Selected Ion Flow Tube Study of the Ion−Molecule Reactions of Monochloroethene, Trichloroethene, and Tetrachloroethene

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Data for the rate coefficients and product cations of the reactions of a large number of atomic and small molecular cations with monochloroethene, trichloroethene, and tetrachloroethene in a selected ion flow tube at 298 K are reported. The recombination energy of the ions range from 6.27 (H_3O^+) through to 21.56 (Ne^+) eV. Collisional rate coefficients are calculated by modified average dipole orientation theory and compared with experimental values. Thermochemistry and mass balance predict the most feasible neutral products. Together with previously reported results for the three isomers of dichloroethene (Mikhailov, V. A.; Parkes, M. A.; Tuckett, R. P.; Mayhew, C. A. *J. Phys. Chem. A* **2006**, *110*, 5760), the fragment ion branching ratios have been compared with those from threshold photoelectron photoion coincidence spectroscopy over the photon energy range of 9−22 eV to determine the importance or otherwise of long-range charge transfer. For ions with recombination energy in excess of the ionization energy of the chloroethene, charge transfer is energetically allowed. The similarity of the branching ratios from the two experiments suggest that long-range charge transfer is dominant. For ions with recombination energy less than the ionization energy, charge transfer is not allowed; chemical reaction can only occur following formation of an ion−molecule complex, where steric effects are more significant. The products that are now formed and their percentage yields are a complex interplay between the number and position of the chlorine atoms with respect to the C=C bond, where inductive and conjugation effects can be important.

1. Introduction

In previous studies our group has examined the photoionization dynamics of the chloroethene molecules $C_2H_xCl_{4-x}$ ($x = 0-2$) by threshold photoelectron photoion coincidence spectroscopy[1,2] and the kinetics and products of cation−molecule reactions for the three isomers of dichloroethene, $C_2H_2Cl_2$.[3] This paper reports results for the reactions of monochloroethene, trichloroethene, and tetrachloroethene with 24 small atomic and molecular cations (H_3O^+, SF_3^+, CF_3^+, CF^+, NO^+, SF_5^+, SF_2^+, SF^+, CF_2^+, SF_4^+, O_2^+, Xe^+, H_2O^+, N_2O^+, OH^+, O^+, CO_2^+, Kr^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+) using a selected ion flow tube (SIFT). The recombination energies (RE) of the cations above span the range of 6.27−21.56 eV. The principal aim of this study is to understand the effect of increasing the number of chlorine substituents on the reactivity of the chloroethenes. To this end comparisons will be drawn between the photoionization results for trichloroethene and tetrachloroethene[1] and between the cation−molecule reactions for all six chloroethenes studied. The six chloroethene molecules are monochloroethene, 1,1-dichloroethene, (*Z*)-1,2-dichloroethene, (*E*)-1,2-dichloroethene, trichloroethene, and tetrachloroethene.

Another reason to examine the reactivity of the chloroethenes is that they are common environmental pollutants and highly resistant to biodegradation.[4] All three chloroethenes studied in this paper, monochloroethene (C_2H_3Cl), trichloroethene (C_2HCl_3), and tetrachloroethene (C_2Cl_4), are industrially important. Monochloroethene is used for the production of the plastic polyvinyl chloride, incomplete combustion of chlorocarbons can produce emissions of trichloroethene,[5] whereas tetrachloroethene has been used as a dry-cleaning agent. All three molecules are suspected carcinogens.

Most of the previously studied ion−molecule reactions have described the reaction of the monochloroethene parent ion ($C_2H_3Cl^+$) with neutral monochloroethene and a range of other neutrals such as methanol, ammonia, and methane.[6−8] There have been very few studies of the reactions of neutral monochloroethene with other cations. Two of interest are the SIFT study of $C_{60}{}^{n+}$ with monochloroethene by Ling et al.[9] and the reactions of rare gas ions with monochloroethene in an ion-beam mass spectrometer.[10] The SIFT study of Ling et al. also included results for the reactions of trichloroethene and tetrachloroethene with $C_{60}{}^{n+}$. Španěl and Smith measured the reactions of trichloroethene and tetrachloroethene with H_3O^+, NO^+, and O_2^+, using a SIFT apparatus adapted for breath analysis.[11]

A secondary aim of this study is to understand the mechanism by which the measured ion−molecule reactions occur. Two limiting mechanisms have been postulated, defined as long-range and short-range electron transfer.[3,12,13] Briefly, in long-range electron transfer the neutral molecule (BC) exchanges an electron with the cation (A^+) at a large internuclear distance (~5Å), and it is assumed that the cation potential energy surface of the neutral molecule is only weakly influenced by the presence of the reacting cation. To all intents and purposes, long-range charge transfer leading to the neutral molecule to donate

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an electron to the reagent ion is energetically the same as resonant photoionization with the photoelectron being produced with zero kinetic energy. Therefore, the product ion branching ratios from long-range transfer ion−molecule reactions and threshold photoelectron photoionization experiments should be similar. For the generic reaction $A^+ + BC \rightarrow AB^+ + C$, these two reactions can be summarized as

$$A^+ + BC \rightarrow A + BC^{+(*)}; \qquad BC^{+(*)} \rightarrow \text{fragments}$$
$$h\nu + BC \rightarrow BC^{+(*)} + e^-; \qquad BC^{+(*)} \rightarrow \text{fragments} \qquad \text{(I)}$$

Short-range electron transfer occurs when the electron jump happens at a much closer separation of the reacting cation and the neutral molecule through the formation of a complex. The cation of the neutral molecule is now formed under the influence of the reacting ion, and this may lead to differences in the product ion branching ratios for the bimolecular compared to the photon-induced reaction. Another mechanism can occur following formation of a collision complex, where bond making and bond breaking may take place; this is our definition of a chemical reaction. Note that for electron transfer, daughter ions form via fragmentation of the parent cation of the neutral molecule, whereas in the chemical mechanism daughter ions are formed in the complex and not with the parent molecular ion as an intermediate. A more detailed discussion of these mechanisms is given elsewhere.[12,13] It should be noted that both the limiting charge-transfer mechanisms can only take place when the RE of the reagent ion is greater than the ionization energy (IE) of the neutral molecule. By contrast, a chemical reaction can take place at any RE of the ion. The IE values, defined as the experimental onset of ionization, for the three neutrals studied here are 9.99 eV for monochloroethene,[14] 9.46 eV for trichloroethene, and 9.30 eV for tetrachloroethene.[1] Of the cations studied, five (H_3O^+, SF_3^+, CF_3^+, CF^+, NO^+) have RE values less than the IE of all three neutrals, whereas SF_5^+ has an RE value less than the IE of monochloroethene. The remaining ions all have RE values greater than the IE of the three chloroethenes, so on energetic grounds charge transfer may occur.

2. Experimental Section

Rate coefficients and products for the ion−molecule reactions have been measured using a SIFT apparatus. Details of its operation are given in several reviews,[15−17] and only a brief description is given here. Reagent ions are generated from a suitable precursor gas or gases in a high-pressure electron ionization source. By transmitting the generated ions through a quadrupole mass filter, the required reactant ion can be selected and admitted into the flow tube. The tube is filled with ca. 0.5 Torr of helium buffer gas moving with a high linear velocity, ca. 100 m s^{-1}. The neutral reagent is injected downstream into the flow tube via one of two different inlets. At the end of the flow tube cations are focused through a 1 mm orifice in a Faraday plate into a second quadrupole mass filter and detected by an off-axis channeltron. The amount of injected neutral is varied from zero to a value which depletes the reactant ion signal by ca. 90%. The loss of reagent ion and the increase in product ions are recorded as a function of neutral reagent concentration under pseudo-first-order conditions. The error in the rate coefficient determined from data analysis is estimated to be 20%, and the apparatus is limited to measuring reactions with rate coefficients greater than ca. 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. Branching ratios are derived from plots of ion signal versus neutral concentration, and extrapolation to zero flow of the neutral molecule allows for the effects of any secondary reactions. We quote an error of 15% in product branching ratios; this error increasing for ratios below 10%. Care is taken to check the linearity of the ln(reactant ion signal) versus neutral concentration rate plot for signs of curvature, since such behavior can indicate the presence of excited reagent ions. Only the reactions of NO^+ showed such curvature. The absence of curvature, however, does not necessarily mean that all ions are in the ground state, since both ground and excited states could react with the same rate coefficient.

