Selected Ion Flow Tube Study of the Reactions between Gas Phase Cations and $CHCl_2F$, $CHClF_2$, and CH_2ClF

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The branching ratios and rate coefficients have been measured at 298 K for the reactions between $CHCl_2F$, $CHClF_2$, and CH_2ClF and the following cations (with recombination energies in the range 6.3−21.6 eV); H_3O^+, SF_x^+ ($x = 1-5$), CF_y^+ ($y = 1-3$), NO^+, NO_2^+, O_2^+, Xe^+, N_2O^+, O^+, CO_2^+, Kr^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+. The majority of the reactions proceed at the calculated collisional rate, but the reagent ions SF_3^+, NO^+, NO_2^+, and SF_2^+ do not react. Surprisingly, although all of the observed product channels are calculated to be endothermic, H_3O^+ does react with $CHCl_2F$. On thermochemical grounds, Xe^+ appears to react with these molecules only when it is in its higher-energy $^2P_{1/2}$ spin−orbit state. In general, most of the reactions form products by dissociative charge transfer, but some of the reactions of CH_2ClF with the lower-energy cations produce the parent cation in significant abundance. The branching ratios produced in this study and by threshold photoelectron−photoion coincidence spectroscopy agree reasonably well over the energy range 11−22 eV. In about one-fifth of the large number of reactions studied, the branching ratios are in excellent agreement and appreciable energy resonance between an excited state and the ground state of the ionized neutral exists, suggesting that these reactions proceed exclusively by a long-range charge-transfer mechanism. Upper limits for the enthalpy of formation at 298 K of SF_4Cl (−637 kJ mol^{-1}), SClF (−28 kJ mol^{-1}), and SHF (−7 kJ mol^{-1}) are determined.

1. Introduction

The study of ion−molecule reactions is of importance in many areas of science, such as plasmas found in industrial applications and in the interstellar medium.[1,2] These fundamental processes underpin the complex reactivity that is evident in these systems. One such mechanism is that of charge transfer, which can occur over either a long range or a short range. The former model states that as an ion (A^+) makes an approach toward a neutral reagent (BC), the ionic charge induces a dipole interaction in the neutral. At a critical separation between the two species, the potential curves of A^+-BC and $A-BC^+$ cross, thus allowing an electron to jump from the neutral to the ion. Factors that exhibit a marked preference for the occurrence of this process include energy resonance between the ground electronic state and an ionic state of the neutral and the extent of shielding in the molecular orbital from which the electron is removed. A guide to the possible energy resonances can be found in the photoelectron spectrum of the neutral species. For the molecular reagent cations, the Franck−Condon factor for neutralizing A^+ can also be important. If the long-range process is unfavorable, then the two species move closer together. The resulting intimate interaction can perturb the relevant potential surfaces to such an extent that a crossing is stimulated, thereby leading to short-range charge transfer. Note that, in this case, although the Franck−Condon factors involved are perturbed, they still need to be appreciable in the isolated molecule for this process to transpire. Short-range charge transfer can compete with chemical reactions, where bonds are broken and formed. Because neither a curve crossing nor a Franck−Condon factor is required for a chemical reaction to occur, this channel can proceed efficiently. A thorough review of the aforementioned three processes has been published by our group.[3]

In this paper, we present a study of the dynamics and kinetics of reactions between ions of known recombination energy and $CHCl_2F$, $CHClF_2$, and CH_2ClF using the well-established selected ion flow tube (SIFT) technique. Correlation between the derived branching ratios and those obtained using tunable energy photons as the excitation source (published elsewhere),[4] alongside the presence of an appreciable band in the threshold photoelectron spectrum (TPES) at the recombination energy of the reagent ion, points toward the occurrence of a long-range charge-transfer mechanism. An absence of these features suggests that other processes dominate. This study is an extension of recent SIFT work performed by Mayhew and collaborators on some halogenated methanes,[5] in addition to previous experiments looking at reactions of the three titled molecules with the anions OH^-, O^-, and O_2^- and an electron attachment study.[6−8]

2. Experimental Section

The SIFT apparatus has been described in detail elsewhere.[9] Briefly, each reagent ion of interest was produced in a high-pressure electron impact ion source containing an appropriate source gas (H_2O for H_3O^+, SF_6 for SF_x^+ (where $x = 1-5$), CF_4 for CF_2^+, CF_3^+ and F^+, C_2F_6 for CF^+, NO for NO^+, NO_2 for NO_2^+, O_2 for O_2^+, Xe for Xe^+, N_2O for N_2O^+, CO for O^+ and CO^+, CO_2 for CO_2^+, Kr for Kr^+, N_2 for N^+ and N_2^+, Ar

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for Ar^+, and Ne for Ne^+). The O_2^+ ions were produced using a mixture comprising a 4:1 ratio of O_2 and N_2 to reduce the chances of filament burnout in the ion source. Only the particular ion of interest was injected into a flow tube holding about 0.5 Torr of high purity (99.997%) helium as a buffer gas. A quadrupole mass filter performs this mass selection. The neutral reactant of choice is then admitted at the far end of the flow region, with subsequent detection of the resultant ionic products using a quadrupole mass spectrometer. The loss of reagent ion signal, alongside the increase in the various product ion signal(s), was recorded as a function of neutral reactant concentration. The amount of neutral was altered between zero and a concentration that depleted the reactant ion signal by about 90%. Plots of the logarithm of the reagent ion signal versus neutral molecule concentration allowed rate coefficients to be determined from a linear least-squares fit. Rate coefficients with a lower limit of about 10^{-13} cm^3 $molecule^{-1}$ s^{-1} can be measured in our apparatus. Percentage branching ratios for each product ion were derived from graphs of the relative product ion counts versus neutral molecule concentration, with extrapolation to zero neutral gas flow to remove any deviations due to secondary reactions. The various chlorine isotopes are accounted for in this procedure. These data can be compared to branching ratio diagrams constructed from photoionization of each of the neutral molecules[4] to shed light on the nature of charge-transfer mechanisms. We quote the error in the branching ratios as ±20% for values greater than 10%. This error increases for smaller branching ratios; indeed, the error associated with branching ratios of 1% is given as ±100%.

Quenching of vibrationally and electronically excited ionic states should be achieved by the use of several Torr of the ion source gases. This is not strictly the case, however, as previous studies in our laboratory have shown that there is about 20% population of the $\upsilon = 1$ and 2 levels of O_2^+ and about 40% in the first excited vibrational level of N_2^+.[10,11] There is also a possibility of population of higher spin−orbit states within atomic ions. The spin−orbit splitting between the $^2P_{3/2}$ ground state and the higher-energy $^2P_{1/2}$ state in ions of the noble gases can vary in magnitude considerably; the values of interest to this work are 0.10, 0.18, 0.67, and 1.31 eV for Ne^+, Ar^+, Kr^+, and Xe^+, respectively.[12] The F^+ ground state exhibits a low-magnitude triplet splitting, whose three levels span an energy range of only 0.06 eV. Given the small energy enhancement that excitation to the higher states would impart, the excited states of F^+, Ne^+, and Ar^+ are expected to have the same reactivity as their respective ground states. However, the larger extent of splitting for Kr^+ and Xe^+ can lead to distinct rates of reaction depending on which state the ion is in prior to reaction. Indeed, under certain circumstances the lower $^2P_{3/2}$ state was found to react faster than the $^2P_{1/2}$ state in reactions with molecules containing between two and five atoms (e.g., CH_4 and C_2H_2).[13] The molecular reagent ions may also have some internal energy excitation, in addition to the thermal contribution expected at 298 K. However, upon inspection of the individual pseudo-first-order kinetic plots, none display curvature of ln(reagent ion signal) versus concentration of neutral co-reactant. This result indicates one of two possibilities. Either the rates of reactions initiated by ions that have some vibrational or spin−orbit excited population are the same as those involving ground state ions, or reaction is only possible from the higher-energy state. Anticipating whether the product ion branching ratios are affected is more problematic, although the small energetic increments involved in most cases are unlikely to make a radical difference to these quantities.

