

Selected ion flow tube study of the gas-phase reactions of CF⁺, CF₂⁺, CF₃⁺, and C₂F₄⁺ with C₂H₄, C₂H₃F, CH₂F₂, and C₂HF₃

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Selected Ion Flow Tube study of the gas-phase reactions of CF^+ , CF_2^+ , CF_3^+ and C_2F_4^+ with C_2H_4 , $\text{C}_2\text{H}_3\text{F}$, CH_2CF_2 and C_2HF_3

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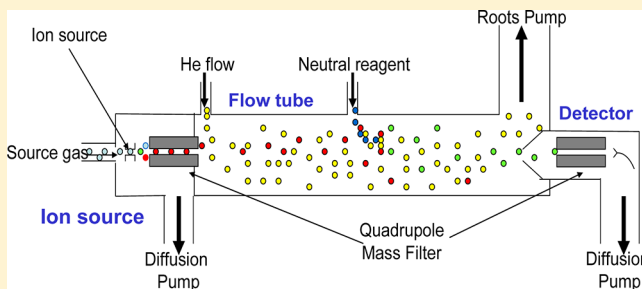
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Selected Ion Flow Tube Study of the Gas-Phase Reactions of CF^+ , CF_2^+ , CF_3^+ , and C_2F_4^+ with C_2H_4 , $\text{C}_2\text{H}_3\text{F}$, CH_2CF_2 , and C_2HF_3 Matthew J. Simpson[#] and Richard P. Tuckett*

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ABSTRACT: We study how the degree of fluorine substitution for hydrogen atoms in ethene affects its reactivity in the gas phase. The reactions of a series of small fluorocarbon cations (CF^+ , CF_2^+ , CF_3^+ , and C_2F_4^+) with ethene (C_2H_4), monofluoroethene ($\text{C}_2\text{H}_3\text{F}$), 1,1-difluoroethene (CH_2CF_2), and trifluoroethene (C_2HF_3) have been studied in a selected ion flow tube. Rate coefficients and product cations with their branching ratios were determined at 298 K. Because the recombination energy of CF_2^+ exceeds the ionization energy of all four substituted ethenes, the reactions of this ion produce predominantly the products of nondissociative charge transfer.

With their lower recombination energies, charge transfer in the reactions of CF^+ , CF_3^+ , and C_2F_4^+ is always endothermic, so products can only be produced by reactions in which bonds form and break within a complex. The trends observed in the results of the reactions of CF^+ and CF_3^+ may partially be explained by the changing value of the dipole moment of the three fluoroethenes, where the cation preferentially attacks the more nucleophilic part of the molecule. Reactions of CF_3^+ and C_2F_4^+ are significantly slower than those of CF^+ and CF_2^+ , with adducts being formed with the former cations. The reactions of C_2F_4^+ with the four neutral titled molecules are complex, giving a range of products. All can be characterized by a common first step in the mechanism in which a four-carbon chain intermediate is formed. Thereafter, arrow-pushing mechanisms as used by organic chemists can explain a number of the different products. Using the stationary electron convention, an upper limit for $\Delta_f H^\circ_{298}(\text{C}_3\text{F}_2\text{H}_3^+$, with structure $\text{CF}_2=\text{CH}-\text{CH}_2^+$) of 628 kJ mol^{-1} and a lower limit for $\Delta_f H^\circ_{298}(\text{C}_2\text{F}_2\text{H}^+$, with structure $\text{CF}_2=\text{CH}^+$) of 845 kJ mol^{-1} are determined.



1. INTRODUCTION

One consequence of the 1987 Montreal Protocol and its many later amendments has been the significant reduction over the last two decades in the use and production of ozone-depleting substances. These chemicals include chlorofluorocarbons (CFCs) and halons, commonly used in applications such as fire protection, refrigeration and aerosols. Many hydrofluorocarbons (HFCs) are considered to be less environmentally unfriendly alternatives to CFCs. This study investigates the effects on reactivity of a series of fluorinated ethenes $\text{C}_2\text{H}_x\text{F}_{4-x}$ ($x = 4, 3, 2, 1$) as the degree of fluorine substitution for hydrogen atoms in ethene increases. Reactivity is studied by determining the kinetics and products of reactions with small gas-phase cations. This work extends earlier similar studies by us of a series of chloroethenes, including the three isomers of dichloroethene.^{1,2} The present study focuses on the reactions of ethene, monofluoroethene, 1,1-difluoroethene and trifluoroethene with the cations CF^+ , CF_2^+ , CF_3^+ , and C_2F_4^+ using a selected ion flow tube (SIFT). This study is not quite as extensive as for the chlorinated ethenes because the two 1,2-difluoroethene isomers of $\text{C}_2\text{H}_2\text{F}_2$, each thermodynamically less stable than the 1,1 isomer by ca. 50 kJ mol^{-1} , have not been investigated.

The results are compared with previous work, where available, on the reactions of CF_n^+ ($n = 1-3$) and C_2F_4^+ ions with tetrafluoroethene and the chlorinated ethenes. This is the

first SIFT study on the reactions of these four cations with $\text{C}_2\text{H}_3\text{F}$, 1,1- CH_2CF_2 , and C_2HF_3 . Using a variety of different techniques, the reactions of small fluorine-containing molecular cations with the related molecules C_2H_4 , 1,2-difluoroethene, and C_2F_4 have been investigated by several groups.³⁻¹² The work by Morris et al.,^{8,9} who also used a selected ion flow tube, is particularly relevant. The reaction of CF_3^+ with C_2H_4 has been investigated by SIFT mass spectrometry¹⁰ and with an ion beam apparatus.¹¹ The reactions of small molecular cations with the full series of fluorinated ethenes $\text{C}_2\text{H}_x\text{F}_{4-x}$ ($x = 0-4$) have also been studied using ion cyclotron resonance mass spectrometry (ICR-MS) by Bowers et al.³⁻⁷

The adiabatic ionization energies (IE) of C_2H_4 , $\text{C}_2\text{H}_3\text{F}$, CH_2CF_2 , and C_2HF_3 are 10.51, 10.37, 10.30, and 10.14 eV, respectively.¹³⁻¹⁵ Comparisons of these values with the recombination energy (RE) of the reagent ion (equal in magnitude to the adiabatic IE of the corresponding neutral) determines if charge transfer is energetically possible.¹⁶ The RE values for CF^+ , CF_2^+ , CF_3^+ , and C_2F_4^+ are 9.11,¹⁷ 11.36,¹⁸ 9.09,^{19,20} and 10.11 eV,^{15,21} respectively, and so charge transfer is only exothermic for the reactions with CF_2^+ .

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Table 1. Results for the Gas-Phase Reactions of CF^+ , CF_2^+ , and CF_3^+ with Ethene and the Fluorinated Ethenes