All samples were purchased from Sigma-Aldrich with stated purities of greater than 99%. Trichloroethene and tetrachloroethene were purified by several freeze−pump−thaw cycles with liquid nitrogen before use.

3. Theory

For comparison to the experimental rate coefficients, k_{exp}, theoretical rate coefficients, k_c, were calculated using the corrected version of the modified average dipole orientation (MADO) model of Su and Chesnavich.[18,19] This calculation requires values for both the polarizability volume and the dipole moment of the neutral reactant. The polarizability volume values for monochloroethene, trichloroethene, and tetrachloroethene are 6.41, 10.03, and 12.02 × 10^{-30} m^3. The values for monochloroethene and trichloroethene were taken from the CRC handbook;[20] the value for tetrachloroethene was estimated using the atomic-hybrid method of Miller which is known to give excellent results.[21] The dipole moments of monochloroethene and trichloroethene are 1.45 and 0.90 D, respectively.[20]

For calculation of enthalpies of reaction, $\Delta_r H°_{298}$, enthalpies of formation at 298 K of ions and neutrals were required. The majority were taken from standard sources,[14,22] exceptions being the enthalpies of formation for CF_3^+ (+406 kJ mol^{-1}),[23] CClF (+31 kJ mol^{-1}),[24] SF_5^+ (+29 kJ mol^{-1}),[25] SF_5 (−915 kJ mol^{-1}),[26] SF_4 (−768 kJ mol^{-1}),[27] SF_2^+ (+693 kJ mol^{-1}),[27] SF_2 (−295 kJ mol^{-1}),[27] SF^+ (+998 kJ mol^{-1}),[27] and NCl (+314 kJ mol^{-1}).[28] The values for the parent neutrals were taken from Manion.[29] The enthalpies of formation for the parent ions formed from trichloroethene and tetrachloroethene were taken from the photoionization study on these molecules,[1] as were $\Delta_f H°_{298}$ values for $C_2HCl_2^+$ (1066 kJ mol^{-1}) and $C_2Cl_3^+$ (984 kJ mol^{-1}). The IE of the three chloroethenes used are 9.99 eV for monochloroethene, 9.46 eV for trichloroethene, and 9.30 eV for tetrachloroethene.

Gaussian 03 calculations have been performed on all three molecules at the MP2 level with a 6-311G+(d,p) basis set. The results for trichloroethene and tetrachloroethene have been reported in the paper on their photoionization dynamics.[1] Among other data, these calculations can give some indication of the orbital from which ionization is taking place.

4. Results

Tables 1−3 show the results from the SIFT experiment for the reactions of 24 cations with monochloroethene, trichloroethene, and tetrachloroethene, respectively. Column 1 lists the reagent ion and its RE value in parentheses. Column 2 lists the experimentally measured rate coefficient and, in square brackets, the rate coefficient determined using the MADO model. Column 3 lists the ion products detected and their respective branching ratio in parentheses. Column 4 lists the proposed neutral products, and column 5 lists the enthalpy for the proposed reaction. The proposed neutral products are based on mass balance, chemical feasibility, and thermochemistry. For simplicity and ease of comparison with the photoionization results

TABLE 1: Rate Coefficients at 298 K, Product Cations and Branching Ratios, and Suggested Neutral Products for Reactions of Gas-Phase Cations with Recombination Energy (RE) in the Range of 6.27−21.56 eV with Monochloroethene, C_2H_3Cl[a,b]

reagent ion (RE/eV)[c]	rate coefficient/10^{-9} cm^3 $molecule^{-1}$ s^{-1}	product ions (%)	proposed neutral products	$\Delta_r H°_{298}$/kJ mol^{-1}
H_3O^+	2.2	$C_2H_3ClH^+$ (100)	H_2O	$-815 + \Delta_f H°_{298}[C_2H_3ClH^+]$
(6.27)	[2.5]			
SF_3^+	no reaction[d]			
(8.32)	[1.5]			
CF_3^+	1.1	$CHFCl^+$ (35)	$C_2F_2H_2$	−2
(9.04)	[1.6]	$C_2H_3^+$ (65)	CF_3Cl	−36
CF^+	2.0	$CHFCl^+$ (27)	C_2H_2	−186
(9.11)	[2.1]	$C_2H_3^+$ (73)	CFCl	−25
NO^+	no reaction			
(9.26)	[2.0]			
SF_5^+	0.4	SF_3^+ (50)	$C_2H_2FCl + HF$	$38 + \Delta_f H°_{298}[C_2H_2FCl]$
(9.78)	[1.4]	$C_2H_3ClF^+$ (50)	SF_4	$-819 + \Delta_f H°_{298}[C_2H_3ClF^+]$
SF_2^+	1.6	$C_2H_3SF_2^+$ (6)	Cl	$-594 + \Delta_f H°_{298}[C_2H_3SF_2^+]$
(10.24)	[1.6]	$C_2H_3Cl^+$ (94)	SF_2	−25
SF^+	1.8	C_2HSF^+ (13)	$H_2 + Cl$	$-899 + \Delta_f H°_{298}[C_2HSF^+]$
(10.31)	[1.8]	C_2SF^+ (22)	$H_2 + HCl$	$-1113 + \Delta_f H°_{298}[C_2SF^+]$
		$C_2H_3Cl^+$ (40)	SF	−31
		$C_2H_3^+$ (25)	SFCl	$80 + \Delta_f H°_{298}[SFCl]$
CF_2^+	1.8	$C_3H_3F_2^+$ (5)	Cl	$-823 + \Delta_f H°_{298}[C_3H_3F_2^+]$
(11.44)	[1.8]	$CHFCl^+$ (25)	$CF + CH_2$	−3
			C_2FH	−75
		$C_2H_3Cl^+$ (70)	CF_2	−140
O_2^+	2.0	$C_2H_3Cl^+$ (100)	O_2	−161
(12.07)	[2.0]			
Xe^+	1.4	$C_2H_3Cl^+$ (78)	Xe	−206
(12.13)	[1.4]	$C_2H_3^+$ (21)	Xe + Cl	+29
		$C_2H_2^+$ (1)	Xe + HCl	+42
H_2O^+	2.4	$C_2H_3ClH^+$ (9)[e]	OH	$-958 + \Delta_f H°_{298}[C_2H_3ClH^+]$
(12.62)	[2.5]	$C_2H_3Cl^+$ (73)	H_2O	−253
		$C_2H_3^+$ (17)	$H_2O + Cl$	−18
N_2O^+	1.7	$C_2H_3Cl^+$ (56)	N_2O	−280
(12.89)	[1.8]	$C_2H_3^+$ (44)	$N_2O + Cl$	−159
OH^+	2.5	$C_2H_3Cl^+$ (−)[e]	OH	−383
(13.25)	[2.6]	$C_2H_3^+$ (−)	OH + Cl	−55
		$C_2H_2^+$ (−)	OH + HCl	−42
O^+	2.1	not recorded[f]		
(13.62)	[2.6]			
CO_2^+	2.0	$C_2H_3Cl^+$ (7)	CO_2	−365
(13.76)	[1.8]	$C_2H_3^+$ (90)	$CO_2 + Cl$	−129
		$C_2H_2^+$ (3)	$CO_2 + HCl$	−116
Kr^+	1.5	$C_2H_3Cl^+$ (1)	Kr	−387
(14.00 (and 14.67))	[1.6]	$C_2H_2Cl^+$ (1)	Kr + H	−114
		$C_2H_3^+$ (91)	Kr + Cl	−152
		$C_2H_2^+$ (7)	Kr + HCl	−138
CO^+	2.1	$C_2H_3Cl^+$ (2)	CO	−388
(14.01)	[2.1]	$C_2H_3^+$ (92)	CO + Cl	−152
		$C_2H_2^+$ (6)	CO + HCl	−139
N^+	2.5	$C_2H_3Cl^+$ (57)	N	−438
(14.53)	[2.7]	$C_2H_3^+$ (41)	N + Cl	−203
		$C_2H_2^+$ (2)	N + HCl	−190
N_2^+	2.0	$C_2H_3Cl^+$ (2)	N_2	−539
(15.58)	[2.1]	$C_2H_2Cl^+$ (8)	$N_2 + H$	−266
		$C_2H_3^+$ (76)	$N_2 + Cl$	−304
		$C_2H_2^+$ (14)	$N_2 + HCl$	−291
Ar^+	1.7	$C_2H_3Cl^+$ (1)	Ar	−557
(15.76)	[1.9]	$C_2H_2Cl^+$ (10)	Ar + H	−284
		C_2HCl^+ (3)	$Ar + H_2$	−306
		HCl^+ (4)	$Ar + C_2H_2$	−179
		$C_2H_3^+$ (68)	Ar + Cl	−322
		$C_2H_2^+$ (13)	Ar + HCl	−309
F^+	2.1	$C_2H_3Cl^+$ (5)	F	−717
(17.42)	[2.5]	$C_2H_2Cl^+$ (13)	F + H	−444
		$C_2H_3^+$ (72)	F + Cl	−481
		$C_2H_2^+$ (10)	F + H + Cl	−37
			F + HCl	−468
Ne^+	2.1	$C_2H_3Cl^+$ (5)	Ne	−1116
(21.56)	[2.4]	$C_2H_2Cl^+$ (1)	Ne + H	−843
		C_2HCl^+ (4)	Ne + H + H	−429
			$Ne + H_2$	−865
		Cl^+ (8)	$Ne + C_2H_3$	−432
		$C_2H_3^+$ (4)	Ne + Cl	−881
		$C_2H_2^+$ (74)	Ne + H + Cl	−478
			Ne + HCl	−868
		C_2H^+ (4)	Ne + H + HCl	−379
			$Ne + H_2 + Cl$	−384