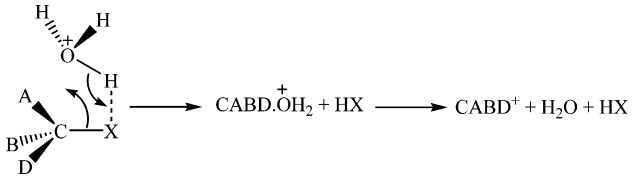
Residual water in the flow tube can cause problems, as removal of an electron from H_2O and the subsequent reaction $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$ results in a signal at $m/z = 19$ due to H_3O^+. This only occurs when ions with recombination energies greater than the ionization energy of neutral water (12.62 eV) are injected. As can be seen later, H_3O^+ only reacts with $CHCl_2F$ out of the three neutrals studied here and is, therefore, only a hindrance in this case. Tuning the ion optics of the entrance quadrupole generally produced a reactant ion signal that was at least 10 times larger than that of H_3O^+; therefore, the smaller signal could be ignored. The impact of this problem was further reduced via cleaning of the He inlet line using a liquid-nitrogen-cooled zeolite trap.

3.Results and Discussion

3.1. Rate Coefficients. The vast majority of the experimentally determined rate coefficients, k_{exp}, have values that approach the capture rate values, k_c, determined using modified-average dipole orientation (MADO) theory,[14] as shown in Tables 1−3. Therefore, these processes occur efficiently, in that most of the ion−molecule collisions lead to reaction. MADO theory accounts for the polar nature of these three systems by including the relevant dipole moments. These were given as 1.29, 1.42, and 1.82 D for $CHCl_2F$, $CHClF_2$, and CH_2ClF, respectively.[12] It also includes the polarizabilities of each molecule, the values for $CHCl_2F$ and $CHClF_2$ being 6.82 and 6.38×10^{-24} cm^3, respectively.[12] No value for the polarizability of CH_2ClF has been published, so the empirical method of adding atomic hybrid components[15] was used to give a value of 4.48×10^{-24} cm^3. Of the cases where $k_{exp} < k_c$, the reactions involving SF_5^+ are the most prominent. In all three reactions, k_{exp} does not get above 60% of the capture value. This suggests that a somewhat congested collision complex is initially formed, as SF_5^+ is the bulkiest reagent ion used in this study, with short-range charge transfer and possible bond cleavage occurring subsequently. It is also worth noting that reactions of SF^+ and SF_4^+ with $CHClF_2$ also proceed slowly, with experimental values that are <50% of the capture coefficients, producing $CHClF^+$ as the single ionic product.

3.2. Branching Ratios. *3.2.1. $CHCl_2F$.* The products resulting from reactions of several cations and $CHCl_2F$ are displayed in Table 1. The proposed neutral products, shown in column 4, are the species that give the lowest value for the enthalpy of reaction at 298 K, $\Delta_r H_{298}°$, while still being chemically reasonable. These values of $\Delta_r H_{298}°$ provide a quantitative guide for the occurrence of the suggested products for each reaction and are listed in column 5. First, we discuss reactions involving ions whose recombination energies are below the onset of ionization of $CHCl_2F$, given in recent work by us as 11.50 ± 0.05 eV.[4]

The reaction between H_3O^+ and $CHCl_2F$ results in three products, which are formed via hydrogen halide, or simply diatomic hydrogen, elimination. This process has been noted before by reactions between H_3O^+ and halomethanes,[16] with the mechanism proceeding thus



where X, A, B, and D are chlorine, fluorine, or hydrogen atoms. The major product, with a branching ratio of 85%, is formed

TABLE 1: Rate Coefficients at 298 K, Product Cations, Branching Ratios, and Suggested Neutral Products for the Reactions of 23 Cations with $CHCl_2F$[o]

reagent ion (RE/eV)	rate coefficient (10^{-9} cm^3 molecule^{-1} s^{-1})	product ion (%)	proposed neutral product	$\Delta_r H_{298}°$ (kJ mol^{-1})
H_3O^+	1.6	CCl_2F^+ (85)	$H_2O + H_2$	+154
(6.27)	[2.2]	$CHCl_2^+$ (11)	H_2O + HF	+65
		$CHClF^+$ (4)	H_2O + HCl	+101
SF_3^+		no reaction		
(8.26)	[1.3]			
CF_3^+	1.3	$CHClF^+$ (83)	$CClF_3$	−88[a]
(9.03)	[1.4]	$CHCl_2^+$ (17)	CF_4	−169[a]
CF^+	1.6	$CHClF^+$ (71)	CClF	−77[b]
(9.10)	[1.8]	$CHCl_2^+$ (29)	CF_2	−146
		CCl_2F^+ (trace)	CHF	−5[c]
NO^+		no reaction		
(9.26)	[1.8]			
SF_5^+	0.4	$CHClF^+$ (73)	SF_5Cl	−42[d]
(9.55)	[1.2]	$CHCl_2^+$ (27)	SF_6	−79[d]
NO_2^+		no reaction		
(9.59)	[1.6]			
SF_2^+		no reaction		
(10.17)	[1.4]			
SF^+	1.5	$CHClF^+$ (92)	SClF	$+28 + \Delta_f H_{298}°(SClF)$[e]
(10.25)	[1.5]	$CHCl_2^+$ (8)	SF_2	−123[e,f]
CF_2^+	1.2	$CHClF^+$ (61)	$CClF_2$	−175[g,h]
(11.43)	[1.5]	$CHCl_2^+$ (39)	CF_3	−218[g,i]
		CCl_2F^+ (trace)	CHF_2	−173[g]
SF_4^+	0.9	$CHClF^+$ (100)	SF_4Cl or	$+637 + \Delta_f H_{298}°(SF_4Cl)$[j] or
(11.92)	[1.2]		SF_4 + Cl	−10[j,k]
O_2^+	1.9	$CHClF^+$ (94)	ClOO or	−40 or
(12.07)	[1.8]		OClO	−41
		CCl_2F^+ (5)	HOO	−176
		$CHCl_2^+$ (1)	FOO	+31, +9, −13[l]
Xe^+	1.2	$CHClF^+$ (97)	Xe + Cl	−23, −149[m]
(12.13/13.44)[m]	[1.2]	CCl_2F^+ (3)	Xe + H	+34, −92[m]
		$CHCl_2^+$ (trace)	Xe + F	+79, −47[m]
N_2O^+	1.1	$CHClF^+$ (95)	N_2 + OCl or	−198 or
(12.89)	[1.6]		N_2O + Cl	−96
		CCl_2F^+ (3)	N_2 + OH or	−301 or
			N_2O + H	−40
		$CHCl_2^+$ (2)	N_2 + OF or	−47 or
			N_2O + F	+6
O^+	1.8	$CHClF^+$ (95)	OCl	−435
(13.62)	[2.4]	$CHCl_2^+$ (5)	OF	−284
		CCl_2F^+ (trace)	OH	−538
CO_2^+	1.4	$CHClF^+$ (99)	CO_2 + Cl	−181
(13.78)	[1.6]	CCl_2F^+ (1)	CO_2 + H	−124
		$CHCl_2^+$ (trace)	CO_2 + F	−79
Kr^+	1.0	$CHClF^+$ (94)	Kr + Cl	−203
(14.00)	[1.3]	$CHCl_2^+$ (3)	Kr + F	−101
		CCl_2F^+ (3)	Kr + H	−147
CO^+	1.7	$CHClF^+$ (95)	COCl	−278
(14.01)	[1.9]	$CHCl_2^+$ (3)	COF	−242
		CCl_2F^+ (2)	COH	−211
N^+	2.5	$CHClF^+$ (92)	NCl	−535[n]
(14.53)	[2.5]	$CHCl_2^+$ (6)	NF	−456
		CCl_2F^+ (2)	NH	−512
N_2^+	1.6	$CHClF^+$ (50)	N_2 + Cl	−355
(15.58)	[1.9]	$CHCl_2^+$ (45)	N_2 + F	−253
		CCl_2F^+ (5)	N_2 + H	−299
Ar^+	1.3	$CHCl_2^+$ (46)	Ar + F	−271
(15.76)	[1.7]	$CHClF^+$ (43)	Ar + Cl	−373
		CCl_2F^+ (6)	Ar + H	−317
		CF^+ (5)	Ar + HCl + Cl	−75
F^+	2.0	CCl^+ (48)	HF + ClF	−557
(17.42)	[2.2]	CF^+ (26)	HF + Cl_2	−615
		$CHClF^+$ (21)	ClF	−784
		$CHCl_2^+$ (5)	F_2	−590
		CCl_2F^+ (trace)	HF	−1046

