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Photoionization mass spectrometry of six isomers of C_7H_8 in the 7–22 eV photon energy range

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Abstract

Photoion mass spectrometry in the 7–22 eV range was used to obtain the parent and fragment photoion yield curves and appearance energies for six isomers of C_7H_8: toluene, cycloheptatriene, norbornadiene, quadricyclane, spiro[2,4]hepta-4,6-diene and 1,6-heptadiyne. The apparent heats of formation of fragment ions m_1^+ were determined for various fragmentation pathways and compared with standard thermochemical values of $\Delta H_f(m_1^+)$ in order to assign the fragmentation channels. Comparisons between the mass spectra of the six isomers obtained by photoelectron–photoion coincidence measurements at a photon excitation energy of 20 eV, and between the respective apparent $\Delta H_f(m_1^+)$ values for these isomers, were used to discuss the possible formation of common isomers during the various dissociative ionization processes. Interconversion of norbornadiene and cycloheptatriene ions is suggested to occur prior to the formation of $C_7H_7^+$ and other fragment ions in these two isomers. For toluene, isomerization does not appear to be necessary for the formation of low-energy fragment ions except for the tropylium form of $C_7H_7^+$ and its sequential product $C_5H_5^+$. The results also suggest that interconversion to an acyclic isomer common to all six species occurs in the formation of the three fragment ions $C_4H_3^+$, $C_3H_3^+$ and $C_2H_3^+$ at high internal energies of the parent ion. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Photoion mass spectrometry (PIMS) over the spectral range 7–22 eV was used to measure the appearance energies of the parent and fragment ions of six C_7H_8 isomers, toluene, cycloheptatriene, norbornadiene, quadricyclane, spiro[2,4]hepta-4,6-diene and 1,6-heptadiyne (Fig. 1). Only very limited data, mainly confined to the $C_7H_7^+$ and $C_5H_5^+$ fragment cations, have previously been available from either photon or electron impact measurements on these compounds. More extensive appearance energy data on these and other fragment ions is important to procure in the context of studies of the dissociative ionization of isotopic [1] and isomeric [2] C_7H_8 species in the 20–100 eV photon excitation range, in particular because this information permits assessment, on thermochemical grounds, of possible ionic and

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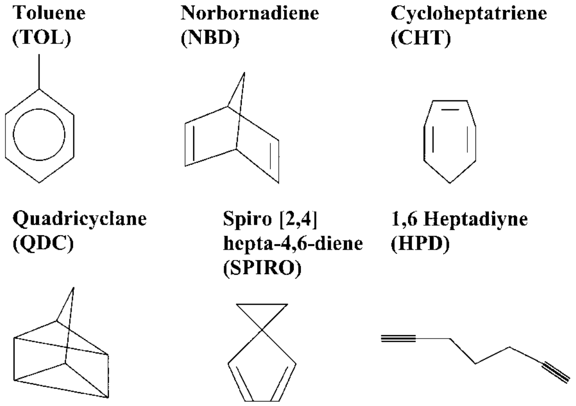

Fig. 1. Six C_7H_8 isomers investigated in the present study.

neutral products, as well as enabling one to choose between alternative dissociation processes.

The measured appearance energies are used to calculate the apparent heats of formation of fragment ions m_1^+ for possible fragmentation pathways. These heats of formation are compared with standard thermochemical values of $\Delta H_\mathrm{f}(\mathrm{m}_1^+)$, thus permitting assignment of particular fragmentation channels. The possible formation of a common isomer during the various dissociative ionization processes is discussed on the basis of two types of data: (i) a comparison between the mass spectra of the six isomers, measured at a photon excitation energy of 20 eV and (ii) correlations between the respective apparent $\Delta H_\mathrm{f}(\mathrm{m}_1^+)$ values for these isomers.

2. Experimental

Photoion yield curves of six C_7H_8 isomers were measured between 7 and 20, 25 or 35 eV using monochromatized synchrotron radiation from the electron storage ring BESSY I at Berlin. The species measured were toluene, cycloheptatriene, norbornadiene, quadricyclane, spiro[2,4]hepta-4,6-diene and 1,6-heptadiyne (Fig. 1). These were commercial products of the highest available purity and were used without further treatment.

The general experimental setup and procedure have been reported elsewhere [3,4] and only a brief summary is given here. The excitation source was monochromatized synchrotron radiation from the electron storage ring BESSY (800 MeV source) at Berlin and the spectrometer used was a 1.5 m modified McPherson 225 normal incidence spectrometer equipped with a 1200 lines per mm grating (Au coated). The monochromatized incident radiation was focussed onto the ionization region of a quadrupole mass spectrometer (Leybold Q200). The bandwidth of the incident monochromatic radiation was 2.3 Å in all experiments. The absolute wavelength is known to better than 0.1 Å. The photon intensity at each wavelength was measured by a sodium salicylate sensitized photomultiplier. The ions were detected by a channeltron multiplier after mass separation by the quadrupole mass spectrometer. Measurements were made of the parent ion M^+ and the most intense fragment ions. Mass spectra were mostly determined at 20 eV photon excitation energy.

The determination and significance of PIMS onsets can be delicate matters from the viewpoint of obtaining thermochemical information since the appearance energies (AE) measured are “effective” values. These values are, in particular, a function of instrumental detection sensitivity, and also reflect effects of thermal energy as well as any activation barriers which could lead to depositing excess energy (i.e. internal and/or kinetic energy) in the fragments. In our case, onset energies of fragments correspond to dissociating ion internal energies at which the particular dissociation rate is of the order of 10^4 s^{-1} [4,5].

Our onset measurements were made on the ion signal curve corrected for the effective detected spectrum of the incident synchrotron radiation. The AEs were determined from the point at which the corrected ion signal curve reached a background line. For most fragment ions, the onsets are quite clearcut, as is easily confirmed by the curve representing the logarithm of the corrected ion signal. In these cases, the error in determining the AE is less than ±0.1 eV. For fragment ions having small intensities, or slowly rising signals, the estimated error in the determined appearance energies is generally less than ±0.3 eV. The average internal (thermal) energy at 300 K of the C_7H_8

isomers is estimated to be of the order of 0.14 eV. From a comparison of our onset energies with those of the few fragment ions ($C_7H_7^+$, $C_6H_5^+$ and $C_5H_5^+$) of the C_7H_8 isomers that have been determined, for example, in ion traps by time-resolved PIMS [6] or other time-resolved ion photodissociation techniques [7], or by comparison with well-established thermochemical limits [8], we estimate our kinetic shift (plus average thermal energy) to be 0.5 ± 0.2 eV in most cases. Any apparent excesses outside this range, with respect to the thermochemical values, are probably due to the existence of activation barriers and are thus dependent on the character of the transition state [1]. The use of our PIMS appearance energies in the determination of fragmentation pathways of toluene isotopic and isomeric species is discussed elsewhere [1,2].