[a] The calculated enthalpy of reaction at 298 K is shown in the fifth column. The solid line indicates the position of the IE of monochloroethene, 9.99 eV, relative to the RE of the cations. [b] The majority of the enthalpies of formation at 298 K for ion and neutral species are taken from standard sources (refs 22 and 35). [c] Recombination energy (RE) of reactant ion. For molecular ions, the RE given is the adiabatic value. [d] No reaction means the rate coefficient is less than ca. 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. [e] We were unable to inject H_2O^+ without OH^+ contamination; the OH^+ signal was 30% of the H_2O^+ signal. Hence, the values for the H_2O^+ branching ratios are approximate. [f] O^+ was produced via collision-induced dissociation from N_2O^+; the signal was too small to allow measurement of branching ratios.

TABLE 2: Rate Coefficients at 298 K, Product Cations and Branching Ratios, and Suggested Neutral Products for Reactions of Gas-Phase Cations with Recombination Energy (RE) in the Range of 6.27−21.56 eV with Trichloroethene, C_2HCl_3[a,b]

reagent ion (RE/eV)[c]	rate coefficient/10^{-9} cm^3 molecule^{-1} s^{-1}	product ions (%)	proposed neutral products	$\Delta_r H°_{298}$/kJ mol^{-1}
H_3O^+	2.1	$C_2HCl_3H^+$ (100)	H_2O	$-815 + \Delta_f H°_{298}[C_2HCl_3H^+]$
(6.27)	[2.2]			
SF_3^+				
(8.32)	[1.2]			
CF_3^+	1.3	$CFCl_2^+$ (24)	C_2HClF_2	$315 + \Delta_f H°_{298}[C_2HClF_2]$
(9.04)	[1.3]	$C_2HCl_2^+$ (54)	CF_3Cl	−33
		CF_2Cl^+ (22)	C_2HCl_2F	$168 + \Delta_f H°_{298}[C_2HCl_2F]$
CF^+	1.8	$CFCl_2^+$ (39)	C_2HCl	−200
(9.11)	[1.8]	$CHCl_2^+$ (23)	CF + CCl	−251
			C_2FCl	$-230 + \Delta_f H°_{298}[C_2FCl]$
		$CHFCl^+$ (37)	C_2Cl_2	−164
NO^+	no reaction[d]			
(9.26)	[1.8]			
SF_5^+	0.4	$C_2HCl_3F^+$ (16)	SF_4	$-780 + \Delta_f H°_{298}[C_2HCl_3F^+]$
(9.78)	[1.1]	$C_2HCl_3^+$ (84)	SF_5	−33
SF_2^+	1.4	$C_2HCl_3^+$ (100)	SF_2	−77
(10.24)	[1.5]			
SF^+	1.2	$C_2HCl_3^+$ (100)	SF	−995
(10.31)	[1.3]			
CF_2^+	1.9	$C_2HCl_3^+$ (100)	CF_2	−193
(11.44)	[1.5]			
SF_4^+	1.5	$C_2HCl_3^+$ (100)	SF_4	−247
(11.99)	[1.1]			
O_2^+	1.8	$C_2HCl_3^+$(100)	O_2	−253
(12.07)	[1.7]			
Xe^+	1.1	$C_2HCl_3^+$ (82)	Xe	−259
(12.13)	[1.1]	$C_2HCl_2^+$ (18)	Xe + Cl	+34
H_2O^+	2.2	$C_2HCl_3^+$ (−)[e]	H_2O	−306
(12.62)	[2.2]	$C_2HCl_2^+$ (−)	H_2O + Cl	−12
N_2O^+	2.0	$C_2HCl_3^+$ (49)	N_2O	−333
(12.89)	[1.5]	$C_2HCl_2^+$ (51)	N_2O + Cl	−39
			N_2 + OCl	−142
OH^+	2.3	$C_2HCl_3^+$ (−)[e]	OH	−343
(13.25)	[2.2]	$C_2HCl_2^+$ (−)	OH + Cl	−50
			O + HCl	−53
			HOCl	−285
O^+	2.3	$C_2HCl_3^+$ (−)[f]	O	−403
(13.62)	[2.3]	$C_2HCl_2^+$ (−)	O + Cl	−109
			OCl	−379
CO_2^+	1.7	$C_2HCl_3^+$ (21)	CO_2	−417
(13.76)	[1.5]	$C_2HCl_2^+$ (79)	CO_2 + Cl	−124
Kr^+	1.3	$C_2HCl_3^+$ (5)	Kr	−440
(14.00 (and 14.67))	[1.2]	$C_2HCl_2^+$ (95)	Kr + Cl	−146
CO^+	1.5	$C_2HCl_3^+$ (11)	CO	−440
(14.01)	[1.8]	$C_2HCl_2^+$ (89)	CO + Cl	−147
			COCl	−221
N^+	3.3	$C_2HCl_3^+$ (44)	N	−491
(14.53)	[2.5]	$C_2HCl_2^+$ (43)	N + Cl	−198
			NCl	−478
		C_2HCl^+ (13)	N + Cl_2	−148
			NCl + Cl	−186
N_2^+	1.3	$C_2HCl_3^+$ (3)	N_2	−592
(15.58)	[1.8]	$C_2HCl_2^+$ (88)	N_2 + Cl	−299
		$CHCl_2^+$ (9)	N_2 + CCl	−96
Ar^+	1.5	$C_2HCl_3^+$ (6)	Ar	−610
(15.76)	[1.6]	$C_2HCl_2^+$ (90)	Ar + Cl	−317
		$CHCl_2^+$ (4)	Ar + CCl	−114
F^+	2.3	$C_2HCl_3^+$ (17)	F	−770
(17.42)	[2.2]	$C_2HCl_2^+$ (18)	F + Cl	−476
			FCl	−727
		C_2HCl^+ (65)	F + Cl_2	−427
			FCl + Cl	−435
Ne^+	2.3	$C_2Cl_2^+$ (13)	Ne + HCl	−1936
(21.56)	[2.1]	C_2HCl^+ (78)	Ne + Cl_2	−826
		CCl^+ (9)	Ne + $CHCl_2$	−1452

[a] The calculated enthalpy of reaction at 298 K is shown in the fifth column. The solid line indicates the position of the IE of trichloroethene, 9.46 eV, relative to the RE of the cations. [b] The majority of the enthalpies of formation at 298 K for ion and neutral species are taken from standard sources (refs 22 and 35). [c] Recombination energy (RE) of reactant ion. For molecular ions, the RE given is the adiabatic value. [d] No reaction means the rate coefficient is less than ca. 10^{-13} cm^3 molecule^{-1} s^{-1}. [e] We were unable to inject H_2O^+ without OH^+ contamination; the OH^+ signal was 30% of the H_2O^+ signal. Hence, the values for the H_2O^+ branching ratios are approximate. [f] O^+ was produced via collision-induced dissociation from N_2O^+; the signal was too small to allow measurement of branching ratios.

emphasis has been given to products formed from charge transfer rather than chemical reaction.