reaction ^a	$\Delta_f H^\circ_{298}$ ^b (kJ mol ⁻¹)	product branching ratio (%)	rate coefficient ^c (10 ⁻⁹ cm ³ molecule ⁻¹ s ⁻¹)
$\text{CF}^+ + \text{C}_2\text{H}_4^d \rightarrow \text{CH}_2\text{F}^+ + \text{C}_2\text{H}_2$	-125	80	1.1 [1.3] 0.85
$\rightarrow \text{C}_3\text{H}_3^+ + \text{HF}$	-268	20	
$\text{CF}^+ + \text{C}_2\text{H}_3\text{F} \rightarrow \text{C}_2\text{H}_3^+ + \text{CF}_2$	-69	88	2.1 [2.0] 1.00
$\rightarrow \text{CHF}_2^+ + \text{C}_2\text{H}_2$	-156	12	
$\text{CF}^+ + \text{CH}_2\text{CF}_2 \rightarrow \text{CF}_3^+ + \text{C}_2\text{H}_2$	-134	88	1.4 [1.9] 0.74
$\rightarrow \text{C}_2\text{H}_2\text{F}^+ + \text{CF}_2$	+2	7	
$\rightarrow \text{CHF}_2^+ + \text{C}_2\text{HF}$	-66	5	
$\text{CF}^+ + \text{C}_2\text{HF}_3 \rightarrow \text{CF}_3^+ + \text{C}_2\text{HF}$	-106	100	1.0 [1.7] 0.59
$\text{CF}_2^+ + \text{C}_2\text{H}_4^e \rightarrow \text{C}_3\text{H}_3\text{F}_2^+ + \text{H}^f$?	55	1.1 [1.1] 1.00
$\rightarrow \text{C}_2\text{H}_4^+ + \text{CF}_2$	-82	45	
$\text{CF}_2^+ + \text{C}_2\text{H}_3\text{F} \rightarrow \text{C}_2\text{H}_3\text{F}^+ + \text{CF}_2$	-96	88	1.8 [1.8] 1.00
$\rightarrow \text{C}_2\text{H}_3^+ + \text{CF}_3$	-111	12	
$\text{CF}_2^+ + \text{CH}_2\text{CF}_2 \rightarrow \text{CH}_2\text{CF}_2^+ + \text{CF}_2$	-103	100	1.6 [1.6] 1.00
$\text{CF}_2^+ + \text{C}_2\text{HF}_3 \rightarrow \text{C}_2\text{HF}_3^+ + \text{CF}_2$	-118	100	1.5 [1.5] 1.00
$\text{CF}_3^+ + \text{C}_2\text{H}_4^g \rightarrow \text{C}_3\text{H}_3\text{F}_2^+ + \text{H}^h$?	60	0.7 [1.1] 0.64
$\rightarrow \text{C}_2\text{H}_3^+ + \text{CHF}_3$	-48	40	
$\text{CF}_3^+ + \text{C}_2\text{H}_3\text{F} \rightarrow \text{C}_2\text{H}_3^+ + \text{CF}_4$	-92	75	1.3 [1.6] 0.81
$\rightarrow \text{CHF}_2^+ + \text{CH}_2\text{CF}_2^j$	-22	25	
$\text{CF}_3^+ + \text{CH}_2\text{CF}_2 \rightarrow \text{C}_2\text{H}_2\text{F}^+ + \text{CF}_4$	-21	50	0.7 [1.5] 0.47,
$\rightarrow \text{C}_3\text{H}_2\text{F}_5^+$ (adduct)	?	44	$p(\text{He}) = 0.5$ Torr
$\rightarrow \text{C}_3\text{HF}_4^+ + \text{HF}^k$?	6	
$\text{CF}_3^+ + \text{C}_2\text{HF}_3^l \rightarrow \text{C}_3\text{HF}_6^+$ (adduct)	?	100	0.2 [1.3] 0.15,
			$p(\text{He}) = 0.5$ Torr

^aThe neutral products of these reactions are not detected in the experiment but are proposed as the most likely candidates. ^bThe reaction enthalpy calculated from 298 K enthalpies of formation. ^cThe experimentally determined rate coefficient, k_{exp} . In square brackets are the collisional values, k_c , and the rate efficiency is given as the ratio of k_{exp} to k_c . ^dValues used for $\Delta_f H^\circ_{298}$ in kJ mol⁻¹, are CF^+ 1122.3,²⁰ C_2H_4 52.5,²⁶ $\text{C}_2\text{H}_3\text{F}$ -140.1,³² 1,1- $\text{C}_2\text{H}_2\text{F}_2$ -350.2,³³ and C_2HF_3 -499.1.²⁰ Data for product species taken from refs 20, 26, and 27. ^eValue used for $\Delta_f H^\circ_{298}(\text{CF}_2^+)$ is 897.1 kJ mol⁻¹.²⁰ Data for product species taken from refs 20, 26, and 27. ^fAssuming this reaction is exothermic, we determine $\Delta_f H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+) < 732$ kJ mol⁻¹. Its structure is almost certainly $\text{CF}_2=\text{CH}-\text{CH}_2^+$. ^gValue used for $\Delta_f H^\circ_{298}(\text{CF}_3^+)$ is 410.2 kJ mol⁻¹.²⁰ Data for product species taken from refs 20, 26, and 27. ^hAssuming this reaction is exothermic, we determine $\Delta_f H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+) < 735$ kJ mol⁻¹. The cis and trans 1,2 isomers both give endothermic reaction enthalpies, and so we propose 1,1-difluoroethene is the neutral product species formed. ⁱAssuming this reaction is exothermic, we determine $\Delta_f H^\circ_{298}(\text{C}_3\text{HF}_4^+) < 333$ kJ mol⁻¹. Its structure is almost certainly $\text{CF}_2=\text{CH}-\text{CF}_2^+$. ^jThe absence of C_2HF_2^+ , presumably with structure $\text{CF}_2=\text{CH}^+$, from this reaction by F^- abstraction suggests that $\Delta_f H^\circ_{298}(\text{C}_2\text{HF}_2^+) > 845$ kJ mol⁻¹.

2. EXPERIMENTAL SECTION

The reactions of the four titled fluorocarbon cations with $\text{C}_2\text{H}_x\text{F}_{4-x}$ ($x = 4, 3, 2, 1$) have been investigated at 298 K using a SIFT apparatus to determine rate coefficients, product ions, and their branching ratios (BRs), and whether the product ion is primary or secondary. The SIFT technique has been described in detail elsewhere.^{22–25} Briefly, the four reagent cations were all generated from perfluoropropane, C_3F_8 , in a high-pressure (ca. 10⁻⁴ mbar) electron ionization source. A quadrupole mass filter was used to select the reagent ion before

injection into the flow tube, 1 m in length and 8 cm in diameter. The carrier gas was He at a pressure of ca. 0.5 Torr, flowing at a velocity of ca. 100 m s⁻¹. Conditions inside the flow tube were thermalized at 298 K, and any excited ions produced in the source should be collisionally cooled by the buffer gas. At a known distance downstream in the flow tube the neutral reactant gas was injected. The reaction gas mixture was sampled at the end of the flow tube through a 1 mm orifice in a Faraday plate. Reactant and product ions were focused into a second

Table 2. Results for the Gas-Phase Reactions of $C_2F_4^+$ with Ethene and the Fluorinated Ethenes

reaction ^a	$\Delta_r H^\circ_{298}$ (kJ mol ⁻¹) ^b	product branching ratio (%)	rate coefficient ^c (10 ⁻⁹ cm ³ molecule ⁻¹ s ⁻¹)
$C_2F_4^+ + C_2H_4^d \rightarrow C_2H_2F_2^+ + C_2H_2F_2^e$	-62 ^f	95	0.7 [1.0] 0.70
$\rightarrow C_3H_3F_2^+ + CHF_2^g$?	5	
$C_2F_4^+ + C_2H_3F \rightarrow C_2HF_3^+ + CH_2CF_2^h$	-34	45	0.6 [1.5] 0.40,
$\rightarrow C_3H_3F_2^+ + CF_3^j$?	40	$p(\text{He}) = 0.5$ Torr
$\rightarrow C_3H_2F_3^+ + CHF_2^k$?	10	
$\rightarrow CH_2CF_2^+ + C_2HF_3$	-18	3	
$\rightarrow C_4H_3F_5^+$ (adduct)	?	2	
$C_2F_4^+ + CH_2CF_2 \rightarrow C_4H_2F_6^+$ (adduct)	?	60	0.7 [1.4] 0.50,
$\rightarrow C_3H_2F_3^+ + CF_3^l$?	30	$p(\text{He}) = 0.5$ Torr
$\rightarrow C_3HF_4^+ + CHF_2^m$?	10	
$C_2F_4^+ + C_2HF_3 \rightarrow C_2HF_3^+ + C_2F_4$	+3	72	0.2 [1.2] 0.17
$\rightarrow C_3HF_4^+ + CF_3^n$?	28	

^aThe neutral products of these reactions are not detected in the experiment but are proposed as the most likely candidates. ^bThe reaction enthalpy calculated from 298 K enthalpies of formation. Absence of a value indicates $\Delta_r H^\circ$ for the product cation is not known. ^cThe experimentally determined rate coefficient, k_{exp} . In square brackets are the collisional values, k_c , and the rate efficiency is given as the ratio of k_{exp} to k_c . ^dValue used for $\Delta_r H^\circ_{298}(C_2F_4^+)$ is 302.7 kJ mol⁻¹. ^eData for product species taken from refs 20, 26, and 27. ^fThe isomeric forms of these two product species are not known; however, it is proposed that both the cation and neutral are the 1,1-isomers of difluoroethene. ^gThe calculated $\Delta_r H^\circ$ value if the two product species are both the 1,1- isomers. ^hAssuming this reaction is exothermic, we determine $\Delta_r H^\circ_{298}(C_3H_3F_2^+) < 605$ kJ mol⁻¹. Its structure is almost certainly $CF_2=CH-CH_2^+$. ⁱBoth cis and trans 1,2 isomers give endothermic reaction enthalpies, and so we propose 1,1-difluoroethene is the neutral product species formed. ^jAssuming this reaction is exothermic, we determine $\Delta_r H^\circ_{298}(C_3H_3F_2^+) < 628$ kJ mol⁻¹. ^kAssuming this reaction is exothermic, we determine $\Delta_r H^\circ_{298}(C_3H_2F_3^+) < 412$ kJ mol⁻¹. Its structure is probably $CF_2=CH-CHF^+$. ^lAssuming this reaction is exothermic, we determine $\Delta_r H^\circ_{298}(C_3H_2F_3^+) < 438$ kJ mol⁻¹. ^mAssuming this reaction is exothermic, we determine $\Delta_r H^\circ_{298}(C_3HF_4^+) < 202$ kJ mol⁻¹. Its structure is probably $CF_2=CH-CF_2^+$. ⁿAssuming this reaction is exothermic, we determine $\Delta_r H^\circ_{298}(C_3HF_4^+) < 418$ kJ mol⁻¹.

quadrupole mass filter and detected by an off-axis channeltron electron multiplier.