Mass spectra of the C_7H_8 isomers were measured by a photoelectron–photoion coincidence (PEPICO) technique at a photon excitation energy of 20 eV. These measurements were carried out using Super-ACO synchrotron radiation (LURE-Orsay) as the excitation energy source, as described elsewhere [1].

3. Results and discussion of photoion yield curves

Photon yield curves for parent and selected fragment ions in their onset regions are shown in Figs. 2–7 for the C_7H_8 isomers studied. The AEs are given in Table 1 and are compared, in Sections 3.1–3.6, with previous relevant data on parent and fragment ions, when available. Application of this information to determination of the apparent heats of formation of fragment ions is reserved for Section 4, within the context of a discussion concerning the possible formation of a common isomer during the photofragmentation processes of the six C_7H_8 isomers. In general, the AEs of the ions given in Table 1 as products of the dissociative ionization of the C_7H_8 isomers are compatible with thermochemically estimated limits as discussed later in Section 4.2 in the context of the apparent heats of formation of the fragment ions. Exceptions to this compatibility are discussed as particular fragment ion cases arise.

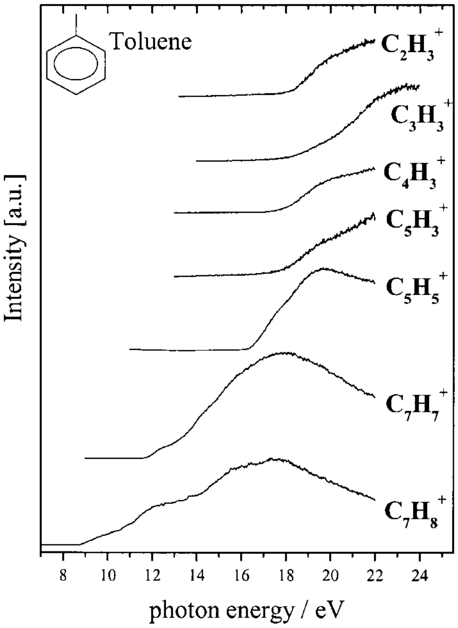

Fig. 2. Photoion yield curves for toluene excited in 7–22 eV energy range.

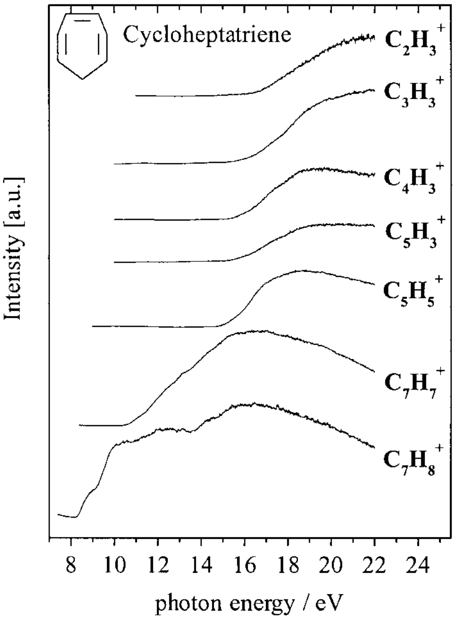

Fig. 3. Photoion yield curves for cycloheptatriene excited in 7–22 eV energy range.

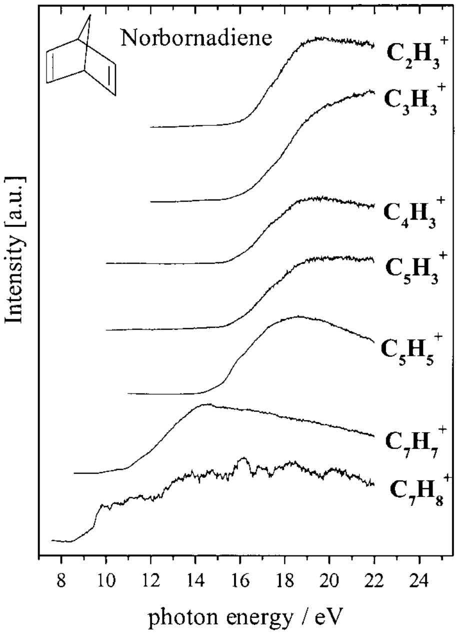

Fig. 4. Photoion yield curves for norbornadiene excited in 7–22 eV energy range.

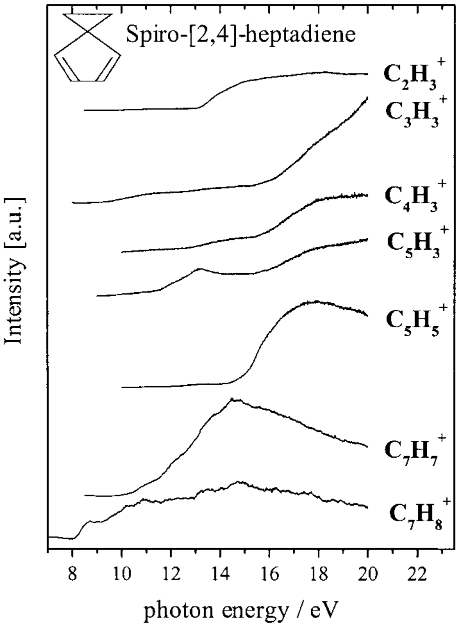

Fig. 6. Photoion yield curves for spiro[2,4]hepta-4,6-diene excited in 7–20 eV energy range.

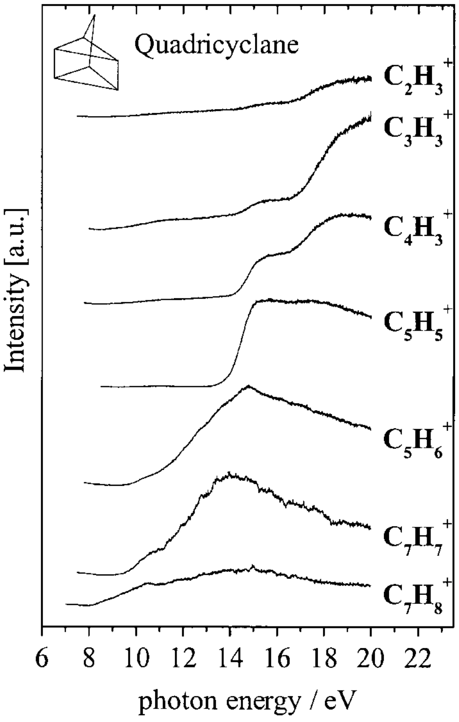

Fig. 5. Photoion yield curves for quadricyclane excited in 7–20 eV energy range.