No rate coefficient for the reaction of SF_4^+ with monochloroethene has been measured. This is because only a small signal of SF_4^+ could be produced from the ion source in conjunction with a large signal of SF_5^+; secondary products from the reaction of SF_5^+ with monochloroethene formed at 107 and 109 u masked the weak SF_4^+ signal at 108 u. For several reactions, branching ratios have not been measured because it was impossible to obtain a clean signal of a single reactant ion, leading to complications in calculating the branching ratios. O_2 was not used to produce O^+ as the filament in the ion source

TABLE 3: Rate Coefficients at 298 K, Product Cations and Branching Ratios, and Suggested Neutral Products for Reactions of Gas-Phase Cations with Recombination Energy (RE) in the Range of 6.27−21.56 eV with Tetrachloroethene, C_2Cl_4[a,b]

reagent ion (RE/eV)[c]	rate coefficient/10^{-9} cm^3 $molecule^{-1}$ s^{-1}	product ions (%)	proposed neutral products	$\Delta_r H^\circ_{298}$/kJ mol^{-1}
H_3O^+	1.1	$C_2Cl_4H^+$ (100)	H_2O	$-809 + \Delta_f H^\circ_{298}[C_2Cl_4H^+]$
(6.27)	[2.0]			
SF_3^+				
(8.32)	[1.1]			
CF_3^+	1.9	$C_2Cl_3^+$ (9)	CF_3Cl	−108
(9.04)	[1.2]	$CFCl_2^+$ (16)	$C_2F_2Cl_2$	$321 + \Delta_f H^\circ_{298}[C_2F_2Cl_2]$
		CF_2Cl^+ (75)	C_2FCl_3	$174 + \Delta_f H^\circ_{298}[C_2FCl_3]$
CF^+	1.8	$CFCl_2^+$ (100)	C_2Cl_2	−197
(9.11)	[1.6]			
NO^+	no reaction[d]			
(9.26)				
SF_5^+	0.6	$C_2Cl_4^+$ (100)	SF_5	−44
(9.78)	[1.0]			
SF_2^+	0.7	$C_2Cl_4^+$ (100)	SF_2	−89
(10.24)	[1.3]			
SF^+	1.2	$C_2Cl_4^+$ (100)	SF	−96
(10.31)	[1.2]			
CF_2^+	1.5	$C_2Cl_4^+$ (100)	CF_2	−204
(11.44)	[1.3]			
SF_4^+	1.0	$C_2Cl_4^+$ (100)	SF_4	−258
(11.99)	[1.0]			
O_2^+	1.3	$C_2Cl_4^+$ (100)	O_2	−265
(12.07)	[1.6]			
Xe^+	0.9	$C_2Cl_4^+$ (55)	Xe	−271
(12.13)	[0.9]	$C_2Cl_3^+$ (45)	Xe + Cl	−41
H_2O^+	1.6	$C_2Cl_4^+$ (−)[e]	H_2O	−317
(12.62)	[2.0]	$C_2Cl_3^+$ (−)	H_2O + Cl	−87
N_2O^+	1.7	$C_2Cl_4^+$ (22)	N_2O	−344
(12.89)	[1.4]	$C_2Cl_3^+$ (78)	N_2O + Cl	−114
OH^+	1.7	$C_2Cl_4^+$ (−)[e]	OH	−342
(13.25)	[2.1]	$C_2Cl_3^+$ (−)	OH + Cl	−131
O^+	2.0	$C_2Cl_4^+$ (−)[f]	O	−414
(13.62)	[2.1]	$C_2Cl_3^+$ (−)	O + Cl	−184
CO_2^+	1.4	$C_2Cl_4^+$ (18)	CO_2	−435
(13.76)	[1.4]	$C_2Cl_3^+$ (82)	CO_2 + Cl	−206
Kr^+	1.1	$C_2Cl_4^+$ (4)	Kr	−451
(14.00 (and 14.67))	[1.1]	$C_2Cl_3^+$ (96)	Kr + Cl	−221
CO^+	1.8	$C_2Cl_4^+$ (7)	CO	−452
(14.01)	[1.7]	$C_2Cl_3^+$ (93)	CO + Cl	−222
N^+	2.3	$C_2Cl_4^+$ (43)	N	−503
(14.53)	[2.3]	$C_2Cl_3^+$ (57)	N + Cl	−273
N_2^+	1.7	$C_2Cl_4^+$ (7)	N_2	−603
(15.58)	[1.7]	$C_2Cl_3^+$ (67)	N_2 + Cl	−373
		CCl_3^+ (3)	N_2 + CCl	−115
			NCN + Cl	−23
		$C_2Cl_2^+$ (17)	$N_2 + Cl_2$	−314
			N_2 + Cl + Cl	−71
		CCl_2^+ (5)	$N_2 + CCl_2$	−77
Ar^+	1.4	$C_2Cl_4^+$ (3)	Ar	−621
(15.76)	[1.4]	$C_2Cl_3^+$ (42)	Ar + Cl	−391
		CCl_3^+ (3)	Ar + CCl	−133
		$C_2Cl_2^+$ (44)	Ar + Cl_2	−332
			Ar + Cl + Cl	−89
		CCl_2^+ (8)	Ar + CCl_2	−95
F^+	1.4	$C_2Cl_2^+$ (100)	F + Cl_2	−492
(17.42)	[2.0]		F + Cl + Cl	−249
			FCl + Cl	−500
Ne^+	2.0	$C_2Cl_3^+$ (1)	Ne + Cl	−950
(21.56)	[1.9]	$C_2Cl_2^+$ (54)	Ne + Cl_2	−891
			Ne + Cl + Cl	−648
		CCl_2^+ (10)	Ne + CCl_2	−654
		C_2Cl^+ (10)	Ne + Cl_2 + Cl	$-1935 + \Delta_f H^\circ_{298}[C_2Cl^+]$
		CCl^+ (25)	Ne + CCl_3	−733
			Ne + CCl_2 + Cl	−453

[a] The calculated enthalpy of reaction at 298 K is shown in the fifth column. The solid line indicates the position of the IE of trichloroethene, 9.30 eV, relative to the RE of the cations. [b] The majority of the enthalpies of formation at 298 K for ion and neutral species are taken from standard sources (refs 22 and 35). [c] Recombination energy (RE) of reactant ion. For molecular ions, the RE given is the adiabatic value. [d] No reaction means the rate coefficient is less than ca. 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. [e] We were unable to inject H_2O^+ without OH^+ contamination; the OH^+ signal was 30% of the H_2O^+ signal. Hence, the values for the H_2O^+ branching ratios are approximate. [f] O^+ was produced via collision-induced dissociation from N_2O^+; the signal was too small to allow measurement of branching ratios.

would rapidly burn out; instead N_2O was used as a source gas for O^+. However, only a small ion signal of O^+ could be generated from N_2O, so no branching ratios have been measured for any reactions of O^+. For the reactions of H_2O^+ and OH^+, it was impossible to separate the two ions using the current injection quadrupole. Therefore, only observed products are listed in the tables. The one exception is reaction with monochloroethene where some allowance could be made for the presence of OH^+, and approximate branching ratios are therefore given in Table 1.

For simplicity we will divide the 24 reactant cations into two groups. The first comprise ions with RE(ion) > IE(neutral), so charge transfer is energetically allowed. The second comprise ions with RE(ion) < IE(neutral), where charge transfer is no longer allowed.

4.1. RE(ion) > IE(neutral). ***4.1.1. Rate Coefficients.*** The majority of the ions fall in this group, ranging from SF_5^+ (RE = 9.78 eV) through to Ne^+ (RE = 21.56 eV). Although SF_5^+ has an RE value which falls just below the IE of monochloroethene, for clarity it will be treated in this group of cations. Comparison of k_c to k_{exp} values shows that the majority of the reactions occur at, or very near to, the collisional rate; for most ions the efficiency, defined as k_{exp}/k_c, is in the range of 70−100%. For some reactions k_{exp} has been measured as 20−30% larger than k_c, although the ±20% error associated with the rate coefficients can explain much of these discrepancies.