The experimental rate coefficients, k_{exp} , were measured under pseudo-first-order conditions by recording the loss of reagent ion as a function of the concentration of neutral reagent. The measurement of the latter's absolute concentration has been described in Appendix II of ref 25. The experimental uncertainty in k_{exp} values was estimated to be $\pm 20\%$, and the apparatus is limited to measuring reactions with $k_{\text{exp}} \geq \text{ca. } 10^{-13}$ cm³ molecule⁻¹ s⁻¹. Product ion BRs were obtained by recording their signals as a function of the concentration of the neutral reagent. The ion signals were then extrapolated to zero concentration to give the BRs, which also allows identification of any secondary ion products. The error in the BRs were considered to be $\pm 20\%$, although this value will be greater for minor products when BRs are below 10%.

C_2H_3F (98%) and C_2HF_3 (97%) were purchased from Apollo Scientific, C_2H_4 (99.5%) and CH_2CF_2 (99+%) from Aldrich, and C_3F_8 (99+%) from Fluorochem. All gases were used without further purification.

3. RESULTS AND DISCUSSION

A summary of the results for the reactions of CF_n^+ ($n = 1-3$) and $C_2F_4^+$ with C_2H_4 , C_2H_3F , CH_2CF_2 , and C_2HF_3 are presented in Tables 1 and 2. The results include the product cations, their BRs and the bimolecular reaction rate coefficient, k_{exp} . In addition, neutral products associated with the product cation are proposed, the corresponding reaction enthalpies

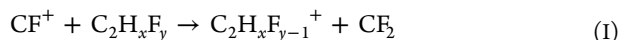
calculated, and collisional rate coefficients, k_c , are included. Reaction enthalpies ($\Delta_r H^\circ_{298}$) were calculated using enthalpies of formation ($\Delta_f H^\circ_{298}$) for the reactant and product species, these values usually being taken from standard sources.^{26,27} New $\Delta_r H^\circ_{298}$ values for the reactant species, shown in the footnotes to Tables 1 and 2, are taken from a study of the photodissociative ionization dynamics of fluorinated ethenes using imaging photoelectron photoion coincidence spectroscopy.²⁰ The k_c values were calculated using the modified average dipole orientation (MADO) model.^{28,29} Comparison of k_{exp} and k_c values can indicate the efficiency of a reaction, yielding information regarding its dynamics. To calculate k_c values, the polarizability volume and dipole moment, if applicable, for the neutral reactant species must be known. The data are shown in Table 3, including that for C_2F_4 because reactions of this molecule have been studied by others.^{4,9,11}

Table 3. Polarizability Volumes and Dipole Moments for Ethene and Four Fluorinated Ethenes

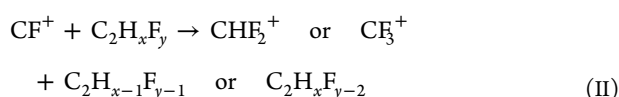
molecule	C_2H_4	C_2H_3F	CH_2CF_2	C_2HF_3	C_2F_4
$\alpha'/\text{\AA}^3$ ^a	4.25 ^c	3.99 ^d	5.01 ^c	4.16 ^d	4.35 ^d
μ_D/D ^b		1.47 ^c	1.39 ^c	1.32 ^c	

^aPolarizability volume, α' , given in \AA^3 where $1 \text{\AA}^3 = 10^{-30} \text{ m}^3$. ^bDipole moment, μ_D , in debyes (D) where $1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$. ^cValue from CRC Handbook of Chemistry and Physics.³⁰ ^dValue calculated using the method of Miller.³¹

3.1. Reactions of CF^+ . Because the RE for CF^+ is 9.11 eV,¹⁷ charge transfer in reactions with all four titled ethenes is endothermic because the IE of the ethene always exceeds this value. Reactions can only occur through a chemical mechanism where bonds are formed and then broken in a reaction complex.¹⁶ The results of Table 1 reveal that only two types of reaction are occurring. One is F^- transferred from the neutral species:



As fluorination increases, reaction I becomes *less* favorable; for $\text{C}_2\text{H}_3\text{F}$ this reaction represents the major product channel (88%), for CH_2CF_2 the BR falls to just 7%, and for C_2HF_3 this reaction is not observed, presumably because it is endothermic. The second type of reaction involves either HF or F_2 abstraction:



For $\text{C}_2\text{H}_3\text{F}$ reaction II represents the minor product channel (12%), although it is more exothermic than the F^- abstraction channel. Now, as the degree of fluorination increases the BR associated with reaction II increases; the BR for CH_2CF_2 is $88 + 5 = 93\%$, and for C_2HF_3 it is 100%.

F^- abstraction, reaction I, suggests that CF^+ attacks the electron-rich fluorine in $\text{C}_2\text{H}_x\text{F}_y$ rather than the $\text{C}=\text{C}$ bond. Thus, it is probably the decrease in dipole moment as fluorination increases (Table 3) which is responsible for the trend in BRs noted; the larger the dipole moment, the more concentrated the electron density on an individual fluorine atom, and the more nucleophilic it becomes. For reaction II, there is no obvious mechanism to explain the observed products, but a tight transition state should be formed. It is also unclear if this mechanism involves breaking the $\text{C}=\text{C}$ bond or not. The reaction of CF^+ with CH_2CF_2 produces two different outcomes from (II); $\text{CF}_3^+ + \text{C}_2\text{H}_2$ and $\text{CHF}_2^+ + \text{C}_2\text{HF}$, with the BR of the former being much greater. We also note that H_2 abstraction is not observed in either the reaction with $\text{C}_2\text{H}_3\text{F}$ or CH_2CF_2 . For CH_2CF_2 , H_2 abstraction is endothermic by 71 kJ mol⁻¹, but from $\text{C}_2\text{H}_3\text{F}$ it is exothermic by 53 kJ mol⁻¹. Although the competition between reactions I and II is not considered to be energetically driven, when considering reaction II alone, F_2 abstraction is more exothermic than HF abstraction which is more exothermic than H_2 abstraction. This suggests that energetics are being reflected in the BRs of the different products via (II).

The reaction of CF^+ with C_2F_4 has been reported by Morris et al.,⁹ and this reaction fits the trends observed from our study; F_2 abstraction, reaction II, is observed as the major product ($\text{CF}^+ + \text{C}_2\text{F}_4 \rightarrow \text{CF}_3^+ + \text{C}_2\text{F}_2$) and reaction I is not observed at all. However, the reaction with C_2F_4 also produces the minor products C_3F_5^+ and C_2F_4^+ by association and charge transfer, respectively. The adiabatic IE of C_2F_4 is 10.11 eV,^{18,21} and so charge transfer to CF^+ ($\nu = 0$) is endothermic. This observation of C_2F_4^+ product by Morris et al. is attributed to the reaction with electronically- or vibrationally excited CF^+ (produced from electron impact ionization of CF_3Br). In our experiments CF^+ ions are produced by electron impact ionization from a different precursor, C_3F_8 . Charge-transfer products from the reaction of CF^+ with $\text{C}_2\text{H}_3\text{F}$, CH_2CF_2 , and C_2HF_3 have not been observed. The results for the reaction of CF^+ with C_2H_4

(Table 1) also fit into the general trend. C_2H_4 has no fluorine substituent nor dipole moment, and reaction I is not observed. The analogous outcome of reaction II, producing $\text{CH}_2\text{F}^+ + \text{C}_2\text{H}_2$, is the dominant channel. We note, however, that HF elimination is observed in this reaction, but not in those of the fluorinated ethenes.

In summary, we suggest that the F^- -transfer reactions between CF^+ and $\text{C}_2\text{H}_3\text{F}$, CH_2CF_2 , and C_2HF_3 are largely dictated by the dipole moments of these neutral species. The outcome of competition between reactions I and II relates to the magnitude of the dipole moment; the larger μ_D , the more preference there is for reaction I to dominate. The different outcomes of reaction II, i.e., F_2 vs HF vs H_2 abstraction, appear to be determined by energetics. They favor F_2 abstraction, and CF^+ attacks the molecule preferentially where more fluorine substituents are present. C_2H_4 and C_2F_4 have no dipole moment, and the outcome is the equivalent of reaction II, i.e., H_2 and F_2 abstraction, respectively.