TABLE 1 (Continued)

reagent ion (RE/eV)	rate coefficient (10^{-9} cm^3 molecule^{-1} s^{-1})	product ion (%)	proposed neutral product	$\Delta_r H_{298}°$ (kJ mol^{-1})
Ne^+	1.9	CHF^+ (43)	Ne + Cl_2	−676
(21.56)	[2.2]	CF^+ (15)	Ne + HCl + Cl	−634
		$CHCl^+$ (15)	Ne + ClF	−600
		$CHClF^+$ (11)	Ne + Cl	−932
		Cl^+ (8)	Ne + CHClF	−531
		$CHCl_2^+$ (4)	Ne + F	−830
		CCl^+ (4)	Ne + HF + Cl	−705
		$CClF^+$ (trace)	Ne + HCl	−872
		CCl_2^+ (trace)	Ne + HF	−906
		CCl_2F^+ (trace)	Ne + H	−876
		$CHCl_2F^+$ (trace)	Ne	−968

[a] $\Delta_f H_{298}°(CF_3^+) = +406$ kJ mol^{-1}.[35] [b] $\Delta_f H_{298}°(CClF) = +31$ kJ mol^{-1}.[36] [c] $\Delta_f H_{298}°(CHF) = +143$ kJ mol^{-1}.[36] [d] $\Delta_f H_{298}°(SF_5^+) = +29$ kJ mol^{-1}.[37] [e] $\Delta_f H_{298}°(SF^+) = +998$ kJ mol^{-1}.[23] [f] $\Delta_f H_{298}°(SF_2) = -295$ kJ mol^{-1}.[23] [g] $\Delta_f H_{298}°(CF_2^+) = +922$ kJ mol^{-1}, calculated from $\Delta_f H_{298}°(CF_2)$ + IE(CF_2).[21] [h] $\Delta_f H_{298}°(CClF_2) = -279$ kJ mol^{-1}.[38] [i] $\Delta_f H_{298}°(CF_3) = -466$ kJ mol^{-1}.[34] [j] $\Delta_f H_{298}°(SF_4^+) = +389$ kJ mol^{-1}.[23] [k] $\Delta_f H_{298}°(SF_4) = -768$ kJ mol^{-1}.[23] [l] The three values quoted are for the enthalpy of reaction at 298 K involving the $v = 0$, 1, and 2 levels of the ground electronic state of O_2^+, using O_2^+ ground-state vibrational spectroscopic constants.[21] [m] The two values quoted are for the enthalpy of reaction at 298 K involving the $^2P_{3/2}$ and $^2P_{1/2}$ spin−orbit states of Xe^+.[12] [n] $\Delta_f H_{298}°(NCl) = +314$ kJ mol^{-1}.[39] [o] The recombination energy (RE) of the ion is shown in column 1. Experimental rate coefficients are shown in column 2; values in square brackets below the experimental data are MADO theoretical capture coefficients (see text). The product ions and their branching ratios are shown in column 3. The most likely accompanying neutral products are given in column 4, with the enthalpy of the proposed reaction given in column 5. These values are generally derived from the usual reference sources for neutrals[22] and ions,[34] unless otherwise indicated. In the interests of brevity, only the proposed neutrals that give the most exothermic $\Delta_r H_{298}°$ are listed, unless specifically discussed in sections 3 or 4.

by H atom loss from the neutral precursor, i.e., X = H. This observation can be explained by the steric effects of the transition state, as the smaller size of a hydrogen atom means that attack by H_3O^+ is least hindered at this position. For this reaction to occur as above, these steps have to occur rapidly to overcome collisional stabilization of the complex.[16] Because the rate of this reaction is close to k_c, we believe that these processes occur efficiently. However, all three observed reactions are appreciably endothermic. Previous work has highlighted that entropic effects can drive such seemingly unfavorable processes,[17−19] but the magnitudes of the endothermicities of the three processes we observe are much larger than those involved in these studies. The overall change in number of moles in the H_3O^+ + $CHCl_2F$ reaction is +1, and we might expect an increase in entropy of the order of 100 J mol^{-1} K^{-1}. However, even if $\Delta_r S_{298}°$ is as large as this, the $T\Delta_r S_{298}°$ term would only contribute about 30 kJ mol^{-1} at room temperature. Therefore, the $T\Delta_r S_{298}°$ term will not be large enough to compensate for the positive $\Delta_r H_{298}°$ values we calculate, and entropy alone does not seem to be a plausible explanation for our results. (Note that $\Delta_r S_{298}°$ would need to be about 500 J mol^{-1} K^{-1} for entropy alone to explain the presence of the most abundant ion product, CCl_2F^+ (85%); this huge value seems very unlikely.) It is also possible that the literature values used to calculate $\Delta_r H_{298}°$ are in error, but the only values where this is potentially the case are those of the product ions; these have not caused such a significant discrepancy in any of the other reactions in this work. A mis-assignment of the ionic products, such as CCl_2F^+ and $CHClF^+$ being $CCl_2{\cdot}H_3O^+$ and $CHCl{\cdot}H_3O^+$, can be discounted, as these proposed complex ions are chemically improbable and would require extensive rearrangement in the transition state. Additionally, such an uncertainty cannot be applied to the $CHCl_2^+$ product. Direct proton transfer to $CHCl_2F$ is not observed in this reaction, which is consistent with room-temperature proton affinity (PA_{298}) data; the PA_{298} of $CHCl_2F$ (676.8 kJ mol^{-1}) has been calculated using ab initio methods[20] and is smaller than the PA_{298} of water (691 kJ mol^{-1}).[21] Therefore, the proton is more likely to reside on the water molecule. In conclusion, we are unable to explain why this reaction proceeds.

Whereas SF_3^+, NO^+, NO_2^+, and SF_2^+ do not react at an observable rate, the remaining ions that fall in this energy range react to form two major products by dissociative charge transfer, namely, $CHClF^+$ and $CHCl_2^+$. The former ion is dominant, being formed with branching ratios of between 92% (with SF^+) and 61% (CF_2^+). All of these reactions also result in a single neutral product. Therefore, Cl atom abstraction via a short-range complex is favored, but removal of a fluorine atom is not insignificant. The enthalpy of formation of SClF, produced in the SF^+ reaction, is unknown. Using the known thermochemistry of the other components, we ascribe this reaction as being exothermic if the unspecified quantity is less than −28 kJ mol^{-1}. As the respective values of $\Delta_f H_{298}°$ for SCl_2 and SF_2 are −18 and −295 kJ mol^{-1}, this seems feasible.[22,23]

At ion recombination energies that are higher than the ionization energy of $CHCl_2F$, long-range charge transfer becomes possible. Over the recombination energy range 11.92−14.53 eV, incorporating reactions with SF_4^+ to N^+ inclusive, the branching ratio for $CHClF^+$ formation is close to unity. It peaks at 100% with SF_4^+, where the heat of formation of the neutral product is not known; this reaction will be exothermic if the $\Delta_f H_{298}°$ of SF_4Cl is less than −637 kJ mol^{-1}. This number is consistent with the $\Delta_f H°_0$ value for SF_4Cl of −761 kJ mol^{-1} determined in previous SIFT work by our group on SF_5Cl.[24] Another set of proposed neutrals is SF_4 + Cl and, if the well-established thermochemistry of these neutrals is used, this reaction is just exothermic. For the reaction with O_2^+, $CHClF^+$ can form with either ClOO or OClO on enthalpy grounds. This suggests that the chlorine atom can form a bond using the electrons from the oxygen double bond or from a lone pair on one of the oxygen atoms. Intuitively, we would expect the former neutral to be the accompanying partner in this reaction, as it does not withdraw electron density from the strong double bond. Both hydrogen and fluorine atom removal are also observed with a low branching ratio, although there appears to be some problem with the thermochemical values used to form $CHCl_2^+$ + FOO. The only way in which this reaction is exothermic is for appreciable vibrational excitation to exist in the O_2^+ reagent ion. However, as stated in section 2, the pseudo-first-order kinetic rate graph displays no curvature, so this cannot

