Elementary Reactions of Energy-Selected Fluoroethene and 1,1-Difluoroethene Ions. 2. The Kinetics of HF-Loss

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The kinetics of unimolecular fragmentation reactions of energy selected fluoroethene and 1,1-difluoroethene ions has been investigated by the threshold photoelectron photoion coincidence (TPEPICO) technique. A systematic comparison of kinetic data recorded in a linear and a reflecting time-of-flight mass spectrometer is presented. From the analysis of the TPEPICO-TOF spectra complete $k(E)$ curves have been derived over a range from 10^4 to 10^7 s^{-1}. The current work complements previous work aimed at the kinetic energy released in the elementary reactions of the title molecules (Güthe, F.; Locht, R.; Leyh, B.; Baumgärtel, H.; Weitzel, K.-M. *J. Phys. Chem. A* **1999**, *103*, 8404).

1. Introduction

In a previous paper we have investigated the unimolecular fragmentation reactions of fluoroethene ($CH_2{=}CHF$) and 1,1-difluoroethene ($CH_2{=}CF_2$) cations with particular emphasize on the kinetic energy released (KER) into the products.[1] From extensive theoretical analysis of experimental data we were able to derive complete kinetic energy release distributions (KERD) of these reactions. Interestingly the KERD for the HF-loss and F-loss reaction channels were found to follow a significantly different energy dependence, i.e., for the HF-loss channel the average KER decreases with increasing energy, while for the F-loss channel the KER increases. In that work also a number of higher energetic reaction channels and consecutive reactions were identified from the breakdown diagram and the kinetic energy release distribution (KERD) up to 20 eV excitation energy.

To complement the work mentioned above, we focus on the metastable reactions near the reaction threshold in the current work. Here, information on the reaction kinetics will be derived by analyzing time-of-flight (TOF) spectra. To the best of our knowledge we will for the first time present a direct comparison of data recorded in a linear and a reflecting TOF (Reflectron). Therefore, it seems appropriate to briefly recall some of the established techniques for rate constant analysis. Pioneering work on the derivation of rate constants from asymmetric TOF distributions in linear TOF spectrometers has been reported by Baer et al.[2] Reflecting TOF spectrometers were first employed by Kühlewind et al.[3,4] for the derivation of rate constants in laser based experiments. That work analyzed the fragment signal originating from different regions of the spectrometer. Reflectrons were also utilized by Castleman et al.,[5] analyzing only signals originating from the acceleration region.

In previous work we have reported the simulation of TOF spectra recorded in a reflectron (RETOF spectra) which took into account the internal energy distribution of the dissociating ions.[6,7] In the current work we apply the same technique to the analysis of data from a linear TOF and present a comparison of results from the two kind of spectrometers.

The unimolecular decay of the fluoroethene cations appear to represent an interesting test case for extensive kinetic analysis. The energetics of chemical reactions of fluoroethene ions and 1,1-difluoroethene ions are in general well-known from electron impact studies,[8,9] photoionization work,[10−12] and from PEPICO work.[13,14] Those investigations agree in that the HF-loss is the energetically lowest reaction channel in both ions. The metastability of the HF-loss from fluoroethene and 1,1-difluoroethene ions has been observed by mass analyzed ion kinetic energy spectroscopy (MIKES).[15−18] The main result of such studies is the kinetic energy released (KER) upon the dissociation of the respective ions. In a recent TPEPICO study we have derived complete KER distributions (KERD) for e.g. the HF- and the F-loss from the title molecules.[1] MIKES experiments also showed a metastable signal for the H-loss from fluoroethene ions and the H- and F-loss from 1,1-difluoroethene ions.[15] In contrast to this, PEPICO experiments[13] only observed slow HF-loss from fluoroethene, with rate constants between 10^4 and 10^5 s^{-1}. Because of the experimental parameters up to 70% of all fragment ions were lost in that study because of discrimination due to the very large KER of the HF-loss channel. Here we note that we did in general not loose more than 10% of the fragment ions in our previous study.[1] Rate constants have also been reported for the cis- and trans- 1,2-difluoroethene,[19] but to our knowledge not for the 1,1-difluoroethene. However, early calculations based on a statistical theory predicted that the rate constant for HF-loss from 1,1-difluoroethene varies from 1.8×10^4 s^{-1} at threshold to 1.9×10^7 s^{-1} at 600 meV above threshold.[20]

The aim of the current work is to shed new light on the fragmentation kinetics of energy selected fluoroethene and 1,1-difluoroethene ions. Particular emphasis will be given to the HF-loss reaction near the dissociation threshold. Here, we will present a comparison of kinetic data obtained from different kinds of TOF spectrometers.

