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Translational Energy-Resolved Collisionally Activated Methyl Cation Transfer from Protonated Methane to Argon, Krypton, and Xenon and from Protonated Fluoromethane to Argon and Molecular Oxygen

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Translational energy-resolved collisionally activated gas-phase reactions of protonated methane with argon, krypton, and xenon and of protonated fluoromethane with argon and molecular oxygen are studied using the method of Fourier transform ion cyclotron resonance mass spectrometry. It appears that translationally activated protonated methane can act as a methyl cation donor if the competing proton transfer is energetically less favored. Translational energy-resolved collisionally activated reactions between protonated methane and argon, krypton, and xenon reveal that the methyl cation transfers resulting in the formation of methylargonium, methylkryptonium, and methylxenonium ions all proceed via transition states which are about 0.6 eV higher in energy than the reactants. The results suggest that in these transition states the weakening of the two-electron three-center C-H-H bond in protonated methane is more advanced than the bond formation between the methyl group and the noble gas atom. Similarly, translationally activated protonated fluoromethane can transfer a methyl cation to argon and molecular oxygen via transition states which are about 0.3 and 0.4 eV higher in energy than the reactants, respectively. It is shown that the product ion from the methyl cation transfer from protonated fluoromethane to molecular oxygen has the methylperoxy cation structure.

Introduction

Radiative association reactions of the methyl cation with various molecules M (eq 1) are considered to be the first stages in the

$$CH_3^+ + M \rightarrow MCH_3^+ + h\nu \tag{1}$$

synthesis of some important interstellar molecules, where M may be H₂, Ne, O₂, CO, CO₂, N₂, HCN, NH₃, etc.¹⁻⁶ This significance in interstellar processes has led to several laboratory studies of methyl cation transfer equilibria reactions,³⁻⁸ from which a methyl cation affinity (MCA) scale has been established.^{8,9}

Methyl Cationized Noble Gases. The first observations of methyl-cationized noble gases were made by Field et al.¹⁰⁻¹² in studies of the ionic reactions in a mass spectrometer with noble gas/methane mixtures. The ions were formed via the ion/molecule reactions (eq 2) The results were reproduced by Jonathan et al.,¹³

$$X^{*+} + CH_4 \rightarrow XCH_3^+ + H^* \qquad (X = Ar, Kr, Xe) \quad (2)$$

who characterized the observed methyl-cationized argon, krypton, and xenon by collision-induced dissociation. To our knowledge no observation of the methyl-cationized neon or helium has been reported.

Alternatively, methyl-cationized noble gases have been generated via β^- decay of the corresponding isoelectronic radioactive halomethanes (eq 3)¹⁴ Holtz et al. demonstrated the formation

131
ICH₃ $\xrightarrow{\beta}$ 131 XeCH₃⁺ (3a)

$${}^{32}\text{BrCH}_3 \xrightarrow{\beta^-} {}^{82}\text{KrCH}_3^+$$
 (3b)

of methyl-cationized xenon in the reaction between xenon and protonated fluoromethane (eq 4a), 15 whereas Hovey et al. 16

1

generated methyl-cationized krypton by similar processes (eqs 4b and 4c).

$$CH_3FH^+ + Xe \rightarrow XeCH_3^+ + HF$$
 (4a)

 $CH_3FH^+ + Kr \rightarrow KrCH_3^+ + HF$ (4b)

$$N_2 CH_3^+ + Kr \rightarrow Kr CH_3^+ + N_2$$
 (4c)

The methyl cation affinities (MCA) have been determined from gas-phase methyl cation transfer equilibrium measurements and found to be 2.2 and 1.9 eV for xenon and krypton, respectively.^{8,16} These MCA's indicate that the "inert" noble gas atoms can establish a remarkably strong bond with the methyl cation which can be considered to have covalent character.

The generally found simple linear relationship between ionization energies, gas-phase proton affinities, and/or methyl cation affinities^{8,16} led to the suggestion that also methylated argon cations would be energetically accessible via a reaction between protonated fluoromethane and argon as follows from the data presented in Figure 1. This figure shows proton affinities (PA) and methyl cation affinities (MCA) of the noble gases, and for comparison, of the hydrogen halides, as a function of their ionization energies.

Since an excellent linear relationship is found between the proton affinities of the noble gases and their ionization energies (Figure 1) it seems reasonable to anticipate a linear relationship between the methyl cation affinities and the ionization energies of the noble gases as well. Based on the methyl cation affinities of xenon and krypton as determined from methyl cation transfer equilibrium measurements (see above), a linear relationship predicts the methyl cation affinity of argon to be about 1.6 eV, which is larger than the experimentally determined methyl cation affinity of hydrogen fluoride of $1.5 \text{ eV}^{8,9}$ (Figure 1). Yet, in the reaction between protonated fluoromethane and argon only a trace of the possible methylated argon product ion has been observed under ambient temperature conditions.^{8,16}

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Figure 1. Experimentally determined proton (PA) and methyl cation affinities (MCA) of the noble gases and the hydrogen halides as a function of their ionization energies.

