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Time-resolved kinetic energy releases in propane

S. Matt-Leubner [a], A. Stamatovic [a,1], R. Parajuli [a], P. Scheier [a],
T.D. Märk [a,b,*], O. Echt [a,2], C. Lifshitz [c]

[a] *Institut für Ionenphysik, Leopold Franzens Universität, Technikerstr. 25, A-6020 Innsbruck, Austria*
[b] *Katedra fyziky plazmy, Univerzita, Mlynska dolina F2, SK-84215 Bratislava, Slovak Republic*
[c] *Department of Physical Chemistry and The Farkas Center for Light Induced Processes,*
The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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Abstract

In this work we present a combined experimental and theoretical study of the time-resolved average kinetic energy release (KER) $\bar{\varepsilon}$ of the $H^{\bullet}$ loss reaction in propane leading to the *sec*-propyl cation, $C_3H_8{}^{\bullet +} \rightarrow sec\text{-}C_3H_7{}^{+} + H^{\bullet}$. The addition of a third field-free region to our double-focusing sector mass spectrometer, combined with previous results obtained by us and others, provides $\bar{\varepsilon}$ values for ion lifetimes ranging from $\tau_{mp} < 0.75$ to 20.4 μs. Their time dependence is nicely reproduced by Finite Heat Bath Theory. Furthermore, an analysis of the dependence of $\bar{\varepsilon}$ on the excess non-fixed energy $E^{\#}$ above the critical energy shows that the fraction $\bar{\varepsilon}/E^{\#}$ approaches a value of 1.0 for the metastable reaction. (Int J Mass Spectrom 222 (2003) 213–219)
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1. Introduction

When unimolecular dissociation reactions of polyatomic ions take place, some of the excess energy of the ion is released as kinetic energy of the two fragments. The kinetic energy release (KER) carries very valuable information concerning the structures of the species involved and concerning the energetics and dynamics of the reactions and this topic has been reviewed recently [1]. Reverse geometry (BE) double-focusing sector mass spectrometers are ideally suited for KER measurements on metastable ions dissociating in the second field-free region (ff2). This has been done very successfully on mass-selected molecular ions using the mass analyzed ion kinetic energy (MIKE) scan technique [2]. The time scale of metastable ion fragmentations has been shortened recently, through the use of electron-induced dissociations [3,4], and extended, through the addition of a third sector (BEE) and of a third field-free region (ff3) [4]. This has enabled the measurement of the KER for metastable ions of a single reaction over a range of ion lifetimes, a study that is the topic of the present presentation.

Experimental results can be compared with expectations from theory. There is a one to one correspondence between the unimolecular rate constant k (i.e.,

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[*] Corresponding author. E-mail: tilmann.maerk@ uibk.ac.at
[1] Permanent address: Faculty of Physics, P.O. Box 638, Yu-11001 Beograd, Yugoslavia.
[2] Permanent address: Department of Physics, University of New Hampshire, Durham, NH 03824, USA.

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the inverse lifetime) and the non-fixed excess internal energy above threshold, $E^{\#} = E - E_0$, where E is the internal energy in the reactant ion and E_0 is the critical activation energy (or threshold energy). For reactions with no reverse activation energy that behave statistically, the KER is expected to rise with increasing excess energy and with decreasing ion lifetime (see references to energy dependences from coincidence work (PEPICO) and to previous work on time dependences [1]).

We have chosen for the present study of time-resolved KERs, the $H^{\bullet}$ loss reaction in propane:

$$C_3H_8{}^{\bullet +} \rightarrow sec\text{-}C_3H_7{}^{+} + H^{\bullet} \qquad (1)$$

It is a simple bond cleavage reaction that has the lowest appearance energy (AE) among all the parallel and consecutive reactions that make up the propane mass spectrum. Rosenstock et al. [5] have used the propane cation-radical to introduce the quasi-equilibrium theory (QET) of mass spectra. It has been a topic of quite a number of studies comparing theory with experiment, including the classical photoionization mass spectrometry study of Chupka and Berkowitz [6]. An interesting observation has been the fact that although methane elimination leading to $C_2H_4{}^{\bullet +}$ from $C_3H_8{}^{\bullet +}$ is a rearrangement reaction and has in addition a higher energy threshold than reaction (1), it is still able to compete very efficiently with reaction (1). This has led to the adoption of a very tight transition state for reaction (1) [7] in theoretical RRKM/QET modeling of the propane mass spectra. This question remained partly unsolved until recently [8] when ab initio calculations were combined with RRKM/QET computations. These calculations demonstrated that the slow rise of the microcanonical rate constant $k(E)$ of reaction (1) with increasing internal energy of the propane cation-radical is due to the changes in vibrational frequencies between the propane ion and the transition state being small for this reaction.