The reactions of SF_5^+ are slow and inefficient (∼25%), except for tetrachloroethene which reacts with an efficiency of 50%. These results are similar to those for the reaction of SF_5^+ with the dichloroethene isomers.[3] SF_5^+ has also been found to react slowly with $CHCl_2F$, $CHClF_2$, and CH_2ClF,[30] as well as with octafluorocyclobutane.[31] There are two possible explanations for the inefficiency of SF_5^+ reactions. First, there could be steric effects associated with the SF_5^+ cation. Second, the RE(SF_5^+) only slightly exceeds the IE for all three isomers of dichloroethenes, trichloroethene, and tetrachloroethene. This could indicate that charge transfer is an inefficient process close to its thermochemical threshold.

For tetrachloroethene, one other reaction, that with SF_2^+ (RE = 10.24 eV), is slow with a reaction efficiency of only 58%. An unfavorable cross section for long-range charge transfer, indicated by the low signal in the C_2Cl_4 threshold photoelectron spectrum around 10 eV, could explain the low reaction efficiency.

4.1.2. Ion−Molecule Branching Ratios. For reactions of monochloroethene, trichloroethene, and tetrachloroethene with the 19 cations having RE values ranging from 9.78 to 21.56 eV, charge transfer is energetically allowed, apart from the one single reaction of SF_5^+ with monochloroethene. For reactions in this energy range, insight into why certain ionic products are observed can be obtained by comparison of product branching ratios with those from photon-induced threshold photoelectron photoion coincidence (TPEPICO) spectroscopy (see section 1). Therefore, reference will be made to TPEPICO data for the dichloroethenes,[2] trichloroethene, and tetrachloroethene,[1] and SIFT results for the dichloroethenes.[3] Unfortunately, no TPEPICO data for monochloroethene is available.

When the RE of the reagent ion is greater than the IE of the neutral molecule, several clear patterns emerge in the ion−molecule branching ratios of all the chloroethenes. Once the RE of the ion just exceeds the IE of the neutral, only the parent ion is formed via charge transfer. After an energy gap of approximately 2−3 eV the first daughter ion caused by fragmentation of the parent ion is formed. This product is always due to loss of one chlorine atom. This daughter ion is formed with a large percentage yield until, after another gap of several electronvolts, a smaller fragment ion is formed involving the loss of two chlorine atoms, or in the case of monochloroethene one chlorine and one hydrogen atom. These are the dominant channels. Other weaker channels may occur which involve loss of hydrogen atoms, either with or without the simultaneous loss of chlorine atoms. In the next three paragraphs, we highlight reactions of particular interest for the three chloroethenes studied in this paper. Then, we highlight trends observed for *all* the chloroethenes, $C_2H_xCl_{4-x}$, including our earlier study of the isomers of dichloroethene.[3]

Two reactions which are interesting to compare for the three titled chloroethenes are those with Kr^+ (RE = 14.00 eV) and CO^+ (RE = 14.01 eV). The RE of these two ions only differs by 0.01 eV, so any difference between the product branching ratios must be due to differences in reaction mechanism rather than energetics. For monochloroethene, the main difference is that for Kr^+ an additional (weak) channel due to loss of a hydrogen atom from the parent ion is observed. By comparison, for trichloroethene and tetrachloroethene no apparent difference is observed between Kr^+ or CO^+. It is possibly due to the presence of some excited Kr^+ ($^2P_{1/2}$) ions in the flow tube with an extra available energy of 0.67 eV, leading to a new fragmentation pathway for monochloroethene. However, the anomaly suggests that monochloroethene may also be reacting with Kr^+ and CO^+ via different mechanisms.

Another interesting ion is N^+ (RE = 14.53 eV). Examination of the branching ratios for reaction of the three titled chloroethenes with N^+ shows that more parent ion is observed than would be expected for ions with comparable RE values. In comparison to the photoionization results, the product ion branching ratios resulting from the reactions of N^+ are more consistent with that for a reagent ion with an RE of approximately 12 eV. If we assume that long-range transfer is occurring, then this would suggest that following electron transfer the majority of the neutral N atoms are formed in an electronically excited state.[13] It is of note that the ^2D excited state of atomic nitrogen is 2.4 eV above the ground state, which is comparable to the shift in energy needed to produce branching ratios consistent with those observed. This proposed decrease in the available RE of N^+ explains the branching ratios determined in many reactions involving N^+, including our recent studies on the isomers of dichloroethene.[3,13,31]

The reactions of Xe^+ and Ar^+ with monochloroethene have previously been studied in a two-stage ion-beam mass spectrometer by Izod and Tedder.[10] For the Xe^+ reaction, our branching ratios agree within experimental error, except no $C_2H_2^+$ is formed in the ion-beam equipment. For the Ar^+ reaction, the branching ratios are in good agreement for formation of both $C_2H_3^+$ and $C_2H_2^+$; however, the only other ion formed in the ion-beam study is $C_2H_3Cl^+$. None of the other three ions seen in our SIFT study, $C_2H_2Cl^+$, C_2HCl^+, and HCl^+, are detected. The differences are undoubtedly due to the different reaction conditions between the two experiments. Finally, the reactions of trichloroethene and tetrachloroethene with O_2^+ have been studied by Španěl and Smith.[11] This work was performed in a SIFT apparatus in which only *relative* rate coefficients were recorded. In both cases O_2^+ reacted to form the parent ion with 100% yield, in excellent agreement with our results. The rate coefficients are in reasonable agreement between the two experiments.

For the reactions of the ions studied in this energy range, four stand out as showing remarkable trends between all six chloroethenes which are listed in the Introduction. The first is SF_5^+. The reaction of monochloroethene and SF_5^+ cannot occur by charge transfer, so it must proceed via a chemical reaction in which bonds break and form. Two ionic products, SF_3^+ and $C_2H_3ClF^+$, are observed, and as expected, neither is due to charge transfer. The production of SF_3^+ is interesting as neutral fluorine atoms have transferred from SF_5^+ rather than a charged species, leaving a fragment of the reagent ion as the product cation; in general, the reagent ion is either incorporated into the product ion or it is left without any charge. F^+ transfer leads to the formation of the other observed product ion, $C_2H_3ClF^+$. For all three dichloroethenes F^+ transfer to form $C_2H_2Cl_2F^+$ is the major channel, with minor channels only forming the parent ion and $C_2H_2Cl^+$.[3] For these reactions the loss of a chloride ion can only be due to a chemical reaction to form SF_5Cl as a neutral partner, since there is not enough energy for charge transfer to be followed by unimolecular dissociation of $C_2H_2Cl_2^+$. This suggests that, because the RE of SF_5^+ is only just above the IE of the dichloroethenes, the cross section for long-range charge transfer is low. Thus, the neutrals and SF_5^+ will probably approach to a small separation and form an ion−molecule complex. It is in this complex that the chemical reactions take place which produce $C_2H_2Cl_2F^+$ and $C_2H_2Cl^+$. The formation of the parent ion, $C_2H_2Cl_2^+$, can take place in two ways; either via a short-range mechanism inside the complex where it is competing with the chemical reaction or at a large separation of ion and neutral. We suggest that long-range charge transfer is inefficient, and a complex is more likely to be formed due to the low rate coefficient of this reaction. It should be noted that, due to uncertainties in thermochemistry, it is possible that only vibrationally excited SF_5^+ can react via charge transfer. It cannot therefore be discounted that the parent ion forms only from the reaction with excited SF_5^+ and that a chemical reaction is the mechanism whereby ground-state SF_5^+ can react. For trichloroethene, the major channel for reaction with SF_5^+ is now formation of parent ion, $C_2HCl_3^+$, with the only other product due to F^+ transfer, $C_2HCl_3F^+$. The reaction is also slightly more efficient than for the dichloroethenes. When tetrachloroethene is the reactant neutral, only nondissociative charge transfer takes place and the reaction is 60% efficient. This large change in product yields across the series $C_2H_xCl_{4-x}$ is most likely due to the decrease in IE of the neutral molecule with increasing chlorine substitution, leading to an increase in the long-range charge-transfer cross section for this reaction. Chemical reaction can still compete for trichloroethene, but for tetrachloroethene long-range charge transfer is so efficient that it dominates over the chemical channel.