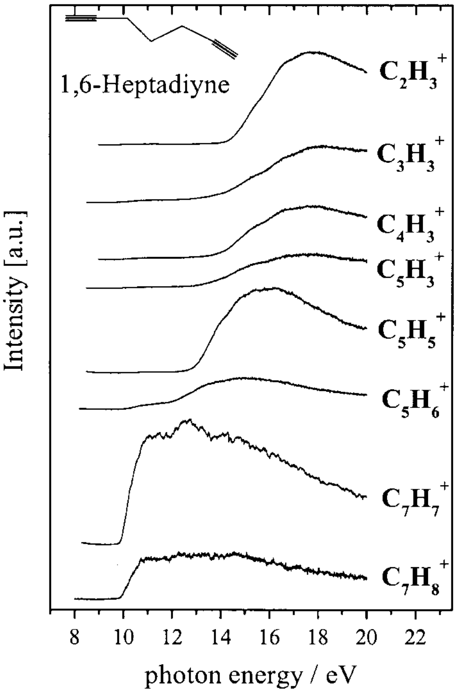

Fig. 7. Photoion yield curves for 1,6-heptadiyne excited in 7–20 eV energy range.

Table 1
PIMS appearance energies of observed ionic fragments in eV

m/z	Fragment ion m_i^+	Toluene	Cycloheptatriene	Norbornadiene	Quadricyclane	Spiro[2,4]hepta-4,6-diene	1,6-Heptadiyne
92	$C_7H_8^+$	8.75	8.2	8.45	7.97	8.06	9.85
91	$C_7H_7^+$	11.43	10.3	9.51/10.8	9.29	9.51	9.85
89	$C_7H_5^+$	13.1	13.6	13.0		13.0	
77	$C_6H_5^+$	13.6	12.6	12.1			
76	$C_6H_4^+$		12.8				
66	$C_5H_6^+$	12.85	10.4	10.8	10.6		9.85/12.1
65	$C_5H_5^+$	13.4/16.0	12.9/14.3	12.6/13.9	13.4	14.3	12.1
64	$C_5H_4^+$	15.0					9.9/11.9
63	$C_5H_3^+$	16.5 ± 0.5	13.8	15.0	14.1	11.5	12.8
62	$C_5H_2^+$					11.2	
53	$C_4H_5^+$	15.11	13.3	12.8/15.2	12.9	13.2	11.9
52	$C_4H_4^+$	14.33	13.6	12.8/15.2	12.9	14.2	11.9
51	$C_4H_3^+$	17.0	15.4	15.2	14.1/16.8	12.7/15.4	13.2
50	$C_4H_2^+$	17.8	15.4	15.4			
41	$C_3H_5^+$	17.1			14.1/16.8	15.3	12.0
40	$C_3H_4^+$	16.44		13.5	13.7/16.6	14.4	11.9
39	$C_3H_3^+$	17.8	15.8	15.2	14.3/16.7	15.4	13.3
38	$C_3H_2^+$			16.2			
27	$C_2H_3^+$	17.6	16.2	15.2	14.3/16.6	13.1	14.0

3.1. Toluene

Our measured value for the ionization potential of toluene is 8.75 ± 0.05 eV. An accurate literature value of 8.8276 ± 0.0006 eV has been obtained by Lu et al. [9] using resonant two-photon ionization techniques. This value is in agreement with that, 8.821 ± 0.010 eV, obtained in earlier photoionization measurements by Watanabe in 1954 [10]. Our own, lower, value is about 0.01 eV outside the respective error limits. This may be due in part to the thermal energy in the toluene ion.

Fragment ion appearance potential measurements have been made previously only for three ions, $C_7H_7^+$, $C_6H_5^+$ and $C_5H_5^+$. In the following, we make a comparison with our own values for these ions.

Our measured onset energy of 11.43 eV for the $C_7H_7^+$ ion agrees well with the value 11.3 ± 0.2 eV that we estimate, from the PEPICO measurements of Bombach et al. [11,12] and their RRKM analysis, as the energy of a toluene ion at a dissociation rate $\approx 10^4$ s^{-1}, and it agrees well with the PIMS measurements, on the microsecond time scale, of Lifshitz et al. [6]. It is higher than the value, 10.71 ± 0.03 eV given by Traeger and McLoughlin [13] from photoionization studies using very high ion detection sensitivity. In their measurements, the $C_7H_7^+$ ion signal is of extremely low intensity between 10.71 and about 11.4 eV, after which there is a fairly rapid rise in intensity, as can be seen in their Fig. 5 [13].

The breakdown curves of the toluene ion obtained by Bombach et al. [12], indicate that the $C_7H_7^+$ yield is unity between 12 and 15.5 eV, dropping to zero at about 17 eV at the same time that the ion $C_5H_5^+$ signal appears at about 16 eV and increases in intensity at higher energies. Electron impact studies by Tajima and Tsuchiya [14] gave 16.4 ± 0.2 eV as onset energy for the formation of $C_5H_5^+$ from toluene-h_8. These authors concluded that the resulting $C_5H_5^+$ ion has the pent-1-yn-3-en-5-yl acyclic structure. In the present PIMS measurements on toluene using synchrotron radiation, a very weak $C_5H_5^+$ signal is observed between 13.4 and 16 eV after which a

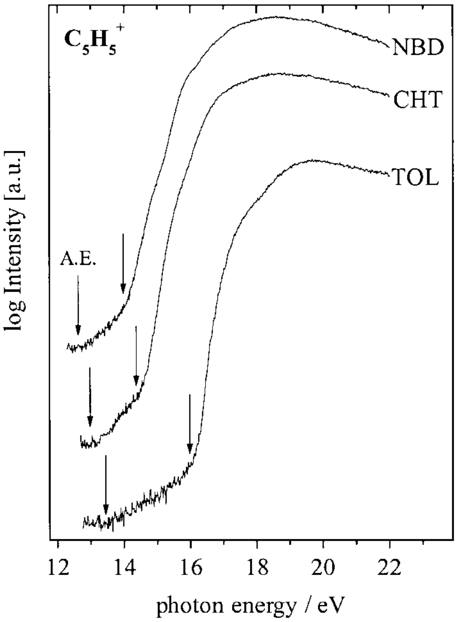

Fig. 8. Photoion yield curves in 12–22 eV energy range of the $C_5H_5^+$ fragment ion for norbornadiene (NBD), cycloheptatriene (CHT) and toluene (TOL). The first and second onset energies are indicated by vertical arrows.

