range charge transfer, the rate coefficients would be expected to be small as is observed. In contrast, the recombination energies of H_2O^+ and D^+ are resonant with the A and B states of CCl_4^+ respectively and have large rate coefficients. This is also indicative of a long-range charge transfer process.

For reactant ions with recombination energies

Table 2
Rate coefficients and product ion distributions for the reactions of SF_6 with common plasma ions

Reactant ion	Product channels[a]	Product ion distribution (%)		Rate coefficient (cm^3 s^{-1})			ΔH° (kcal mol^{-1})
		Present	Previous[b]	Present	Previous[b]	Langevin	
H_3O^+	No reaction	. . .	. . .	≤2(−12)	<5(−12)	1.5(−9)	. . .
H_3^+	$SF_5^+ + HF + H_2$	. . .	100	. . .	3.1(−9)	3.5(−9)	−14.8
H_2O^+	$(OSF_4)^+ + 2\ HF$	$(OSF_4)^{+}$[c]	. . .	1.9(−10)	. . .	1.5(−9)	. . .
	$(OHSF_5)^+ + HF$	$(OHSF_5)^+$					
	$(H_2OSF_6)^+$	$(H_2OSF_6)^+$					
D^+	$SF_4^+ + DF + F$	5	. . .	4.7(−9)	. . .	4.2(−9)	−25.9
	$SF_5^+ + DF$	95					−116.9
N^+	$SF_3^+ + F_2 + NF$	2		1.8(−9)	1.4(−9)	1.7(−9)	−6.9
	$SF_5^+ + NF$	98	100				−78.0
D_2^+	$SF_5^+ + DF + D$	100	. . .	3.6(−9)	. . .	3.0(−9)	−54.0
N_2^+	$SF_5^+ + F + N_2$	100	100	1.2(−9)	1.3(−9)	1.2(−9)	−25.6
Ar^+	$SF_5^+ + F + Ar$	. . .	100	. . .	9.3(−10)	1.1(−9)	−29.7
Ne^+	$SF_3^+ + F_2 + F + Ne$	91	. . .	7.8(−10)	. . .	1.4(−9)	−92.5
	$SF_4^+ + F_2 + Ne$	3[d]					−110.6
	$SF_5^+ + F + Ne$	6[d]					−163.6
He_2^+	$SF_3^+ + F_2 + F + 2\ He$	86	. . .	2.0(−9)	. . .	2.2(−9)	−107.6
	$SF_4^+ + F_2 + 2\ He$	14					−125.7
He^+	$SF_3^+ + F_2 + F + He$	94	SF_3^{+}[e]	2.1(−9)	2.0(−9)	3.0(−9)	−162.2
	$SF_4^+ + F_2 + He$		SF_4^+				−180.3
	$SF_5^+ + F + He$	6	SF_5^+				−233.3

The enthalpy changes, ΔH°, in the reactions were calculated using thermochemical data from [45,46].

[a] Only the less fragmented neutral products are reported.

[b] See [18].

[c] All product observed (see text).

[d] Product ion could be a result of reactions of SF_6 with $HeNe^+$ and Ne_2^+ contaminant ions (from a Ne impurity in the He) which could result in a maximum 10% combined contribution.

[e] All products observed with no percentage ion information given.

above threshold, this does not necessarily mean that the reactions will proceed by long-range charge transfer. For example, this could be indicated by the He_2^+ and Ne^+ reactions which are efficient even though there is no peak in the PES spectrum. The correlation between the PES spectrum and charge transfer reactivity should not be taken too far because the PES additionally requires the ejection of an electron with the balance of the energy appearing as electron kinetic energy. If this process is not uniformly efficient for all electron energies then the form of the resonance indicated by the PES peak could be different from that appropriate for the charge transfer reactions. Because of this difference between PES studies and the studies reported here, there should be caution that the PES studies are not over-generalized. In PES, the excitations to all accessible states are occurring simultaneously and the most dominant resonances will be those which are most facile. In the present study, for a given reaction in which long-range charge transfer occurs, only a fixed amount of energy is generally transferred into ionization of the neutral and thus competition with the production of other states cannot occur. What matters here is the process efficiency in absolute terms (i.e. within the time that the reactants are in the same vicinity), rather than the time before a competitive channel occurs which could be much shorter.

