On the photodissociation of propadienylidene, l-C_3H_2†

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We investigate the photochemistry and photodissociation dynamics of the linear C_3H_2 isomer propadienylidene by two-colour photofragment Doppler spectroscopy at excitation wavelengths between 260 and 230 nm, corresponding to excitation into the $C\,{}^1A_1$ state. Propadienylidene is generated by pyrolysis from IC_3H_2Br. Almost complete conversion of the precursor can only be achieved at high pyrolysis temperatures. Two reaction channels, H-atom loss and loss of H_2 molecules, are energetically close. Our results show that H-atom loss is indeed important in the investigated energy range. The Doppler profiles indicate that 34–37% of the excess energy is released as translation. The rates for H-atom loss are faster than the time resolution of our nanosecond-laser setup, $k_H > 10^8\ s^{-1}$.

Introduction

In this paper we present an investigation of the photochemistry and photodissociation dynamics of the linear C_3H_2 isomer propadienylidene, l-C_3H_2, by H-atom photofragment Doppler spectroscopy. Small carbenes play a key role in the chemistry of the interstellar space[1] and in combustion processes. They are also important model systems for theoretical chemistry due to the large number of low-lying electronic states.[2] Propadienylidene itself, depicted on the right hand side of Scheme 1, was characterised by microwave spectroscopy,[3] discovered in translucent clouds[4] and observed in a cyclopentene flame by VUV photoionisation.[5] Due to its importance in reactive environments there is considerable interest in elucidating its photochemistry and photodissociation dynamics upon interaction with high energy radiation.

Propadienylidene has C_{2v} symmetry and a singlet ground state, $X\,{}^1A_1$. The transition into the symmetry forbidden $A\,{}^1A_2$ state was observed in a cavity ringdown experiment.[6,7] Most relevant for the photochemistry of the carbene is the transition into the $C\,{}^1A_1$ state. It can be considered to be a $\pi\pi^*$ transition. The spectrum, like the $B\,{}^1B_1$–$X\,{}^1A_1$ transition, was observed in an Ar- and Ne-matrix and assigned by comparison with calculations.[8,9] In the experiment described below, we excite l-C_3H_2 into this UV band, using excitation wavelengths between 260 and 230 nm, corresponding to 460–520 kJ mol^{-1}. The most important reaction channels accessible at these photon energies are summarised in Fig. 1. All energies are given in kJ mol^{-1} relative to l-C_3H_2. They are based on computations. Most of the energies are taken from the paper by Mebel *et al.*[10] The energy difference between the cyclic and linear isomer of C_3H was derived from computations by Ochsenfeld *et al.*[11] As is visible, the lowest dissociation threshold corresponds to

$$C_3H_2 \rightarrow C_3\ (X\,{}^1\Sigma_g^+) + H_2\ \Delta_RH\ (0\ K) = +250\ kJ\ mol^{-1} \quad (1)$$

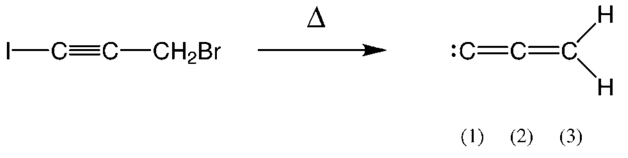
However, there is a considerable barrier (+357 kJ mol^{-1}) associated with this channel. This brings it energetically close to H-atom loss and formation of either the cyclic or the linear isomer of C_3H.

$$C_3H_2 \rightarrow c\text{-}C_3H\ (X\,{}^2B_2) + H\ \Delta_RH\ (0\ K) = +366\ kJ\ mol^{-1} \quad (2a)$$

$$C_3H_2 \rightarrow l\text{-}C_3H\ (X\,{}^2A') + H\ \Delta_RH\ (0\ K) = +374\ kJ\ mol^{-1} \quad (2b)$$