The technique of electron-induced dissociation has been applied by some of us recently [4,9] to reaction (1) in propane. The average KER for electron-induced dissociation of $C_3H_8{}^{\bullet +}$ was found to be about 42% larger than for the spontaneous reaction. The present paper is an extension of the previous experimental presentation [9] giving in addition the KER for the spontaneous reaction (1) in the ff3 for the first time. Since the microcanonical rate constant of reaction (1) rises slowly with excess internal energy [8], it is ideally suited for an experimental study of time-resolved KERs of metastable ions that are due to a simple bond cleavage and have a negligible reverse activation energy. The situation is also ripe for theoretical modeling of such experimental results. The present paper presents a combined experimental and theoretical modeling study of the time-resolved KER dependence of metastable ions from reaction (1).

2. Experimental

Details of the experimental setup and data analysis have been published elsewhere [9,10]. As shown in Fig. 1, the apparatus consists of a high resolution double-focusing mass spectrometer (Varian MAT CH5-DF) of reversed Nier–Johnson-type BE1 geometry combined with a second electrostatic analyzer E2. Propane is introduced into the collision chamber of a Nier-type ion source via a capillary leak gas inlet system where the molecules are ionized by an electron beam of variable energy and current. Ensuing cations are extracted by a weak electric field and accelerated through a potential drop of $U_{ac} = 3\,kV$ into the spectrometer. They pass through the first field-free region (ff1, length 61 cm), a magnetic sector field B, a second field-free region (ff2, length 33.3 cm), a 90° electric

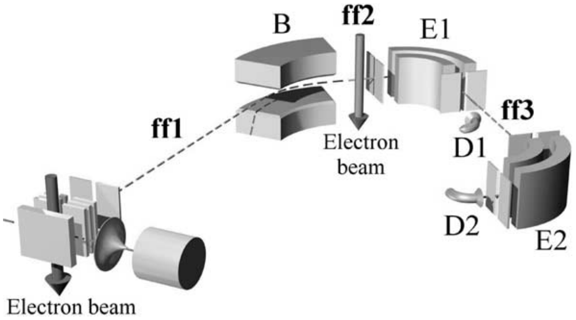

Fig. 1. Schematic drawing of the experimental setup.

sector field (E1), a third field-free region (ff3, length 92 cm), and another electrostatic sector field (E2, geometry identical with E1) past which they are detected by a channeltron multiplier, D2. Alternatively, another channeltron multiplier D1 can be moved into the ion beam to register all ions that pass through the exit slit of E1.

In addition, a high-performance, home-built electron gun is mounted in ff2, just before the defining aperture between the magnetic sector and the first electric sector, approximately mid-way between the sectors. The electron beam intersects the ion beam at 90°. In the present work, we chose an electron energy of 150 eV and an electron beam current of 7 mA. For further details, see Ref. [9].

With this setup we can record decay reactions of mass selected ions in either ff2 or ff3 by applying the MIKE technique [1,2]. The magnet is tuned to the mass m_p of the desired parent ion (in this work assumed to be singly charged). Decay in ff2 is analyzed by varying the voltage of E1 and using detector D1. Stable ions will have a kinetic energy of 3 keV and pass E1 at a nominal sector field voltage of $U_\mathrm{p} = 509\,\mathrm{V}$. Fragment ions of mass m_f formed in ff2 will pass E1 at a voltage

$$U_\mathrm{f} = \frac{m_\mathrm{f}}{m_\mathrm{p}} U_\mathrm{p} \tag{2}$$

The same relation holds if decay is analyzed in ff3, by selecting the parent ion with the magnet, setting E1 to $U_\mathrm{p} = 509\,\mathrm{V}$, scanning the second sector field E2 and using detector D2 to record the spectrum.