In sharp contrast with the above-predicted MCA of argon of 1.6 eV, Hiraoka et al. have reported a MCA of only 0.5 eV (Figure 1) as determined from equilibrium association measurements of the methyl cation and argon in a high-pressure ion source.¹⁷ The authors claim that this value can be reproduced by ab initio calculations.¹⁷ Surprisingly, they state that the MCA of 0.5 eV is unexpectedly high!¹⁷

Methyl-Cationized Molecular Oxygen. To our knowledge no bimolecular methyl cation transfer to molecular oxygen has been reported. Yet, $CH_3O_2^+$ has been generated via ternary ion/ molecule association reactions.³ The observed methyl transfer to molecular nitrogen (eq 5) strongly indicates that the ion has the methylperoxy ion structure. Much attention has been paid

$$CH_3O_2^+ + N_2 \rightarrow CH_3N_2^+ + O_2 \tag{5}$$

to the reaction of the molecular ion of oxygen with the methane molecule.¹⁸⁻²² Although a large number of possible exothermic reaction channels are open at room temperature, the dominant product of the reaction is $CH_3O_2^+$. The structure of this ion has been the subject of many studies. The 8-keV collision-induced dissociation (CID) spectra of several isomeric $CH_3O_2^+$ ions generated from different precursors have been reported.²³ From these results it has been established that the $CH_3O_2^+$ ion generated via the reaction of the molecular ion of oxygen with the methane molecule has a hydroperoxymethyl cation structure, CH_2OOH^+ .²⁰⁻²²

The relative energies of 18 structural, geometric, and electronic isomers of $CH_3O_2^+$ ions have been predicted by ab initio calculations.²⁴ These calculations show that several isomers, such as the protonated formic acid, are considerably lower in energy (>4 eV) than the lowest triplet state of the methylperoxy cation. Therefore, it is quite peculiar that the methylperoxy cation can have a lifetime of more than a millisecond.^{3,22} A possible reason why isomerization is hindered may be spin conservation. The methyl-cationized molecular oxygen, formed via a ternary association reaction, most likely is formed in the lowest triplet state, because the lowest state of molecular oxygen is a triplet state (the first electronic excited singlet state, ${}^{1}\Delta_{g}$, is ≈ 1.0 eV higher in energy²⁵). If for the isomerization spin conservation is required, the energy of the triplet state of the methylperoxy cation must be compared with the triplet state of the other isomers. Although to our knowledge the energies of these states are not known, they may well be a few electronvolts higher than the energies of the lowest singlet states and consequently spin conservation may hamper any isomerization of the methylperoxy cation. Such a "spin forbidden" isomerization is also predicted to play an important role in the stabilization of the triplet methyl-cationized oxygen atom, +OCH₃.^{26,27}

The theoretical calculations show that the MCA of molecular oxygen is $0.8 \text{ eV}.^{24}$

Protonated Methane as Methyl Cation Donor. In a previous study we have demonstrated the ability of protonated ethane to react as a methyl cation donor.²⁸ Also, the poor capability of

protonated methane to react as methyl cation donor was discussed briefly. To our knowledge, the methyl cation affinities of methane and molecular hydrogen have not been determined by methyl cation transfer reactions. If it is assumed that the ions formed by protonation of ethane and methane are identical to the ones generated by methyl cation transfer to methane and molecular hydrogen, respectively, the methyl cation affinities may be calculated using the relation

$$MCA(M) = \Delta H_{f}(CH_{3}^{+}) + \Delta H_{f}(M) - \Delta H_{f}(MCH_{3}^{+})$$
(6)

where $\Delta H_{\rm f}({\rm MCH_3^+})$ may be deduced from the known proton affinity of the MCH_2 neutral molecules. If this relation is used, the methyl cation affinities of methane and hydrogen are found to be 1.8 and 1.9 eV, respectively.²⁹ Therefore, it is expected that protonated methane can react with several neutral molecules M via a methyl cation transfer. Only a few reactions in which CH₅⁺ transfers a methyl cation have been reported, i.e., in which M was molecular nitrogen,³ atomic nitrogen,^{30,31} and atomic oxygen.³⁰ As reported previously,²⁸ the difference in reactivity of protonated methane and protonated ethane toward water is remarkable. Although both reaction systems are comparable as far as energetics of the starting and final products are concerned, protonated ethane exhibits a fair competition between proton and methyl cation transfer to water, whereas protonated methane exclusively transfers a proton to water. In contrast with the methyl cation transfer reactions from protonated ethane, it seems that the methyl transfer reactions from CH₅⁺ are hampered by a considerable barrier.

These previous findings²⁸ led us to a further study on the ability of protonated methane to react as a methyl cation donor. To this end, the dependence of the translational energy of the protonated methane on the observed reactivity has been examined in the reactions with argon, krypton, and xenon. Similarly, the dependence of the translational energy of the protonated fluoromethane on the observed reactivity in the reactions with argon and molecular oxygen has been examined.