A great deal of additional understanding can be obtained from comparisons with the PEPICO and He^m Penning ionization studies of Kischlat and Morgner [26] and the TPEPICO studies of Smith et al. [23] where the ions produced by the ionization process were identified. These show that the B, A, and X states of CCl_4^+ fragment to CCl_3^+ the C state to CCl_2^+ and the D state to CCl^+ with the small unidentified

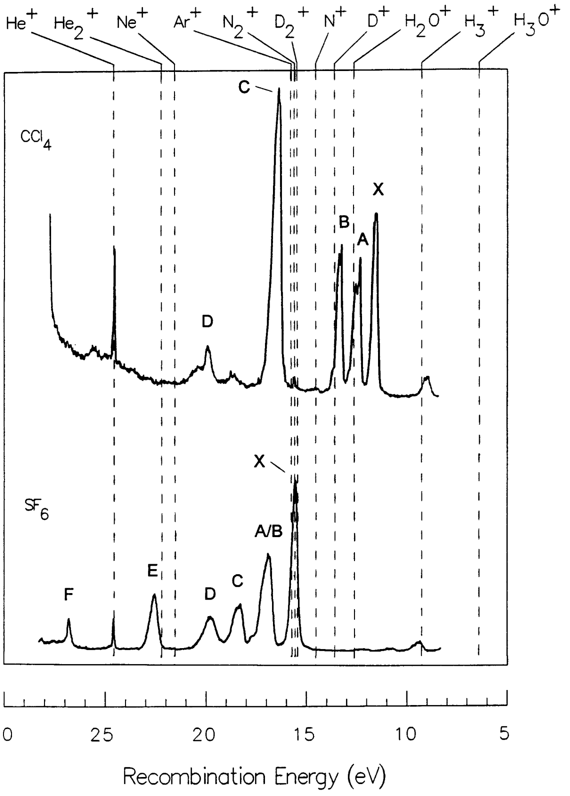

Fig. 2. Photoelectron spectra for CCl_4 [32] and SF_6 [33] obtained with 30.4 nm photons with the product ion states identified. The recombination energies of all of the reactant ions (given in Table 3) are indicated. Note that the values for the H and D atom variants will not be signficantly different.

peak between the C and D states giving mainly CCl_2^+ and perhaps some CCl^+. It should be noted that there is little evidence from our studies to determine whether the dissociation is the unimolecular decomposition of a bound state, predissociation or direct dissociation from a repulsive curve. CCl_3^+ was observed as the only product ion for the H_3O^+, D_3^+, and H_2O^+ reactions with CCl_4. D_3^+ and H_3O^+ are special cases because CCl_3^+ production is endothermic. However, in the D_3^+ reaction if the D atom is bonded to the ejected Cl as DCl, the reaction is exothermic. But even with this mechanism, the H_3O^+ reaction is still predicted to be endothermnic by 1.3 kcal mol^{-1}. This is not possible because the rate coefficient is at the gas kinetic limit, implying that either the literature value of the heat of formation of CCl_3^+ is too large or that of H_3O^+ is too small. Our observation of CCl_3^+ as the only product ion from H_2O^+ reaction is consistent with concidence data because the recombination energy of H_2O^+ is resonant with the A state. Resonance with the B state occurs for the recombination energy of D^+, again consistent with CCl_3^+ being the major product ion. The following possible explanations exist for the presence of the minor product ions CCl_2^+ and CCl^+ (assuming the impurity ions HeD^+ and NeD^+ are not significantly distorting the distribution): (1) Burton et al. [36] are correct in their observation of a weak CCl_2^+ signal that occurs at a threshold of 13.5 ± 1 eV despite the conflicting results of Golovin et al. [25], Kischlat and Morgner [26], and Smith et al. [23]. (2) The reaction is intimate forming DCl (bond strength of 4.52 eV) as a neutral product which would result in a more energetic reaction allowing greater fragmentation. In such a case, photoionization data would only be relevant if the $D^+ \ldots CCl_4$ complex that is formed initially is only weakly bonded such that the CCl_4/CCl_4^+ potential curves are undistorted. When charge transfer occurs, the ion-induced dipole energy could thus be involved in the interaction moving the resonance higher in energy. Following this charge transfer to form the $D \ldots CCl_4^+$, the Cl would be abstracted from the unstable CCl_4^{+*} to form DCl and the observed CCl_3^+. (3) For an intimate charge transfer reaction, the possible distortion of the potential curves could result in favorable Franck-Condon overlap with the C state.