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2. Experimental Methods

The dissociation of fluoroethene and 1,1-difluoroethene ions has been investigated by means of the threshold photoelectron photoion coincidence technique (TPEPICO).[21,22] The experimental setup has been described in detail in previous work.[23,24] Only a brief account will be given here. All measurements were performed in an effusive beam at room temperature. The molecules were ionized by radiation from the synchrotron radiation facility BESSY I in Berlin, dispersed in the 3 m NIM1 beamline. Energy selection of ions is achieved by detecting threshold photoelectrons and photoions in coincidence. The electron energy analyzer (steradiancy principle) is designed to transmit threshold electrons preferentially. The experiments discussed in this paper have been performed at an overall resolution (fwhm) of ca. 15−20 meV (determined by the slits of the monochromator (200 μm) and the extraction field (E_{acc}) in the ionization region) with a weak “hot electron tail” toward high electron energies (corresponding to lower internal energies for the ions).

Two different mass spectrometer setups have been used to analyze these metastable reactions. One consists of a linear two stage time-of-flight spectrometer of Wiley McLaren-type[25] (E_{acc} = 17 V/cm, ion energy 300 V, field free drift region D = 30 cm). The other one is a reflecting ion time-of-flight (reflectron) spectrometer (E_{acc} = 40 V/cm, ion energy 600−1500 V, overall length = ca. 100 cm), which has been optimized for the investigation of metastable reactions.[23,26] Time-of-flight (TOF) spectra were recorded by employing threshold electrons as a start and ions as a stop signal for a time to amplitude converter (TAC) thus enforcing the coincidence condition.

3. Data Analysis

In this work two different methods have been used to derive kinetic data on the metastable reaction from experimental TOF distributions, which will be described in the following section.

Simulation of TOF Spectra in the Linear TOF Mass Spectrometer. In a linear TOF mass spectrometer, metastable reactions lead to asymmetric ion time-of-flight distributions. These originate from the distribution of locations in the acceleration region of the spectrometer, where the fragmentation occurs. While fragment ions formed instantaneously within the ion source arrive at the detector at the TOF of the daughter ion, those fragment ions formed in the field free drift region arrive at the TOF of the parent ion, and are thus indistinguishable from the latter. Fragment ions formed in the acceleration region arrive at the detector at an intermediate TOF. In the past such TOF spectra were in general simulated based on just one or two rate constants.[21,27] A more rigorous approach is clearly the simulation of several ion TOF spectra recorded at different excitation energies, taking into account the corresponding distribution of ion internal energies associated with a complete $k(E)$ curve. In general, this distribution of internal energies can arise from the finite instrumental resolution and from the thermal energy distribution of the sample. In the current work, we employ such an approach taking into account a complete distribution of ion internal energies associated with a complete rate constant curve $k(E)$. In a previous study of the HCl loss from chloroethane we have also taken into account a distribution of ion internal energies corresponding to a distribution of rate constants.[28]

More specifically the internal energy distribution of parent ions $P_{ion}(E)$ is here obtained by a convolution of the thermal energy of neutral molecules $P_{nrv}(E)$ and the experimental instrument function, $P_{res}(E)$, as has been described for the decay of ethane cations.[6] $P_{res}(E)$ is derived from a convolution of the optical resolution of the monochromator and the resolution of the electron energy analyzer. The latter can be estimated from a transmission function for steradiancy analyzers described by Spohr et al.[29] The resulting instrument function is found to agree with the measured TPE spectrum of the argon $^2P_{1/2}$ peak. As mentioned above the overall resolution is about 20 meV in this work. $P_{nrv}(E)$ is calculated from the known vibrational frequencies using vibrational densities of state calculated by the Beyer−Swinehart algorithm[30] and convoluted with the rotational density of states as described in previous work.[6] The frequencies employed in this work are listed in Table 1. The index n gives the number of active rotational degrees of freedom. How many of the three external rotors are active in the fragmentation reaction has to be determined from the analysis. However, since the HF-loss reaction is most likely dominated by a tight transition state we expect that n should be close to 1. As one example, Figure 1 shows the thermal energy distribution of neutral 1,1-difluoroethene molecules $P_{1rv}(E)$ and the instrument function $P_{res}(E)$, together with the ion internal energy distribution $P_{ion}(E)$, which is obtained by convolution of the two former functions. Note that the hot electron tail of the steradiancy analyzer leads to ions of small internal energy, whereas the Boltzmann tail of the thermal energy distribution of the sample leads to ions of high internal energy. The structure between 50 and 100 meV in Figure 1 arises from the 4 lowest vibrational