Experimental Section

The ion/molecule reactions were studied in a Bruker Spectrospin CMS 47X FT-ICR mass spectrometer, equipped with a 4.7-T magnet and an external ion source. The general operating procedures, for ion manipulation (selection/detection), have been described previously.³²⁻³⁴

The reactant ions were prepared in the external chemical ionization source. Protonated methane was generated by selfprotonation of methane, protonated fluoromethane was generated by self-protonation of fluoromethane. Typical chemical ionization pressures used in the source were ≈ 3 Pa in the case of methane and 1 Pa in the case of fluoromethane. Primary ions were generated by bombardment with relatively low energy electrons (20-30 eV). The relative amounts of primary and secondary ions extracted from the external source were controlled by adjusting both the chemical ionization gas pressure and the repeller potential. The generated ions, extracted from the source, were transferred via a set of electrical lenses to the FT-ICR cell, which was kept at a temperature of 298 K. Background pressure in the FT-ICR cell was less than 1.0×10^{-7} Pa. All the substrates (methyl cation acceptors) were leaked into the FT-ICR cell via a Balzers precision valve up to pressures of about 5.0×10^{-6} Pa. The ion beam from the external ion source was gated for 30 ms. After an ion trapping delay of 0.5 s all ions except for the reactant CH_5^+/CH_3FH^+ ions were ejected from the FT-ICR cell by resonant single-frequency excitation fields of about 1 ms duration. The electric field strength used was about 300 V/m. Following this selective ion ejection, an additional delay of 1.5 s was incorporated to achieve collisional relaxation of the harmonic trapping motion of the ions. This relaxation is essential in order to secure that the reactant ions have no more than thermal velocities prior to the determination of the reaction threshold energies (see below). Following this relaxation delay during which no reaction occurred, the reactant CH,+/ CH₃FH⁺ ions were translationally excited by a resonant singlefrequency excitation field of variable duration (between 0.6 and 30 μ s). In each individual experiment the actual amplitude of the field potential applied to the excitation electrodes of the FT-ICR cell was measured. For the excitation of the protonated methane ions an electric field strength of 312 V/m was used, whereas for the excitation of the protonated fluoromethane ions an electric field strength of 292 V/m was used. It was calculated that the maximum cyclotron radius of the translationally excited ions after an excitation duration of 30 μ s was less than 0.1 cm. After the reactant ion excitation event a reaction delay of 0.5 s was applied, during which the translationally excited ions were allowed to react with the neutral gaseous molecules in the FT-ICR cell. Finally, the normalized abundances of all the reactant and product ions were individually determined from the high-resolution heterodyne mass spectra as a function of the duration of the translational excitation of the reactant ion, and thus as a function of the center-of-mass collision energy which was calculated by eq 7, where $T_{\rm exc}$ is the duration of the reactant ion excitation event,

$$E_{\text{center of mass}} = T_{\text{exc}^2} \frac{q \omega_{\text{eff}} E_0^2}{8B} \left(\frac{M_{\text{t}}}{M_{\text{p}} + M_{\text{t}}} \right)$$
(7)

 $\omega_{\rm eff}$ is the angular cyclotron frequency of the reactant ion, B is the magnetic field strength, $M_{\rm p}$ and $M_{\rm t}$ are the masses of the reactant ion and the neutral collision/reaction partner, and E_0 is the strength of the excitation field.

Determination of Center-of-Mass Collision Energy Thresholds of Uni- and Bimolecular Reactions via Energy-Resolved Collisional Activation. In recent years, collisional activation has been used to study the energy dependence of unimolecular reactions in the low translational energy range (0-100 eV) using various mass spectrometric techniques such as guided ion beam instruments, 35-37 flowing afterglow triple quadrupole instruments,^{38,39} quadrupole ion-trap instruments,⁴⁰ tandem instruments of the BEQQ type,^{41,42} and Fourier transform ion cyclotron resonance (FT-ICR) instruments.43-47 The applicability of FT-ICR instruments to perform translational energy-resolved measurements has been disputed³⁷ as it was suggested that rf excitation of the ions in an ICR cell would result in very broad energy distributions, which may not be characterized easily. However, recent FT-ICR translational energy-resolved collisional activation studies44,46,47 have shown that the obtained energy threshold values of unimolecular reactions agreed remarkably well with the known literature values. Low translational energy resolved collisional activation has proven to be successful in the determination of the thermochemistry of ions^{36,38,44,47} and neutral molecules.³⁹ Translational energy dependence of bimolecular ion/molecule reactions has been studied with guided ion beam³⁵⁻³⁷ and more recently also with FT-ICR instruments.⁴⁷ For reaction systems in which competitive reactions occur, the shape of the product ion "appearance" curves can be complex and difficult to describe theoretically. An empirical method for the description of the curve representing the translational energy dependence of the product ion yields of endothermic reactions has been developed by Armentrout et al.^{36,48,49} This model describes the energy dependence of the product ion yield, $\sigma(E)$, by eq 8, in which σ_0 is an empirical energy independent

$$\sigma(E) = \sigma_0 (E_{\rm cm} - E_{\rm threshold})^n / E_{\rm cm}^m \tag{8}$$

scaling factor, $E_{\rm cm}$ is the center-of-mass collision energy, $E_{\rm threshold}$ is the threshold energy, and *n* and *m* are variables. The threshold energy is obtained by optimizing σ_0 , $E_{\rm threshold}$, *n*, and *m* to obtain a best fit to the experimental curve. This empirical model has proven to be successful for the determination of accurate threshold reaction energies.^{36,39,44} In addition, information about the reaction mechanisms involved has been be deduced from the shape of the calculated product ion "appearance" curves.⁴⁷