As for D_2^+, only CCl^+, CCl_2^+ and CCl_3^+ major ions are reported with no percentage information given. Though the reaction has high efficiency, no apparent resonance at the D_2^+ recombination energy is present. Therefore either the reaction is intimate as in the D_3^+ and H_3O^+ reactions and/or some energy is dissipated as kinetic energy and/or internal energy in the product D_2, resulting in resonance with the states that give the CCl_3^+ fragment ion. CCl_2^+ and CCl^+ production is problematic in that the only reported states to give these ions are the C and D state respectively, with the small unidentified peak between the C and D states giving both ions. All lie higher in energy than the D_2^+ recombination energy. This reaction channel is exothermic if the molecular neutral products are 2 DCl or D_2 and Cl_2, the former requiring an intimate interaction.

N^+ lies lower in energy than Ar^+ and N_2^+, and shows a much larger CCl_3^+ product (in both percentage terms and in terms of the absolute magnitude of the rate coefficient into this channel) consistent with it being closer to the high vibrational levels of the B, A, and X states or with the fact that less energy would need to be dissipated kinetically to occupy these states. As stated earlier when discussing the D^+ reaction, Burton et al. [36] observed a weak CCl_2^+ signal at a threshold of 13.5 ± 1 eV, which could explain the small CCl_2^+ signal for the N^+ reaction. The products observed in the Ar^+ and N_2^+ reactions are CCl_2^+ and CCl_3^+ in approximately equal quantities. The recombination energies of these ions lie between the B, A, and X state grouping and the C state. Population of the former grouping of states (with the production of CCl_3^+) requires either that ~2.5 to 4 eV of the available energy is converted into kinetic energy of the neutralized reactant ion and the primary product CCl_4^+ with some as internal energy in the CCl_4^+ (also in the N_2 in the case of the N_2^+ reaction) or that high vibrational levels of these states are populated whose Franck-Condon overlap for photoionization is small. The fact that N_2 internal excitation can occur, may be responsible for the higher proportion of CCl_3^+ in this case. The C state population can be inferred from the CCl_2^+ product percentages (if Burton et al. [36] are not correct) for the Ar^+ and N_2^+ reactions, and, from an Arrhenius approach, this suggests that the reaction channel is endothermic by a maximum of 0.03 and 0.06 eV, respectively. This implies that the CCl_4^+ (C, v = 0) ← CCl_4 (X, v = 0) transition has a small Franck-Condon overlap and occurs below the peak maximum in Fig. 2 or perhaps that the energy scale is slightly shifted. Tsuji et al. [30], who previously studied the Ar^+ reaction, suggested that CCl_2^+ is formed through near-resonant high vibrationally excited levels of the B state and/or low vibrational levels of the C state in the 15.4 (appearance potential from CCl_4) − 15.76 eV (Ar^+ recombination energy) energy range, noting that the Franck-Condon factors for ionization into the levels would be very small. For CCl_3^+, they state that the most probable precursor state would be the B state on the basis of the energy-resonance rule.

For the He_2^+ and Ne^+ reactions, the recombination energies lie somewhat above the D state consistent with the large CCl^+ product because Smith et al. [23] have reported a high energy tail for this state that extends to at least 23.3 eV (the end of their scan range). Alternatively, some of the energy could be dissipated as kinetic energy bringing the available internal energy closer to that of the D state. A similar tail has been observed for the C state between approximately 17.5 and 20.0 eV. As a result, the small contribution of CCl_2^+ to the product distributions for the Ne^+ and He_2^+ reactions could be explained by this state. Though the recombination energy of Ne^+ is closer to the above range, yet has a smaller proportion of CCl_2^+ than the He_2^+ reaction, the latter reaction could have some energy taken up in kinetic energy of dissociation of the two He atoms after charge transfer, making the available energy smaller. CCl^+ is also the major product for the He^+ reaction. For resonance with the D state to occur, the reaction would need to be intimate with a proportion of the energy being dissipated as kinetic energy. Cl^+ is an important product in all these three reactions but has not been observed as a fragmentation product by any of the coincidence techniques. It may originate from the unresolved peak lying at energies above the D state for the He^+ reaction or, for all of the reactions, the Cl^+ product could be the result of an intimate reaction. For Ne^+, this assumes that the smaller Cl^+ contribution is not because of the minor $HeNe^+$ or Ne_2^+ impurity ions (from a Ne impurity in the He).