TABLE 1: Experimental, Vibrational Frequencies of the Neutral Fluoroethene and 1,1-Difluoroethene Listed in Order of Increasing Frequency

fluoroethene/ frequency (cm^{-1})	1,1-difluoroethene/ frequency (cm^{-1})
490[a]	438[d]
713[a]	550[d]
863[a]	590[d]
923[a]	611[d]
929[a]	803[d]
1157[a]	926[d]
1305[a]	955[d]
1380[b]	1302[d]
1656[a]	1414[d]
3052[c]	1728[d]
3080[c]	3060[d]
3115[c]	3103[d]

[a] Reference 36. [b] Reference 37. [c] Reference 38. [d] Reference 39.

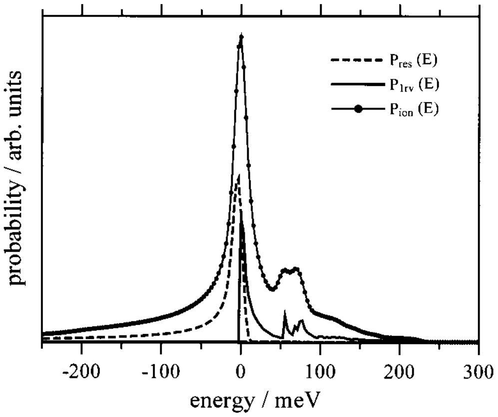

Figure 1. Energy distributions used for the simulation: (a) experimental energy resolution $P_{res}(E)$, (b) internal energy distribution of neutral 1,1-difluoroethene for one active rotor $P_{1rv}(E)$, and (c) convolution of both leading to the internal energy distribution for the parent ions $P_{ion}(E)$.

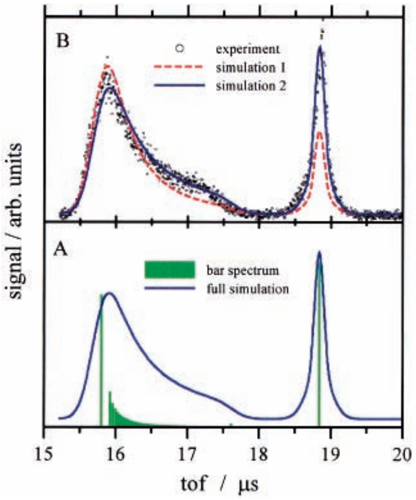

Figure 2. Simulations and experimental spectra for 1,1-difluoroethene: (A) projection of t_{life} in the TOF domain as block diagram and resulting simulation after convolution with thermal energy and KER. (B) Experiment in an effusive beam at 14.33 eV and simulations with only one single k value (simulation 1) as well as a distribution of k values (simulation 2).

frequencies of the 1,1-difluoroethene molecule between 438 and 611 cm^{-1} (cf. Table 1).

Assuming first-order decay of the parent ion the main task of the kinetic analysis is the transformation of the decay probability from the lifetime to the flight time domain (see, for example, ref 31). The first step of the simulation will then lead to a bar spectrum as indicated in Figure 2A. The distribution of TOF is here originating from the distribution of locations, where the fragmentation takes place. To take into account the conservation of linear momentum of the parent ion upon fragmentation and—more importantly—the kinetic energy released into the fragments during bond breaking this bar spectrum is convoluted with appropriate Gaussian functions. The average kinetic energy of the parent molecules (300 K) is about 39 meV, the average total KER for the HF-loss channel is about 1 eV at the threshold of the reaction.[1] A typical simulated TOF spectrum is shown in Figure 2A as a solid line.