The reactions of CF^+ with chlorinated ethenes have been performed by Mikhailov et al. using the Birmingham SIFT apparatus.^{1,2} The reactions of CF^+ with $\text{C}_2\text{H}_x\text{Cl}_{4-x}$ ($x = 0-3$) follow the general trends observed for the fluorinated ethenes. That is, the equivalent of reactions I and II describes all the observed products, with the dominance of reaction I, i.e., Cl^- transfer, decreasing as the number of chlorine atoms increases. The results from the chlorinated ethenes reveal information about reaction II, which is not possible from this fluorinated ethene study. For example, the reaction of CF^+ with C_2HCl_3 produces 23% $\text{CHCl}_2^+ + \text{C}_2\text{HCl}$, with the neutral substituted ethyne product containing the fluorine atom. In the analogous reaction with C_2HF_3 it might be assumed that the atoms in the neutral product, C_2HF , all originate from the C_2HF_3 reactant. The chlorinated ethene study shows that this may not be true, and a more complicated mechanism is probably occurring. The study of the three isomers of dichloroethene also reveals additional information.¹ Most significantly, the reaction of *cis*-1,2-dichloroethene shows no products from the equivalent of reaction I whereas with $\text{C}_2\text{H}_3\text{Cl}$ and CH_2CCl_2 this reaction dominates. This is surprising because of these three chlorinated ethenes it is the *cis*-1,2 isomer that has the largest dipole moment. In fact, of the complete series of chlorinated ethenes reacting with CF^+ , only $\text{C}_2\text{H}_3\text{Cl}$ and CH_2CCl_2 show products from reaction I; all others only show products from reaction II. It could be significant that these two species are the ones where the chlorine substituents are on the same carbon atom. Yet, if this factor is important in determining if reaction I or II dominates, it is not obvious why reaction II dominates (88% $\text{CF}_3^+ + \text{C}_2\text{H}_2$) with CH_2CF_2 , but reaction I dominates (69% $\text{C}_2\text{H}_2\text{Cl}^+ + \text{CFCl}$) with CH_2CCl_2 .

3.2. Reactions with CF_2^+ . The RE for CF_2^+ is 11.36 eV.¹⁸ The results for the reactions of this cation with C_2H_4 , $\text{C}_2\text{H}_3\text{F}$, CH_2CF_2 , and C_2HF_3 are presented in Table 1. Because this value exceeds the IE of all four neutral molecules, charge transfer in all reactions is exothermic, and this process does dominate the products. All reactions occur with 100% efficiency. Nondissociative charge transfer is the only channel observed with CH_2CF_2 and C_2HF_3 . The reaction of CF_2^+ with $\text{C}_2\text{H}_3\text{F}$ yields two different ionic products, although the major product still arises from nondissociative charge transfer. The minor product is C_2H_3^+ , produced by F^- abstraction:

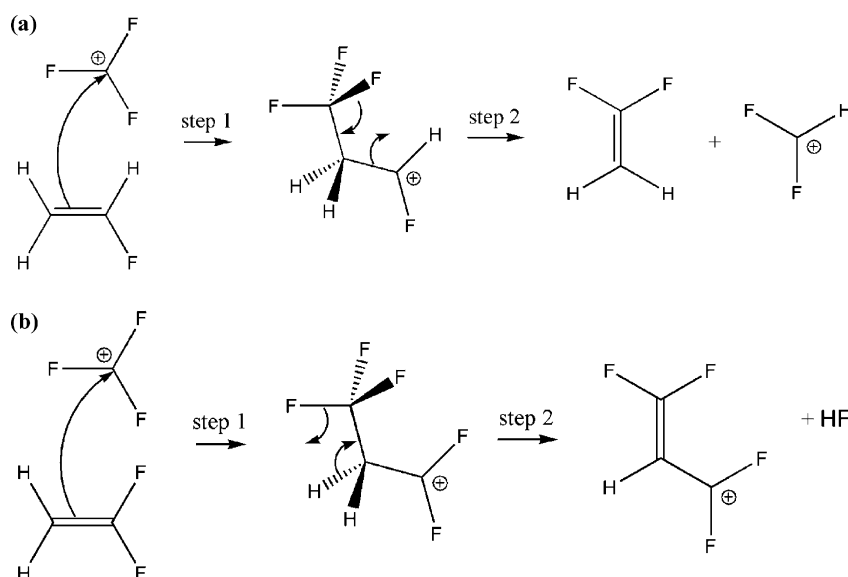
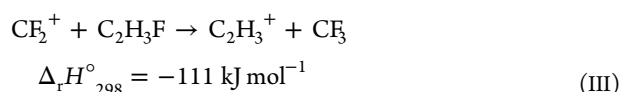


Figure 1. Proposed mechanism for (a) the reaction $\text{CF}_3^+ + \text{C}_2\text{H}_3\text{F} \rightarrow \text{CHF}_2^+ + \text{CH}_2\text{CF}_2$ and (b) the reaction $\text{CF}_3^+ + \text{CH}_2\text{CF}_2 \rightarrow \text{C}_3\text{HF}_4^+ + \text{HF}$.



Dissociative charge transfer, $\text{CF}_2^+ + \text{C}_2\text{H}_3\text{F} \rightarrow (\text{C}_2\text{H}_3\text{F}^+)^* + \text{CF}_2 \rightarrow \text{C}_2\text{H}_3\text{F}^+ + \text{F} + \text{CF}_2$, is endothermic by 235 kJ mol^{-1} .

The results from the reaction with C_2H_4 are anomalous; charge transfer is observed, but it is the minor channel. In addition, the formation of the major product $\text{C}_3\text{H}_3\text{F}_2^+$ by H-atom elimination from the adduct is surprising. However, this product has also been observed in the reactions of CF_3^+ and C_2F_4^+ with ethene, and from C_2F_4^+ with $\text{C}_2\text{H}_3\text{F}$ (Tables 1 and 2). The structure of this cation is unknown, but its frequent observation suggests it is relatively stable. Unfortunately, its $\Delta_f H^\circ$ value is unknown, so $\Delta_r H^\circ$ values for reactions where it is produced cannot be calculated. Assuming that the $\text{CF}_2^+ + \text{C}_2\text{H}_4$ reaction is exothermic, we can only determine an upper limit for its enthalpy of formation, $\Delta_f H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+) < 732 \text{ kJ mol}^{-1}$, where the stationary electron convention for cations at $T > 0 \text{ K}$ is used.²⁷ Its structure is almost certainly $\text{CF}_2=\text{CH}-\text{CH}_2^+$.

The adiabatic IE of C_2F_4 is 10.11 eV,^{15,21} so charge transfer in its reaction with CF_2^+ is also exothermic. This reaction has been reported by Morris et al.,⁹ and unsurprisingly, this reaction proceeds exclusively by charge transfer at the collisional rate.

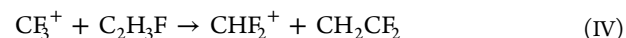
3.3. Reactions of CF_3^+ . The RE for CF_3^+ is 9.09 eV,^{19,20} so as with CF^+ charge transfer is endothermic for all four reactions. Data for the reactions of CF_3^+ with $\text{C}_2\text{H}_x\text{F}_{4-x}$ ($x = 1-4$) are presented in Table 1. Where an association adduct is observed, the He buffer gas pressure is quoted due to its involvement in collisionally stabilizing the energized intermediate formed. We note that this value for the IE of the CF_3 radical, $9.090 \pm 0.015 \text{ eV}$,¹⁹ is slightly higher than many recent determinations in the range 9.00–9.05 eV, but there is strong evidence that this latest value is the most accurate.