In the present study the center-of-mass collision energy thresholds, E_{t} , for the studied reactions are obtained by optimizing σ_0 , $E_{threshold}$, and n in eq 8 to accomplish the best fit to the experimental data. The analysis was restricted to the form where m = 1 since it was shown that this form is one of the most useful in deriving accurate thermochemistry,^{47,50} whereas in addition this form has been predicted theoretically for translationally driven reactions.⁵¹

TABLE I: Energetics (ΔH) and Determined Center-of-Mass Collision Energy Thresholds (E_{thres}) (eV)

reaction no.	reaction	products	$\Delta H_{\text{reaction}}$ (lit.) ^a	$E_{\rm thres}{}^b$	nc
11a	$CH_5^+ + Ar \rightarrow$	$CH_{3}^{+} + H_{2} + Ar$	1.9	1.9	1.45
116	2	ArH́+ + CH₄	1.9		
11c		$ArCH_1^+ + H_2$	1.4	0.6	1.45
12a	$CH_{s}^{+} + Kr \rightarrow$	$CH_{1}^{+} + H_{2} + Kr$	1.9	1.9	1.49
12b	5	KrH ⁺ + CH₄	1.3	2.9	1.50
12c		$KrCH_3^+ + H_2$	0.0	0.5	1.50
13a	CH ₅ ⁺ + Xe →	$CH_{3}^{+} + H_{2} + Xe$	1.9	1.9	1.59
13b	•	XeH ⁺ + CH₄	0.5	0.4	1.62
13c		$XeCH_3^+ + H_2$	-0.3	0.6	1.62
14a	$CH_{3}FH^{+} + Ar \rightarrow$	$CH_3^+ + HF + Ar$	1.5	1.5	1.13
14b	2	ArH ⁺ + CH ₃ F	2.5		
14c		ArCH ₁ ⁺ + HF	1.0	0.3	1.53
15a	$CH_3FH^+ + O_2 \rightarrow$	$CH_{1}^{+} + HF + O_{2}$	1.5	1.4	1.35
15b	5 2	$O_{2}H^{+} + CH_{3}F$	1.9		
15c		$0.CH^{+} + HF$	0.7	0.4	1.38

^a The energetics of the reactions are calculated from the data taken from ref 29. In addition, the heat of formation of ArCH₃⁺ is calculated from the MCA of argon of 0.5 eV, as determined from association equilibrium measurements and ab initio calculations in ref 17. The heats of formations of KrCH₃⁺ and XeCH₃⁺ are calculated from the MCA of krypton and xenon of 1.9 and 2.2 eV, respectively, as determined from methyl cation transfer equilibrium measurements in ref 8. The heat of formation of CH₃O₂⁺ is calculated from the MCA of molecular oxygen of 0.8 eV, as obtained by ab initio calculations in ref 24. ^b For method of determination see text. Estimated experimental uncertainty is 0.15 eV. ^cOptimized value for variable *n* in eq 8 obtained from the best fit to the experimental data (see text).

The obtained threshold energies were corrected for Doppler broadening by adding $3[M_p/(M_p + M_t)]kT$, where k is the Boltzmann constant and T the estimated temperature (298 K).^{44,52}

It should be noted that special care was taken to avoid excess internal and translational excitation of the reactant ions (due to off-resonance and/or so-called z-excitation, effectuated by rf-fields used to eject unwanted ions from the ICR cell³⁴) prior to translational excitation by the rf field (see above). The ratio of probabilities, Q_2/Q_1 , for the reactant ion to undergo two and one collisions with the target molecules during the reaction period, T_{react} , can be estimated using eq 9,^{44,47} in which C_n is the number

$$\frac{Q_2}{Q_1} = \frac{C_n \pi e (r_p + r_t)^2 E_0 T_{exc} T_{react}}{4M_p}$$
(9)

density of the target gas molecules, e is the electronic charge, and r_p and r_t are the average radii of the reactant ion and the target molecule. By using eq 9 it can be estimated that, for the studied reaction systems under the experimental conditions given above, the ratio, Q_2/Q_1 , for reactant ions excited to a translational energy above the reaction threshold energy, is maximally 0.35. Although this value indicates that multiple collisions can occur, it may be argued that low energy (nonreactive) multiple collisions of a translationally excited reactant ion with a stationary reaction gas molecule stepwise can deposit more energy in the reaction complex than calculated with eq 7.