If it is necessary to take into account the ion internal energy distribution and the corresponding rate constant curve $k(E)$, the probability for a fragmentation event at time t_{life} in the lifetime domain is given by

$$P(t_{\mathrm{life}}) = \int_0^{\infty} P_{\mathrm{ion}}(E_{\mathrm{ion}}) \exp[-k(E_{\mathrm{ion}}) t_{\mathrm{life}}] \mathrm{d}E_{\mathrm{ion}} \qquad (1)$$

where E_{ion} is the ion internal energy. For correlating the internal energy distribution with a $k(E)$ distribution a guess on the steepness of the $k(E)$ curve is necessary. Since several TOF spectra recorded for different excitation energies have to be simulated on the basis of the same $k(E)$ curve, reliable and consistent information on the latter will be derived.

Figure 2B compares the best simulation for a single rate constant and that for a distribution of rate constants with the experimental TOF spectrum. Clearly the agreement is significantly better, when a distribution of rate constants is taken into account. We particularly note the good agreement achieved in the region of the parent ion, which is generally extremely difficult to fit, and which in the past was normally omitted from the kinetic analysis. Because of the high KER of the HF-loss channel, the decay of parent ions in the field free drift region leads to a broad signal observable as a background to the stable parent ion signal. This represents a rare case where metastable decay can be observed in the field free drift region of a linear TOF spectrometer.[26]

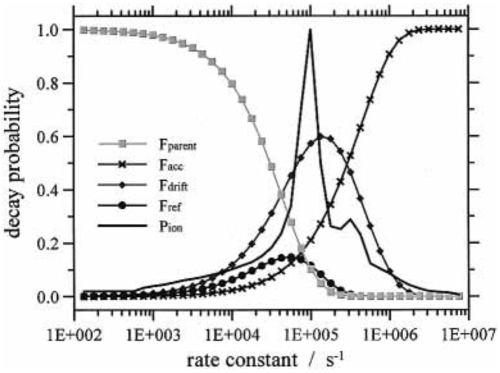

Figure 3. Relative decay probability in different spectrometer sections for 1,1-difluoroethene. The dotted line represents the energy distribution P_{ion}.

Simulation of TOF Spectra in the Reflectron. There are several differences in the mode of operation between a linear TOF and a reflectron, which consequently lead to differences in the data analysis. First, while linear TOF spectrometers are in general operated at homogeneous (very small) electric fields, allowing for the simulation of complete TOF distributions, reflectrons are often operated under pulsed electric fields. This makes a simulation of TOF distributions at least extremely difficult. The analysis of reflectron TOF spectra is, therefore, based on the signal intensity originating from different regions of the spectrometer. Second, the advantage of the reflectron is its ability to identify fragmentation processes taking place in the first field free drift region[6,32] between the acceleration region and reflector. Considering identical electric fields in a linear and a reflecting TOF spectrometer this immediately indicates the higher sensitivity of the latter with respect to small rate constants.

In the kinetic analysis of reflectron TOF spectra we first have to calculate the integrated parent and fragment signal originating from the three relevant regions of the spectrometer, the acceleration, the first drift, and the reflector region. The corresponding fractional abundances F_{acc}, F_{drift}, F_{ref}, and F_{parent} are given by eqs 2−5

$$F_{\mathrm{acc}} = 1 - \mathrm{e}^{-k(E)t_{\mathrm{acc}}} \qquad (2)$$

$$F_{\mathrm{drift}} = \mathrm{e}^{-k(E)t_{\mathrm{acc}}} - \mathrm{e}^{-k(E)(t_{\mathrm{acc}}+t_{\mathrm{drift}})} \qquad (3)$$

$$F_{\mathrm{ref}} = \mathrm{e}^{-k(E)(t_{\mathrm{acc}}+t_{\mathrm{drift}})} - \mathrm{e}^{-k(E)(t_{\mathrm{acc}}+t_{\mathrm{drift}}+t_{\mathrm{ref}})} \qquad (4)$$

$$F_{\mathrm{parent}} = \mathrm{e}^{-k(E)(t_{\mathrm{acc}}+t_{\mathrm{drift}}+t_{\mathrm{ref}})} \qquad (5)$$

where t_{acc}, t_{drift}, and t_{ref} are the residence times of the parent ion in the different regions of the spectrometer. These fractional abundances are plotted in Figure 3 as a function of the rate constant $k(E)$ for the case of the 1,1-difluoroethene. This plot illustrates the sensitivity of this spectrometer for certain $k(E)$'s. It is directly evident, that the spectrometer is sensitive to rate constants ranging from 2×10^3 s^{-1} to 2×10^6 s^{-1}. In the further analysis signal from the reflector region will not be taken into account, since this signal is spread out over a large TOF range and difficult to analyze. Again, at this point either a single rate constant or a full distribution of $k(E)$ values can be used for further analysis. As pointed out above the distribution of rate