Additional information on the reaction mechanisms can be obtained by considering the body of evidence on product ions as a function of available energy. From Table 1, it can be seen that there is a very obvious trend of increasing fragmentation (from CCl_3^+ to Cl^+) with increasing recombination energy of the reactant ion. This is shown graphically in Fig. 3 (a) where the product distributions are plotted as a function of recombination energy (the recombination energies of the reactant ions are given in Table 3). The thresholds for production of several of the fragmen-

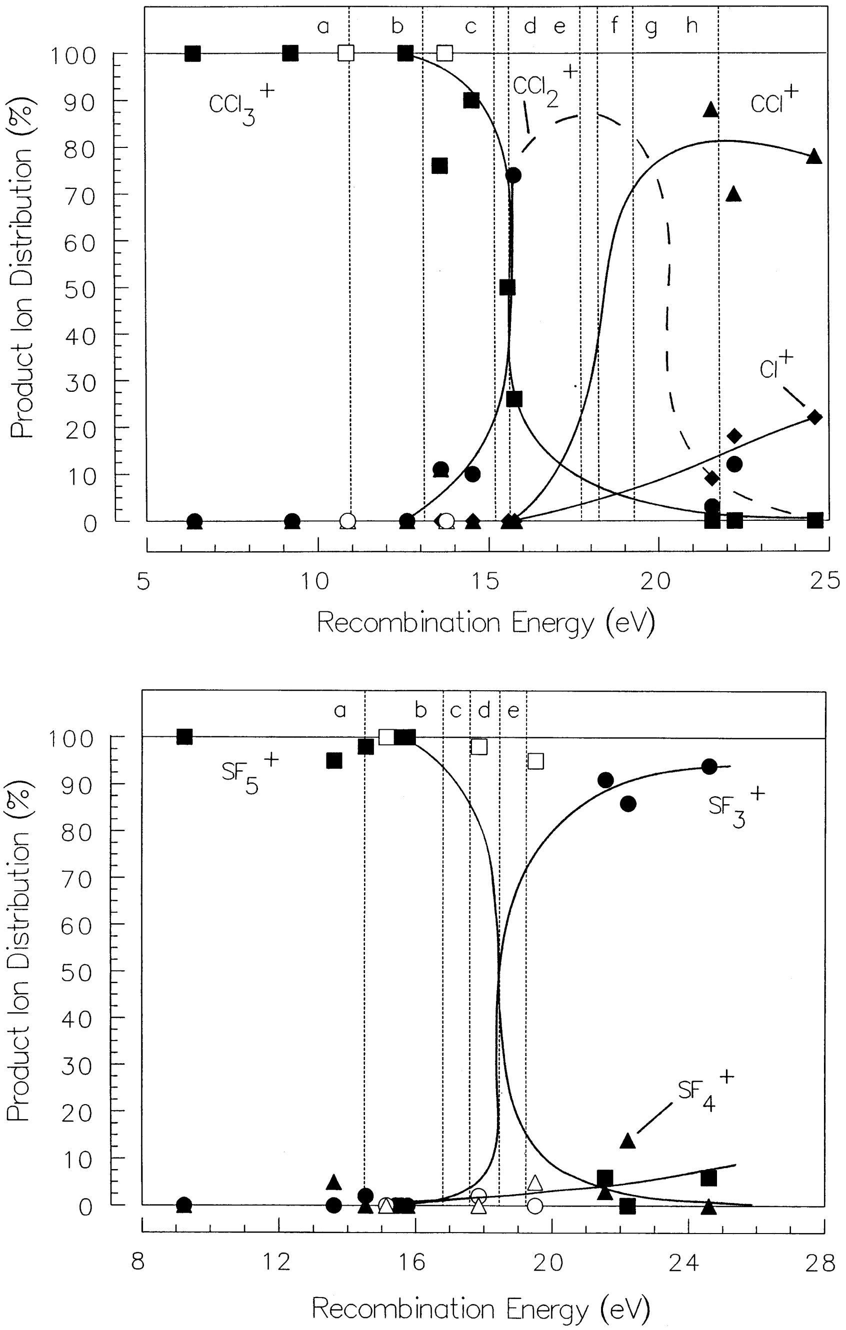

Fig. 3. Variation in the degree of fragmentation in dissociative charge transfer with reactant ion recombination energy for (a) CCl_4 and (b) SF_6. Thresholds for CCl_4 dissociative channels are denoted by the following: a) $CCl_4 \rightarrow CCl_3^+ + Cl + e$, b) $\rightarrow CCl_2^+ + Cl_2 + e$, c) $\rightarrow CCl^+ + Cl_2 + Cl + e$, d) $\rightarrow CCl_2^+ + 2\,Cl + e$, e) $\rightarrow CCl^+ + 3\,Cl + e$, f) $\rightarrow Cl^+ + CCl_2 + Cl + e$, g) $\rightarrow Cl^+ + CCl + Cl_2 + e$, h) $\rightarrow Cl^+ + CCl + 2\,Cl + e$. Thresholds for SF_6 dissociative channels are denoted by the following: a) $SF_6 \rightarrow SF_5^+ + F + e$, b) $\rightarrow SF_4^+ + F_2 + e$, c) $\rightarrow SF_3^+ + F_2 + F + e$, d) $\rightarrow SF_4^+ + 2\,F + e$, e) $\rightarrow SF_3^+ + 3\,F + e$. The thresholds that are shown in the figures are for those dissociative channels that are in best agreement with experimental data. Unfilled data points are for the reactions with the bond strengths of HCl/DCl, HF/DF, and NF accounted for (see text).

Table 3
Recombination energies of the reactant ions [45,47]

Reactant ion	Recombination energy (eV)
H_3O^+	6.40[a]
H_3^+	9.25[b]
H_2O^+	12.61
D^+	13.60
N^+	14.53
D_2^+	15.47
N_2^+	15.58
Ar^+	15.76
Ne^+	21.56
He_2^+	22.22
He^+	24.59

[a] $H_3O^+ + e \rightarrow H_2O + H$.
[b] $H_3^+ + e \rightarrow H_2 + H$.