According to recent anion photodetachment spectra the $A\,{}^2A_1$ state of c-C_3H (+463 kJ mol^{-1}) is, in principle, also energetically accessible.[12] Rupture of a C–C bond constitutes an alternative pathway, but dissociation into acetylene and ground state carbon C (${}^3P$), corresponding to +395 kJ mol^{-1},[10,13] is spin forbidden. Neither formation of C (${}^1D$) plus acetylene (+568 kJ mol^{-1}), nor formation of C_2H + CH (+550 kJ mol^{-1}) are energetically possible under our conditions.[10] These pathways will not thus be further considered, although crossed-beam experiments of acetylene and C (${}^3P$) yielded an evidence for the minor role of spin–forbidden reactions.[14]

In recent years we investigated the unimolecular dissociation of various radicals by depositing sufficient energy for dissociation by optical excitation. The dissociation dynamics and kinetics were then studied by time-resolved detection of H-atoms and by Doppler spectroscopy.[15–17] The detection of



Scheme 1

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† Electronic supplementary information (ESI) available: Synthesis, wavenumbers used in the RRKM calculations, H-atom action spectrum, and laser power information. See DOI: 10.1039/b807049k

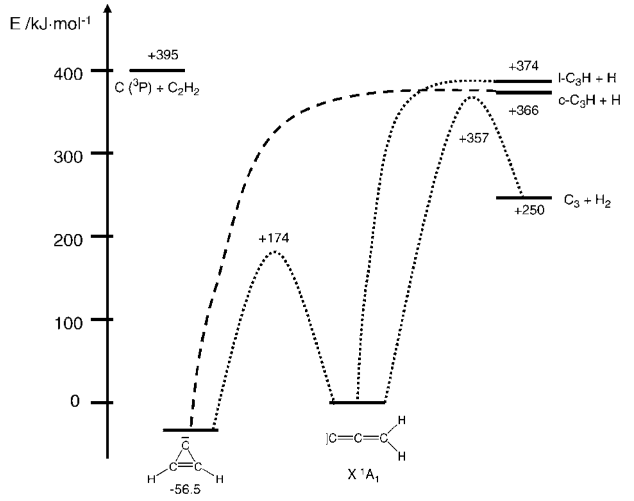

Fig. 1 Energetically accessible reaction channels for propadienylidene. All energies are given in kJ mol^{-1}. Loss of a H_2 molecule and formation of C_3 is the lowest energy product channel, but is associated with a considerable reverse barrier. Therefore loss of an H-atom becomes competitive. The C (^3P) + acetylene channel is spin-forbidden from the singlet ground state of propadienylidene.

hydrogen atoms by Lyman-α radiation was shown to be a sensitive tool for the observation of reactions of reactive intermediates. Here we apply it to the investigation of carbene photochemistry, but emphasise that our approach is only sensitive to reaction channels (2a) and (2b), not to channel (1).

Experimental

All experiments were carried out in a differentially pumped standard molecular beam apparatus, equipped with a 0.5 m time-of-flight mass spectrometer. In the experiments described below a molecular beam of propadienylidene was produced by supersonic jet flash pyrolysis of 3-bromo-1-iodopropyne, seeded in 1–2 bar of helium, according to Scheme 1. The precursor was synthesized following the procedure outlined in the literature.[18] Alternatively, 1,3-dibromopropyne[19] and 1,2-diiodopropyne were employed. The synthesis of the latter[20] is described in the ESI,† together with the one of 3-bromo-1-iodopropyne. The design of our pyrolysis nozzle is based on the one described elsewhere,[21] but is combined with a water cooled solenoid valve to achieve stable operation at higher pyrolysis temperatures. The radical beam passes through a skimmer into the main chamber where it is crossed by two counterpropagating laser beams: one for excitation of propadienylidene and one for the detection of H-atoms.