very rapid rise occurs (Table 1). These double onsets can be clearly seen in the semi-log ion yield plots of $C_5H_5^+$ in Fig. 8. We note that direct photodissociation experiments on the $C_7H_7^+$ ion [15] revealed an apparent onset for $C_5H_5^+$ production at 2.3 eV excitation energy, the weak signal of which rose rapidly beyond 3.4 eV. Since the amount of internal energy in the initial $C_7H_7^+$ ion is uncertain in the photodissociation experiments [15], the 2.3 and 3.4 eV photodissociation energy values must be considered as lower limits. In our PIMS experiments, the differences in energy between the onset for $C_7H_7^+$ formation (11.4 eV) and the weak and strong onsets for $C_5H_5^+$ formation (Table 1) are 2.0 ± 0.2 and 4.6 eV, respectively. Our 13.4 eV onset energy for $C_5H_5^+$ agrees well with that deduced from the photodissociation spectra, but the second onset at 16 eV is more than 1 eV above the total energy corresponding to the increase in the $C_5H_5^+$ photodissociation yield at 3.4 eV. The $C_7H_7^+$ photodissociation measurements [15] do not go beyond 4.6 eV photon energy and therefore it is not known from this work whether there is a further increase in $C_5H_5^+$ yield which might correspond to our second onset at 16 eV. However, a sharp rise in $C_5H_5^+$ yield at 4.8 eV internal energy was observed by McCrery and Freiser [16] in studies of the photodissociation spectrum of the benzylium $C_7H_7^+$ ion. This value is consistent with our second onset energy at 16 eV.

The PEPICO experiments of Bombach et al. [12] gave a single onset for $C_5H_5^+$ formation from toluene at about 16 eV. The weak signal between 13.4 and 16 eV observed in our PIMS experiments may indicate that there are two processes leading to the formation of $C_5H_5^+$, having onsets at 13.4 and 16 eV, respectively. This is discussed in more detail elsewhere [1].

The $C_6H_5^+$ ion has an onset energy at 13.6 eV from our PIMS measurements, agreeing well with the value 13.7 eV obtained from an electron impact study on toluene [17]. The ion obtained from dissociative photoionization of toluene is, most probably, a phenyl ion since trapped ion mass spectrometry experiments [18] have shown that the $C_6H_5^+$ ion obtained by dissociative electron impact ionization of benzene and of monohalogenated benzenes has the structure of the phenyl species. On this basis, a thermochemical estimation of 11.3 eV for the AE of the $C_6H_5^+$ ion by the dissociative photoionization process $C_7H_8 + h\nu \rightarrow C_6H_5^+ + CH_3$ is in satisfactory agreement with our observed value, given that the products of this reaction probably contain considerable internal energy, as discussed elsewhere [1].

We note that the fragment ions $C_5H_2^+$ and $C_3H_2^+$, observed in PEPICO measurements on toluene at 20 eV photon excitation energy [1], could not be measured with sufficient accuracy in our PIMS experiments to provide reliable appearance energies (Table 1).

3.2. Cycloheptatriene

Our measured value for the ionization potential of cycloheptatriene is 8.20 ± 0.05 eV (Table 1). This is in satisfactory agreement with the value 8.29 ± 0.01 eV obtained as an *upper limit* by photoionization mass spectrometry [13].

The appearance energy of the $C_7H_7^+$ ion that we have measured, 10.3 eV, is close to that, 10.4 ± 0.1

eV, determined by Myerson and Rylander [19] in an electron impact experiment on cycloheptatriene, but is lower than the electron impact value 10.73 eV given by Hoffman [17]. A much lower value, 9.36 ± 0.02 eV has been given by Traeger and McLoughlin [13] for measurements using much higher ion-detection sensitivity than in our case, and also possibly involving isomerization effects. It is probable that in the experiment of Traeger and McLoughlin [13], it is the tropylium ion Tr-$C_7H_7^+$ that is formed, since we estimate from the data in Tables 1–3 that the thermochemically calculated AE for the dissociative ionization of cycloheptatriene by the process $C_7H_8 + h\nu \rightarrow \text{Tr-}C_7H_7^+ + H$ is 9.12 eV, whereas the AE of the benzylium ion Bz-$C_7H_7^+$ is calculated to be at least 0.3 eV higher than the experimental value of Traeger and McLoughlin. In our experiment, it is possible that the $C_7H_7^+$ ion population contains both benzylium and tropylium (and perhaps tolyl) cations. It has been shown that the actual relative percentage of these $C_7H_7^+$ isomers depends both on the parent molecule and on the method of excitation [20–23].

The $C_5H_5^+$ ion from the dissociative ionization of cycloheptatriene has an initial, weak, onset at 12.9 eV, followed by a much stronger signal starting at 14.3 eV (Fig. 8). We note that an analogous double onset for the $C_5H_5^+$ ion was observed in our PIMS study of toluene, as discussed above. The literature values of the $C_5H_5^+$ AE from cycloheptatriene, 16.0 [24] and 16.66 eV [25] from electron impact measurements dating from the early 1960s, are much higher than those that we have measured by photon impact. No other measurements, either by electron or by photon impact, have been reported. The double onset we observed in cycloheptatriene could indicate that there are two processes leading to the formation of $C_5H_5^+$, as has been discussed for the case of toluene [1], and elsewhere for cycloheptatriene [2]. Indeed, estimations of the thermochemical value of the AE of $C_5H_5^+$ from cycloheptatriene, assuming the cyclopentadienyl ion structure for the fragment ion, give AEs of 11.75 and 14.25 eV for the respective processes $C_7H_8 + h\nu \rightarrow C_5H_5^+ + C_2H_3$ and $C_7H_8 + h\nu \rightarrow C_5H_5^+ + C_2H_2 + H$, values which are compatible with our observed two onset values. The possibility of other $C_5H_5^+$ isomers being formed is discussed in Section 4.2.

The PIMS onset energy of 12.6 eV for the $C_6H_5^+$ ion formed by dissociative ionization of cycloheptatriene (Table 1) is also much lower than the electron impact value 14.17 eV reported by Hoffman [17]. Assuming that the $C_6H_5^+$ ion formed is a phenyl cation, the thermochemical appearance energy of $C_6H_5^+$ is calculated to be 11.3 eV, which is compatible with our measured value if one considers a possible energy barrier resulting from the skeletal reorganization energy necessary to produce a phenyl ion from a cycloheptatriene cation.

The case of the $C_5H_6^+$ fragment ion merits some discussion. Assuming a cyclic form (cyclopentadiene [1]) for this ion, the value of $\Delta H_f(C_5H_6^+) = 9.98$ eV calculated on the basis of its PIMS appearance energy is greater than, but uncomfortably close to, the standard [1] literature value $\Delta H_f(C_5H_6^+) = 9.92$ eV [8], whereas for the other C_7H_8 isomers (see Table 3), the PIMS-based $\Delta H_f(C_5H_6^+)$ is at least 0.5 eV greater than the standard value, as is reasonable, given the possibility of activation barriers in the formation of this fragment ion as well as kinetic shift effects. Other forms of $C_5H_6^+$ must therefore also be considered in order to account for the low AE of this fragment ion in the case of cycloheptatriene.