The reactions of SF_2^+ (RE = 10.24 eV) and SF^+ (RE = 10.31 eV) also show trends across the six chloroethenes. For all neutral molecules charge transfer is energetically allowed, so parent ions can be formed. With monochloroethene, the parent ion is the major product for both reactions, but several other products also form. For reaction with SF_2^+, the other product is $C_2H_3SF_2^+$ which can only be formed by a chemical reaction. For reaction with SF^+, the other products are C_2HSF^+, C_2SF^+, and $C_2H_3^+$. All three form from a chemical reaction, and there is not enough energy to form a parent ion which would fragment to $C_2H_3^+$ + Cl. For the other five neutral molecules, reaction with SF_2^+ only forms parent ions, whereas the reactions of the dichloroethenes with SF^+ yield several non-charge-transfer products.[3] For the 1,2 isomers of dichloroethene two other ions, $C_2H_2ClSF^+$ and C_2HClSF^+, are formed in small yields, along with the parent ion. For the 1,1 isomer, in addition $C_2H_2Cl^+$ and $CHCl_2^+$ are formed as products. Apart from the parent ion, all these products must form via a chemical reaction. For trichloroethene and tetrachloroethene, only the parent ion is formed with SF^+. As the number of chlorine atoms in $C_2H_xCl_{4-x}$ increases, this pattern of increasing parent ion production via charge transfer at the expense of product ions formed via a chemical reaction is exactly as observed with the reactions of SF_5^+. The pattern can be explained in a similar way. For monochloroethene and dichloroethene, the RE of SF_2^+ and SF^+ is not much greater than the IE of the neutrals. So, although charge transfer is energetically favorable, it may be inefficient, and not all reactant pairs of ion and neutral react via charge transfer. It is likely that only charge transfer occurs for the dichloroethenes reacting with SF_2^+ because no chemical reactions are energetically open. For trichloroethene and tetrachloroethene, however, the RE of the ions far exceeds the IE of the neutrals; long-range charge transfer is now efficient, and no ion−molecule complexes are formed.

This trend is confirmed for the reaction of monochloroethene with CF_2^+ (RE = 11.44 eV). For all the other chloroethenes this ion only reacts via charge transfer, but for monochloroethene, although the parent ion is dominant, two other "chemical" products are also formed, $C_3H_3F_2^+$ and $CHFCl^+$. The final ion in this energy range which does not just react by charge transfer is the reaction of H_2O^+ (RE = 12.62 eV) with monochloroethene; a small percentage of protonated monochloroethene, $C_2H_3ClH^+$, is formed. However, it should be noted that there was some OH^+ present with approximately 30% of the intensity of the H_2O^+ signal.

4.1.3. Comparison of SIFT and TPEPICO Branching Ratios. Parts a−f of Figure 1 show, as discrete data points, the branching ratios from the product cations of the ion−molecule reactions recorded on the SIFT with all six chloroethenes over the RE range of 9.7−21.6 eV. It should be noted that for monochloroethene only a single Cl atom can be lost, so the blue circles represent loss of one Cl atom and one H atom, not loss of two Cl/H atoms. In Figure 1b−e the branching ratios from the photon-induced TPEPICO data using continuously tunable vacuum-UV radiation for the three dichloroethenes and trichloroethene are also plotted as continuous lines.[1,2] The TPEPICO branching ratios for tetrachloroethene are not produced here as the data quality was too poor.[1] No TPEPICO study has been performed on monochloroethene; however, there are some photoionization and mass-analyzed threshold ionization studies from which comparisons can be drawn[32,33] and a recent theoretical study of the photodissociation of $C_2HCl_3^+$.[34]

Parts b−e of Figure 1 show that the agreement between the SIFT and TPEPICO branching ratios is, in general, good, and overall trends are mirrored in the two sets of data; we note that in the range of 9.7−12.0 eV there is no disagreement at all for trichloroethene. That is, after onset the parent ion is formed, followed by fragmentation by chlorine-atom loss at higher energies. From 12−15 eV the agreement between branching ratios is not quite as good, but except for N^+ (RE = 14.53 eV) the overall trends are the same for the two sets of data. For N^+ the yield of parent ions is around 50% in all six chloroethenes. As mentioned previously, N^+ is often an anomalous ion, seeming to act as a softly ionizing species compared to photons of this energy. For F^+ (RE = 17.42 eV) and Ne^+ (RE = 21. 56 eV) the agreement between the SIFT and TPEPICO branching ratios is fairly good. It should be noted that for Ne^+ other ions are formed which are not seen in the TPEPICO data. The broad agreement between the experiments for Ne^+ suggests that the charge-transfer mechanism is largely of a long-range nature with some interaction leading to production of CCl^+ as well. In general, all the ion−molecule reactions where the RE(ion) > 13 eV produce a greater percentage of parent ion than with photoionization at the comparable photon energy.

Although data for the TPEPICO branching ratios of monochloroethene and tetrachloroethene are not available, some comparisons can be made. The trends in product formation from the ion−molecule reactions agree well with the photoionization data.[1,32] This suggests that the majority of the ion−molecule reactions studied in this energy range for monochloroethene and tetrachloroethene react via long-range type charge transfer. The first appearance of $C_2Cl_3^+$ in the SIFT experiments with C_2Cl_4 occurs with ions whose RE is around 12 eV. This observation seems to confirm that the true value of $AE_{298}(C_2Cl_3^+)$ is 11.40