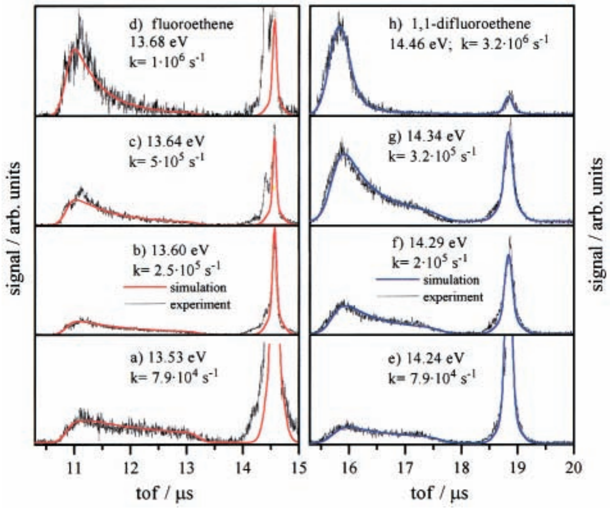

Figure 4. TOF spectra of fluoroethene and 1,1-difluoroethene for various excitation energies in the region of metastable decay in a linear TOF spectrometer.

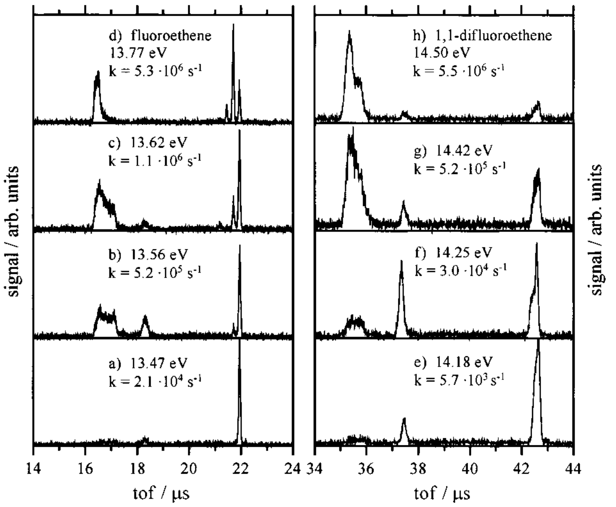

Figure 5. RETOF spectra of fluoroethene and 1,1-difluoroethene for various excitation energies in the region of metastable decay in a reflectron.

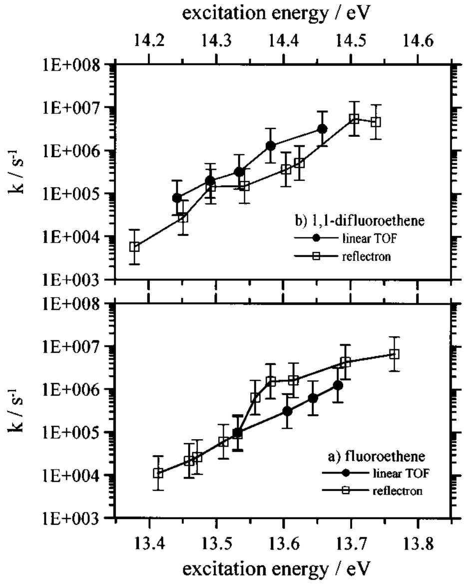

Figure 6. $k(E)$ curves for (a) fluoroethene and (b) 1,1-difluoroethene measured with in a linear TOF spectrometer and in a reflectron.

constants turned out to be important for the current data. In this procedure a $k(E)$ curve is defined numerically and adjusted until best agreement is observed between simulation and experiment. Note that at a given excitation energy each internal energy of the ion is uniquely associated with a rate constant as indicated in Figure 3.