Hydrogen atoms were detected by multiphoton ionisation.[22] The output of a dye laser, pumped by a Nd:YAG laser and operating with pyridine 2, was frequency doubled in a KDP crystal, producing around 6–12 mJ at 365 nm, and focused by a 150 mm lens into a cell filled with 90 mbar of krypton in order to produce VUV radiation around 121.6 nm (Lyman-α). Since the bandwidth of the fundamental is around 0.1 cm^{-1}, we estimate a bandwidth of 0.3 cm^{-1} for the VUV pulse. The VUV light was focused into the ionisation region by a 100 mm MgF_2 lens mounted at the exit of the cell. Absorption of 121.6 nm radiation excites hydrogen atoms from the ^2S ground state to the ^2P state and the residual fundamental ionises the excited atoms, which are subsequently detected in a Wiley–McLaren time-of-flight spectrometer. Fields of 300 and 1000 V cm^{-1} were employed in the two acceleration regions. The ions were detected by a microchannel plate detector. The signals were recorded in a digital storage oscilloscope, averaged over typically 200 shots, and transferred to a computer. For the 118 nm photoionisation mass spectra the dye laser was tuned to 355 nm and focused into the same cell, filled with 20 mbar of xenon. For excitation of the radicals the frequency-doubled output of another Nd:YAG laser pumped dye laser was employed. Typically, 2 mJ of the unfocused laser were employed for excitation. The two laser systems were synchronised externally by a digital delay generator to within better than 2 ns.

Results and discussion

Photoionisation mass spectra were recorded at 118 nm in addition to the usual 121.6 nm, because the ionisation energy of l-C_3H_2 is known to be around 10.43 eV and thus above the energy of a single 121.6 nm photon. In Fig. 2 a number of 118 nm photoionization mass spectra relevant for our conditions are presented. With the pyrolysis source turned off (top trace) the signal of the

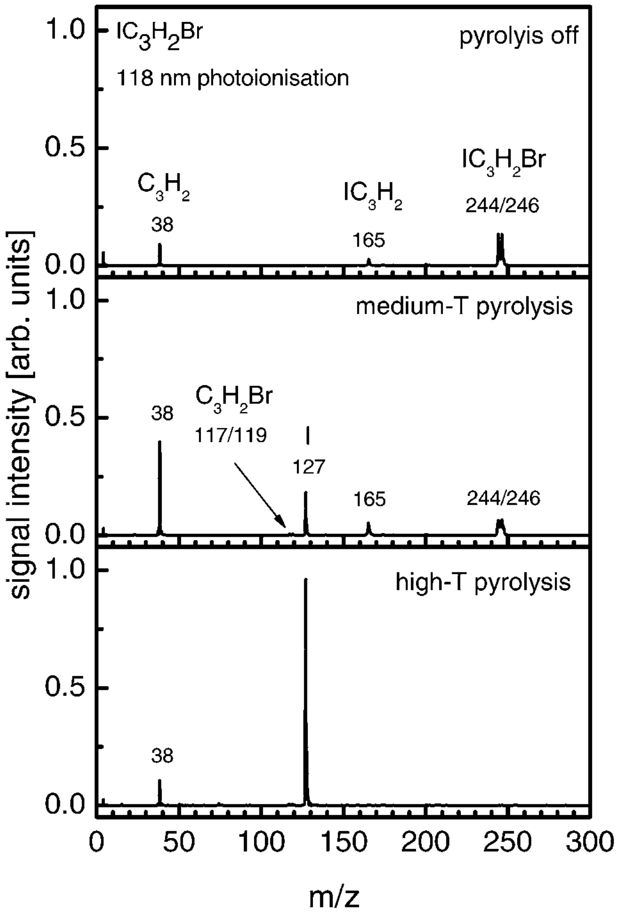

Fig. 2 118 nm (10.51 eV) photoionisation mass spectra of propadienylidene relevant for our conditions. The 118 nm spectra show that quantitative conversion of the precursor is only achieved at high pyrolysis temperature.