tation product ions are shown in the figure and this threshold behavior is evident in the experimental data. (The dissociative channels are listed in Table 4.) This implies that, for recombination energies close to threshold, the reaction proceeds by long-range charge transfer followed by unimolecular decomposition so that the available energy goes into ionization and fragmentation with little being dissipated in kinetic and internal energy of the products. For this a bound, rather than a repulsive potential curve must be accessed. That such reactions proceed by long-range charge transfer with little distortion of the molecular potential curves during the interaction (for the diatomic reactant ions also, that little if any of the reaction exothermicity goes into internal excitation of the neutralized ion) has been previously suggested by Bowers and others [37–41] to occur in some other cases. Little energy was thought to be partitioning into kinetic energy of the products of the initial nondissociative charge transfer process.

Table 4
Enthalpy changes, ΔH°, for dissociative channels for CCl_4 and SF_6 (determined from heats of formation in [45–47])

Reactant neutral	Dissociative channel	ΔH° (eV)
CCl_4	$\rightarrow CCl_3^+ + Cl + e$	10.93
	$\rightarrow CCl_2^+ + Cl_2 + e$	13.09
	$\rightarrow CCl_2^+ + 2Cl + e$	15.61
	$\rightarrow CCl^+ + Cl_2 + Cl + e$	15.18
	$\rightarrow CCl^+ + 3\,Cl + e$	17.69
	$\rightarrow Cl^+ + CCl_3 + e$	16.09
	$\rightarrow Cl^+ + CCl_2 + Cl + e$	18.21
	$\rightarrow Cl^+ + CCl + Cl_2 + e$	19.25
	$\rightarrow Cl^+ + CCl + 2\,Cl + e$	21.77
	$\rightarrow Cl^+ + Cl_2 + C + Cl + e$	23.95
	$\rightarrow Cl^+ + C + 3\,Cl + e$	26.46
SF_6	$\rightarrow SF_5^+ + F + e$	14.50
	$\rightarrow SF_4^+ + F_2 + e$	16.80
	$\rightarrow SF_4^+ + 2\,F + e$	18.45
	$\rightarrow SF_3^+ + F_2 + F + e$	17.59
	$\rightarrow SF_3^+ + 3\,F + e$	19.23

As stated above, only in the cases of D_3^+ and H_3O^+ are the products ions apparently produced below threshold and at the gas kinetic rate. This implies, in these cases, that the reactions are intimate with $CCl_3^+ + DCl/HCl$ being produced. Taking account of the DCl/HCl bond energy (4.52/4.47 eV) makes these data points consistent with the behavior of the other reactions illustrated in Fig. 3(a).