In the standard thermochemical tables [8], the cyclopentadiene ion is considered to be the lowest energy form of $C_5H_6^+$. We therefore searched the appropriate literature in order to see whether a previously unknown form of lower energy exists or whether there is an error in the previously established heat of formation of the cyclopentadiene ion. Indeed, we do find a lower heat of formation of $C_5H_6^+$ that can be determined from the measured appearance energy of this ion in electron impact studies of two isomers of C_7H_{10}, bicyclo[2.2.1] heptene-2-ene (i.e. norbornene) for which $AE(C_5H_6^+) = 9.22 \pm 0.01$ eV and tricyclo[2.2.1.$0^{2.6}$]heptane (i.e. nortricyclene) where

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[1] Standard values of the heats of formation refer to values that are accepted in thermochemical tables [8].

$AE(C_5H_6^+) = 9.44 \pm 0.01$ eV [26]. In both cases, C_2H_4 is the neutral product of the parent ion fragmentation. The value of $\Delta H_f(C_5H_6^+)$ can be obtained from the relation $\Delta H_f(C_5H_6^+) = AE(C_5H_6^+) - \Delta H_f(C_2H_4) + \Delta H_f(C_7H_{10})$ (see Section 4.2). Substituting in this relation the $AE(C_5H_6^+)$ values and $\Delta H_f(C_2H_4) = 0.54$ eV [8] and $\Delta H_f(C_7H_{10}^+) = 0.93$ and 0.88 eV for the respective C_7H_{10} isomers, we obtain the values $\Delta H_f(C_5H_6^+) = 9.61$ and 9.78 eV from the C_7H_{10} isomers. These values are decidedly lower than the standard value for the cyclopentadiene cation and are compatible with the apparent AEs measured in our PIMS study of cycloheptatriene. Further work is required in order to determine the structure of the $C_5H_6^+$ ion formed in the dissociative ionization of the C_7H_{10} isomers.

3.3. Norbornadiene

Our measured value for the ionization potential of norbornadiene is 8.45 ± 0.05 eV. This agrees well with the 8.42 ± 0.02 and 8.35 ± 0.01 eV values derived from photoionization mass spectrometry respectively by Demeo and El-Sayed [27] and by Traeger and McLoughlin [13], and with the photoelectron spectroscopy vertical ionization value 8.43 eV [28].

The only literature values for an appearance energy of an ionic fragment from norbornadiene are for the $C_7H_7^+$ ion, reported as 9.6 [29] and 9.75 eV [30] by electron impact and 9.25 eV by photoionization [13]. Our PIMS observation of a shallow rising signal whose onset is at 9.51 eV is in reasonable agreement with these values, taking into account the higher sensitivity for ion detection in the photoionization technique of Traeger and McLoughlin [13].

3.4. Quadricyclane

Our PIMS value for the ionization potential of quadricyclane is 7.97 ± 0.05 eV (Table 1). This is much lower than the electron impact value, 8.70 eV, given by Dolejsek et al. [30], but agrees well with the adiabatic ionization potential given as 7.86 eV from the HeI photoelectron spectrum onset [28,31]. The vertical ionization potential is 8.33 eV as determined by photoelectron spectroscopy [31].

The only ionic fragment from quadricyclane whose electron impact appearance energy has been measured is the $C_7H_7^+$ ion. Its AE has been reported as 9.56 eV [30]. Our PIMS measurements give $AE(C_7H_7^+) = 9.29$ eV (Table 1).

3.5. Spiro[2,4]hepta-4,6-diene

The PIMS ionization potential of spiro[2,4]hepta-4,6-diene is 8.06 ± 0.05 eV, in good agreement with the vertical ionization photoelectron spectroscopy value, 8.14 eV, measured by Gleiter et al. [32].

Similar to the case of of norbornadiene and quadricyclane, the only ionic fragment from spiro[2,4]hepta-4,6-diene whose AE has been measured previously is the $C_7H_7^+$ ion, the electron impact value of which has been reported as 10.45 ± 0.10 eV [33]. Our PIMS value of 9.51 ± 0.10 eV is somewhat lower than the electron impact value but is more consistent with thermochemical and structural considerations (see Section 4.2).

3.6. 1,6-Heptadiyne

The species 1,6-heptadiyne is the only acyclic isomer of the C_7H_8 series studied here. The PIMS ionization potential is 9.85 ± 0.05 eV (Table 1). Although the PIMS signal of the parent ion is weak, our value is in excellent agreement with the reported photoionization and photoelectron spectroscopy adiabatic values, 9.85 ± 0.01 eV [13].

The 1,6-heptadiyne parent ion is suggested by Traeger and McLoughlin [13] to undergo vibrational predissociation. Indeed the $C_7H_7^+$ PIMS signal is much stronger than that of the parent ion, as is also reflected in the mass spectrum taken at 20 eV photon excitation energy. The PIMS appearance energy of $C_7H_7^+$, 9.85 eV is the same as that of the parent ion, consistent with the parent ion undergoing predissociation. The ion $C_7H_7^+$ is the only ionic fragment from 1,6-heptadiyne whose electron impact appearance potential has been measured.

The electron impact AE has also been reported as being identical with the ionization potential of this isomer [13]. Our results are therefore consistent with the electron impact study. We note, furthermore, that two other fragment ions, $C_5H_6^+$ and $C_5H_4^+$, have appearance energies close to 9.85 eV, which suggests that there are three competitive vibrational predissociation channels which are open at the ion formation onset of this acyclic species.

4. Fragmentation via a common isomer?

In much of the earlier work on the electron or photon impact dissociative ionization of the toluene isomers, it has often been stated that their molecular ions fragment through a common isomer. Two main arguments have been offered in favour of this conclusion: (1) the quasi-identical mass spectra of these isomers [29,30,34]; (2) the fact that, on the basis of the appearance energies, the apparent heat of formation of the ion $C_7H_7^+$ is closely similar for the several isomers [19,29]. It is recognized that a similarity in apparent heat of formation might simply reflect a constant activation energy for the reaction giving $C_7H_7^+ + H$ and so does not necessarily imply a common intermediate. We note that in the case of the dissociative photoionization of the isomers naphthalene and azulene [35], the concordance between the heats of formation of their corresponding fragment ions showed the existence of a common isomer as intermediates in the fragmentation processes.

In order to determine whether the $C_7H_8^+$ species form a common isomer before fragmentation, we investigated these two characteristics on the basis of our much more extensive data than that previously available.

4.1. Photoionization mass spectra

The mass spectra of the six isomers, except spiro[2,4]hepta-4,6-diene, were measured at 20 eV photon excitation energy in PEPICO experiments with a reflectron mass analyzer. The data for the principal mass peaks are given in Table 2 as parent or fragment ion signals relative to the total ion count. The $C_7H_7^+$ ion is the major ion in each case but there are considerable differences between the mass spectra of the isomers. This is also true of the corresponding electron impact mass spectra taken with 70 eV electrons [36]. The relative ion peak intensities for a particular isomer are not identical in the photon and electron impact mass spectra, due to differences in the ionization sources, mass analyzers and ion transmitivity in the two cases. We note that time-of-flight mass analysis, as used in the PEPICO measurements at 20 eV photon energy, exhibits no pronounced variation of detection sensitivity with ion mass.