precursor 3-bromo-1-iodopropyne (*m*/*z* = 244/246) is detected. All masses and fragments containing bromine are easily recognized by the $^{79}Br/^{81}Br$ isotopic pattern. In addition, signals at mass 165 (IC_3H_2) and 38 (C_3H_2) are present that presumably originate from dissociative ionization. When the pyrolysis source is turned on (centre trace), the intensity of the signal at mass 38 increases significantly. In addition a strong I^+ signal appears. As is visible, the precursor is not converted completely and a signal of IC_3H_2 is also present. The signal at the mass of C_3H_2Br is negligibly small. Obviously the C–Br bond in the precursor is more easily cleaved than the C–I bond, as can be deduced from further experiments employing BrC_3H_2Br and IC_3H_2I as precursors. By moving from BrC_3H_2Br to IC_3H_2Br the efficiency of the pyrolysis was strongly increased. On the other hand, using IC_3H_2I did not improve the efficiency further. The intermediate IC_3H_2 radical can be stabilised by interaction of the radical site with the π-system of the triple bond, whereas the corresponding C_3H_2Br radical is of sigma character. When the pyrolysis nozzle is heated further (bottom trace), the precursor is almost completely converted and only very little IC_3H_2 is present. In addition, a small HI signal is also observed. It has been shown before in experiments utilizing synchrotron radiation that bimolecular reaction products can be formed in the nozzle,[23] however, their concentration is comparatively small in nanosecond laser experiments that are carried out on the leading edge of the gas pulse. The pyrolysis parameters were varied over a large range. The best conversion efficiency and smallest number of side products were observed with the heating electrodes as close together as possible and the SiC tube heated to the maximum possible temperature.

It showed that mass spectra at 121.6 nm (10.20 eV) had to be recorded as well in order to optimise the conditions of carbene generation. They are presented in Fig. 3. The spectra in the top and centre trace were recorded without an excitation laser. At low and medium temperature pyrolysis (top trace) a small amount of l-C_3H_2 is discernible in the spectra recorded at 121.6 nm, despite its high ionization energy of 10.43 eV. No dependence on the VUV wavelength was observed, ruling out a speculation that we hit an accidental resonance in the VUV. When the temperature of the pyrolysis nozzle was increased further (centre trace) the carbene signal disappeared. The experiments described here differ from many earlier experiments on radicals in one important aspect: since two bonds have to be cleaved sequentially in order to produce l-C_3H_2, a second intermediate (IC_3H_2 in this case) appears in the carbene generation process. Most likely, even after complete conversion of the precursor, C_3H_2 can be formed by photodissociation of some IC_3H_2 intermediate that is still present. These carbene molecules contain a significant amount of internal energy and can perturb the photodissociation experiments described below. No information on the thermochemistry (ionisation and dissociation energies) of IC_3H_2 is available in the literature. It is thus essential to increase the pyrolysis up to the point where the 118 nm mass spectrum indicates complete conversion of the precursor and the carbene signal due to photodissociation of IC_3H_2 disappears at 121.6 nm. This corresponds to a pyrolysis nozzle that glows bright white. Note that an isomerisation to c-C_3H_2 in the pyrolysis nozzle can be ruled out because the latter has an IE of 9.15 eV[19] and would thus be detected at 121.6 nm ionisation.