Trends in the reactions of the fluorinated ethenes with CF_3^+ are apparent. F^- abstraction from the neutral appears less favorable as the degree of fluorine substitution increases or the dipole moment decreases; with $\text{C}_2\text{H}_3\text{F}$ the BR is 75%, with CH_2CF_2 only 50%, and with C_2HF_3 this reaction is not

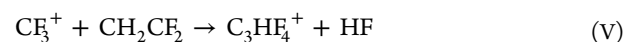
observed. The same trend is apparent in the analogous reaction with CF^+ ; the smaller the dipole moment of the fluorinated ethene, the less likely F^- abstraction appears to occur. Three points should be made regarding F^- transfer to CF_3^+ compared to CF^+ . First, only the reaction of $\text{C}_2\text{H}_3\text{F}$ with CF_3^+ can be compared directly with CF^+ because the same two product cations are observed. Second, as the BR for F^- abstraction decreases, there is no common mechanism in all three reactions taking its place; i.e., there is no significant competition to the F^- abstraction reaction. Third, although the value for $\Delta_f H^\circ_{298}(\text{C}_2\text{HF}_2^+)$ is not known, F^- abstraction in the reaction with C_2HF_3 is expected to be endothermic; if this is true, using the stationary electron convention $\Delta_f H^\circ_{298}(\text{C}_2\text{HF}_2^+) > 845 \text{ kJ mol}^{-1}$.²⁷ Its structure is almost certainly $\text{CF}_2=\text{CH}^+$.

We note the trend in the reaction enthalpies in Table 1, and furthermore, that the reaction $\text{CF}_3^+ + \text{C}_2\text{F}_4 \rightarrow \text{C}_2\text{F}_3^+ + \text{CF}_4$ is endothermic by 110–120 kJ mol^{-1} , depending on the value used for $\Delta_f H^\circ_{298}(\text{C}_2\text{F}_3^+)$.^{20,27} Thus it seems that energetics are more likely to be important in interpreting the results from the CF_3^+ reactions. Supporting evidence is that, unlike CF^+ , adduct formation is observed, and the BR increases with increasing fluorine substitution; no adduct is formed in the reaction with $\text{C}_2\text{H}_3\text{F}$, the BR for adduct formation is 44% with CH_2CF_2 , and with C_2HF_3 the BR is 100%. Thus, as F^- abstraction becomes energetically less favorable, the lifetime of the reaction complex increases, so it becomes more likely to be collisionally stabilized and observed.

There are also other reactions occurring which do not lead to F^- abstraction or adduct formation; for example, the observation of CHF_2^+ as the minor product (25%) from the reaction of CF_3^+ with $\text{C}_2\text{H}_3\text{F}$:



The proposed neutral product is the 1,1 isomer of difluoroethene because this is the only exothermic outcome. (The cis and trans isomers of 1,2-difluoroethene give reaction enthalpies endothermic by 53 and 57 kJ mol^{-1} , respectively.^{20,27}) Another minority reaction with a BR of 6% which does not fit the general trend is that of CF_3^+ with CH_2CF_2 :



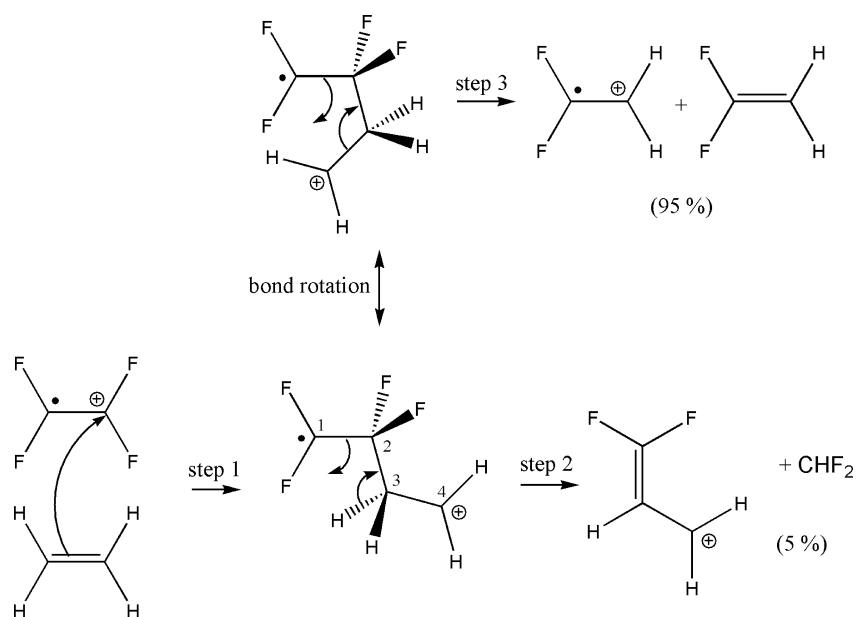


Figure 2. Proposed mechanism for the reaction between C_2F_4^+ and ethane, C_2H_6 .

Reactions IV and V represent thermodynamically favorable exit channels from the adduct that is formed. Proposed mechanisms are presented in Figure 1. We note also that previous work has shown that CF_3^+ reacts with neutral C_2F_4 to produce covalently bonded C_3F_7^+ .⁹ Finally, in the reaction of CF_3^+ with C_2H_4 , H^- abstraction is observed. This process is not observed in the reactions with the fluorinated ethenes, presumably because it cannot compete with F^- abstraction. We recall the comparisons made above between F^- abstraction in the reactions of both CF^+ and CF_3^+ with the fluorinated ethenes, but the same comment cannot be made regarding H^- abstraction in ethene because this outcome in the reaction with CF^+ is endothermic by 63 kJ mol^{-1} . The other product from the reaction of CF_3^+ with C_2H_4 is $\text{C}_3\text{H}_3\text{F}_2^+$, produced by HF elimination with a BR of 60%. HF elimination is also observed from the reaction with CH_2CF_2 but as the *minor* product, further demonstrating the dominance of the F^- abstraction channel in the fluorinated ethenes and the less dominant H^- abstraction reaction from C_2H_4 . Tsuji et al. have studied the reaction of CF_3^+ with ethene in an ion beam,¹⁰ and the results are in satisfactory agreement; the dominant product is $\text{C}_3\text{H}_3\text{F}_2^+$, the minor product is C_2H_3^+ , and the rate coefficient at 300 K is $(1.3 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A SIFT study by Morris et al.⁸ obtained similar branching ratios but a slower rate of $0.98 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, closer to our value.

Previous work on chlorinated ethenes report their gas-phase reactions with CF_3^+ .^{1,2} Similarities with the fluoroethenes are noted in the reaction with $\text{C}_2\text{H}_3\text{Cl}$ and CH_2CCl_2 , particularly the former. CF_3^+ reacts with $\text{C}_2\text{H}_3\text{Cl}$ to produce $\text{C}_2\text{H}_3^+ + \text{CF}_3\text{Cl}$ (65%) and $\text{CHFCl}^+ + \text{C}_2\text{H}_2\text{F}_2$ (35%),² very similar to the reaction with $\text{C}_2\text{H}_3\text{F}$ (Table 1). In both reactions, the $\text{C}_2\text{H}_2\text{F}_2$ product can only be the 1,1 isomer because the two 1,2 isomers give endothermic reaction enthalpies. The similarities in the reaction of CH_2CF_2 and CH_2CCl_2 are less striking; $\text{CF}_3^+ + \text{CH}_2\text{CCl}_2$ exclusively produces $\text{C}_2\text{H}_2\text{Cl}^+ + \text{CF}_3\text{Cl}$ via Cl^- abstraction, whereas the analogous F^- abstraction reaction with CH_2CF_2 forms only 50% of the observed products (Table 1). Also, Cl^- abstraction is observed in the reactions of C_2HCl_3 and C_2Cl_4 , but the analogous F^- abstraction reaction is *not* observed

from C_2HF_3 (this work) or C_2F_4 .⁸ The latter two reactions are expected to be endothermic (see earlier), whereas the former two reactions are clearly exothermic. In fact, new reactions observed in the chlorinated ethenes, which are not equivalently observed in the fluorinated ethenes, appear to arise simply because of the new atom involved, chlorine. For example, $\text{CF}_3^+ + \text{C}_2\text{HCl}_3$ produces 24% $\text{CFCl}_2^+ + \text{C}_2\text{HClF}_2$, whereas this reaction for C_2HF_3 is thermoneutral and produces products identical to the reactants. So, although initially it might appear that the differences in the reactions of CF_3^+ with fluorinated and chlorinated ethenes are significant, they are not and appear to have two dominant explanations. First, Cl^- abstraction reactions are energetically more favorable than the equivalent reactions involving F^- abstraction. Second, reactions with chlorinated ethenes involve the atoms C, H, F, and Cl, allowing for a larger number of dynamically- and energetically viable exit channels to be available to the reaction complex.