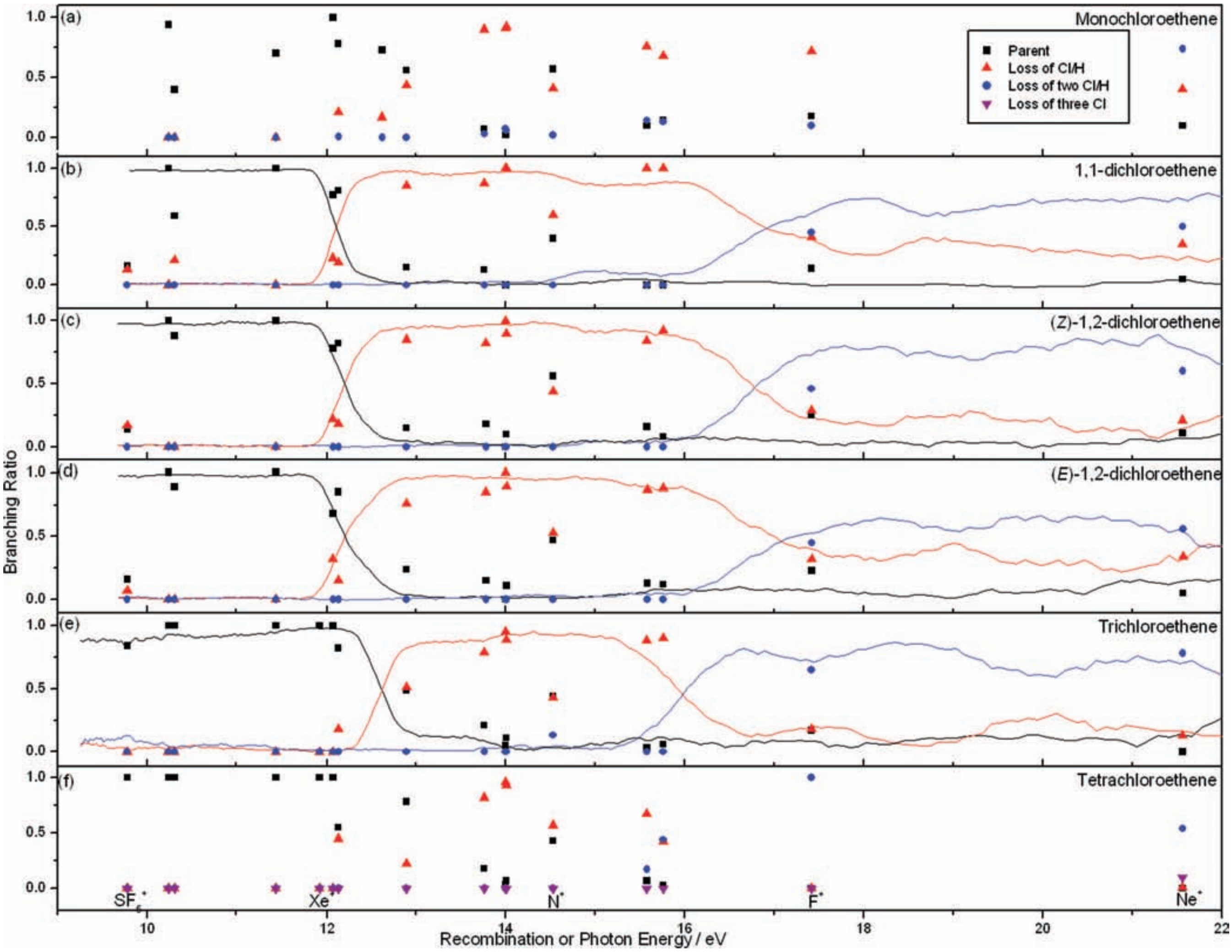

Figure 1. Comparison of the ionic products from ion−molecule studies of six chloroethenes (a−f) with TPEPICO photoionization branching ratios (b−e) over the range of 9−22 eV. The optical resolution in the TPEPICO experiments is 0.3 nm. The resolution of the time-of-flight mass analyzer in the coincidence apparatus is not sufficient to differentiate unambiguously the loss of one Cl atom from loss of an HCl molecule (or loss of two Cl atoms from loss of H and 2Cl). To make comparisons with branching ratios from the SIFT data, therefore, the *sum* of the branching ratios of appropriate ions in the SIFT experiment is plotted.

eV, and not the lower value of 9.48 eV apparently observed from the TPEPICO data. More details are given in ref 1.

For several reactions, products seen in the SIFT experiment are very different from those observed anywhere in TPEPICO experiments. In the case of C_2HCl_3 they are $C_2HCl_3F^+$ from the SF_5^+ reaction, $CHCl_2^+$ from the N_2^+ and Ar^+ reactions, and CCl^+ from the Ne^+ reaction. In the case of C_2Cl_4 they are CCl_2^+ and CCl_3^+ from N_2^+ and Ar^+ reactions and CCl^+, CCl_2^+, and C_2Cl^+ from the Ne^+ reaction. Apart from production of $C_2HCl_3F^+$, the other ionic products can all be formed via charge transfer. It is likely that the reactions are mainly long-range in nature, with either some short-range character to the transfer or the short-range transfer occurs in competition.

4.2. RE(ion) < IE(neutral). In this section, we consider the reactions of the five ions whose RE values range from 6.27 to 9.11 eV with monochloroethene, trichloroethene, and tetrachloroethene. These RE values are all below the IE values of the three neutrals, making charge transfer forbidden on energetic grounds. The ions are H_3O^+ (RE = 6.27 eV), SF_3^+ (RE = 8.32 eV), CF_3^+ (RE = 9.04 eV), CF^+ (RE = 9.11 eV), and NO^+ (RE = 9.26 eV).

4.2.1. Rate Coefficients. Two of the ions, SF_3^+ and NO^+, do not react with any of the chloroethenes. For NO^+ there was indication of some reaction, but it was very slow and there was a large amount of curvature in the plot of ln(NO^+ signal) versus neutral concentration from which the rate coefficient is derived. This suggests that all of the reaction was due to vibrationally or electronically excited NO^+ ions. The reaction of NO^+ with trichloroethene and tetrachloroethene has previously been studied by Španěl and Smith,[11] where they reported an adduct being the only product.

Unlike the reactions where RE(ion) > IE(neutral), the measured rate coefficients here show a large variation in the efficiency of reaction. Such reactions can only occur following formation of a collision complex and the breaking and making of chemical bonds. These chemical reactions only occur when the ion and neutral are in close contact. Thus, steric effects, i.e., the orientation of the ion and neutral molecule relative to each other, can make significant changes to reaction efficiencies. Also, there could be exit-channel barriers and energetic constraints for some product channels. The most prominent example is for the reactions of H_3O^+ (RE = 6.27 eV). With monochloroethene and trichloroethene the experimental rate coefficient is essentially the same as the collisional value; however, for tetrachloroethene the reaction is only 50% efficient. A comparison with the isomers of dichloroethene highlights this result;[3]

for 1,1-dichloroethene the rate coefficient is essentially collisional, but for the two 1,2-dichloroethene isomers the reactions are only ca. 15% efficient. Such differences must be due to the structures of the molecules, the relative positions of the chlorine atoms, and the energetics of the protonated products.

The reactions of all three chloroethenes studied in this paper with CF^+ are fairly efficient. With CF_3^+, the efficiency shows more variation across the chloroethenes, ranging from 70% for monochloroethene through to 100% for trichloroethene and tetrachloroethene.

4.2.2. Branching Ratios. *4.2.2.1. Reactions of H_3O^+.* H_3O^+ reacts with monochloroethene, trichloroethene, and tetrachloroethene by proton transfer to form the protonated parent ion. This is in agreement with the results of Španěl and Smith.[11] For tetrachloroethene a small percentage yield of $C_2Cl_3^+$ was also detected by Španěl and Smith, but we did not observe this product. As all three chloroethenes react with H_3O^+ by proton transfer, their proton affinity (PA) must be larger than that of H_2O, 691 kJ mol^{-1}.[35] Upper limits for $\Delta_fH°_{298}$ values for protonated monochloroethene, trichloroethene, and tetrachloroethene are determined to be 815, 815, and 809 kJ mol^{-1}, respectively, assuming that $\Delta_rH°_{298} \leq 0$ for all three reactions. Interestingly, when H_3O^+ reacts with the isomers of dichloroethene, not only is protonated parent ion detected, but for the 1,2-dichloroethenes, two extra products are seen.[3] They are $C_2HClOH_2^+$ with HCl formed as the neutral partner and the adduct $C_2H_2Cl_2{\cdot}H_3O^+$. These results show the importance of the position and number of chlorine atoms to the reactivity of the chloroethenes. Combining the rate coefficients and branching ratios gives insight into the H_3O^+ reaction mechanism. It appears that monochloroethene and trichloroethene have no barrier to protonation as they react rapidly to form only one product. For tetrachloroethene, the reaction is fairly slow. We conclude that the presence of four bulky Cl atoms blocks access of H_3O^+ to the reaction site or reaction leads to an unfavorable structure of $C_2Cl_4H^+$.

4.2.2.2. Reactions of CF_3^+. The reactions of CF_3^+ produce a range of different products formed from three reactions. Examples are shown below:

$$CF_3^+ + C_2H_3Cl \rightarrow C_2H_3^+ + CF_3Cl \tag{II}$$

$$CF_3^+ + C_2HCl_3 \rightarrow CF_2Cl^+ + C_2HCl_2F \tag{III}$$

$$CF_3^+ + C_2Cl_4 \rightarrow CFCl_2^+ + C_2F_2Cl_2 \tag{IV}$$

Reactions of type II–IV are seen for the reactions with trichloroethene and tetrachloroethene, but reactions II and IV are only seen for monochloroethene. Reaction II is a simple Cl^- transfer driven by formation of the stable CF_3Cl neutral molecule. Reactions III and IV involve rearrangement of the halogen atoms to form new halogenated ethenes. The reaction efficiencies are 69% for monochloroethene and 100% for trichloroethene. Tetrachloroethene reacts with a rate coefficient which is larger than the collisional value, but the difference falls within the normal experimental error.

In our previous study of reactions of CF_3^+ with the isomers of dichloroethene, it was found that to explain reactions in which the C=C bond was completely broken it was necessary for the neutral product to be a halogenated ethene;[3] formation of a new C=C π-bond in the product helps compensate for the energy required to break the original C=C π-bond. Therefore, we have assumed that new halogenated ethenes must be formed in reactions III and IV of this study, and furthermore no other reaction products could be found that were chemically reasonable. So, for the reaction of monochloroethene with CF_3^+ to form $CHFCl^+$, analogous to reaction IV, the product is $C_2F_2H_2$ and the enthalpy of reaction is −2 kJ mol^{-1}. For trichloroethene and tetrachloroethene, the enthalpies of formation of the fluorochloroethenes formed from reactions III and IV are not known. Assuming that the products must contain a C=C bond and that the enthalpy of reaction is negative, lower limits are set on the enthalpy of formation for these fluorochloroethenes: $\Delta_fH°_{298}(C_2HClF_2) \geq 315$ kJ mol^{-1}, $\Delta_fH°_{298}(C_2HCl_2F) \geq 168$ kJ mol^{-1}, $\Delta_fH°_{298}(C_2F_2Cl_2) \geq 321$ kJ mol^{-1}, and $\Delta_fH°_{298}(C_2FCl_3) \geq 174$ kJ mol^{-1}.