4. Results and Discussion

The unimolecular fragmentation reactions of energy selected fluoroethene and 1,1-difluoroethene ions have been investigated in the energy range between 13.4 and 14.6 eV where the HF-loss reactions from the two molecules are metastable. The adiabatic ionization energies of the fluoroethene and the 1,1-difluoroethene are 10.35 and 10.29 eV, respectively.[12]

In the following we will first discuss the results obtained in the linear TOF spectrometer. A selection of TPEPICO-TOF spectra recorded for both title molecules in the linear TOF setup is shown in Figure 4 together with simulations based on a distribution of rate constants as discussed in section 3. For both molecules pronounced asymmetric TOF distributions, indicative of metastable decay are observed. The energetically lowest reaction channel in both molecules is the HF-loss, and the focus of the kinetic analysis will be on this reaction channel. Although each spectrum has been simulated based on a distribution of rate constants, one particular rate constant is shown in each spectrum, to illustrate the variation of $k(E)$ with the excitation energy. These rate constants refer to those ions with zero internal energy (cf. Figure 1). For the 1,1-difluoroethene, the HF-loss apparently dominates over the entire energy range covered. For the fluoroethene, however, at least one other reaction channel opens up above 13.64 eV, i.e., the H-loss channel. Note that for both molecules the smallest rate constant accessible in the linear TOF setup is here on the order of 8×10^4 s^{-1}.

The corresponding TPEPICO-RETOF spectra recorded for both title molecules with the reflectron setup are shown in Figure 5. For the fluoroethene spectra (left part of Figure 5) at the lowest excitation energy (13.47 eV), only the parent ion and its ^{13}C isotopologue (around 22 μs), and the $C_2H_2^+$ signal originating from the drift region (18.3 μs) and the acceleration region (16.5−17.3 μs), are observed. At the highest excitation energy (13.77 eV) additional signals from H-loss (21.7 μs) and H_2-loss (21.5 μs) are observed. For the 1,1-difluoroethene, the three signals observed correspond to the parent ion (42.6 μs), and the C_2HF^+ ion signals originating from the drift region (37.5 μs) and the acceleration region (35.3−36.1 μs). In analogy to the procedure adopted for the linear TOF spectra, we also assign that rate constant to the respective spectrum, which corresponds to ions of zero internal energy. It is important to note that the lowest excitation energy at which spectra could be recorded in the reflectron is 50 meV (fluoroethene), respectively 60 meV (1,1-difluoroethene) smaller than in the case of the linear TOF spectrometer. Again this gives evidence of the significantly higher sensitivity of the reflectron toward smaller rate constants. Here, the smallest rate constants are on the order of 10^4 s^{-1} in the reflectron.

A comparison of all rate constants derived in this work is shown in Figure 6 for the 1,1-difluoroethene (upper part) and the fluoroethene (lower part). Within the error bars shown for both molecules the rate constants obtained in the linear TOF spectrometer agree with those from the reflectron. However, evidently the agreement is worst in the intermediate energy range, i.e., around 14.37 eV for the 1,1-difluoroethene and 13.57

eV for the fluoroethene. This might be connected to the onset of additional reactions, particularly for the fluoroethene (see below). One of the most important results of the current work concerns the range of rate constants accessible in the different spectrometers. Here, we show that the reflectron data cover a range from 5×10^3 s^{-1} to 5×10^6 s^{-1}. The data from the linear TOF cover a significantly smaller range from about 8×10^4 s^{-1} to 5×10^6 s^{-1}.

The kinetic analysis presented in this work focused on the energetically lowest reaction channel in the fluoroethene and 1,1-difluoroethene ions, i.e., the HF-loss reaction. In the energy range, where this is the only reaction channel, the rate constant derived is directly the specific rate constant for HF-loss. As soon as another reaction channel opens, the overall rate constant is the sum of all specific rate constants of the competing reaction channels. From different experiments,[1,10,12] including our own, it is known that the onset of H-loss from fluoroethene ions occurs at about 13.6 eV. The onset of F-loss from 1,1-difluoroethene ions occurs at about 14.4 eV. Consequently, eqs 2−5 would in principle need to be modified. However, this would require the inclusion of additional specific $k(E)$ curves as parameters of the analysis. This was not considered to be justified for the time being. Further studies are necessary in order to account for the competition of reaction channels.