3.4. Reactions of C_2F_4^+ . The RE for C_2F_4^+ is 10.11 eV.^{15,21} Like the reactions of CF^+ and CF_3^+ , charge transfer with all fluoroethenes is therefore endothermic. Results for the reactions of C_2F_4^+ with $\text{C}_2\text{H}_x\text{F}_{4-x}$ ($x = 1-4$) are given in Table 2. Where an association reaction is observed, as with CF_3^+ reactions the He buffer gas pressure is quoted. All reactions are relatively slow with $k_{\text{exp}} < k_0$, so three-body processes can compete with bimolecular reactions. Many of the ionic products are relatively large, containing three or four carbon atoms. This complicates the data analysis for two reasons. First, it is difficult to suggest confidently an isomeric structure for these product ions. Second, many $\Delta_f H^\circ_{298}$ values are not known, which prevents $\Delta_r H^\circ_{298}$ from being calculated for these reactions. Assuming, however, that the reaction is exothermic, it is possible to determine an upper limit for the enthalpy of formation of the product ion (Table 2 and section 4).

We discuss the structure of the reagent ion, C_2F_4^+ . Perfluorination of neutral ethene significantly weakens the $\text{C}=\text{C}$ bond, the bond strength being ca. 720 kJ mol^{-1} in C_2H_4 but only 274 kJ mol^{-1} in C_2F_4 .^{20,26} Electron removal from the π -framework weakens the bond even further. Su and Kevan³⁴

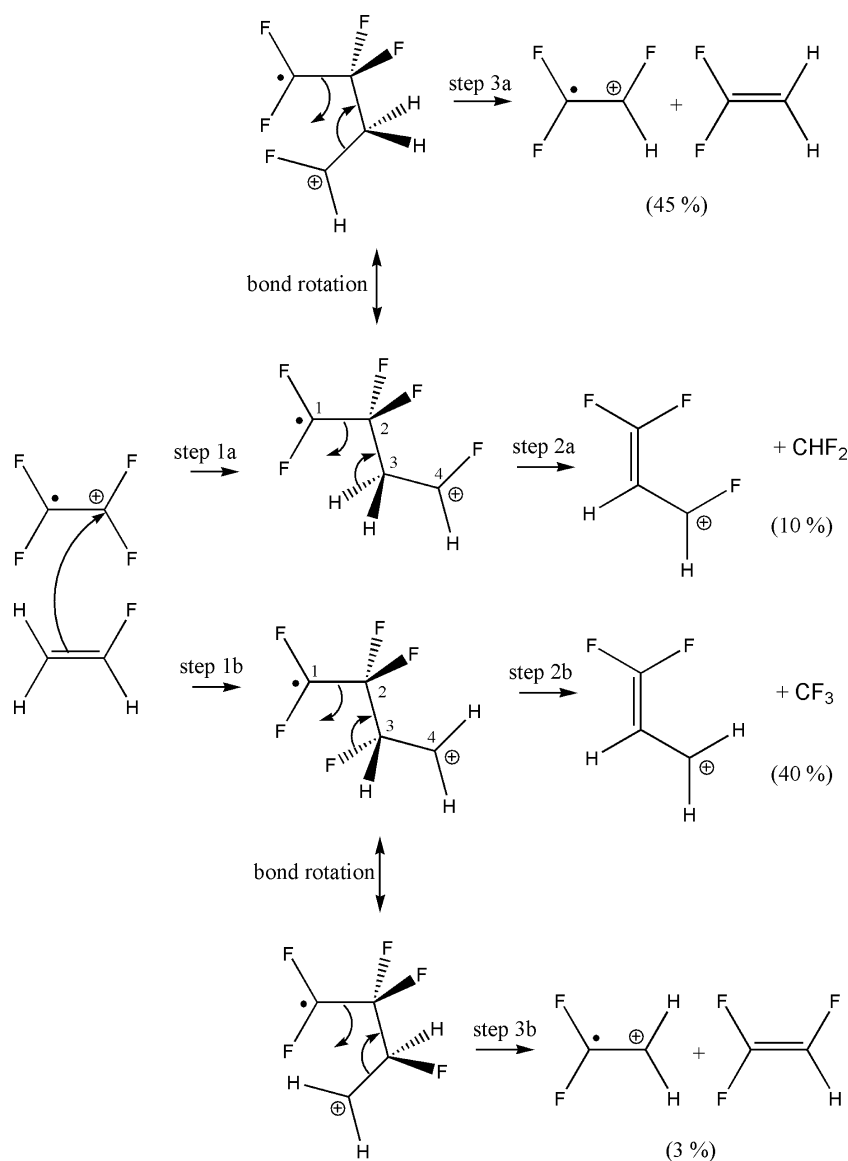
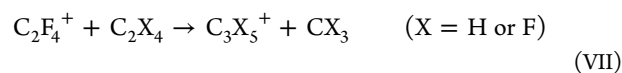
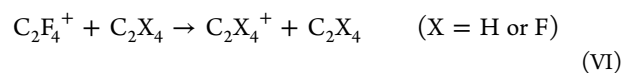


Figure 3. Proposed mechanism for the reaction between $C_2F_4^+$ and monofluoroethene, C_2H_3F .

have shown that $C_2F_4^+$ is metastable and will produce CF_3^+ by collision induced dissociation. This involves F-atom migration and cleavage of the carbon–carbon bond. We note also that the first fragment ion formed from dissociative photoionisation of C_2F_4 is CF_3^+ , and not $C_2F_3^+$ or CF_2^+ from a single bond cleavage.^{20,35,36} $C_2F_4^+$ is therefore represented as $\cdot CF_2-CF_2^+$ throughout this section. All the products can be divided into three categories. The first is observation of the adduct species. The second is observation of a fluorinated ethene cation which is *different* to the neutral reactant, reaction VI. The third is observation of a cation containing three carbon atoms with the corresponding neutral species being either CHF_2 or CF_3 , reaction VII.



We suggest that products from any of these categories may be explained by one common mechanism, involving formation of a

four-carbon chain adduct that may subsequently fragment either to eliminate CX_3 , reaction VII, or to produce two fluorinated ethenes with one retaining the positive charge. Figure 2 shows this mechanism for the reaction of $C_2F_4^+$ with C_2H_4 , both the observed product channels (Table 2) being produced from the same four-carbon chain intermediate formed by step 1. This mechanism suggests the product channel $C_2H_2F_2^+ + C_2H_2F_2$ forms both species as the 1,1 isomer, also the most exothermic outcome. From the BRs, there is an apparent preference for step 3, and not step 2, to follow step 1. The same trend is seen in the reactions of $C_2F_4^+$ with the fluorinated molecules (Table 2 and discussion below); the channel eliminating CHF_2 is always minor, and the product channels analogous to that in step 3, where possible, have a significant BR. It appears that step 2 in Figure 2 is unfavorable and relatively slow, allowing bond rotation to occur in the intermediate species and step 3 to dominate. Using the upper limit value for $\Delta_r H_{298}^\circ(C_3H_3F_2^+)$ of 732 kJ mol^{-1} determined from the $CF_2^+ + C_2H_4$ reaction, we determine $\Delta_r H_{298}^\circ(C_2F_4^+ + C_2H_4 \rightarrow C_3H_3F_2^+ + CHF_2)$ to be $+127 \text{ kJ mol}^{-1}$. Even though the BR of this reaction is only 5%, this clearly cannot be