3.2. SF_6 reactions

As for the CCl_4 reactions, rate coefficients are generally close to the collisional value except for Ne^+ (which is a factor of 2 smaller), H_2O^+ (a factor of 8 smaller) and H_3O^+ (no reaction). Where comparison with previous data (N_2^+ and N^+) is possible, there is agreement in both the rate coefficients and the product ion distributions [18]. From the PES spectrum (Fig. 2) there are no resonances at the recombination energies of Ne^+ and H_2O^+ which is consistent with the smaller rate coefficients, but there are also no resonances for other reactions (He^+, D^+ and H_3^+) which proceed with high efficiency. (The H_3^+ recombination energy is resonant with an unidentified peak in Fig. 2 and for H_3O^+ there are no PES data available at its recombination energy.) Even so, it is interesting to note that the reactions which proceed with an efficiency of 0.85 or greater either have resonances (i.e. He_2^+, Ar^+, N_2^+, D_2^+, and N^+ (the recombination energy is close to the low energy shoulder of X state) in the PES spectrum or the reaction is intimate producing DF and HF as in the cases of D^+ and H_3^+.

The product ion types in the case of the SF_6 reactions are fewer than for CCl_4 with only the dissociative charge transfer products SF_3^+, SF_4^+, and SF_5^+ generally being observed, except for the reaction of H_2O^+ where the ions $(OSF_4)^+$, $(OHSF_5)^+$ and $(H_2OSF_6)^+$ were observed. The the production of $(OSF_4)^+$ and $(OHSF_5)^+$ is possibly driven by the formation of HF molecules. The H_2O^+ reaction is unusual in this sequence in that the reaction requires bond breaking and making in the product ion and thus an intimate encounter. This is the first report to our knowledge of an ion reacting with SF_6 to give a product not of the type SF_n^+.

Additional understanding of the SF_6 reactions can be gained by comparing the product ion distributions with the recent TPEPICO data of Creasey et al. [27] and PIMS data of Creasey et al. [28]. These experiments show that the X, A, and B states of SF_6^+ fragment to SF_5^+. The E and F state have been shown to fragment to SF_3^+ and SF_2^+, respectively. However, for the C and D states there are some inconsistencies. The TPEPICO data show the branching ratio of the C state to be 8 to 1 for SF_5^+ to SF_4^+, whereas the PIMS data only reported SF_4^+ for this state. Creasey et al. [27] have observed that the branching ratios change when different regions of the C state are accessed; they assigned SF_4^+ formation to the higher vibrational levels and SF_5^+ formation to the lower levels. For the D state, TPEPICO gives a branching ratio of 2.0:1.8:1.0 for SF_4^+:SF_3^+:SF_5^+, which is fairly consistent with the data of Hitchcock and Van der Wiel [42], but for PIMS, only SF_3^+ is observed as a fragment ion which is in agreement with the data of Berkowitz [43].