Results

Reactivity of Thermal Protonated Methane and Protonated Fluoromethane. The studied reaction systems are listed in Table I, which includes the estimated reaction enhalpies for the a priori conceivable reaction channels. None of these reaction systems are observed to give rise to product ions. This behavior is to be expected for the reaction systems 11, 14, and 15 where no conceivable exothermic reaction channels are open. However, methyl cation transfer from protonated methane to krypton (eq 12c) and xenon (eq 13c) is thermoneutral and slightly exothermic, respectively (Table I). Yet, even after a reaction delay of 25 s no methyl-cationized krypton and xenon could be observed, indicating that the corresponding reaction rate constants at thermal energies are lower than 10^{-13} cm³ mol⁻¹ s⁻¹. Therefore, it has to be assumed that these reactions are hampered by a considerable barrier.

Reactivity of Translationally Excited Protonated Methane and Protonated Fluoromethane. Reaction between Protonated Methane



Figure 2. Relative cross sections for the formation of product ions in the reaction between protonated methane and argon determined as a function of the center-of-mass collision energy. Zooming in on the data on the formation of $ArCH_3^+$ is shown in the inset of the figure where the magnitude of the indicated error bars is estimated from the average noise level of the individually detected narrow band ion signal responses.



Figure 3. Relative cross sections for the formation of product ions in the reaction between protonated methane and krypton determined as a function of the center-of-mass collision energy.

and Argon. Increasing the translational energy of the protonated methane ions in an atmosphere of argon gas has been observed to open both the reaction channels towards dissociation of the CH_5^+ ions into $CH_3^+ + H_2$ fragments (eq 11a) and the methyl cation transfer to argon (eq 11c). The appearance curves of the CH_3^+ and $ArCH_3^+$ ions are given in Figure 2 which gives a direct indication of the relative cross sections of these two processes. The cross section for the methyl cation transfer reaction is at a center-of-mass collision energy of about 4 eV at a maximum, but even at this energy the cross section of the methyl-transfer reaction is a factor of 30 smaller than the cross section for collision-induced dissociation into CH_3^+ and H_2 as shown by the inset in Figure 2. The obtained center-of-mass collision energy thresholds (for the method of determination of the threshold energies see above) are given in Table I.

Formation of ArH^+ ions (eq 11b) has not been observed, implying that the cross section for this process is even smaller than for the formation of $ArCH_3^+$ ions.

Reaction between Protonated Methane and Krypton. Increasing the translational energy of the protonated methane ions in an atmosphere of krypton gas has been observed to open the reaction channels toward dissociation of the CH_5^+ ions into $CH_3^+ + H_2$ fragments (eq 12a), the proton transfer to krypton (eq 12b), and the methyl cation transfer to krypton (eq 12c). In the heterodyne high-resolution detection mode, only the normalized abundances of ⁸⁴KrH⁺ and ⁸⁴KrCH₃⁺ have been measured. The actual normalized abundances of the KrH⁺ and KrCH₃⁺ product ions summed over all the Kr isotopes have been obtained by multiplying the normalized abundances of the ⁸⁴KrH⁺ and ⁸⁴KrCH₃⁺ product ions by (100/56.90) (the natural contribution of the ⁸⁴Kr isotope is 56.90%). Figure 3 shows the resulting appearance curves for the CH₃⁺, KrH⁺, and KrCH₃⁺ product ions. As for the reaction



Figure 4. Narrow-band heterodyne mode mass spectra of CH_3^+ , ¹³²XeH⁺, and ¹³²XeCH₃⁺ product ions generated in the reaction of translationally activated protonated methane and xenon showing the relative contributions of these product ions to the total product ion yield at various center-of-mass collision energies. To obtain the actual relative abundance of the XeH⁺ and XeCH₃⁺ product ions summed over all the Xe isotopes the relative abundances of the ¹³²XeH⁺ and ¹³²XeCH₃⁺, product ions have to be multiplied by (100/26.89) (the natural contribution of the ¹³²Xe isotope is 26.89%).

system 11, the collision-induced dissociation into CH_3^+ and H_2 is dominant at higher energies. At center-of-mass collision energies above about 10 eV the proton-transfer reaction gains importance and starts to dominate over the methyl cation transfer reaction. The obtained center-of-mass collision energy thresholds for the three competing reaction channels are given in Table I.

Reaction between Protonated Methane and Xenon. Increasing the translational energy of the protonated methane ions in an atmosphere of xenon gas has been observed to open the reaction channels toward dissociation of the CH_5^+ ions into $CH_3^+ + H_2$ fragments (eq 13a), the proton transfer to xenon (eq 13b) and the methyl cation transfer to xenon (eq 13c).

In Figure 4 typical heterodyne high-resolution mass spectra of the ¹³²XeH⁺, ¹³²XeCH₃⁺, and CH₃⁺ ions are shown for various center-of-mass collision energies. In the heterodyne high-resolution detection mode, only the normalized abundances of ¹³²XeH⁺ and 132 XeCH₃⁺ have been measured. The actual normalized abundances of the XeH⁺ and XeCH₃⁺ product ions summed over all the Xe isotopes have been obtained by multiplying the normalized abundances of the ¹³²XeH⁺ and ¹³²XeCH₃⁺ product ions by (100/26.89) (the natural contribution of the ¹³²Xe isotope is 26.89%). Figure 5 shows the resulting appearance curves for the CH_3^+ , XeH⁺, and XeCH₃⁺ product ions. The results in Figure 5 show that both the translational energy driven proton and methyl cation transfer reactions are highly efficient. Over the total translational energy range studied, the proton transfer (eq 13b) cross section is higher than the cross section of the competing unimolecular dissociation (eq 13a), whereas for the methyl cation transfer (eq 13c) the cross section comes down under the cross



Figure 5. Relative cross sections for the formation of product ions in the reaction between protonated methane and xenon determined as a function of the center-of-mass collision energy.