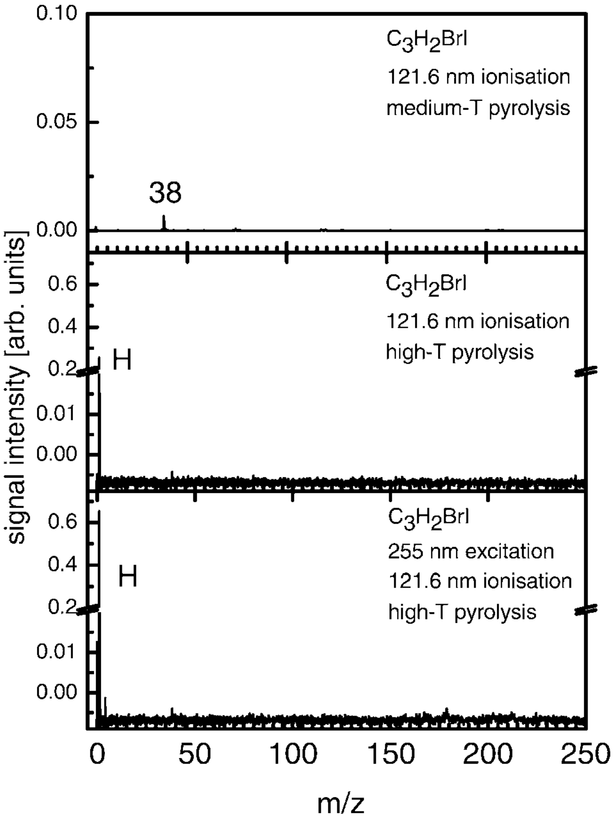

Fig. 3 121.6 nm (10.20 eV) photoionisation mass spectra of IC_3H_2Br under various conditions. At low and medium pyrolysis temperatures (top trace) C_3H_2 appears in the spectrum, despite its ionisation energy of 10.43 eV. Thus only at high pyrolysis temperatures (center and bottom trace) a beam of internally cold C_3H_2 is produced. As is visible, a H-atom background is present without excitation (centre trace), but the signal increases significantly when the excitation laser is turned on (bottom trace).

The spectrum in the centre trace shows the presence of a H-atom background signal at high pyrolysis temperature. The one-colour background appears due to H-atoms formed in the pyrolysis source. Since it is almost absent at lower pyrolysis temperatures it does not originate from dissociative photoionisation with the 121.6 nm or the 365 nm radiation alone. In the bottom trace a two-colour spectrum is depicted, using 121.6 nm for detection and the 255 nm excitation laser in addition. As can be seen, a strong enhancement of the signal at *m*/*z* = 1 is present, indicating that H-atom loss is an important reaction channel. The magnitude of the H-atom signal depended linearly on the excitation laser power (see ESI).†

We then investigated the H-atom loss as a function of excitation wavelength between 260 and 230 nm (460 to 520 kJ mol^{-1}), corresponding to excitation into the $C\,^2A_1$ state. In a simple molecular orbital picture an electron is excited from the $1b_1$ π-orbital located at the $C_{(2)}$–$C_{(3)}$ bond (see Scheme 1 for a definition of the subscripts) into the $2b_1$ orbital that can be viewed as a nonbonding π-orbital.[24,25] The empty p-orbital at $C_{(1)}$ can interact with the $C_{(2)}$–$C_{(3)}$ π-orbital, whereas the $C_{(1)}$–$C_{(2)}$ π-orbital is oriented perpendicular to the symmetry plane of the former.

Information on the product energy distribution can be obtained from Doppler profiles. Most of the energy released