For both title molecules the rate constant $k(E)$ on the average increases by 1 order of magnitude for an increase in excitation energy of 120 ± 20 meV. This slope should be compared to other information from the literature. This slope is compatible with the data from Dannacher et al.[13] However, the current data cover a significantly larger range of rate constants. For the HF-elimination from 1,1-difluoroethene ions no experimental rate constants were available to date. Apart from the 1,1-difluoroethene there are two other isomers of the difluoroethene, i.e., the *cis*- and the *trans*-1,2-difluoroethene. Ab initio calculations suggest that the barriers for isomerization between all three isomers are probably lower than the experimentally observed onset of fragmentation.[33] In this regard it seems interesting to note that the slope of the $k(E)$ curve derived for HF-loss from 1,1-difluoroethene ions in this work is compatible with data measured for the cis- and the *trans*-1,2-difluoroethene ion.[19] Again the range of rate constants covered in this work is significantly larger than in ref 19. The agreement in the slope could imply that the HF-loss from the three difluoroethene isomers takes place from a common intermediate. At this point the question remains: what is the mechanism of HF-loss? For the difluoroethene ions the ab initio calculations indicate a tight 4-center cyclic transition state.[33] The energy of this transition state, however, is calculated to be 163 kJ/mol above the energetic limit of product formation. The experimentally observed onset occurs at 95 kJ/mol above the thermochemical limit. If a barrier for HF-loss in fact exists, then this reaction could only take place by tunneling. Tunneling of H atoms through a transfer barrier has previously also been invoked for the HCl loss from ethyl chloride ions[28] and the H_2 loss from ethane.[6,34] Here, tunneling leads to significantly smaller rate constants than expected for a classical reaction over the top of a barrier. In fact, in previous work the inability to model slow rate constants by classical statistical theories often gave a hint that tunneling might be important. In this context it is important to note that early statistical calculations for the HF-loss from 1,1-difluoroethene predicted a rate constant of 1.8×10^4 s^{-1} at threshold for a classical fragmentation. For the time being we cannot resolve the question of tunneling in the HF-loss from the title molecules. This problem requires additional experiments, e.g. on deuterated fluoroethenes. Finally it seems worthwhile to note that the slope of the $k(E)$ curve observed for HF-loss in this work is a factor of 5 to 10 smaller than that observed for H_2 loss from ethene[7] and ethane.[6] The slope found for the HCl-loss from ethyl chloride[28] was about a factor of 2 smaller than that of HF-loss from the different fluoroethene ions.

5. Summary

The fragmentation reactions of energy selected fluoroethene and 1,1-difluoroethene ions have been investigated in a TPEPICO experiment at variable excitation energies. The focus of the current work was on the HF-loss reaction for which the rate constant was measured over a range of about 400 meV starting from the respective threshold. For the first time we presented a comparison of data recorded in a linear and a reflecting TOF mass spectrometer. Within the error limits the agreement is good. However, it seems worthwhile to study this comparison in the future with emphasis on the competition of several reaction channels. The experiment performed in the reflectron has the advantage that it can easily be combined with any technique employing pulsed electric fields. This approach is rarely applied for the investigation of metastable reactions in a linear TOF spectrometer, although it is possible to pulse fields in order to vary the residence time of ions in the spectrometer (see, for example, ref 35). The second advantage of the reflectron is that it is sensitive to significantly smaller rate constants than a comparable linear TOF spectrometer. Therefore, in general the kinetic shift is smaller in the reflectron. In the current work the largest rate constants determined are similar for both types of spectrometer, i.e., on the order of a few times 10^6 s^{-1}. This upper limit is however given by the onset of another fast reaction channel, i.e., the F-loss, which makes a further analysis of the HF-loss difficult. In the case of a single reaction channel, the linear TOF can measure slightly larger rate constants than the reflectron. From one point of view the simulation of linear TOF data is more critical and thus more sensitive to small variations of the rate constant, since always the entire TOF profile is analyzed. The range of accessible rate constants can in general be increased toward larger $k(E)$ by increasing the electric field. Often, the range can be extended toward smaller $k(E)$ by decreasing the electric field or increasing the length of the spectrometer. Decreasing the electric field may, however, lead to severe discrimination of fragment ions in the case of a large KER. In fact the HF-loss reactions from fluoroethene- and difluoroethene ions are accompanied by a very large KER indicative of a significant barrier for reverse reaction.[1,13,16,18] A discrimination of up to 70% was, for example, observed by Dannacher et al. in the HF loss from fluoroethene ions because of very small electric fields.[13] We finally note that for comparable fields and spectrometer size the reflectron is in general sensitive to a larger range of rate constants than the linear TOF spectrometer.

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