For H_3O^+ there is no available coincidence data at its recombination energy. Furthermore, it is energetically unfavorable to produce any SF_n^+ ions from H_3O^+. This is all in agreement with our reported $\leq 2(-12)$ $cm^3\,s^{-1}$ rate coefficient. The recombination energy of H_3^+ is not resonant with any of the identified states of SF_6. However, considering the energetics, the H_3^+ reaction must give HF as a neutral product to explain the observed SF_5^+, i.e. an intimate interaction. This is further supported by the product ion distribution data of Fig. 3(b) and by our preliminary IR studies of gas phase ionic reactions where ground electronic state emissions are observed from HF produced in this reaction [14]. The H_2O^+ recombination energy is also not resonant with any ions from reaction state and has no energetically favorable channels to produce any SF_n^+ ions from reaction with SF_6. One might expect to produce HF similarly to the H_3^+ reaction, however no significant SF_5^+ was seen. Note that ground state of H_3 is unstable whereas that of H_2O is not, thus favoring HF production in the former case. Also, as mentioned above, the H_2O^+ reaction is unique amongst the SF_6 reactions in that there are non-SF_n^+ products formed. Based on energetics, D^+ must produce DF as a neutral product for SF_4^+ and SF_5^+ to be observed. This is further supported by the agreement obtained by placing the product ion distribution of the D^+ reaction 5.90 eV higher in energy (the HF bond dissociation energy) in Fig. 3(b) and the fact that no resonance exists at the recombination energy of D^+. The D_2^+, N_2^+, and Ar^+ recombination energies are resonant with the X state, and this is consistent with the SF_5^+ production and with the reactions having high efficiencies. SF_5^+ is produced in the N^+ reaction also. Although a strong resonance is not observed, in contrast to the D_2^+, N_2^+, and Ar^+ reactions, the recombination energy of N^+ is only slightly lower than the low energy shoulder of the X state and therefore the large rate coefficient for SF_5^+ production is not unreasonable. The small observed SF_3^+ signal (2% and at the detection limit) cannot be produced via long-range charge transfer because this is endothermic and there is no energy resonance with an SF_6^+ state dissociating to this ion. Production of SF_3^+ thus requires a close interaction in which F_2 and NF neutral products are generated to make the overall reaction exothermic. That the N^+ is not electronically excited was confirmed by its reactivity with CO and therefore its reaction cannot be the source of the SF_3^+. The Ne^+ reaction gives mainly SF_3^+ but Ne^+ is somewhat lower than the E state peak, the lowest state that generates only SF_3^+. Therefore, Franck-Condon factors for the lower vibrational levels must be significant so that they can be resonant with Ne^+. Also, because the peak is ~1 eV above the recombination energy of Ne^+ and the reaction proceeds with 0.5 efficiency, this would tend to imply that resonance of these lower vibrational levels is occurring. As mentioned in Sec. 3.1, all states in the photoelectron spectrum are accessed simultaneously whereas in the present studies only a single state is accessed by direct charge transfer. Thus, a transition that is not competitive in photoelectron spectroscopy because of small Franck-Condon factors could be important in the present studies. As for the small percentages of SF_4^+ and SF_5^+ observed in the product ion distribution, the higher vibrational levels of the D state could be involved. Two important points should be mentioned, (1) the above statements assume that SF_4^+ and SF_5^+ are not because of the minor $HeNe^+$ and/or Ne_2^+ impurity ions and (2) there are some discrepancies in the photoelectron spectroscopy measurements of the dissociation of the D state as mentioned above. More straightforwardly, He_2^+ is resonant with the E state and thus the results are in agreement with the major product ion being SF_3^+. If the D state, like the C state, fragments to different ions depending on which region of the potential curve is being accessed, then an He_2^+ resonance with its upper vibrational levels could explain the observation of the minor SF_4^+ product. It is noted that for the He_2^+ reaction, energy can additionally be taken up in kinetic energy of dissociation of two He atoms after charge transfer, bringing it into closer resonance with the D state. The He^+ recombination energy lies between the F and E states. The F state has no dissociative channels to either SF_3^+ or SF_5^+ (only to SF_2^+), leaving the most likely population to be the high vibrational levels of the E state, with an analogous argument to the Ne^+ case for the production of the minor SF_5^+ channel. In addition, a small peak in the TPES (threshold photoelectron spectroscopy) data [44] has been observed which would be resonant with He^+.

The product ion distributions are plotted in Fig. 3(b) versus recombination energy and, as for CCl_4, show a clear trend. As mentioned earlier, only for the cases of the H_3^+ and D^+ reactions, are the product ions apparently produced below threshold, but the reactions still proceed essentially at the gas kinetic rate. This implies that the reactions of H_3^+ and D^+ are intimate, with SF_5^+ + HF/DF and SF_4^+ + DF + F being produced. (This assumes that SF_4^+ is not because of impurity ions.) Taking account of the HF bond energy (5.90 eV) makes the data consistent with the threshold behavior of the other reactions.