TABLE 2: Rate Coefficients at 298 K, Product Cations, Branching Ratios, and Suggested Neutral Products for the Reactions of 23 Cations with $CHClF_2$[p]

reagent ion (RE/eV)	rate coefficient (10^{-9} cm^3 molecule^{-1} s^{-1})	product ion (%)	proposed neutral product	$\Delta_r H_{298}°$ (kJ mol^{-1})
H_3O^+		no reaction		
(6.27)	[2.3]			
SF_3^+		no reaction		
(8.26)	[1.4]			
CF_3^+	1.0	CHF_2^+ (55)	CF_3Cl	−28[a,b]
(9.03)	[1.5]	$CHClF^+$ (40)	CF_4	−115[a]
		$CClF_2^+$ (5)	CHF_3	−93[a]
CF^+	2.0	$CHClF^+$ (85)	CF_2	−91
(9.10)	[1.9]	CHF_2^+ (15)	CClF	−17[b,c]
		$CClF_2^+$ (trace)	CHF	+19[d]
NO^+		no reaction		
(9.26)	[1.9]			
SF_5^+	0.8	$CHClF^+$ (100)	SF_6	−25[e]
(9.55)	[1.3]			
NO_2^+		No reaction		
(9.59)	[1.7]			
SF_2^+		No reaction		
(10.17)	[1.5]			
SF^+	0.5	$CHClF^+$ (100)	SF_2	−69[f,g]
(10.25)	[1.6]			
CF_2^+	1.7	$CHClF^+$ (59)	CF_3	−163[h,i]
(11.43)	[1.6]	CHF_2^+ (30)	$CClF_2$	−115[b,h,j]
		$CClF_2^+$ (11)	CHF_2	−149[h]
SF_4^+	0.6	$CHClF^+$ (100)	SF_5	−80[k,l]
(11.92)	[1.3]			
O_2^+	1.7	CHF_2^+ (70)	ClOO or	+19, −3, −25[b,m]
(12.07)	[1.9]		OClO	+18, −4, −26[m]
		$CHClF^+$ (25)	FOO	+85, +63, +41[m]
		$CClF_2^+$ (5)	HOO	−153
Xe^+	1.3	CHF_2^+ (94)	Xe + Cl	+36, −90[b,n]
(12.13/13.44)[n]	[1.3]	$CHClF^+$ (6)	Xe + F	+134, +7[n]
		$CClF_2^+$ (trace)	Xe + H	+57, −69[n]
		$CHClF_2^+$ (trace)	Xe	+5, −121[n]
N_2O^+	1.5	CHF_2^+ (97)	N_2 + OCl or	−139[b] or
(12.89)	[1.7]		N_2O + Cl	−37[b]
		$CHClF^+$ (3)	N_2 + OF or	+8 or
			N_2O + F	+60
O^+	2.4	CHF_2^+ (86)	OCl	−376[b]
(13.62)	[2.5]	$CHClF^+$ (14)	OF	−229
CO_2^+	1.5	CHF_2^+ (94)	CO_2 + Cl	−122[b]
(13.78)	[1.7]	$CHClF^+$ (6)	CO_2 + F	−25
Kr^+	1.3	CHF_2^+ (76)	Kr + Cl	−144[b]
(14.00)	[1.4]	$CHClF^+$ (24)	Kr + F	−47
CO^+	2.0	CHF_2^+ (88)	COCl	−218[b]
(14.01)	[2.0]	$CHClF^+$ (12)	COF	−188
N^+	2.7	CHF_2^+ (84)	NCl	−476[b,o]
(14.53)	[2.6]	$CHClF^+$ (16)	NF	−402
N_2^+	2.0	$CHClF^+$ (63)	N_2 + F	−199
(15.58)	[2.0]	CHF_2^+ (37)	N_2 + Cl	−296[b]
		$CHClF_2^+$ (trace)	N_2	−327
Ar^+	1.7	$CHClF^+$ (69)	Ar + F	−217
(15.76)	[1.7]	CHF_2^+ (31)	Ar + Cl	−314[b]
		$CHClF_2^+$ (trace)	Ar	−345
F^+	2.1	$CHClF^+$ (69)	F_2	−535
(17.42)	[2.3]	CF^+ (25)	HF + ClF	−467
		CHF_2^+ (5)	ClF	−725[b]
		$CHClF_2^+$ (1)	F	−505
Ne^+	1.7	Cl^+ (27)	Ne + CHF_2	−465
(21.56)	[2.3]	CHF_2^+ (25)	Ne + Cl	−873[b]
		CHF^+ (14)	Ne + ClF	−528
		$CHClF^+$ (14)	Ne + F	−776
		CF_2^+ (12)	Ne + HCl	−769[h]
		CF^+ (7)	Ne + HF + Cl	−616
		$CClF_2^+$ (1)	Ne + H	−852

[a] $\Delta_f H_{298}°(CF_3^+) = +406$ kJ mol^{-1}.[35] [b] $\Delta_f H_{298}°(CHF_2^+) = +604$ kJ mol^{-1}.[28] [c] $\Delta_f H_{298}°(CClF) = +31$ kJ mol^{-1}.[36] [d] $\Delta_f H_{298}°(CHF) = +143$ kJ mol^{-1}.[36] [e] $\Delta_f H_{298}°(SF_5^+) = +29$ kJ mol^{-1}.[37] [f] $\Delta_f H_{298}°(SF^+) = +998$ kJ mol^{-1}.[23] [g] $\Delta_f H_{298}°(SF_2) = -295$ kJ mol^{-1}.[23] [h] $\Delta_f H_{298}°(CF_2^+) = +922$ kJ mol^{-1}, calculated from $\Delta_f H_{298}°(CF_2) + IE(CF_2)$.[21] [i] $\Delta_f H_{298}°(CF_3) = -466$ kJ mol^{-1}.[35] [j] $\Delta_f H_{298}°(CClF_2) = -279$ kJ mol^{-1}.[38] [k] $\Delta_f H_{298}°(SF_4^+) = +389$ kJ mol^{-1}.[23] [l] $\Delta_f H_{298}°(SF_5) = -915$ kJ mol^{-1}.[40] [m] The three values quoted are for the enthalpy of reaction at 298 K involving the $v = 0$, 1, and 2 levels of the ground electronic state of O_2^+, using the O_2^+ ground-state vibrational spectroscopic constants.[21] [n] The two values quoted are for the enthalpy of reaction at 298 K involving the $^2P_{3/2}$ and $^2P_{1/2}$ spin−orbit states of Xe^+.[12] [o] $\Delta_f H_{298}°(NCl) = +314$ kJ mol^{-1}.[39] [p] The recombination energy (RE) of the ion is shown in column 1. Experimental rate coefficients are shown in column 2; values in square brackets below the experimental data are MADO theoretical capture coefficients (see text). The product ions and their branching ratios are shown in column 3. The most likely accompanying neutral products are given in column 4, with the enthalpy of the proposed reaction given in column 5. These values are generally derived from the usual reference sources for neutrals[22] and ions,[34] unless otherwise indicated. In the interest of brevity, only the proposed neutrals that give the most exothermic $\Delta_r H_{298}°$ are listed, unless specifically discussed in sections 3 or 4.