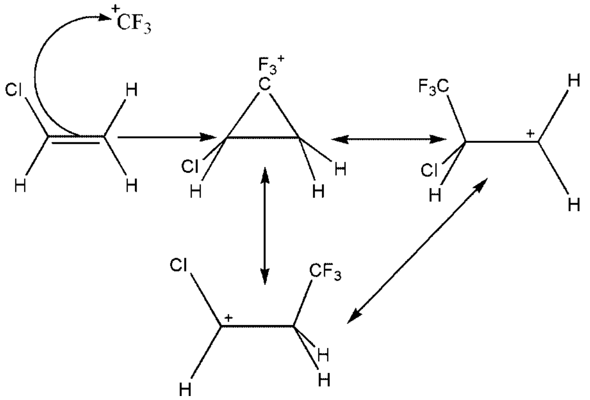

Figure 2. Inital insertion step of CF_3^+ into a chloroethene double bond.

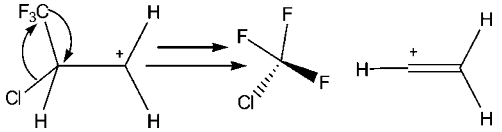

Figure 3. Proposed scheme for the reaction of monochloroethene with CF_3^+, reaction II. The double arrow implies there are many steps to form the products.

To explain these results, attempts have been made to suggest reaction mechanisms. The starting point for all mechanisms is to assume that CF_3^+ attacks electrophilically at the π orbitals of the double bond, as postulated in the reactions of chloroethenes with neutral free radicals.[36,37] Figure 2 shows this proposed first step for monochloroethene. Insertion forms the trigonal-bridged intermediate cation shown in step 2. The CF_3^+ can then move from one side or another to form the two resonance structures shown. It is assumed that this insertion step occurs for all the reactions. Figure 3 shows the proposed mechanism for formation of $C_2H_3^+$ from monochloroethene, reaction II. Any of the other reactions in which Cl^- transfer to CF_3^+ takes place should follow the same, or a similar, mechanism. First, CF_3^+ adds to the C=C bond. This is followed by the migration of the Cl to the CF_3 group. The next step is cleavage of the C−CF_3 bond. These two steps may be either sequential or concerted. We assume that the chlorine transfer, and subsequent loss, takes place when the CF_3 group is attached to the same carbon atom as the chlorine atom. The $C_2H_3^+$ product is formed by rearrangement of the initially formed cation carbene after the loss of $CClF_3$.

Both reactions III and IV are more complicated than reaction II. Although the simplest mechanism would be exchange of chlorine and fluorine atoms between the CF_3 group and the adjacent carbon atom, this simple mechanism is unlikely, due to the position of the positive charge following insertion of the CF_3^+ group. Because of these complications no reaction schemes are given. However, it is proposed that the reaction must involve exchange of chlorine and fluorine atoms between the two carbon atoms on the ethene group. Ab initio calculations are ongoing to attempt to understand these complicated reactions.

In the absence of values for any energy barriers, which channels are open and which are closed undoubtedly depends on the structure of the chloroethenes and the energetics of the reactions. It is interesting to note that, as the number of chlorine atoms increases, reaction III, loss of CF_2Cl^+, dominates. One possible explanation is that, the more Cl atoms are present, the likelihood that a chlorine atom can transfer back to the CF_2^+ group of the intermediate increases. It could also be that transfer of chlorine atoms in the trigonal-bridging intermediate is more favorable. For example, in tetrachloroethene it is unfavorable to have the positive charge next to two chlorine atoms, so by transferring a chlorine across the double bond the positive charge is moved so that it is only next to one chlorine and a CF_3 group, relieving the unfavorable interaction. It is clear that the relative branching ratios for the competing reactions depend on a complex interplay between inductive effects and conjugation due to the chlorine atoms on the stability of the cation intermediates. It is hoped that theoretical calculations on the reaction pathways, coupled with experiments on isotopically labeled samples, will help elucidate the dynamics of these reactions.

4.2.2.3. Reactions of CF^+. Monochloroethene, trichloroethene, and tetrachloroethene all react with CF^+ with similar ionic products detected as from CF_3^+, but now the reactions are nearly all 100% efficient. Monochloroethene reacts to form the same two ionic products, $CHFCl^+$ and $C_2H_3^+$, with similar percentage yields as with CF_3^+. It is therefore assumed that the reaction mechanisms are the same as for CF_3^+ but with different neutral partners, i.e., ethynes rather than ethenes are formed. Trichloroethene reacts to form three ionic ions. $CFCl_2^+$ is also observed for reaction with CF_3^+, but the other two products, $CHCl_2^+$ and $CHClF^+$, are new. Neither $C_2HCl_2^+$ nor CF_2Cl^+ is detected for the reactions of CF^+ with trichloroethene. Tetrachloroethene reacts with CF^+ to form only $CFCl_2^+$. Due to similarities in the products formed from CF^+ and CF_3^+, it is assumed that their reaction mechanisms will probably be similar, although we note that there is no reason to suppose that the mechanisms will necessarily be the same for production of the same product ions.

Since $CHCl_2^+$ is formed from the reaction of CF^+ with trichloroethene but not with CF_3^+, there may be a barrier to formation of this product from the latter reaction. Any barrier is unlikely to be high because there is only 0.07 eV extra energy available with CF^+. The reactions with CF^+ also allow a new channel, formation of $CHClF^+$, to open for the reactions with trichloroethene, a channel which has previously been seen only for the reaction of CF_3^+ with monochloroethene. Although this suggests that $CHClF^+$ forms as a product from reaction IV, it is also possible that a different mechanism is taking place for CF^+. One possible way to test whether there is a barrier to reaction or whether it is chemical-specific is to perform experiments in which the collision energy of the ion−neutral system is varied, for example, by changing the temperature. Another method would be to use a guided ion beam of CF^+ or CF_3^+. If there is a barrier to formation of products, then as the energy of the ion beam is increased the product channels should "switch on" at their threshold for formation; if there is no barrier but the effect is due to chemical differences between CF^+ and CF_3^+, then no such onsets should occur. It is noted that simple Cl^--transfer channel is not observed at all for trichloroethene and tetrachloroethene, even though it is energetically allowed if CFCl is the neutral partner. The reasons for this are unclear.

5. Conclusions

The reactions of monochloroethene, trichloroethene and tetrachloroethene with a range of cations with REs in the range of 6.27−21.56 eV have been studied. The majority of the reactions have not been studied before. For the 19 ions with recombinations energies which exceed the IE of the chloroethenes, comparisons have been made with photoionization studies to attempt to understand the nature of the charge transfer that takes place. Owing to the good agreement between the product ion branching ratios from ion−molecule and photon−molecule reactions, it appears that the majority of charge-transfer reactions take place via a long-range mechanism. For the few exceptions, chemical reaction or short-range charge-transfer mechanisms are postulated.

The reactions of the three titled molecules with five cations (H_3O^+, SF_3^+, CF_3^+, CF^+, and NO^+) whose REs are below the IEs of the chloroethenes have been studied. Only H_3O^+, CF_3^+, and CF^+ react. Data from the reactions with H_3O^+ have allowed an upper limit to be placed on the PA of monochloroethene, trichloroethene, and tetrachloroethene. The reactions with CF_3^+ has shown several different reaction pathways. Many of these pathways involve breaking of the C═C double bond in the chloroethene and formation of a new double bond. Similar channels have also been seen for reactions with CF^+. It seems that a complex interplay between the number and position of the chlorine atoms with respect to the C═C double bond dictates which product channels are formed and their relative yields. The stabilities of the intermediate cations formed in the reaction pathways are clearly important. Future work will perform ab initio calculations on this series of reactions to attempt to elucidate more detailed pathways.

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Note Added in Proof. The following reference describes a TPEPICO study on monochloroethane: Shuman, N.S.; Ochieng, M. A.; Sztáray, B.; Baer, T. *J. Phys. Chem. A* **2008**, *112*, 5647. The results of this study support our conclusion of the nature of charge transfer for the reactions of monochloroethene studied using the SIFT.

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