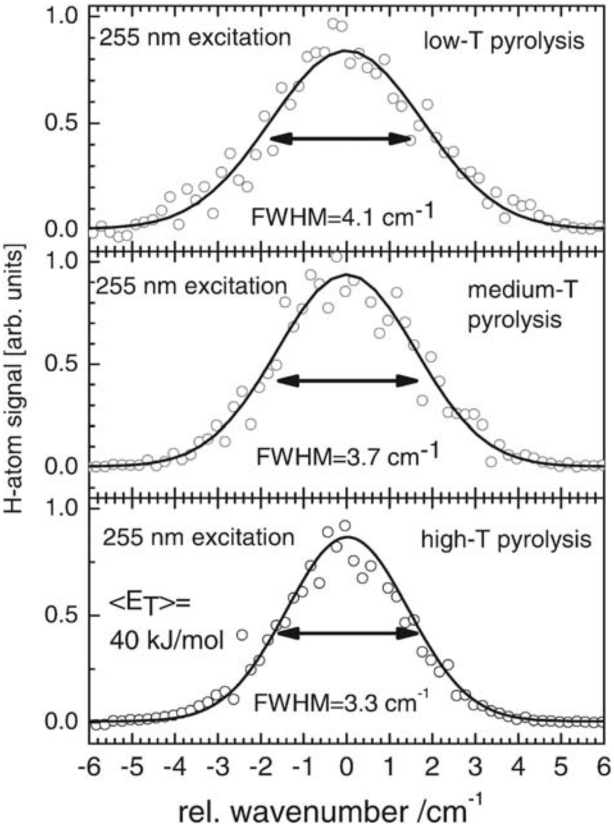

Fig. 4 Doppler profiles of the H-atom photofragment at 255 nm excitation. The full width at half maximum decreases with increasing temperature of the pyrolysis source. At the highest pyrolysis temperature (bottom trace), where quantitative conversion of the precursor is achieved, a translational energy release of 40 kJ mol^{-1} is obtained.

into translation will be carried away by the hydrogen atom on account of momentum conservation, leading to a Doppler broadening of the absorption line. In Fig. 4 three Doppler profiles recorded at 255 nm under different pyrolysis conditions are presented. The one-colour background signal recorded in spectra without the excitation laser was subtracted. All three absorption profiles are well fitted by a Gaussian (solid line), indicating a Maxwellian speed distribution. The contributions of the fine structure splitting and the laser bandwidth to the total broadening were neglected. As is evident from Fig. 4, the full width at half maximum (FWHM) of the Doppler profile decreases with increasing pyrolysis temperature. This dependence was observed at all excitation wavelengths and indicates the possible presence of a second source of hydrogen atoms in addition to the pyrolytically produced l-C_3H_2.

The most likely reason for the decreasing FWHM of the Doppler profile is obtained from the mass spectra in Fig. 2 and 3, as discussed above. They show that at low and medium temperatures conversion of the precursor is not complete and some IC_3H_2 intermediate is present. Some of this intermediate is converted to carbene by photolysis in the interaction region. This photolytically produced carbene possesses significant internal energy, as indicated by the appearance of a carbene signal in the 121.6 nm spectra in Fig. 3 (top trace) and might even be produced in the excited triplet state. H-atoms generated from such photolytically produced carbenes will carry away more translational energy, leading to a broader Doppler profile. Therefore we should consider only the profiles recorded at high pyrolysis temperature. Using the usual textbook formulae,[26] we extract an expectation value for the translational energy release of 40 kJ mol^{-1} from the FWHM of 3.3 cm^{-1}.

Another possibly interfering species might be HI, which is present in small amounts in the mass spectrum and is known to be a source of fast H-atoms.[27] However, in the energy range of interest its absorption cross section is continuously increasing to the blue and reaches its maximum at 222 nm.[28] At the 255 nm excitation discussed above, HI contributions will be negligible. Therefore this rather long excitation wavelength at the red edge of the absorption band was chosen for a detailed analysis of the dependence of the Doppler profile on the pyrolysis temperature.

Loss of a hydrogen atom can lead to two products, linear (l-) and cyclic (c-) C_3H. As both channels are energetically very close and do not exhibit a reverse barrier (see Fig. 1), it is not possible to distinguish them. At first glance l-C_3H seems to be the most likely reaction product, but inspection of Fig. 1 reveals that the by far lowest reaction barrier is the isomerisation barrier to c-C_3H_2. Thus energised l-C_3H_2 is able to access the c-C_3H reaction channel as well. In a thermal reaction, a dissociation on the c-C_3H_2 part of the ground state surface will lead to c-C_3H while dissociation on the l-C_3H_2 part of the surface will lead to l-C_3H. This picture assumes a fast internal conversion of propadienylidene to the electronic ground state, followed by a statistical dissociation. The almost perfect Gaussian shape of the Doppler profile supports a statistical mechanism. The measured translational energy release of $\langle E_T \rangle = 40$ kJ mol^{-1}, corresponding to 37% of the excess energy, based on the computed heat of reaction of path (2a), is comparatively large. When the maximum H-atom velocity is extracted from the wavenumber of the Doppler profile at which the signal has decayed to zero, we arrive even at the highest pyrolysis temperature at a maximum excess energy of 115–120 kJ mol^{-1} instead of the computational value of 104 kJ mol^{-1} for c-C_3H + H. Typical vibrational temperatures of pyrolytically generated radicals are 100–200 K, corresponding to only 1–2 kJ mol^{-1} of internal energy. There are two possible reasons, either (a) the dissociation energy is slightly lower than computed or (b) even at the highest pyrolysis temperatures still a small amount of carbene is present that contains some internal energy. If we assume that the dissociation energy is $\approx$12 kJ mol^{-1} smaller than computed, the translational energy release corresponds to $\langle E_T \rangle \approx 34\%$. This translational energy release is comparatively high for a statistical reaction, but not completely outside the usual range.