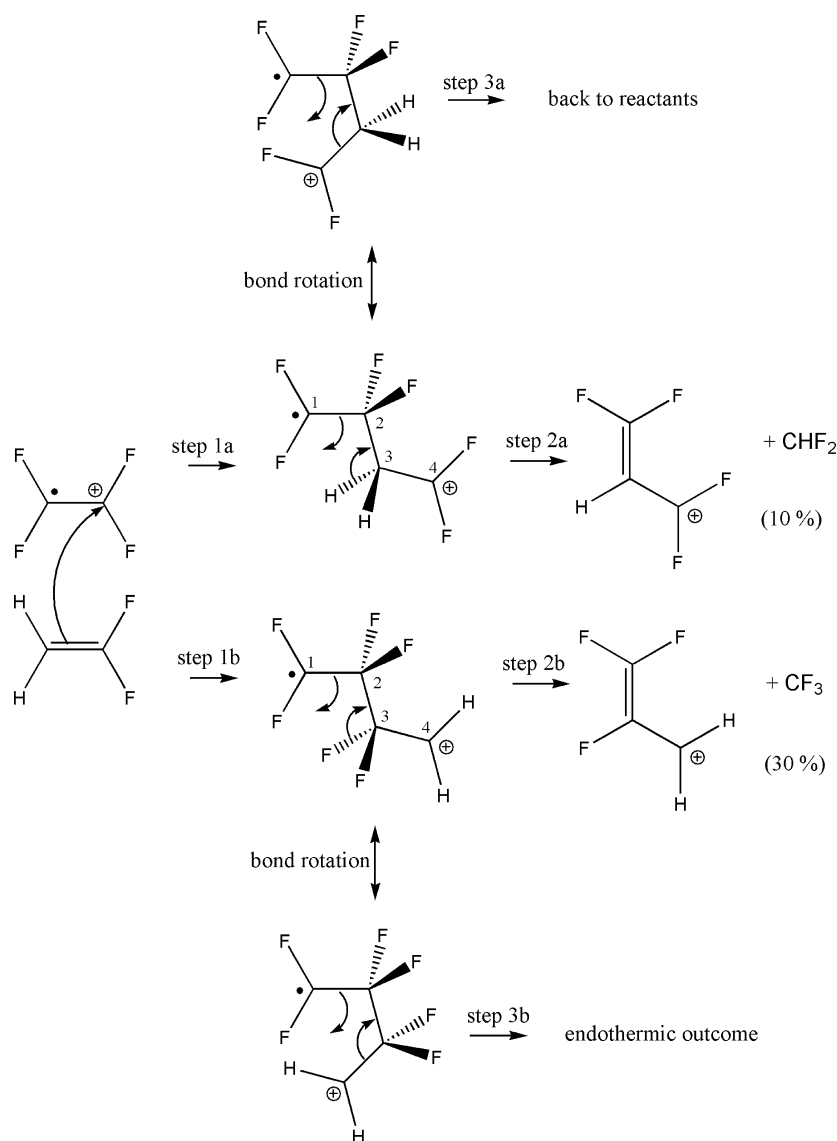


Figure 4. Proposed mechanism for the reaction between C_2F_4^+ and 1,1-difluoroethene, CH_2CF_2 .

possible unless $\Delta_f H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+)$ is significantly less than 732 kJ mol^{-1} , i.e., $\Delta_f H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+) < 605 \text{ kJ mol}^{-1}$. The enthalpy change for the dominant channel is exothermic, -62 kJ mol^{-1} , as expected.

Figure 3 shows the proposed mechanism for the reaction between C_2F_4^+ and $\text{C}_2\text{H}_3\text{F}$, and all products (Table 2) can be produced by this mechanism. Steps 1a and 1b show that two isomerically different intermediate adducts can form, depending on which carbon in $\text{C}_2\text{H}_3\text{F}$ forms the bond with a carbon in C_2F_4^+ . Step 1a followed by 2a will produce $\text{C}_3\text{H}_2\text{F}_3^+$ and CHF_2 , with both substituents on carbon 3 in the adduct being hydrogen. Step 1b, however, produces carbon 3 with one hydrogen and one fluorine substituent in the adduct, so a mixture of $\text{C}_3\text{H}_2\text{F}_3^+$ (+ CHF_2) and $\text{C}_3\text{H}_3\text{F}_2^+$ (+ CF_3) is produced; note that Figure 3 only shows the latter outcome. From the product BRs there is a preference for elimination of CF_3 over that of CHF_2 . Fluorine is a larger and more polarizable atom than hydrogen, and the C–F bond distance is greater. These facts may explain qualitatively why step 2b preferably eliminates CF_3 rather than CHF_2 , and why step 2b occurs more readily than step 2a. The other products shown in Figure 3 are C_2HF_3^+ and CH_2CF_2^+ , resulting from steps 3a and

3b, respectively. C_2HF_3^+ is the major product (BR = 45%), whereas CH_2CF_2^+ is only a minor product (BR = 3%). A bond rotation is required for either step 3a or 3b to occur, both sterically unfavorable. Therefore, the more favorable step 2b is, the less likely 3b is. The same comment is made with respect to steps 2a and 3a. This may explain why, following step 1a, formation of C_2HF_3^+ by step 3a is the dominant outcome, whereas following step 1b, elimination of CF_3 by step 2b is dominant. An ICR-MS study of the reaction $\text{C}_2\text{F}_4^+ + \text{C}_2\text{H}_3\text{F}$ revealed the products C_2HF_3^+ (62%), $\text{C}_3\text{H}_3\text{F}_2^+$ (31%) and $\text{C}_3\text{H}_2\text{F}_3^+$ (7%), in good agreement with the dominant products observed in our study. If *only* the mechanism in Figure 3 is considered, then the adduct species, observed as the minor product with BR = 2%, can be produced by either steps 1a or 1b. Given the number of hydrogen and fluorine atoms in the two reactants, the observed adduct may also predominantly be a hydrogen-bonded, rather than a covalent-bonded, species. Because $\text{C}_2\text{F}_4^+ + \text{C}_2\text{H}_3\text{F} \rightarrow \text{C}_3\text{H}_3\text{F}_2^+ + \text{CF}_3$ has a BR as large as 40%, this reaction is clearly exothermic. We then determine $\Delta_f H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+) < 628 \text{ kJ mol}^{-1}$, consistent with the upper limit of 605 kJ mol^{-1} derived from the $\text{C}_2\text{F}_4^+ + \text{C}_2\text{H}_4$ reaction.

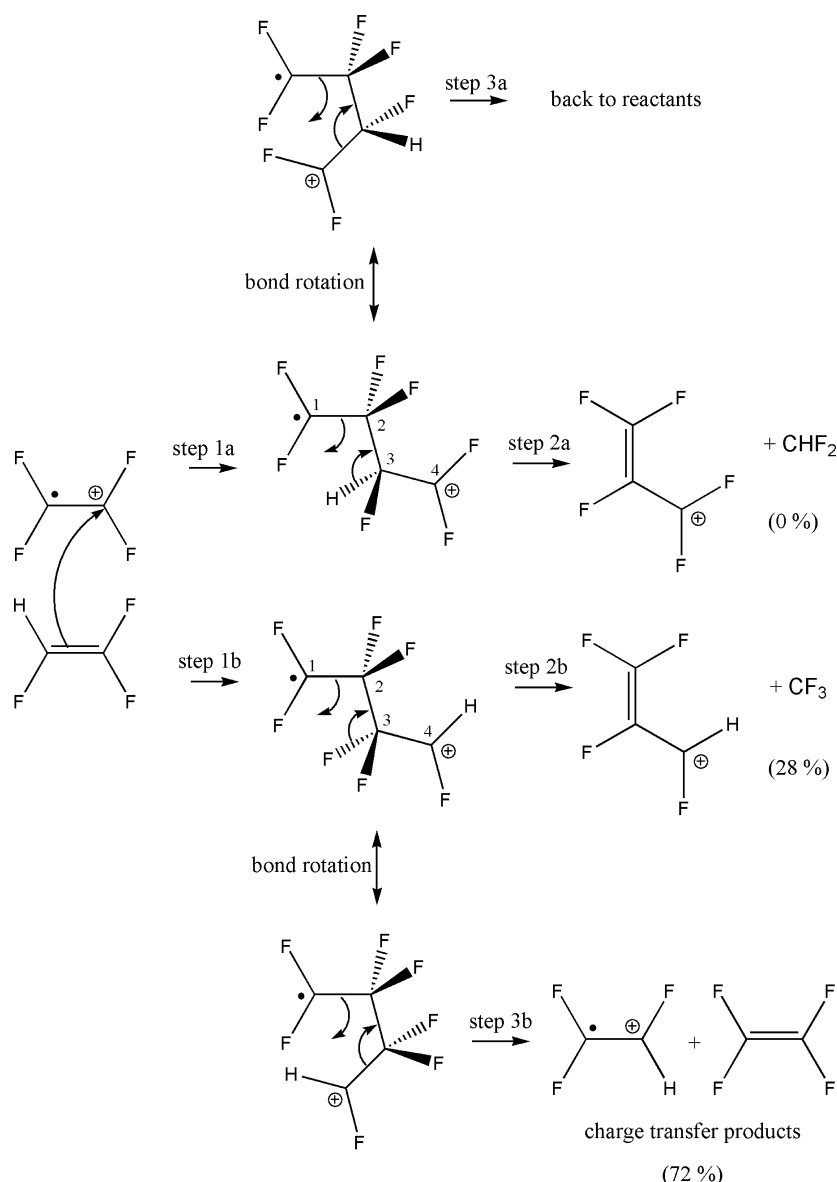


Figure 5. Proposed mechanism for the reaction between C_2F_4^+ and trifluoroethene, C_2HF_3 .