In general, the parent ion will have a finite width and a distinct shape; these are also imposed on the fragment ion through Eq. (2). Any kinetic energy ε that is released in the reaction will further modify the peak shape of the fragment. A common situation, encountered in the present work, are fragment ion peaks that are Gaussian. This holds if the kinetic energy release distribution (KERD) is a three-dimensional Maxwell–Boltzmann distribution, and no discrimination against fragment ions occurs [1,2]. In this situation, the full-width at half-maximum, ΔU, of the MIKE peak (derived by using non-linear least-squares fitting techniques, and correcting for the finite width of the parent ion peak), provides a robust measure of the average KER, $\bar{\varepsilon}$, through the relation

$$\bar{\varepsilon} = 2.16 \frac{{m_\mathrm{p}}^2 U_\mathrm{ac}}{16 m_\mathrm{f} (m_\mathrm{p} - m_\mathrm{f})} \left(\frac{\Delta U}{U_\mathrm{p}} \right)^2 \tag{3}$$

Furthermore, in this situation the transition state temperature $T^\#$ of the reaction is easily derived from $\bar{\varepsilon}$,

$$\bar{\varepsilon} = 1.5 k_\mathrm{B} T^\# \tag{4}$$

where k_B is the Boltzmann constant [1].

An important difference between scanning E1 and E2 is that different metastable time scales, hence different metastable rate constants, are being accessed. Spontaneous (metastable) reactions in ff2 will sample the time interval $11.2 \leq t \leq 14.2\,\mu\mathrm{s}$ after formation of the parent ion $\mathrm{C_3H_8}^{\bullet+}$ in the ion source, while spontaneous (metastable) reactions in ff3 will sample the time interval $16.6 \leq t \leq 24.7\,\mu\mathrm{s}$.

A third, much shorter time window will be accessed if E1 is scanned with the electron source in ff2 being turned on. In this case, induced reactions that occur within $t \leq 0.75\,\mu\mathrm{s}$ after electron excitation will contribute to the MIKE spectrum. However, spontaneous reactions of metastable $\mathrm{C_3H_8}^+$ will also contribute, therefore, the experimental KER that is obtained in this mode does not represent an ensemble of parent ions having a well-defined distribution of internal energies.

The use of a second electrostatic analyzer has additional advantages as described by Beynon and coworkers [11]. First of all, in a "normal" MIKE spectrum recorded in ff2, the decay of fragment ions m_2 produced in ff1 from precursor ions m_1 with $m_1 > m_\mathrm{p}$ will also contribute if their apparent mass $m^* = {m_2}^2/m_1$ is approximately equal to m_p. MIKE spectra recorded in ff3 are free of these artifact peaks because those fragment ions will not pass through E1.

Another advantage is the possibility to analyze decay reactions occurring in ff2 by simultaneously scanning E1 and E2 [11]. In this "linked scan" mode the energy resolution is determined by E1. One closes the exit slit behind E1 as much as possible while using an open collector slit behind E2; this enhances the sensitivity. We have tested our BE1E2 system by measuring H loss from $C_3H_8^{\bullet+}$ with this linked scan technique and obtained $\bar{\varepsilon} = 8.33 \pm 0.67$ meV. Our previous result for this reaction, using a normal MIKE scan [9], was $\bar{\varepsilon} = 9.3 \pm 1.5$ meV which agrees within the uncertainty.

The smaller uncertainty with the new setup is significant. We have changed the aperture in the focal plane of the magnetic and electrostatic sector fields from 0.2 to 2 mm in order to have sufficient intensity past E2. As a result, the resolution in a normal MIKE spectrum has deteriorated from 0.5 V (parent ion width) to 0.9 V. However, with the linked scan we now achieve a width of less than 0.3 V.

3. Results and discussion

3.1. MIKE spectra and average KERs

Fig. 2 presents the MIKE spectrum obtained for reaction (1), the hydrogen atom loss from propane, obtained for ff3. The average KER is deduced from the widths of the parent and metastable ion peaks in this spectrum, as has been explained in Section 2. The average KERs, obtained in Innsbruck from similar spectra for spontaneous dissociations in ff2 and ff3 and from the electron-induced reaction, respectively, are summarized in Table 1, and previous results by Holmes [12] and Medved et al. [13] are included as well. If metastable ions enter a field-free region at time t_1 and leave it at time t_2, they dissociate with a distribution of rate coefficients [3]. The most probable experimental rate coefficient is equal to the most probable inverse ion lifetime, $k_{mp} = 1/\tau_{mp}$ that in turn depends upon whether the reaction is spontaneous or electron induced and which field-free region is involved; k_{mp} is obtained from the maximum of the rate constant distribution as [3,14]:

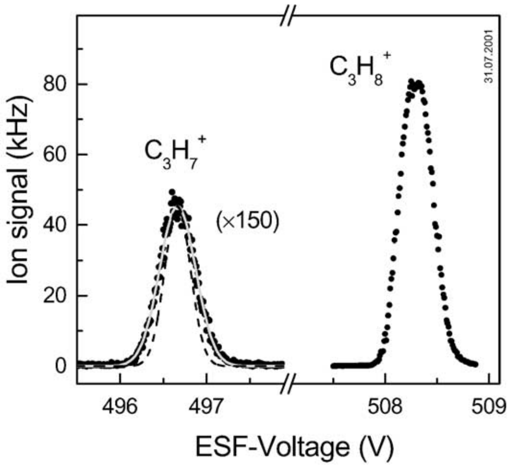

Fig. 2. MIKE spectra of *sec*-$C_3H_7^+$ produced from metastable $C_3H_8^{\bullet+}$ in the third field-free region. The fragment ion intensity has been scaled by a factor of 150. The solid line represents a Gaussian fit to the fragment; the dashed line indicates the width of the metastable peak that one would expect if the KERs were zero.

Table 1
Time-resolved average KERs for reaction (1) in propane

τ_{mp} (μs)	k_{mp} (s^{-1})	$\bar{\varepsilon}$ (meV)	Comments
≤0.75 ± 0.05	$\geq 1.33 \times 10^6$	13.2 ± 2	Electron induced
2.0 ± 0.7	5×10^5	12.5 ± 0.5	[12]
7.5	1.33×10^5	9.6 ± 0.3	[13]
12.5 ± 0.5	8×10^4	8.33 ± 0.67	ff2
20.4 ± 0.5	4.9×10^4	7.17 ± 0.57	ff3

$$k_{mp} = \frac{1}{t_2 - t_1} \ln[t_2/t_1] \tag{5}$$

The most probable ion lifetimes in microseconds are given in Table 1, for the various experiments, under the column τ_{mp}. Table 1 thus summarizes the time-resolved experimental average KER results obtained for reaction (1).

3.2. Data analysis and modeling

The experimental data were analyzed and modeled using the Finite Heat Bath Theory (FHBT) developed by Klots [15]. From the transition state temperature $T^{\#}$ [Eq. (4)] one derives the isokinetic temperature T_b of a canonical ensemble that would produce in an infinite heat bath the same rate constant $k(T_b)$ as the microcanonical rate constant $k(E)$ sampled [1,16]. The isokinetic bath temperature T_b is calculated using [1,17,18]:

$$T_b = T^{\#} \frac{\exp[\gamma/(C-1)] - 1}{[\gamma/(C-1)]} \tag{6}$$

where $k_B C$ is the vibrational heat capacity of the parent ion. The Gspann parameter γ is defined as

$$\gamma = \ln\frac{A}{k_{mp}} = \frac{E_a}{k_B T_b} \quad (7)$$

In Eq. (7), k_{mp} is the most probable decay rate constant, A is the pre-exponential in the Arrhenius relation, T_b is the canonical temperature, and E_a is the activation energy.

Modeling the experimental data was carried out using Eqs. (4), (6) and (7). This necessitated the prior adoption of the best possible values of the activation parameters, A and E_a for reaction (1). A first trial value for the pre-exponential A factor was calculated on the basis of the scaled ab initio vibrational frequencies of the reactant and transition state for reaction (1) via the activation entropy calculated by McAdoo et al. [8], $\Delta S^{\#} = -5\,\mathrm{J\,mol^{-1}K^{-1}}$ (at 298 K) and Tables S1 and S2 of the Supporting Information of Ref. [8]. This resulted in $A = 9.26 \times 10^{12}\,\mathrm{s^{-1}}$. It is well known from modeling of PEPICO studies [19] that the transition state properties calculated by DFT are less certain than those of the reactants and they are usually treated as somewhat free parameters. The value $A = 9.26 \times 10^{12}\,\mathrm{s^{-1}}$ was treated as a parameter; in the final calculations that gave the best fit with the experimental results obtained in ff3, $A = 6.9 \times 10^{13}\,\mathrm{s^{-1}}$. Chupka and Berkowitz [6] determined experimentally by photoionization mass spectrometry, the 0 K threshold for production of the $C_3H_7^+$ ion at 11.59 ± 0.01 eV. We based the activation energy, adopted for reaction (1) on this value and upon the value for the ionization energy of propane IE = 10.94 ± 0.05 eV recommended by the NIST tables [20], $E_a = 11.59 - 10.94 = 0.65$ eV.