We also recorded the H-atom signal as function of the delay time between excitation and ionisation laser. In principle, a reaction rate can be extracted from the rise time of the signal. As is visible in Fig. 6, the signal rises within a few nanoseconds or less at all excitation wavelengths, thus the rate of H-atom loss is faster than the time resolution of our setup (5–10 ns). Note that the signal decay is due to the motion of the H-atoms out of the observation region and has no chemical significance. To support the experiments, we performed simple RRKM calculations utilizing the B3LYP frequencies and CCSD(T) barriers of Mebel *et al.*[10] and augmenting them with our own B3LYP/ 6-311G** frequency calculations for some transition states. The frequencies are summarised in the ESI.† The RRKM calculations neglect the rotations of the reactant and TS. The results indicate that H-atom loss of l-C_3H_2 is the dominant reaction channel in the energy range investigated in the present paper. At 230 nm excitation the calculations predict a rate constant of 8.2×10^{10} s^{-1} for the formation of l-C_3H, 3.5×10^{10} s^{-1} for the loss of H_2 and 2.0×10^{10} s^{-1} for the formation of c-C_3H, following fast isomerisation to cyclopropadienylidene. At 260 nm the rates are calculated to be 9.8×10^9 s^{-1}, 6.1×10^9 s^{-1} and 3.0×10^9 s^{-1}, respectively. The ratios of the calculated rates indicate that the channel for the loss of H_2 decreases in importance at shorter wavelengths compared to the loss of H-atoms. It thus seems that l-C_3H is the dominant reaction product. However, the numbers are so close that even small changes in the barriers and frequencies have a significant impact and might reverse the relative order. Nevertheless the measured subnanosecond rate is indeed in agreement with simple RRKM computations and is therefore to be expected in the case of a statistical dissociation. On the other hand, experiments on several alkyl radicals showed rates that were slower than expected.[29–31] It is therefore interesting to note that propadienylidene, like unsaturated radicals,[16,32] does not show such an unexpectedly slow H-atom loss. Since the time resolution of our nanosecond setup is insufficient, we intend to carry out femtosecond time-resolved experiments to gain further insight into the excited state dynamics of this carbene.

We also recorded an H-atom photofragment excitation (action) spectrum, given in the ESI.† The H-atom signal rises between 260 and 255 nm and reaches a maximum around 249 nm. When compared with the only available spectrum of this state, recorded in a rare gas matrix,[8,9] both spectra have a similar appearance in the red. However, the matrix spectrum continues to rise to the blue and reaches its maximum around 237 nm, in addition, the vibronic structure is discernible. Several reasons could be responsible for the differences: First, our experimental approach is sensitive to only one possible reaction channel, no information is available on the second one, loss of a H_2 molecule. Second, at the very high temperatures corresponding to Fig. 5 the stability of the pyrolysis source might not be sufficient for a long scan over a large energy range, thus a complete conversion of both precursor and IC_3H_2 intermediate cannot be ensured.