Figure 6. Relative cross sections for the formation of product ions in the reaction between protonated fluoromethane and argon determined as a function of the center-of-mass collision energy.

section of the competing unimolecular dissociation above center-of-mass collision energies above 9 eV.

The obtained center-of-mass collision energy thresholds for the three competing reaction channels are given in Table I.

Reaction between Protonated Fluoromethane and Argon. Increasing the translational energy of the protonated fluoromethane in an atmosphere of argon gas has been observed to open both the reaction channels toward dissociation of the CH₃FH⁺ ions into CH_3^+ + HF fragments (eq 14a) and the methyl cation transfer to argon (eq 14c). In addition, CH_2F^+ ions have been observed as minor contribution to the product ion mixture, but the formation of this ion has not been studied in more detail. The thermicities of the unimolecular dissociations of protonated methane into CH_3^+ + HF and CH_2F^+ + H₂ are almost equal. However, the latter process is believed to proceed via a considerable barrier.53 No evidence has been found for the formation of ArH+ (eq 14b). Since this proton-transfer reaction channel (eq 14b) is estimated to be about 1 eV more endothermic than the competing unimolecular dissociation (eq 14a) (Table I), it was to be expected that the cross section for the formation of ArH⁺ is very small. The appearance curves of the CH_3^+ and $ArCH_3^+$ ions are The cross section of the methyl-transfer given in Figure 6. reaction is at a center-of-mass collision of ≈ 2.5 eV at a maximum. At this energy the cross section of the methyl-transfer reaction is a factor of 3 smaller than the cross section for collision-induced dissociation into CH₃⁺ and HF. Clearly, the translationally driven methyl cation transfer from protonated fluoromethane to argon is much more efficient than the translationally driven methyl cation transfer from protonated methane to argon (see above)

The obtained center-of-mass collision energy thresholds for the formation of CH_3^+ and $ArCH_3^+$ are given in Table I.

Reaction between Protonated Fluoromethane and Molecular Oxygen. Increasing the translational energy of the protonated fluoromethane in an atmosphere of molecular oxygen gas has been observed to open both the reaction channels toward dissociation of the CH_3FH^+ ions into $CH_3^+ + HF$ fragments (eq 15a) and the methyl cation transfer to molecular oxygen under formation





Figure 7. Relative cross sections for the formation of product ions in the reaction between protonated fluoromethane and molecular oxygen determined as a function of the center-of-mass collision energy.

of $CH_3O_2^+$ (eq 15c). As for the reaction with argon, CH_2F^+ ions have been observed as minor contribution to the product ion mixture, but the formation of this ion has not been studied in more detail (see above). As mentioned in the Introduction, at least four possible isomers of this ion are known. The present route of generation indicates that the ion has a methylperoxy ion structure. This structure is supported by the low-energy collision-induced dissociation of the $CH_3O_2^+$ product ion, which exclusively shows the loss of the oxygen molecule. Moreover, the $CH_3O_2^+$ product ion has been observed to efficiently transfer a methyl cation to both molecular nitrogen and fluoromethane, which is characteristic for the methylperoxy ion structure.

No evidence has been found for the formation of O_2H^+ (eq 15b). Since this proton-transfer reaction channel (eq 15b) is estimated to be about 0.4 eV more endothermic than the competing unimolecular dissociation (eq 15a) (Table I), it was to be expected that analogous to the formation of ArH⁺ in the reaction system 14, the cross section for the formation of O_2H^+ in the reaction system 15 is very small.

The appearance curves of the CH_3^+ and $O_2CH_3^+$ ions are given in Figure 7. The cross section of the methyl-transfer reaction is at a center-of-mass collision energy of ≈ 2.0 eV at a maximum. At this energy the cross section of the methyl-transfer reaction is a factor of 4 smaller than the cross section for collision-induced dissociation into CH_3^+ and HF, indicating that the translationally driven methyl transfer from protonated fluoromethane to molecular oxygen is a relatively efficient process.

The obtained center-of-mass collision energy thresholds for the formation of CH_3^+ and $O_2CH_3^+$ are given in Table I.

Reaction of Protonated Fluoromethane with Neon. Increasing the translational energy of the protonated fluoromethane in an atmosphere of neon gas exclusively has been observed to open the reaction channel toward unimolecular dissociation of the CH_3FH^+ ions. No evidence has been found for the formation of either NeH⁺ or NeCH₃⁺, indicating that the cross sections of the formation of these product ions are orders of magnitude smaller than the cross section of the unimolecular dissociation of protonated fluoromethane.

Discussion and Conclusions

For the reaction systems studied (eqs 11-15) only translational energy driven reactions have been observed.