Figure 4 shows how the same mechanism can explain the products observed from the reaction of C_2F_4^+ with CH_2CF_2 . In particular, it shows how elimination of CF_3 and CHF_2 are observed, yet fluorinated ethene cation products from steps 3a or 3b are not; step 3a reverts back to reactants, whereas step 3b is endothermic. Again, a preference to eliminate CF_3 over CHF_2 is observed. The major difference of this reaction compared to that of C_2F_4^+ with C_2H_4 , $\text{C}_2\text{H}_3\text{F}$ or C_2HF_3 is the large BR recorded for the adduct species: 60%, compared to 0%, 2%, and 0%, respectively. There is no obvious explanation. In the SIFT study of the reaction of C_2F_4^+ with C_2F_4 , no adduct is observed and the only product is C_3F_5^+ ($+\text{CF}_3$).⁹ Furthermore, the ICR-MS study of the C_2F_4^+ + CH_2F_2 reaction showed that the only product was $\text{C}_3\text{H}_2\text{F}_3^+$ ($+\text{CF}_3$).⁷

Figure 5 shows the same mechanism for the reaction of C_2F_4^+ with C_2HF_3 . Consistent with the results discussed above, the preference for the intermediate species to eliminate CF_3 rather than CHF_2 is observed, but now the BR for CHF_2 elimination is zero. For this reaction, Anicich and Bowers observed the products C_3HF_4^+ ($+\text{CF}_3$) and C_3F_5^+ ($+\text{CHF}_2$)

with BRs of 92% and 8%, respectively.⁷ We observe rather different products: C_2HF_3^+ + C_2F_4 and C_3HF_4^+ + CF_3 with BRs of 72% and 28%, respectively (Table 2). Step 2a shows how CHF_2 elimination is possible, but this step could also lead to CF_3 elimination given that carbon 3 in the intermediate species has both one hydrogen and one fluorine atom attached. We therefore propose that the channel leading to 28% CF_3 elimination is dominated by step 2b. C_2HF_3^+ ($+\text{C}_2\text{F}_4$) is detected with the largest BR of 72%. Figure 5 shows how this can arise from step 3b, but a simple charge-transfer mechanism could also be occurring. In ion–molecule reactions where charge transfer is observed, it is commonly the dominant product channel, but this reaction is endothermic, albeit by only 3 kJ mol^{-1} ; the IE of C_2F_4 is 10.11 eV, that of C_2HF_3 is 10.14 eV.¹⁵ Therefore, the high BR observed for C_2HF_3^+ is not surprising and could result from vibrationally excited C_2F_4^+ in the flow tube, or from the high-energy tail of the thermal distribution of the reactants overcoming the small endothermicity. A charge-transfer reaction normally implies that the two species do not react intimately, but rather an electron from the

neutral molecule hops over to the cation at a significant intermolecular distance.¹⁶ These reactions are usually fast and occur at the collisional rate. Evidence to support the alternative mechanism for $C_2HF_3^+$ production comes from the low value of the reaction efficiency, 17% (Table 2). If the dominant product was formed from fast long-range charge transfer, it is unlikely that the efficiency would be so low. In addition, this efficiency for the reaction of $C_2F_4^+$ with C_2HF_3 is much lower than that for $C_2F_4^+$ with C_2H_4 (70%), C_2H_3F (40%) or CH_2CF_2 (50%), and none of the products from these three reactions can arise from "fast" processes.

In earlier studies of the ion–molecule reactions of substituted ethene species, it was suggested that a cyclic intermediate, rather than a four-carbon chain, formed which then dissociated to products.^{4,7} (Note that in these earlier studies a four-carbon chain intermediate was still needed to explain the $C_3X_5^+$ products ($X = H$ or F) shown in Figures 2–5 by steps 2a and 2b.) The four-carbon chain intermediate is preferred to the cyclic intermediate for two reasons. First, the cycloaddition reaction requires $C_2F_4^+$ to be represented as $CF_2=CF_2^+$. If the preferred descriptor of $^{\bullet}CF_2-CF_2^+$ is used, it becomes impossible to rationalize the formation of a cycloadduct in step 1. Second, excluding the adduct, the relative BRs of the observed products are best explained by one common mechanism involving one branched, *noncyclic* four-carbon adduct.

4. CONCLUSIONS

The gas-phase reactions of CF^+ , CF_2^+ , CF_3^+ , and $C_2F_4^+$ with C_2H_4 , C_2H_3F , CH_2CF_2 , and C_2HF_3 have been studied using a selected ion flow tube at 298 K. The reactions with CF_2^+ proceed predominantly by nondissociative charge transfer, whereas those with CF^+ , CF_3^+ , and $C_2F_4^+$ produce products from an adduct complex in which bonds are broken and new ones form.

The dipole moment of the fluorinated ethene is probably a significant factor in the determination of BRs because it is a measure of the nucleophilicity of a fluorine atom in the molecule. This is highlighted by their reactions with CF^+ and CF_3^+ . The dynamics involved with F^- abstraction are favored when the dipole moment of the fluorinated ethene is large, and the branching into this channel decreases as the dipole moment decreases. However, as branching into F^- abstraction decreases, so does the exothermicity of the reaction; in both CF^+ and $CF_3^+ + C_2HF_3$ the reaction is expected to be endothermic. It is therefore not easy to separate totally the effects of μ_D of the fluorinated ethene from the energetics. It also appears that energetics is the major factor responsible for the apparent preference for F_2 -abstraction over HF -abstraction over H_2 -abstraction in the reactions of CF^+ with CH_2F_2 and C_2HF_3 . The reactions of CF_3^+ and $C_2F_4^+$ show some similarities. Relative to those of CF^+ and CF_2^+ , the rate coefficients and efficiencies in both sets of reactions, are small, ca. 10^{-10} cm³ molecule⁻¹ s⁻¹ and sometimes <50%, respectively. Indeed, it is only for reactions of CF_3^+ and $C_2F_4^+$ where adduct products are observed, but some bimolecular products are also observed from these reactions, for example the neutral product CH_2CF_2 from the reactions with C_2H_3F , and the ionic product $C_3HF_4^+$ from the reactions with CH_2CF_2 .

The reactions with $C_2F_4^+$ show many products, but the majority can be explained by a first step that is common to all four of the titled neutral molecules; a four-carbon chain adduct, and not a four-membered ring, is formed. Two pathways then

compete. In one, the intermediate dissociates to yield two fluorinated ethene products (generically described by reaction VI), in the other, CF_3 or CHF_2 is eliminated from the intermediate (reaction VII). In reaction VII, a preference for CF_3 over CHF_2 elimination is observed.

$C_3H_3F_2^+$ is observed as a product from four of the reactions involving CF_2^+ , CF_3^+ , and $C_2F_4^+$ (Figures 2 and 3). The structure of this cation is almost certainly $CF_2=CH-CH_2^+$, and from these four measurements, we determine indirectly $\Delta_f H_{298}^\circ(C_3H_3F_2^+) < 628$ kJ mol⁻¹, possibly as low as 605 kJ mol⁻¹ (stationary electron convention). $C_3H_2F_3^+$ is observed as a product of two reactions involving $C_2F_4^+$. We determine $\Delta_f H_{298}^\circ(C_3H_2F_3^+) < 438$ kJ mol⁻¹, possibly as low as 412 kJ mol⁻¹. We note that Figure 3 suggests that this ion has structure $CF_2=CH-CHF^+$ whereas Figure 4 suggests a different isomeric structure of $CF_2=CF-CH_2^+$. $C_3H_1F_4^+$ is produced from three reactions involving CF_3^+ and $C_2F_4^+$. Two reactions (Figures 1b and 4) suggest the structure is $CF_2=CH-CF_2^+$, one (Figure 5) that it is $CF_2=CF-CHF^+$. Three upper limits for $\Delta_f H_{298}^\circ(C_3H_1F_4^+)$ are determined: 418, 333, and 202 kJ mol⁻¹. To our knowledge, there are no other experimental or ab initio values of these enthalpies of formation at 298 K of $C_3H_xF_{5-x}^+$ ($x = 1-3$) for comparison. The value for $C_3H_5^+$ at 298 K is well established, 955.4 ± 2.5 kJ mol⁻¹,³⁷ that for $C_3F_5^+$ only has an approximate upper limit determined of 84 ± 20 kJ mol⁻¹.³⁸ As expected, the upper limits we have determined for $\Delta_f H_{298}^\circ(C_3H_xF_{5-x}^+)$ ($x = 1-3$) all fall between these anchor values, and ab initio calculations will be performed in the future. Furthermore, no attempt has yet been made to calculate stationary points of the proposed reaction mechanisms involving $C_2F_4^+$, i.e., the energetics of the four-carbon intermediates shown in Figures 2–5. Finally, we note that the absence of the $C_2HF_2^+$ product, presumably with structure $CF_2=CH^+$, from the reaction of CF_3^+ with C_2HF_3 suggests that $\Delta_f H_{298}^\circ(CF_2=CH^+) > 845$ kJ mol⁻¹.

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Notes

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