The results obtained for l-C_3H_2 are also relevant to earlier work on the propargyl radical, C_3H_3. Fahr *et al.* examined the absorption spectrum of propargyl in the UV range[33] and reported a maximum at around 242 nm. In later work on the photodissociation dynamics of the radical an H-atom action spectrum was recorded that appeared rather similar.[32] The data were confirmed by photofragment translational energy spectroscopy.[34] Recent computational work questioned this assignment and suggested a C_3H_2 isomer to be the carrier of the H-atom signal.[35,36] In principle, propadienylidene might be formed by overheating propargyl in the nozzle. However, the data presented here rule out such a contribution for the following reasons: (1) the Doppler profile at the highest temperature shows a FWHM of 3.3 cm^{-1} and is thus significantly broader than the one obtained for propargyl at the same wavelengths (FWHM = 2.4 cm^{-1}); (2) a sub-nanosecond dissociation time was obtained, thus H-atom loss occurs at least two orders of magnitude faster than in propargyl. In addition, neither the action spectrum recorded by us nor the earlier matrix absorption spectrum of propadienylidene resemble the H-atom action spectrum recorded for propargyl. Therefore, we conclude that propadienylidene does not contribute to the absorption[33] or the H-atom action spectrum[32] of the propargyl radical.

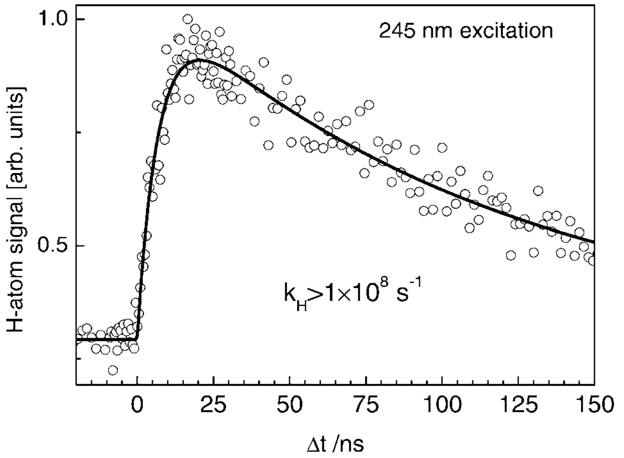

Fig. 5 H-atom signal as a function of the time delay between excitation and ionization laser pulse, showing a rise time that is faster than the time resolution of our setup. The H-atom loss occurs within less than a few nanoseconds.

Summary and conclusion

A free jet of propadienylidene (l-C_3H_2) was generated by flash pyrolysis of 1-iodo-3-bromopropyne. Complete conversion of the precursor was only achieved at high pyrolysis temperatures. We investigated the photochemistry of the carbene by laser excitation into the $C\,^2A_1$ state between 260 and 230 nm. In this energy range two channels are expected to be competitive in the photodissociation dynamics of the carbene, loss of a H_2 molecule, leading to C_3, and loss of an H-atom, associated with the formation of either linear or cyclic C_3H. Our approach, photofragment Doppler spectroscopy of hydrogen atoms is only sensitive to the latter channel. The Doppler profile has a Gaussian shape, supporting a statistical dissociation. The FWHM of the Doppler profiles depends strongly on the pyrolysis temperature, because some l-C_3H_2 is formed by photolysis of the IC_3H_2 intermediate in the interaction region at insufficient pyrolysis temperatures. From the profiles recorded at the highest pyrolysis temperatures a translational energy release of $\langle E_T \rangle$ = 34–37% of the excess energy is extracted. It is important to work under conditions where both the IC_3H_2Br precursor and the IC_3H_2 intermediate are completely converted in the pyrolysis source. In agreement with RRKM computations the H-atom loss is fast and could not be time-resolved with our nanosecond setup. The results rule out that propadienylidene photodissociation perturbs the data obtained for the photodissociation of propargyl, as indicated in recent theoretical papers.[35,36]

Acknowledgements

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