TABLE 3: Rate Coefficients at 298 K, Product Cations, Branching Ratios, and Suggested Neutral Products for the Reactions of 23 Cations with CH_2ClF[o]

reagent ion (RE/eV)	rate coefficient (10^{-9} cm^3 molecule^{-1} s^{-1})	product ion (%)	proposed neutral product	$\Delta_f H_{298}°$ (kJ mol^{-1})
H_3O^+		no reaction		
(6.27)	[2.6]			
SF_3^+		no reaction		
(8.26)	[1.6]			
CF_3^+	1.5	CH_2Cl^+ (84)	CF_4	−118[a]
(9.03)	[1.7]	$CHClF^+$ (10)	CHF_3	−98[a]
		CH_2F^+ (6)	$CClF_3$	−19[a]
CF^+	1.7	CH_2Cl^+ (96)	CF_2	−95
(9.10)	[2.2]	CH_2F^+ (4)	CClF	−8[b]
		$CHClF^+$ (trace)	CHF	+14[c]
NO^+		no reaction		
(9.26)				
SF_5^+	0.7	CH_2Cl^+ (100)	SF_6	−29[d]
(9.55)	[1.5]			
NO_2^+	[1.9]	no reaction		
(9.59)				
SF_2^+	[1.7]	no reaction		
(10.17)				
SF^+	1.5	CH_2F^+ (45)	SClF	$+97 + \Delta_f H_{298}°$(SClF)[e]
(10.25)	[1.9]	$CHClF^+$ (42)	SHF	$+7 + \Delta_f H_{298}°$(SHF)[e]
		CH_2Cl^+ (13)	SF_2	−73[e,f]
CF_2^+	1.6	CH_2Cl^+ (85)	CF_3	−167[g,h]
(11.43)	[1.9]	CH_2F^+ (15)	$CClF_2$	−106[g,i]
		$CHClF^+$ (trace)	CHF_2	−154[g]
SF_4^+	1.1	CH_2Cl^+ (100)	SF_5	−83[j,k]
(11.92)	[1.6]			
O_2^+	2.1	CH_2ClF^+ (61)	O_2	−34
(12.07)	[2.2]	$CHClF^+$ (31)	HOO	−158
		CH_2Cl^+ (8)	FOO	+82, +60, +37[l]
Xe^+	1.3	CH_2ClF^+ (57)	Xe	−40, −166[m]
(12.13/13.44)[m]	[1.5]	$CHClF^+$ (29)	Xe + H	+52, −74[m]
		CH_2F^+ (13)	Xe + Cl	+46, −81[m]
		CH_2Cl^+ (1)	Xe + F	+130, +4[m]
N_2O^+	1.5	CH_2ClF^+ (54)	N_2 + O or	+54 or
(12.89)	[2.0]		N_2O	−113
		CH_2F^+ (39)	N_2 + OCl or	−130 or
			N_2O + Cl	−28
		CH_2Cl^+ (7)	N_2 + OF or	+4 or
			N_2O + F	+56
O^+	2.2	CH_2F^+ (63)	OCl	−367
(13.62)	[2.8]	CH_2Cl^+ (25)	OF	−233
		$CHClF^+$ (8)	O	−183
		CH_2ClF^+ (4)	OH	−519
CO_2^+	1.7	CH_2F^+ (73)	CO_2 + Cl	−112
(13.78)	[2.0]	CH_2Cl^+ (12)	CO_2 + F	−28
		$CHClF^+$ (8)	CO_2 + H	−106
		CH_2ClF^+ (7)	CO_2	−198
Kr^+	1.4	CH_2F^+ (83)	Kr + Cl	−135
(14.00)	[1.7]	CH_2Cl^+ (11)	Kr + F	−51
		$CHClF^+$ (3)	Kr + H	−128
		CH_2ClF^+ (3)	Kr	−220
CO^+	2.3	CH_2F^+ (93)	COCl	−209
(14.01)	[2.3]	CH_2Cl^+ (4)	COF	−192
		$CHClF^+$ (2)	COH	−193
		CH_2ClF^+ (1)	CO	−221
N^+	3.3	CH_2F^+ (55)	NCl	−466[n]
(14.53)	[3.0]	CH_2Cl^+ (19)	NF	−405
		$CHClF^+$ (16)	NH	−494
		CH_2ClF^+ (10)	N	−271
N_2^+	2.1	CH_2F^+ (73)	N_2 + Cl	−287
(15.58)	[2.3]	CH_2Cl^+ (20)	N_2 + F	−203
		$CHClF^+$ (4)	N_2 + H	−280
		CH_2ClF^+ (3)	N_2	−372
Ar^+	2.6	CH_2F^+ (79)	Ar + Cl	−305
(15.76)	[2.0]	CH_2Cl^+ (17)	Ar + F	−221
		$CHClF^+$ (4)	Ar + H	−298
F^+	2.5	CH_2Cl^+ (81)	F_2	−539
(17.42)	[2.6]	CH_2F^+ (17)	ClF	−715
		CH_2ClF^+ (2)	F	−550

TABLE 3 (Continued)

reagent ion (RE/eV)	rate coefficient (10^{-9} cm^3 molecule^{-1} s^{-1})	product ion (%)	proposed neutral product	$\Delta_r H_{298}°$ (kJ mol^{-1})
Ne^+ (21.56)	2.0 [2.6]	CHF^+ (36)	Ne + HCl	−789
		Cl^+ (21)	Ne + CH_2F	−480
		CH_2^+ (14)	Ne + ClF	−482
		CF^+ (8)	Ne + H_2 + Cl or	−563 or
			Ne + HCl + H	−558
		CH_2F^+ (7)	Ne + Cl	−864
		CCl^+ (6)	Ne + HF + H	−630
		$CHCl^+$ (4)	Ne + HF	−844
		$CHClF^+$ (3)	Ne + H	−857
		CH_2Cl^+ (1)	Ne + F	−780
		CH_2ClF^+ (trace)	Ne	−949

[a] $\Delta_f H_{298}°(CF_3^+) = +406$ kJ mol^{-1}.[35] [b] $\Delta_f H_{298}°(CClF) = +31$ kJ mol^{-1}.[36] [c] $\Delta_f H_{298}°(CHF) = +143$ kJ mol^{-1}.[36] [d] $\Delta_f H_{298}°(SF_5^+) = +29$ kJ mol^{-1}.[37] [e] $\Delta_f H_{298}°(SF^+) = +998$ kJ mol^{-1}.[23] [f] $\Delta_f H_{298}°(SF_2) = -295$ kJ mol^{-1}.[23] [g] $\Delta_f H_{298}°(CF_2^+) = +922$ kJ mol^{-1}, calculated from $\Delta_f H_{298}°(CF_2)$ + IE(CF_2).[21] [h] $\Delta_f H_{298}°(CF_3) = -466$ kJ mol^{-1}.[35] [i] $\Delta_f H_{298}°(CClF_2) = -279$ kJ mol^{-1}.[38] [j] $\Delta_f H_{298}°(SF_4^+) = +389$ kJ mol^{-1}.[23] [k] $\Delta_f H_{298}°(SF_5) = -915$ kJ mol^{-1}.[40] [l] The three values quoted are for the enthalpy of reaction at 298 K involving the $\upsilon = 0$, 1, and 2 levels of the ground electronic state of O_2^+, using O_2^+ ground-state vibrational spectroscopic constants.[21] [m] The two values quoted are for the enthalpy of reaction at 298 K involving the $^2P_{3/2}$ and $^2P_{1/2}$ spin−orbit states of Xe^+.[12] [n] $\Delta_f H_{298}°(NCl) = +314$ kJ mol^{-1}.[39] [o] The recombination energy (RE) of the ion is shown in column 1. Experimental rate coefficients are shown in column 2; values in square brackets below the experimental data are MADO theoretical capture coefficients (see text). The product ions and their branching ratios are shown in column 3. The most likely accompanying neutral products are given in column 4, with the enthalpy of the proposed reaction given in column 5. These values are generally derived from the usual reference sources for neutrals[22] and ions,[34] unless otherwise indicated. In the interest of brevity, only the proposed neutrals that give the most exothermic $\Delta_r H_{298}°$ are listed, unless specifically discussed in sections 3 or 4.

be the case. The fault for this discrepancy may be the uncertainty in the $\Delta_f H_{298}°$ value for FOO, which has caused many problems for theoretical chemists because of the large number of lone pairs of electrons.[25,26] The O_2^+ reaction has been studied previously using a selected ion drift tube apparatus,[27] where the measured k_{exp} exactly matches our value but with the branching ratios for the ionic products only broadly agreeing with the data we report; the values they give for $CHClF^+$ and CCl_2F^+ are 70 and 30%, respectively.