The dissociative channels that are possible for SF_3^+, SF_4^+, and SF_5^+ production are listed in Table 4. There is good agreement between the SF_5^+ threshold and our experimental data except for the special cases of D^+ and H_3^+ as discussed above. Because of the lack of reactant ion recombination energies in the range where SF_3^+ and SF_4^+ threshold would appear, either unbound or bound fluorine channels could be in agreement with the available experimental data.

3.3. H_2 reactions

In the studies of Cl_2^+, CCl_2^+, CCl_3^+ (Cl^+ and CCl^+ have been measured previously [15]), SF^+, SF_2^+, SF_3^+, SF_4^+, and SF_5^+ with H_2, all ions (except Cl^+) are unreactive (i.e. $k \leq 1.0(-12)$ cm^3 s^{-1}). However, for Cl_2^+, CCl_2^+, and CCl_3^+, exothermic channels to produce HCl are available. They are the following:

$$Cl_2^+ + H_2 \rightarrow HCl^+ + HCl + 15.2 \text{ kcal mol}^{-1} \tag{3}$$

$$CCl_2^+ + H_2 \rightarrow HCCl^+ + HCl + 2.1 \text{ kcal mol}^{-1} \tag{4}$$

$$CCl_3^+ + H_2 \rightarrow HCCl_2^+ + HCl + 9.1 \text{ kcal mol}^{-1} \tag{5}$$

Although the reactions of Cl^+ and CCl^+ with H_2 to produce HCl are not energetically favorable, there are exothermic channels. For example, Cl^+ can energetically produce $HCl^+ + H$ and H_2Cl^+ with exothermicities of 4.1 and 121 kcal mol^{-1} respectively; CCl^+ can energetically produce CH_2Cl^+ with an exothermicity of 67.8 kcal mol^{-1}. Cl^+ reacting with H_2 has been measured to give 100% HCl^+ at 7.2(−10) cm^3 s^{-1} [15]. Therefore, with the reactions being below the detection limit (excluding Cl^+), large energy barriers must be present or some steric factors must be important.

For SF_n^+ ions (n = 1 to 5), only SF^+, SF_4^+ and SF_5^+ can energetically produce HF,

$$SF^+ + H_2 \rightarrow HS^+ + HF + 28.6 \text{ kcal mol}^{-1} \tag{6}$$

$$SF_4^+ + H_2 \rightarrow SF_3^+ + HF + H + 13.9 \text{ kcal mol}^{-1} \tag{7}$$

$$SF_4^+ + H_2 \rightarrow SF_2^+ + 2\,HF + 64.0 \text{ kcal mol}^{-1} \tag{8}$$

$$SF_5^+ + H_2 \rightarrow SF_3^+ + 2\ HF + 58.9\ \text{kcal mol}^{-1} \qquad (9)$$

For SF_2^+ and SF_3^+ there are apparently no exothermic channels which can be determined with the energetic information that is available (energetics for channels leading to the production of $H_mSF_n^+$ with $m = 1$ or 2 and $n = 1$ to 3 could not be calculated). Therefore, as in the CCl_4 cases, there must be large energy barriers for SF^+, SF_4^+ and SF_5^+ or some steric effects.

4. Conclusions

The body of data presented here on the reactions of common plasma ions with CCl_4 and SF_6 suggests that the major reaction process is dissociative charge transfer for reactant ions not containing H/D atoms, initially producing CCl_4^{+*} or SF_6^{+*} which then dissociates (unimolecular or predissociation or direct access to a repulsive product state) giving the observed fragment ion products. Further, the magnitudes of the rate coefficients and the overall consistency of many of the major products with data on unstable excited states of CCl_4^+ and SF_6^+ previously obtained by photoelectron spectroscopy, suggests that in many cases the reactions proceed by a long-range electron transfer where the potential curves of the isolated reactant neutral are not significantly distorted. This is consistent with the original suggestion by Bowers and co-workers that charge transfer is, to a large degree, controlled by Franck-Condon overlap between the neutral and initial product ion states. Not all reaction channels can be explained in this way however, especially those leading to the less abundant products. In cases where the ion contains H/D atoms there is evidence for the production of HF/DF and of HCl/DCl which is indicative of a short-range interaction; indeed for some of these, formation of HX or DX (X = F or Cl) is the only energetically favorable route to the observed product ions. Spectroscopic studies are needed to establish the states of excitation of the products and the proportion of the available energy that goes into such excitation. Studies of this type are currently in progress.

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