Collision-Induced Dissociation of CH_5^+ and CH_3FH^+. For the loss of a hydrogen molecule from CH_5^+ induced by collisions with argon (eq 11a), krypton (eq 12a), and xenon (eq 13a) the determined threshold center-of-mass collision energy is 1.9 eV (Table I). The results of a study on the temperature dependence of the association between the CH_3^+ and H_2^3 and the hydrogen exchange between these reaction partners⁵⁴ indicate that the loss of a hydrogen molecule from CH_5^+ proceeds without significant reverse activation energy. Consequently, the determined threshold energy can be associated with the endothermicity of this reaction channel. Therefore, the perfect agreement between the reaction endothermicity and the determined threshold energy (Table I) gives credibility to the presently used method.

This is further supported by the determined threshold center-of-mass collision energy of 1.5 and 1.4 eV associated with the loss of a HF molecule from CH₃FH⁺ induced by collisions with argon (eq 14a) and molecular oxygen (eq 15a), respectively. Also, these threshold energies agree with the reaction endothermicity, which is to be expected given the negligible reverse activation energy as indicated by the small kinetic energy release which accompanies the loss of a HF molecule from the metastable CH₃FH⁺ ions, which is found to be between 4⁵⁵ and 25 meV.⁵³

Translational Energy Driven Proton-Transfer Reactions of CH_5^+ and CH_3FH^+ . The 1.9-eV endothermic proton transfer from translationally activated CH_5^+ ions to argon (eq 11b) has been observed not to compete with the unimolecular dissociation channel (eq 11a). This may not be surprising given the endothermicity of this proton-transfer reaction channel which is very close to the endothermicity of the entropy-favored dissociation channel.

On the other hand, the 1.3-eV endothermic proton transfer from the translationally activated CH_5^+ ions to krypton (eq 12b) has been observed to compete with the unimolecular dissociation channel (eq 12a). However, the determined threshold energy of 2.9 eV suggests that the activation energy is around 1.5 eV higher than the endothermicity of the proton transfer (Table I). This result seems very unrealistic and it thus appears that the actual threshold of this proton transfer with a very small cross section (Figure 3) is obscured by the very dominant dissociation channel.

The 0.5-eV endothermic proton transfer from translationally activated CH_5^+ ions (eq 13b) is the most dominant channel in the reaction with xenon (Figure 5). The determined threshold center-of-mass collision energy of 0.4 eV is very close to the endothermicity of this proton transfer (Table I) which indicates that this process proceeds without significant reverse activation energy.

Proton transfers from translationally activated CH_3FH^+ ions to both argon (eq 14b) and molecular oxygen (eq 15b) are energetically and entropically less favored than the competing unimolecular dissociation into CH_3^+ and HF (eqs 14a and 15a). Consequently, the cross sections of these proton-transfer reactions are so low that these processes cannot compete with the unimolecular dissociation channel.

Translational Energy Driven Methyl Cation Transfer Reactions of CH₅⁺ and CH₃FH⁺. The methyl cation transfer from translationally activated CH₅⁺ ions to argon (eq 11c) shows a threshold center-of-mass collision energy of only 0.6 eV. In conflict, this threshold energy is 0.8 eV lower than the endothermicity of this process estimated on the basis of the MCA of argon of 0.5 eV (Table I) as reported by Hiraoka et al., who obtained this value from equilibrium association measurements of the methyl cation and argon in a high-pressure ion source.¹⁷ However, the determined threshold energy of 0.6 eV is 0.3 eV higher than the endothermicity of the methyl cation transfer estimated on the basis of the MCA of argon of 1.6 eV as predicted by the linear relationship between the MCA's of the noble gases and their ionization energies as shown in Figure 1 (see above). This result suggests a reverse activation energy for this methyl cation transfer of around 0.3 eV!

Moreover, the methyl cation transfer from translationally activated CH₃FH⁺ ions to argon (eq 14c) shows a threshold center-of-mass collision energy of only 0.3 eV. Again in conflict, this threshold energy is 0.7 eV lower than the endothermicity of the methyl cation transfer reaction based on the MCA of argon of 0.5 eV as determined by Hiraoka et al.¹⁷ (Table I). However, based on the MCA of argon of 1.6 eV the determined threshold of 0.3 eV is about 0.4 eV higher than the thermicity of the methyl cation transfer, suggesting a reverse activation energy for this methyl cation transfer of around 0.4 eV! It thus appears from the presently determined center-of-mass collision energy thresholds for the formation of $ArCH_3^+$ (eqs 11c and 14c) that the MCA of argon is much closer to 1.6 eV than to 0.5 eV! The methyl cation transfer from translationally activated CH5⁺ ions to krypton (eq 12c) and xenon (eq 13c) shows a threshold center-of-mass collision energy of 0.5 and 0.6 eV, respectively (Table I). Since the methyl cation transfer to krypton is thermoneutral and the



Figure 8. Experimentally determined methyl cation affinities of oxygen-containing compounds as a function of the corresponding oxygen 1s electron binding energies. Methyl cation affinities are taken from refs 8 and 9, and oxygen 1s electron binding energies are taken from ref 60.

methyl cation transfer to xenon is 0.3 eV exothermic the determined center-of-mass collision energy thresholds indicate that the reverse activation energies for these processes are 0.5 and 0.9 eV, respectively.