Employing Eq. (7) and using the adopted values for the activation parameters given earlier, we proceeded to calculate the temperature T_b and the Gspann parameter γ as a function of the most probable ion lifetime $\tau_{mp} = 1/k_{mp}$.

The heat capacity, C, of the propane cation was next calculated as a function of temperature T_b using the scaled vibrational frequencies of the ion ([8], Table S1 of the Supporting Information). The temperature T_b and the corresponding heat capacity $C(T_b)$ as well as the Gspann parameter γ were introduced into Eq. (6) to calculate the transition state temperature $T^{\#}$ as a function of τ_{mp}.

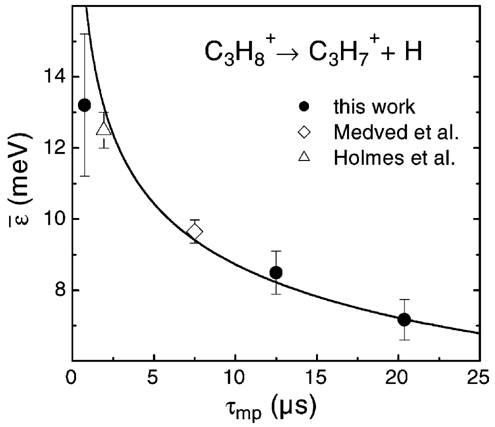

Fig. 3. Average KER, $\bar{\varepsilon}$, for $H^{\bullet}$ loss from $C_3H_8^{\bullet+}$ as a function of the most probable lifetime. The symbols (filled—present results and open—Refs. [12,13]) are experimental; the continuous curve is calculated (see text).

Finally, Eq. (4) was used to calculate from $T^{\#}$ the average KER $\bar{\varepsilon}$ as a function of τ_{mp}.

The computed dependence of the average KER, $\bar{\varepsilon}$ upon the most probable ion lifetime τ_{mp} is compared with the experimental data from Table 1 in Fig. 3. The agreement between experiment and calculation is very good. The drop of the average KER from the values of Holmes [12] and of Medved et al. [13] of 12.5 meV at 2.0 µs and of 9.65 meV at 7.5 µs, respectively, to the value 7.17 meV in ff3 is beautifully reproduced. Even the electron-induced value is reproduced quite well by the calculation. However, as explained in the experimental section, this value has fairly large error limits; it does not pertain to an ensemble with a well-defined most probable ion lifetime. It would be interesting to see how the average KER for the induced reaction changes when the energy deposition function is changed, for example by varying the energy of the exciting electron beam.

The nice agreement observed between experimental and computed time-resolved KERs for reaction (1) (Fig. 3) is for activation parameters $A = 6.9 \times 10^{13}\,\mathrm{s^{-1}}$ and $E_a = 0.65\,\mathrm{eV} = 62.7\,\mathrm{kJ\,mol^{-1}}$. In changing the

A factor from the originally calculated value of $A = 9.26 \times 10^{12}\,\mathrm{s}^{-1}$, we have accommodated possible errors in the heat capacity, stemming from uncertainties in the frequencies. The activation energy $E_a = 62.7\,\mathrm{kJ\,mol^{-1}}$ based upon the photoionization experiment [6] is somewhat lower than the ab initio calculated value [8], $E_a = 75\,\mathrm{kJ\,mol^{-1}}$. The latter value [8] predicts a calculated RRKM rate constant at threshold, $k \sim 2 \times 10^6\,\mathrm{s}^{-1}$ whereas the experimentally observed rate constant at threshold is considerably lower, $k \le 4.9 \times 10^4\,\mathrm{s}^{-1}$ (Table 1). A lower activation energy, like the one we have adopted, $E_a = 62.7\,\mathrm{kJ\,mol^{-1}}$ would predict an even higher rate constant at threshold. Fragmentation of $CH_4^{\bullet+}$ ions has been interpreted in the past [21] by tunneling through a rotational (centrifugal) barrier. This model was in line with the low lifetimes observed for the $H^\bullet$ loss reaction as well as with the increased intensity and increased KER observed as the temperature is raised. An analogous mechanism for reaction (1), i.e., tunneling through a centrifugal barrier, cannot be easily invoked, however, because the KER has been demonstrated to be independent of temperature of the sample [13]. In other words, the chosen activation parameters, $A = 6.9 \times 10^{13}\,\mathrm{s}^{-1}$ and $E_a = 62.7\,\mathrm{kJ\,mol^{-1}}$, reproduce our experimental time-resolved KERs but do not give the right RRKM rate constants and further work is required to understand this discrepancy. As the results stand, we undoubtedly observe (see Table 1) rather slow dissociation with most probable experimental microcanonical rate constants in the range $4.9 \times 10^4\,\mathrm{s}^{-1} < k_{mp} < 1.33 \times 10^6\,\mathrm{s}^{-1}$. The KER data analysis by FHBT provides activation parameters that allow us to predict canonical rate constants for reaction (1). These can conceivably be tested using blackbody infrared radiative dissociation (BIRD) as a means of activation of the unimolecular reaction by ambient blackbody radiation [22]. The character of the unimolecular decomposition of propane ions near threshold will be elucidated further in coming investigations of time-resolved KERs for deuterated propanes including the possibility of tunneling through centrifugal barriers [23,24].