A further inconsistency is evident in the thermochemistry of the reaction involving Xe^+, as the two minor channels are only exothermic if the reagent ion is in the higher-energy $^2P_{1/2}$ state. The major product channel, $CHClF^+$ with a 97% branching ratio, is exothermic when Xe^+ is in either state. No curvature of any rate plot is observed. Assuming the thermochemistry is correct, we can only conclude that the reactions of Xe^+ with $CHCl_2F$ to produce CCl_2F^+ and $CHCl_2^+$ can only proceed from the higher $^2P_{1/2}$ spin−orbit state of Xe^+. In other words, Xe^+ is not thermalized under our experimental conditions. By contrast, the reactions of Kr^+ to produce all three product ions are substantially exothermic from its $^2P_{3/2}$ ground state. We should note, however, that reactions of Kr^+ could also be occurring from both spin−orbit states with identical rate coefficients. The neutral products resulting from the N_2O^+ reaction merit discussion, in that forming N_2 + OX as neutral partners is thermochemically more favorable than the more intuitive route to N_2O + X (where X = Cl, H, or F). The latter set of neutrals might be expected, as they occur from the breaking of one C−X bond, whereas the more enthalpically favored route involves cleavage of both the C−X and the N═O bonds plus formation of an O−X bond. It is possible, therefore, that either set of neutrals may accompany the detected product ions. Reactions with the N_2^+ and Ar^+ ions result in more even distributions of major products, with approximately equal branching ratios between $CHClF^+$ and $CHCl_2^+$. At higher recombination energies, greater fragmentation is observed. Both CCl^+ and CF^+ are observed as the dominant products from the F^+ reaction, with formation of CHF^+ ions taking precedence with Ne^+.

In Figure 1, the branching ratios resulting from our recent threshold photoelectron−photoion coincidence (TPEPICO) study of $CHCl_2F$ are displayed.[4] Composite ion yields are displayed due to resolution difficulties, outlined elsewhere.[4] The SIFT branching ratios for ions with recombination energies in the range 12−22 eV, corrected so that the sum of the pertinent data equals unity, are overlaid. From this diagram, it is clear that both sets of data agree very well, with the contours for the $CHClF^+$ and $CHCl_2^+$ ions matching within experimental error. The only discrepancy of note is with the F^+ data, which overestimates the $CHClF^+$ branching ratio with respect to the photoionization results, at the expense of the combined CHF^+/CF^+ branching ratio. For a reaction to be considered as proceeding by a pure long-range charge-transfer mechanism, the recombination energy of the reagent ion should correspond to an ionization energy in the neutral reagent where good Franck−Condon factors exist.[3] Such a situation is denoted by an appreciable signal in the TPES.[4] From this information, we can infer that the reactions between $CHCl_2F + O_2^+$ or N^+ occur via long-range charge transfer, while the reactions of the other ions above the ionization energy of $CHCl_2F$ probably occur by short-range charge transfer, even though the branching ratios match those that would result from the long-range model.

3.2.2. $CHClF_2$. Table 2 displays the products of the reactions between a variety of cations and $CHClF_2$, alongside proposed neutral products and thermochemistry. We initially consider reactions involving ions whose recombination energies are below 12.15 ± 0.05 eV, which is the onset of ionization for $CHClF_2$ determined by our recent work.[4] Five of the cations used in this study did not react with $CHClF_2$, namely, H_3O^+, SF_3^+, NO^+, NO_2^+, and SF_2^+. The CF_y^+ ions, where $y = 1$, 2, or 3, display competitive bond cleavage between C−F and C−Cl, with a limited tendency toward hydrogen abstraction. The SF_x^+ ions that do react, however, favor fluorine abstraction exclusively, but all three of these reactions take place nonefficiently ($k_{exp} \ll k_c$). The reaction with O_2^+ displays the same thermochemical limitations as those described in section 3.2.1, with the additional uncertainty in the heats of formation of ClOO and OClO. The thermochemistry suggests that the $\upsilon \geq 1$ level of the reagent ion reacts to form CHF_2^+, although an absense of curvature in the pseudo-first-order rate plot makes this possibility difficult to prove. As only one-fifth of the population

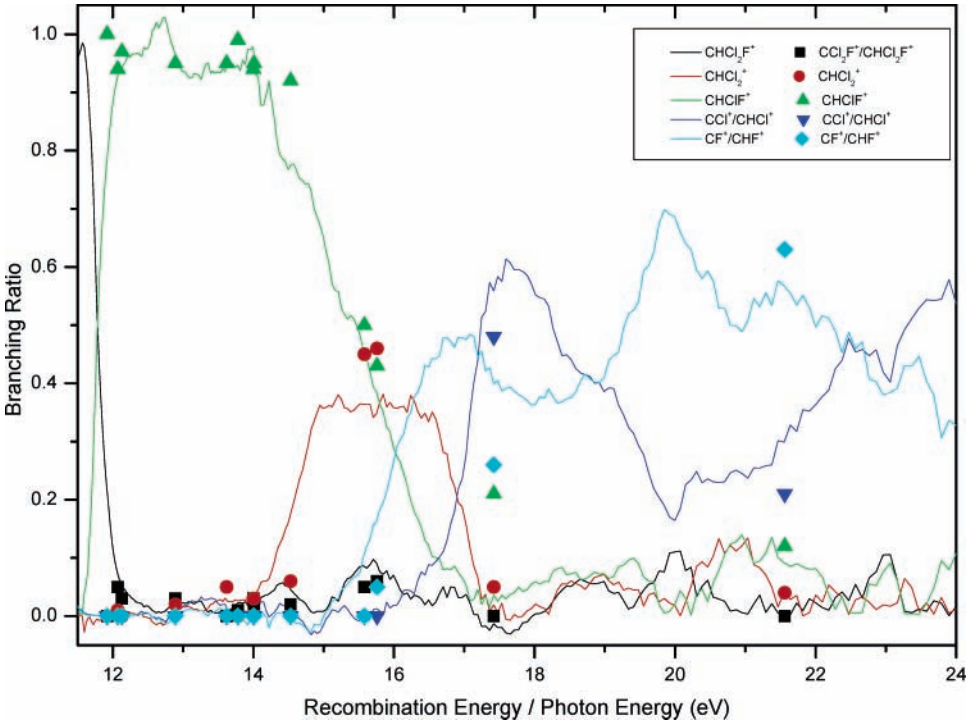


Figure 1. Comparison of the ionic products from ion−molecule studies of $CHCl_2F$ with TPEPICO photoionization branching ratios over the energy range 12−24 eV. The SIFT branching ratios are corrected so that the sum of the relevant data equals unity.

of O_2^+ is in its higher vibrational levels,[10] and yet they yield the major ionic product with a 70% branching ratio, this cannot be a satisfactory explanation for the observed phenomenon. In addition to the thermochemical issues regarding the neutral species, we note that the value quoted for CHF_2^+, +604 kJ mol^{-1}, is an upper limit to $\Delta_f H_{298}°$.[28] Another study of this reaction using a selected ion drift tube gave an inverted product distribution, with $CClF_2^+$ and CHF_2^+ having branching ratios of 74 and 26%, respectively.[27] Additionally, k_{exp} is given as 0.85×10^{-10} cm^3 s^{-1}, which is less than half the MADO capture value calculated by us. We cannot explain why this study appears to give concurrent results for the $O_2^+ + CHCl_2F$ reaction but significantly different results for $O_2^+ + CHClF_2$. The results for the reaction with Xe^+ show the same inconsistency as described in section 3.2.1, in that the thermochemistry points toward reaction only occurring with the $^2P_{1/2}$ excited state. The observed straight line rate graph demonstrates that both spin−orbit states react at the same rate or that the $^2P_{3/2}$ level has insufficient energy to react. This effect is now also true for the major product channel, CHF_2^+ with 94% branching ratio.