Table 2 reveals marked, but not perfect, similarities between the mass spectra of toluene and cycloheptatriene on one hand and, to a lesser extent, norbornadiene and quadricyclane on the other hand. The mass spectrum of 1,6-heptadiyne, which is the only acyclic isomer, is very different from the spectra of the other isomers.

These results argue against a common isomer as intermediate for the majority of the decomposition pathways although for some fragment ions there may be common channels in some of these isomers, in particular for toluene and cycloheptatriene and the pair norbornadiene and quadricyclane. From the structures of these pairs of ions, as judged from their neutral forms in Fig. 1, we can speculate that common transition states are easy to construct for each pair. The formation of the $C_7H_7^+$ ion in toluene, cycloheptatriene [1] and, as shown in Section 4.2, norbornadiene and spiro[2,4]hepta-4,6-diene, may also proceed by common pathways. We note that some theoretical attention has been given to the rearrangement of the toluene and cycloheptatriene molecular ions involved in the formation of the tropylium fragment ion [37]. We remark also that the similarity between the mass spectra of norbornadiene and quadricyclane is somewhat intriguing in view of the conjecture that interconversion between the ground states of the pair of ions norbornadiene$^+$/quadricyclane$^+$ is state-symmetry forbidden [28, 38]. This implies that if isomerization takes place between these species it proceeds via excited electronic states.

Table 2
Percentage of total ion yield of observed fragment ions from ReTOF–PEPICO measurements at 20 eV photon energy

m/z	Fragment ion m_i^+	Toluene	Cycloheptatriene	Norbornadiene	Quadricyclane	1,6-Heptadiyne
93	$^{13}CC_6H_8^+$	1	1	1	1	
92	$C_7H_8^+$	26	17	16	9	4
91	$C_7H_7^+$	53	45	31	32	30
90	$C_7H_6^+$	1	1	1	1	1
89	$C_7H_5^+$	1	1		1	1
79	$C_6H_7^+$		1			
78	$C_6H_6^+$		1			
77	$C_6H_5^+$		1		1	
76	$C_6H_4^+$					
67	$C_5H_7^+$		1	2	1	
66	$C_5H_6^+$	1	5	17	18	1
65	$C_5H_5^+$	7	10	8	13	4
64	$C_5H_4^+$				1	1
63	$C_5H_3^+$	1	1	1	1	2
62	$C_5H_2^+$					
53	$C_4H_5^+$		1	1	1	9
52	$C_4H_4^+$		1	1	1	4
51	$C_4H_3^+$	2	2	1	3	4
50	$C_4H_2^+$		1	1		1
43	$C_3H_7^+$					1
41	$C_3H_5^+$		1	1	1	1
40	$C_3H_4^+$		1	4	5	6
39	$C_3H_3^+$	2	5	5	7	9
38	$C_3H_2^+$		1	1		1
30	$C_2H_6^+$			1		
27	$C_2H_3^+$		1	1	1	16

4.2. Apparent heats of formation

We have calculated the apparent heats of formation $\Delta H_f(m^+)$ of the fragment ions formed by processes

$$M + h\nu \rightarrow M^+ + e^- \rightarrow m_1^+ + m_i \qquad (1)$$

where M is the parent isomer, m_1^+, the fragment ion whose AE has been measured, and m_i are the i neutral products formed directly or sequentially in the fragmentation reaction studied. The apparent heat of formation of m_1^+ is given by the following relation:

$$\Delta H_f(m_1^+) = AE(m_1^+) - \sum(\Delta H_f(m_i)) + \Delta H_f\ (M) \qquad (2)$$

This procedure was used for the following fragment ions: $C_7H_7^+$, $C_7H_5^+$, $C_6H_5^+$, $C_5H_6^+$, $C_5H_5^+$, $C_5H_3^+$, $C_4H_5^+$, $C_4H_4^+$, $C_4H_3^+$, $C_3H_3^+$, and $C_2H_3^+$. The results are given in Table 3. The fragmentation products $m_1^+ + m_i$ given in Table 3 are those that were the most probable in a study of the dissociative ionization of toluene isotopomers [1]. The number of possible pathways are too great for meaningful conclusions to be drawn for the other fragment ions. The thermochemical data on the m neutrals were mostly taken from standard collections [8] and are given in Table 4.

Taking into account the possibility of different kinetic shifts (within the range 0.5 ± 0.2 eV) for the various isomers, and uncertainties in the measurement of the fragmentation onset energies, similar values of the apparent heats of formation were found for the various fragment ions as discussed below:

$C_7H_7^+$: The parent ions toluene, cycloheptatriene, norbornadiene and spiro[2,4]hepta-4,6-diene

Table 3
Apparent heats of formation ΔH_f of fragment ions m_1^+ for C_7H_8 isomers in eV