The methyl cation transfer from translationally activated CH_3FH^+ ions to molecular oxygen (eq 15c) shows a threshold center-of-mass collision energy of only 0.4 (Table I). Unfortunately, only an experimental upper limit of the MCA of molecular oxygen is available as follows from the observed methyl cation transfer from the methyl-cationized molecular oxygen to molecular nitrogen (see above), for which an experimental MCA has been established of 2.1 eV.⁸ Ab initio calculations²⁴ show that the MCA of molecular oxygen is around 0.8 eV. An independent indication for the MCA of molecular oxygen can be obtained by correlating the oxygen 1s core electron binding energies with the known methyl cation affinities of methyl-cationized oxygen containing compounds. It has been demonstrated that a linear relationship exists between the oxygen 1s core electron binding energies^{56,57} and the proton affinities.^{58,59} Analogously, it is presently shown in Figure 8 that also a linear correlation exists between the oxygen 1s core electron binding energies and the corresponding methyl cation affinities.

The empirical relationship between the oxygen 1s core electron binding energies and the gas-phase methyl cation affinities is given by eq 10, in which O 1s ESCA is the oxygen 1s core electron

$$MCA(X) = 361.73 - 0.6646(O \ 1s \ ESCA) \ (eV) \ (10)$$

binding energy. The square of the correlation coefficient found for this linear relation is 0.96. Unfortunately, the lack of data for oxygen-containing compounds with relatively low methyl cation affinities requires a hazardous extrapolation to O_2 . Yet, given the reported oxygen 1s core electron binding energy of molecular oxygen of 543.1 eV^{60} the above correlation predicts a MCA for molecular oxygen between 0.6 and 1.0 eV. Based on these values the endothermicity of the methyl cation transfer from CH₃FH⁺ to molecular oxygen (eq 15c) can be estimated between 0.5 and 0.9 eV. This estimated endothermicity is slightly higher than the presently determined threshold energy for this reaction of 0.4 eV (Table I), which corresponds to an MCA of molecular oxygen of about 1.1 eV. Yet, since the determined threshold energy is close to the endothermicity it may be concluded that the methyl cation transfer from CH₃FH⁺ to molecular oxygen proceeds without a significant reverse activation energy.

From the above results it appears that CH_5^+ can act as a methyl cation donor if the competing proton transfer is energetically less favored as in the reactions with argon, krypton, and xenon (Table I). If a MCA for argon is adopted of 1.6 eV (see discussion above) the double-minimum potential energy reaction profile for the methyl cations transfers can be constructed on the basis of the estimated reaction enthalpies of 0.3, 0, and -0.3 eV and threshold energies of 0.6, 0.5, and 0.6, for the reaction with argon, krypton, and xenon, respectively. The potential energy reaction profiles are pictured in Figure 9. The studied methyl cation transfers



Figure 9. Outline of the potential energy reaction profiles for the methyl cation transfers from protonated methane to argon, krypton, and xenon, constructed on the basis of the estimated reaction enthalpies of 0.3, 0, and -0.3 eV (see text) and the determined threshold energies of 0.6, 0.5, and 0.6, respectively.

from protonated methane suffer from considerable reaction barriers (see Table I and Figure 9). Surprisingly, the activation energies for the methyl cation transfers from protonated methane to all studied noble gas atoms are very close, whereas the reverse activation energy increases in the series argon, krypton, and xenon. Because the activation energy does not significantly vary with the methyl cation acceptor it looks that in the transition state there is little specific interaction between CH_5^+ and the noble gas atom. This points to transition states in which the weakening of the two-electron three-center C-H-H bond in protonated methane is poorly assisted by bond formation between the methyl group and the noble gas atom.

Because the methyl cation affinities of argon and molecular oxygen are not known accurately it is not clear whether the reactions between protonated fluoromethane and argon/molecular oxygen are hampered by significant energy barriers. However, in contrast to protonated methane, protonated fluoromethane transfers readily a methyl cation to krypton,¹⁶ methane,²⁸ and xenon.¹⁵ Yet, the reaction enthalpies for the methyl cation transfer from protonated methane to xenon (-0.3 eV, Table I) and from protonated fluoromethane to krypton ($-0.4 \text{ eV}^{8,16}$) or methane (-0.3 eV²⁸) are similar. Furthermore, it was found previously²⁸ that the methyl cation transfer from protonated methane to water is also hampered by a considerable energy barrier, in contrast with the again energetically similar methyl cation transfer from protonated ethane to water. Therefore, it seems plausible that the observed reaction barriers in the methyl cation transfer reactions of protonated methane are characteristic for this species. The reason most likely is the specific type of bonding of H₂ to the methyl group in protonated methane.

The methyl cation transfers from protonated fluoromethane only involve the breaking of a relatively weak two-center C-FH bond,⁵³ whereas methyl cation transfers from protonated methane involve a more complex breaking of the two-electron three-center C-H-H bond.

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