An alternative analysis of the data involves the dependence of the average KER upon the excess non-fixed energy above threshold, $E^{\#} = E - E_0$. Classically the average KER is expected to increase linearly with excess energy above threshold, $\bar{\varepsilon} = E^{\#}/N$, where N is the number of vibrational degrees of freedom. An empirical linear relation, $\bar{\varepsilon} = E^{\#}/0.44N$, due to Franklin and coworkers [25], has been used in the past. This relation has no sound theoretical basis and Klots [14] derived a better equation by combining RRKM/QET with Langevin collision theory. In the case in which there is a centrifugal barrier and Eq. (4) prevails:

$$E^{\#} = \left(\frac{R}{2}\right) k_B T^{\#} + \sum_i h\nu_i [\exp(h\nu_i / k_B T^{\#}) - 1]^{-1} \tag{8}$$

where R is the number of rotational degrees of freedom in the reaction products and ν_i are the frequencies of the N vibrational degrees of freedom. The experimental evaluation of the average KER $\bar{\varepsilon}$ as a function of $E^{\#}$ at low values of $E^{\#}$ is of particular interest since Eq. (8), contrary to Franklin's equation, predicts that

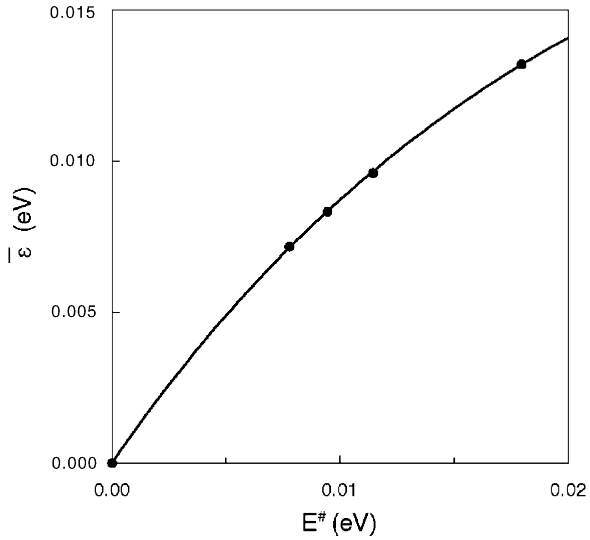

Fig. 4. Average KER, $\bar{\varepsilon}$, for $H^\bullet$ loss from $C_3H_8^{\bullet+}$ as a function of the excess non-fixed energy in the transition state, $E^{\#} = E - E_0$. The points are the experimental $\bar{\varepsilon}$ without error limits as a function of $E^{\#}$, calculated using Eq. (8) and adding a point for $E^{\#} = 0$, with an assumed $\bar{\varepsilon} = 0$; the continuous line is the best non-linear fit just to lead the eye through the points.

in this energy range the fraction of energy acquired as kinetic energy ($\bar{\varepsilon}/E^{\#}$) should increase rapidly as $E^{\#}$ decreases [26]. The excess energies $E^{\#}$ can be derived for reaction (1) from expression (8) because the vibrational frequencies have now been determined by ab initio calculations [8] and the temperatures $T^{\#}$ are known from Eq. (4) and from the experimentally determined average KERs. Fig. 4 represents the calculated dependence of $\bar{\varepsilon}$ upon $E^{\#}$. As expected, the fraction ($\bar{\varepsilon}/E^{\#}$) is quite high and increases as $E^{\#}$ decreases approaching 1 for the longest lifetimes sampled.

Acknowledgements

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