m/z	Fragment ion m_1^+	Neutral fragments m_i	Toluene	Cycloheptatriene	Norbornadiene	Quadricyclane	Spiro[2,4]hepta-4,6-diene	1,6-Heptadiyne	Literature value $\Delta H_f(m_1^+)$ (see text)
91	$C_7H_7^+$	H	9.69	9.98	9.78/11.07	10.51	9.72	11.69	8.8[a], 9.32[b]
89	$C_7H_5^+$	$H + H_2$	11.36	13.28	13.27		13.21		10.36 (?)
77	$C_6H_5^+$	CH_3	12.61	13.03	13.12				11.68
66	$C_5H_6^+$	C_2H_2	11.01	9.98	10.97	11.72		11.54/13.84	9.92[c]
65	$C_5H_5^+$	C_2H_3	11.17/13.77	12.09/13.49	12.38/13.69	14.13	14.02	13.45	10.49, 10.9, 11.73, 11.87, 12.0[d]
		$H + C_2H_2$	9.3/11.9	10.12/11.62	10.41/11.82	12.26	12.15	11.58	
63	$C_5H_3^+$	$H_2 + C_2H_3$	14.27	12.99	14.78	14.83	11.22	14.15	12.79, 13.66, 14.26[d]
		$H + H_2 + C_2H_2$	12.4	11.12	12.91	12.96	9.35	12.28	
		$H + C_2H_4$	14.22	12.94	14.73	14.78	11.17	14.10	
53	$C_4H_5^+$	$c\text{-}C_3H_3$	11.06	10.28	10.47/13.17	11.82	11.11	11.44	10.28, 10.66, 10.94, 11.13[d]
		$l\text{-}C_3H_3$	12.07	11.29	11.48/14.18	12.83	12.12	12.45	
52	$C_4H_4^+$	C_3H_4[e]	12.87	13.56	13.35/15.75	14.40	14.69	14.02	12.54, 12.64, 12.77[d]
		C_3H_4[f]	12.92	13.61	13.4/15.8	14.45	14.74	14.07	
		C_3H_4[g]	11.98	12.67	12.46/14.86	13.51	13.8	13.13	
		$H + c\text{-}C_3H_3$	8.03	8.72	8.51/10.91	9.56	9.85	9.18	
		$H + l\text{-}C_3H_3$	9.04	9.73	9.52/11.92	10.57	10.86	10.19	
51	$C_4H_3^+$	$C_2H_2 + CH_3$	13.64	13.46	13.85	13.7	11.29/13.99	13.42	12.49
		$H_2 + c\text{-}C_3H_3$	12.96	12.78	13.17	13.02	10.61/13.31	12.74	
		$H_2 + l\text{-}C_3H_3$	13.97	13.79	14.18	14.03	11.02/14.32	13.75	
		C_3H_5[h]	15.78	15.60	15.99	15.84	13.43/16.13	15.56	
		C_3H_5[i]	14.84	14.66	15.05	14.90	12.49/15.19	14.62	
		$H + C_3H_4$[e]	13.28	13.10	13.49	13.34	10.93/13.63	13.06	
		$H + C_3H_4$[f]	13.33	13.15	13.54	13.39	10.98/13.68	13.11	
		$H + C_3H_4$[g]	12.39	12.21	12.60	12.45	10.04/12.74	12.17	
39	$C_3H_3^+$	$C_2H_3 + C_2H_2$	13.21	12.63	12.62	12.67/15.07	12.76	12.29	11.14[c], 12.22[j]
		$H + 2C_2H_2$	11.34	10.76	10.75	10.8/13.2	10.89	10.42	
27	$C_2H_3^+$	$c\text{-}C_5H_5$	15.62	15.64	15.23	15.28/17.58	13.07	15.60	11.19, 11.45, 11.53, 11.63, 11.79[d]
		$l\text{-}C_5H_5$	14.26	14.28	13.87	13.92/16.22	11.71	14.24	

$M + h\nu \rightarrow m_1^+ + m_i$ (m_i : neutral fragments).

[a] Tropylium.

[b] Benzylium.

[c] Cyclic.

[d] According to different m_1^+ isomers.

[e] Allene.

[f] Propyne.

[g] Cyclopropene.

[h] Allyl.

[i] Cyclopropyl.

[j] Linear.

Table 4
Heats of formation of parent molecules and neutral fragments m_i[a]

Species	ΔH_f (eV)
Toluene	0.52
Cycloheptatriene	1.94
Norbornadiene	2.53
Quadricyclane	3.48
Spiro[2,4]hepta-4,6-diene	2.47
1,6-Heptadiyne	4.10
H	2.26
H_2	0
CH_3	1.51
C_2H_2	2.36
C_2H_3	2.75
C_2H_4	0.54
c-C_3H_3	4.56
l-C_3H_3	3.55
C_3H_4	1.98[b], 1.93[c], 2.87[d]
C_3H_5	1.74[e], 2.68[f]
c-C_5H_5[g]	2.50
l-C_5H_5[h]	3.86

[a] Data from Ref. [8].
[b] Allene.
[c] Propyne.
[d] Cyclopropene.
[e] Allyl.
[f] Cyclopropyl.
[g] Cyclopentadienyl.
[h] Pent-1-en-4-yn-3-yl.

give rise to $C_7H_7^+$ ions having similar apparent heats of formation, whose average value is $\Delta H_f(C_7H_7^+) = 9.79$ eV (Table 3). We remark that for the tropylium ion form of $C_7H_7^+$, the literature value of $\Delta H_f(\text{Tr-}C_7H_7^+) = 8.80$ eV, whereas for the benzylium ion $\Delta H_f(\text{Bz-}C_7H_7^+) = 9.32$ eV [8]. Formation of $C_7H_7^+$ from quadricyclane which has an apparent heat of formation of 10.51 eV (Table 3) appears to involve considerable activation energy, whereas the high value $\Delta H_f(C_7H_7^+) = 11.69$ eV for 1,6-heptadiyne results from this fragment ion, which is unlikely to be either benzylium or tropylium, being formed at the onset energy for parent ion formation. Indeed, the apparent heat of formation of $C_7H_7^+$ from 1,6-heptadiyne is 2.26 eV less than the heat of formation of the parent ion. We note that the second onset energy of $C_7H_7^+$ in norbornadiene, at 10.8 eV, corresponds to an apparent heat of formation $\Delta H_f(C_7H_7^+) = 11.07$ eV, similar to that in quadricyclane, $\Delta H_f(C_7H_7^+) =$ 10.51 eV, perhaps indicating a second common fragmentation pathway for norbornadiene.

$C_7H_5^+$: For the three isomers, cycloheptatriene, norbornadiene and spiro[2,4]hepta-4,6-diene, this fragment ion has similar apparent heats of formation, nearly 2 eV higher than that for toluene (no PIMS measurements on $C_7H_5^+$ could be made for quadricyclane and 1,6-heptadiyne). The apparent heats of formation of the presumed precursor ion $C_7H_7^+$ are similar for the four isomers toluene, cycloheptatriene, norbornadiene and spiro[2,4]hepta-4,6-diene (see above). However, $C_7H_5^+$ has a lower apparent heat of formation in toluene as compared with the other isomers. This indicates that in toluene, the formation of $C_7H_5^+$ occurs from the parent ion by initial loss of H_2, i.e. $C_7H_8^+ \rightarrow C_7H_6^+ + H_2$, followed by $C_7H_6^+ \rightarrow C_7H_5^+ + H$, whereas in the other three isomers, the initial loss is of a hydrogen atom, to form $C_7H_7^+$, followed by H_2 loss (see Table 3). Note that our PIMS results provide the first experimental value of $\Delta H_f(C_7H_5^+) \leqslant 11.36$ eV. A previous semi-empirical value is $\Delta H_f(C_7H_5^+) = 10.36$ eV [39].

$C_6H_5^+$: Data on this fragment ion is available only for the three isomers toluene, cycloheptatriene and norbornadiene. It is reasonable that for cycloheptatriene and norbornadiene, the value of the apparent $\Delta H_f(C_6H_5^+)$ is 0.4–0.5 eV higher than in the case of toluene (Table 3). The phenyl ion is formed in toluene by simple bond rupture of the C–C bond linking the aromatic ring and the methyl radical, whereas in cycloheptatriene and norbornadiene reorganization energy must be expended for loss of CH_3 to occur. The apparent heat of formation of $C_6H_5^+$ for the three C_7H_8 isomers considered is compatible with the standard value $\Delta H_f(C_6H_5^+) = 11.68$ eV [8]. Since $C_6H_5^+$ was not observed in our PIMS experiments on the other three isomers, the formation of this fragment probably involves high energy cost processes in these cases.