At recombination energies between 12.15 and 14.53 eV, CHF_2^+ production is by far the most dominant route, with its branching ratio not falling below 76% over this energy range. The reaction with N_2O^+ that forms $CHClF^+$ at the 3% level does not have the option to produce $N_2O + F$ as the accompanying neutrals, unlike the major product channel producing $N_2O + Cl$, due to the inherent endothermicity, +60 kJ mol^{-1}, of producing these neutrals. Therefore, the near thermoneutral reaction forming $CHClF^+ + N_2 + OF$ is the only accessible pathway. At even higher energy, the major product formed from the reactions involving N_2^+, Ar^+, and F^+ is $CHClF^+$ produced at the about 65% level. Appreciable formation of CHF_2^+ still occurs in reactions with the former two ions, although with F^+ the emergence of smaller ions such as CF^+ is evident. This trend is extended further in the reaction involving Ne^+, where the major product is Cl^+, an atomic ion. A range of other product ions is also observed, although not the parent ion. The composite breakdown diagram resulting from the photoionization of $CHClF_2$ using the TPEPICO technique,[4] alongside the corrected SIFT branching ratios, is shown in Figure 2. Reasonable agreement exists between the two sets of data, although the data for Ne^+ appears to show a reversal in the branching ratios for CF^+/CHF^+ and CF_2^+/CHF_2^+ and a vastly increased yield of $CHClF^+$. From the TPES for this molecule,[4] it can be demonstrated that only the reactions of $CHClF_2$ with N_2O^+, Kr^+, CO^+, N_2^+, and Ar^+ appear to have sufficient Franck−Condon overlap to occur via the long-range charge-transfer mechanism. Any other results that resemble the TPEPICO data are assumed to fit the short-range model, even though the products match those expected from the long-range model.

3.2.3. CH_2ClF. The ionic and proposed neutral products of reaction between atomic and molecular ions with CH_2ClF are listed in Table 3. Below the onset of ionization of CH_2ClF, determined by us as 11.63 ± 0.05 eV,[4] only CF_y^+, where y = 1, 2, or 3, SF_5^+, and SF^+ react at an observable rate. The CF_y^+ species show a preference for fluorine atom removal, with the subsequent ion CH_2Cl^+ being the most dominant product with a branching ratio of about 90%. The CF_3^+ reaction has been studied previously using an ion cyclotron resonance mass spectrometer (ICR-MS), but the results are very different.[29] In this earlier study, CH_2F^+ was the major product (95%) together with only 5% of CH_2Cl^+, and the reaction proceeds with a much lower rate coefficient. These observations may be explained by the formation of a longer-lived transition state than is indicated by our efficient reaction.[30] Additionally, the operating pressure inside an ICR-MS is much lower than that inside a SIFT, resulting in non-thermalized reagents and different product distributions. As an extension of the aforementioned CF_y^+ trend, the SF_5^+ reaction proceeds via C−F bond cleavage to form CH_2Cl^+, now with a yield of 100%. This may be due to the stabilization that formation of SF_6 conveys. Competition between Cl and H atom removal is observed in the SF^+ reaction, as the respective resultant ionic products have approximately

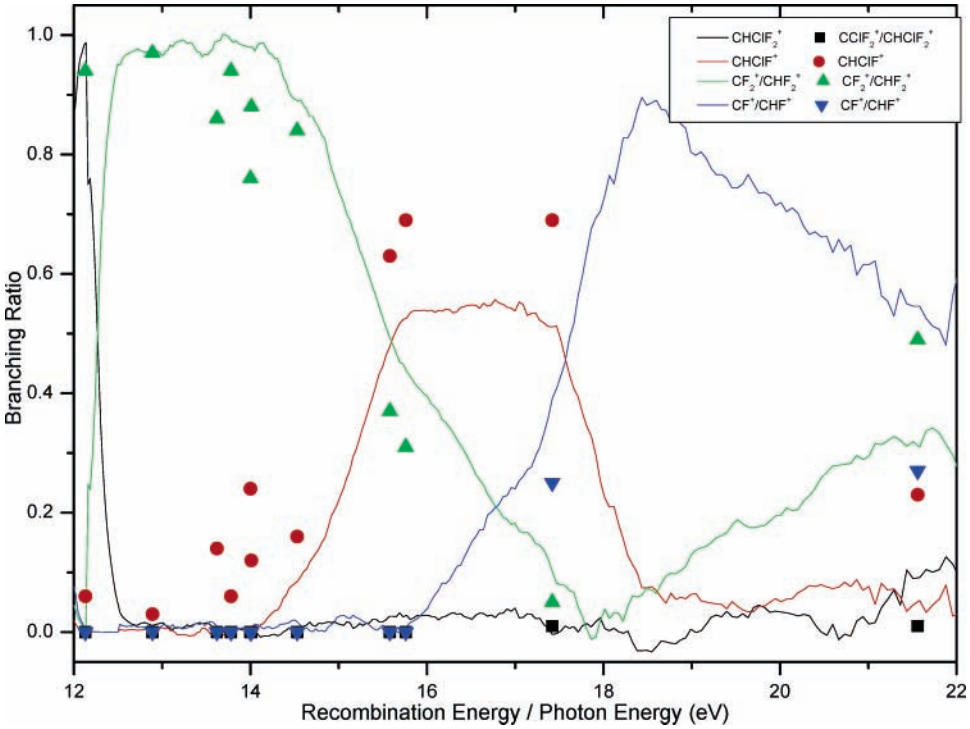


Figure 2. Comparison of the ionic products from ion−molecule studies of $CHClF_2$ with TPEPICO photoionization branching ratios over the energy range 12−22 eV. The SIFT branching ratios are corrected so that the sum of the relevant data equals unity.

the same branching ratio. The heats of formation for the suggested neutrals SClF and SHF have not been established, but these reactions would occur spontaneously if the $\Delta_f H_{298}°$ for these two molecules were less than −97 and −7 kJ mol^{-1}, respectively. As the heats of formation at 298 K for SCl_2, SH_2, and SF_2 are −18, −21, and −295 kJ mol^{-1}, respectively, these suggestions seem plausible.[22,23]

Above the onset of ionization of CH_2ClF there is the opportunity for long-range charge transfer to happen. Interestingly, SF_4^+ reacts to give solely CH_2Cl^+. As for the SF_5^+ reaction, a possible explanation is the formation of the comparatively stable SF_5 species, with $\Delta_f H_{298}° = -915$ kJ mol^{-1}. From 12.07 (O_2^+) to 12.89 eV (N_2O^+), the major product is the parent ion. There is also an appreciable amount of $CHClF^+$ detected over this range. The uncertainty in the thermochemistry of the FOO radical may explain the production of CH_2Cl^+ at 8% from $O_2^+ + CH_2ClF$, despite $v^+ = 0-2$ of O_2^+ being endothermic reactions. The reactions of Xe^+ once again display the inconsistencies described in detail for $CHCl_2F$ in section 3.2.1, and the arguments are not repeated here. Neither the O_2^+ nor the Xe^+ reaction displays any curvature in its respective rate plot. It is worth noting that the major product of the Xe^+ reaction may be formed from either spin−orbit state of the reagent ion and that the parent ion formed by N_2O^+ can only be formed with N_2O as the neutral partner. This is the only time this molecule is a preferred neutral product in any of the N_2O^+ reactions studied here. Within the energy range 13.62−15.76 eV, CH_2F^+ is the dominant product, with a branching ratio between 55 and 93%. Varying amounts of CH_2Cl^+, $CHClF^+$, and the parent ion are observed from all the reactions in this range. The F^+ reaction strongly favors CH_2Cl^+ formation, possibly because F_2 is a stable neutral partner. The reaction with Ne^+ forms a multitude of smaller ions, with CHF^+ figuring prominently. The CF^+ product can be formed with either $H_2 + Cl + Ne$ or $HCl + H + Ne$, as both of these reactions are approximately isoenthalpic. With reference to Figure 3, which depicts the breakdown diagram from the TPEPICO experiment[4] and the corrected branching ratios from this work, it is clear that the fit between the two data sets is not as close as for the other two molecules. Anomalies include reactions with SF_4^+, where completely different products are observed, and N_2^+, Ar^+, and Ne^+, where an increase in one product is offset with a decrease in another. Using the intensities of peaks in the TPES of CH_2ClF as a guide to Franck−Condon factors,[4] it can be concluded that the reactions of Kr^+, CO^+, and N^+ occur via long-range charge transfer. All other reactions occur by other mechanisms, even if the products match those of the long-range model.

4. Conclusions

The branching ratios and rate coefficients have been measured at 298 K for the reactions between $CHCl_2F$, $CHClF_2$, and CH_2ClF and the following cations: H_3O^+, SF_x^+ (where $x = 1$, 2, 3, 4, or 5), CF_y^+ (where $y = 1$, 2, or 3), NO^+, NO_2^+, O_2^+, Xe^+, N_2O^+, O^+, CO_2^+, Kr^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+. Comparisons between experimental and calculated rate coefficients indicate that the vast majority of reactions occur efficiently. No reactions are observed between any of the neutrals and SF_3^+, NO^+, NO_2^+, and SF_2^+. This is attributed to the endothermic nature of all the available reaction processes. The H_3O^+ ion only reacts with $CHCl_2F$, even though all of the observed channels are apparently endothermic. Attempts to rationalize this observation using entropic effects and incorrect thermochemistry fall short of a plausible explanation. The CF_y^+ series all react via single bond dissociation of the neutral in the collision complex to form a single neutral halocarbon species. All of the reagent ions in the SF_x^+ series react inefficiently with $CHClF_2$ forming $CHClF^+$ as the sole ionic product, implying that fluorine-atom transfer is hindered in these complexes. The reactions involving O_2^+ demonstrate that the $\Delta_f H_{298}°$ for FOO is not established, in agreement with recent theoretical work.[25,26] Xe^+ appears to react either when it is only in its higher-energy $^2P_{1/2}$ spin−orbit state or when both spin−orbit states react with

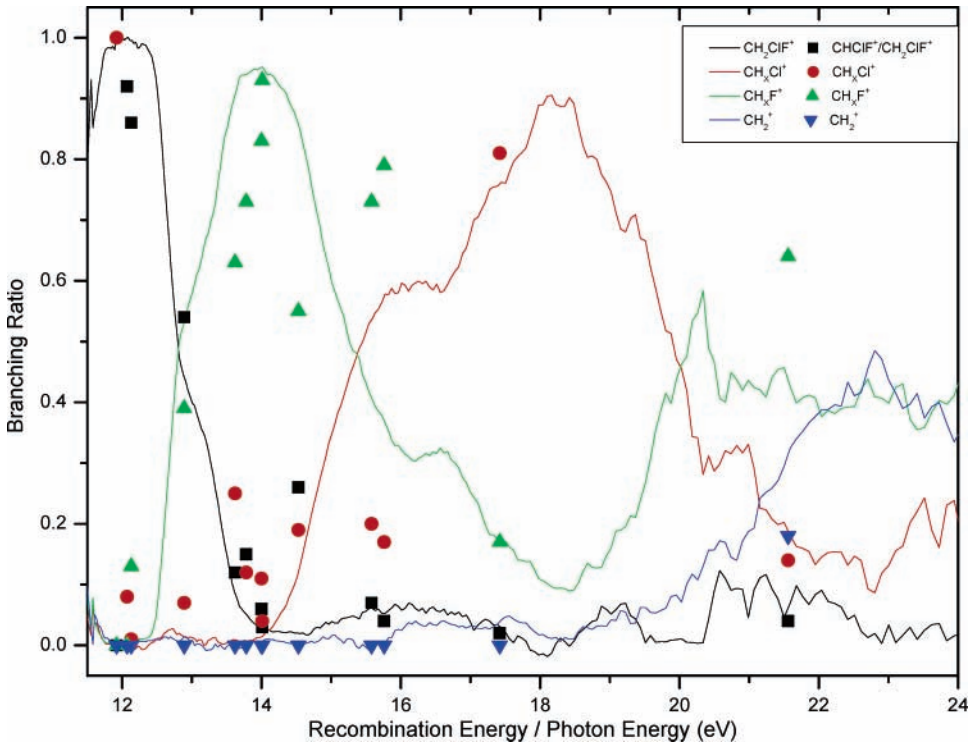


Figure 3. Comparison of the ionic products from ion−molecule studies of CH_2ClF with TPEPICO photoionization branching ratios over the energy range 12−24 eV. The SIFT branching ratios are corrected so that the sum of the relevant data equals unity.

the same rate coefficient. This result appears to contradict previous data from our SIFT apparatus involving Xe^+, where different rates were observed for each spin−orbit state, with the $^2P_{3/2}$ state reacting significantly faster.[13,31] We can only conclude that the operating conditions of the ion source and flow tube were different in these two studies. From a thermochemical perspective, the reactions of N_2O^+ may proceed via charge transfer with dissociation in both the reagent cation and neutral, although extensive rearrangements are required. Chlorine-atom abstraction is favored for reactions with Xe^+, N_2O^+, O^+, CO_2^+, Kr^+, CO^+, and N^+ ions, except in the case of the first two ions with CH_2ClF. This favorable trend can be justified using the relative bond strengths available in the neutral molecules, where C−Cl is clearly the weakest bond.[4,32] This is further supported by the Cl lone pair and C−Cl σ-bonding orbital character evident in all three neutrals over the energy region that corresponds to the recombination energies of these reagent ions.[4] It is interesting to note that the product branching ratios resulting from reactions with atomic and molecular ions that possess virtually identical recombination energy are exceedingly similar, as demonstrated by the Kr^+ and CO^+ data. Equivalent results are noted when comparing the N_2^+ and Ar^+ results, where competition between chlorine or fluorine removal exists. As expected, increased fragmentation is noted at the highest recombination energies, with Cl^+, CF^+, and CHF^+ products figuring prominently. Upper limits for $\Delta_f H_{298}°$, where values could not be sourced from the literature, can be useful guides to thermochemistry. These are derived for the molecules SClF, SF_4Cl, and SHF as −28, −637, and −7 kJ mol^{-1}. The value for SClF is taken from the reaction between SF^+ and $CHCl_2F$, rather than with CH_2ClF, as the former gives a higher branching ratio for SClF production.

Genuine long-range charge transfer, where substantial overlap between the ground state and an accessible ionic state in the neutral molecule exists at the recombination energy of the reagent ion plus an agreement between TPEPICO and SIFT branching ratios,[3] is observed in about 10 out of a total of 55 reactions studied. The only results which notably conflict with those of the TPEPICO study, rather than display systematic differences, are the $F^+ + CHCl_2F$, $Ne^+ + CHClF_2$, and, to a lesser extent, $Ne^+ + CH_2ClF$. These three reactions take place at recombination energies that coincide with the lowest intensity on the relevant TPES, thereby emphasizing the importance of the Franck−Condon overlap on the accord between the two sets of results. Generally, the results for $CHCl_2F$ and $CHClF_2$, where dissociative charge transfer dominates and parent ion signal is rarely seen in major abundance, are similar to those found in the recent SIFT studies performed on the analogous $CHBr_2F$ and $CHBrF_2$ molecules, respectively.[5] The profile of the product ion signal variation as a function of neutral reagent for each individual reaction indicates which secondary processes are occurring at higher neutral gas flow. The vast majority of these graphs for $CHCl_2F$ and $CHClF_2$ mimic those obtained using a high-pressure mass spectrometer,[33] in that $CHClF^+$ reacts on to form $CHCl_2^+$ in the former case and CHF_2^+ produces $CHClF^+$ at high flows of the neutral reactant. The only exceptions to this consensus are those plots derived from reactions involving ions with high recombination energies, where the presence of more fragmented products complicates this matter. However, derivative processes such as these only warrant a cursory mention, as the branching ratios derived from extrapolation to zero flow of the neutral gas are the prime focus of this study. The CH_2ClF results fall into a separate group than those of the other two molecules of interest to this work, as nondissociative charge transfer is evident in increased levels and even dominates in some cases. These findings concur with the recent work performed on CH_2BrF and CH_2BrCl.[5]

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