$C_5H_6^+$: There are similarities in the apparent $\Delta H_f(C_5H_6^+)$ values for the pairs of isomers toluene/norbornadiene and quadricyclane/heptadiyne. On structural grounds (for the neutral isomer, Fig.1), one might expect the formation of cyclic $C_5H_6^+$, which has the lowest reported heat of formation of the known isomers of this ion [8], to be easiest

in the case of norbornadiene, yet it is cycloheptatriene which has the lowest apparent $\Delta H_f(C_5H_6^+) = 9.98$ eV, i.e. 1 eV less than for norbornadiene (no data are available for spiro[2,4]hepta-4,6-diene). This may indicate that in cycloheptatriene, the $C_5H_6^+$ ion is perhaps easily formed by a 1,3 sigmatropic shift and C_2H_2 elimination. However, as discussed in Section 3.2, the apparent $\Delta H_f(C_5H_6^+) = 9.98$ eV appears to be too close to the standard value $\Delta H_f(C_5H_6^+) = 9.92$ eV [8], indicating that for cycloheptatriene the $C_5H_6^+$ fragment ion has other than the cyclic form or that its standard heat of formation is in error. As mentioned earlier, other known isomers of $C_5H_6^+$ have higher ΔH_f values [8], but in Section 3.2, we have derived lower values of $\Delta H_f(C_5H_6^+)$, based on the AEs of this ion in electron impact studies of C_7H_{10} isomers. Our PIMS results on cycloheptatriene, besides calling into question standard ΔH_f values of $C_5H_6^+$, points to particularities in the pathways of formation of this fragment ion in the various $C_7H_8^+$ isomers.

$C_5H_5^+$: This fragment ion is important as a species in combustion processes [40–42]. In our PIMS measurements, there are "double" onsets for the appearance of this ion in toluene, cycloheptatriene and norbornadiene (Table 1). The apparent $\Delta H_f(C_5H_5^+)$ values are similar for cycloheptatriene and norbornadiene at the first onset, and for toluene, cycloheptatriene and norbornadiene at the second onset, along with 1,6-heptadiyne (Table 3). The apparent $\Delta H_f(C_5H_5^+)$ values are also similar for the pair of isomers quadricyclane/spiro[2,4]hepta-4,6-diene.

There are two pathways in the formation of the $C_5H_5^+$ fragment from the parent ions (Table 3). Five isomers of $C_5H_5^+$ are known either experimentally or on the basis of calculations. These are respectively the vinylcyclopropenyl cation, $\Delta H_f = 10.49$ eV, the cyclopentadienyl cation, $\Delta H_f = 10.90$ eV, the acyclic radical cations pent-1-en-4-yn-3-yl, $\Delta H_f = 11.73$ eV [8] and pent-1-yn-3-en-5-yl, $\Delta H_f = 12.0$ eV [43] and a pyramidal cation, of C_{4v} symmetry, calculated to have $\Delta H_f = 11.87$ eV [44].

Table 3 shows that the apparent heats of formation of $C_5H_5^+$ based on the first AEs (first onset) and the $H + C_2H_2$ loss channel in toluene, cycloheptatriene and norbornadiene are smaller than the standard heats of formation for the five $C_5H_5^+$ isomers mentioned above. This shows that at the first PIMS onset energy of $C_5H_5^+$ for these three $C_7H_8^+$ isomers, the fragment ion formed must be by the C_2H_3 loss channel and not the $C_2H_2 + H$ channel. Furthermore, a comparison between standard and apparent heats of formation shows that the acyclic $C_5H_5^+$ cations and the pyramidal cation can be excluded as the fragment ion products formed at the first onset by the C_2H_3 loss mechanism, certainly for toluene and probably for cycloheptatriene.

$C_5H_3^+$: Similarities exist in $\Delta H_f(C_5H_3^+)$ for norbornadiene, quadricyclane and toluene (AE error bar of ±0.5 eV for toluene, Table 1) and also possibly for 1,6-heptadiyne. There are serious discrepancies between theoretical and experimental enthalpies of formation of $C_5H_3^+$ [44–47]. The value of this quantity is important in theories of combustion, in particular concerning soot formation [40,44].

Theoretical studies of 12 isomeric structures of $C_5H_3^+$ have been carried out [45] from which it was concluded that the most stable structure is the ethynylcyclopropenylium ion, whose calculated $\Delta H_f(C_5H_3^+) = 16.3$ eV. Experimental values are (i) $\Delta H_f(C_5H_3^+) = 13.66$ eV for the pentadiynyl ion $HC{\equiv}C{-}C{\equiv}C{-}CH_2^+$ [46], from which Weiner et al. [45] deduced the "experimental" value $\Delta H_f(C_5H_3^+) = 12.79$ eV for the ethynylcyclopropenylium ion, (ii) $\Delta H_f(C_5H_3^+) < 14.83$ eV for an unknown $C_5H_3^+$ structure [47], possibly the $CH_3C{\equiv}C{-}C{\equiv}C^+$ structure [46] and (iii) $\Delta H_f(C_5H_3^+) = 14.26$ eV for an unknown structure [48]. These values, as well as our apparent heats of formation $\Delta H_f(C_5H_3^+)$ in Table 3, clearly show that the $\Delta H_f(C_5H_3^+) = 16.3$ eV value calculated by Weiner et al. for the lowest energy form of $\Delta H_f(C_5H_3^+)$ is far too high. Examination of the apparent heats of formation for $C_5H_3^+$ in Table 3 indicates, in particular from the values for spiro[2,4]hepta-4,6-diene, that $\Delta H_f(C_5H_3^+) \leqslant 11.22$ eV. This is not very different from the value obtained semiempirically, $\Delta H_f(C_5H_3^+) = 11.66$ eV [39].

From Table 3, it appears probable that the $C_5H_3^+$ structure is different when formed by dissociative ionization of spiro[2,4]hepta-4,6-diene than in other parent isomer cases. It is highly desirable that accurate values of the heat of formation of $C_5H_3^+$ be obtained for its various isomeric structures. We note, nevertheless, that our finding for spiro[2,4]hepta-4,6-diene that the heat of formation $\Delta H_f(C_5H_3^+) \leqslant 11.22$ eV (see Table 3) indicates that this particular form of $C_5H_3^+$ is thermodynamically of similar stability to the lowest energy forms of $C_5H_5^+$. Thus, contrary to the affirmations of Weiner et al. [45], based on their high value for $\Delta H_f(C_5H_3^+)$, the reaction $C_5H_5^+ \rightarrow C_5H_3^+ + H_2$ could very well proceed in a sooting flame, even if $C_5H_5^+$ was in the lowest energy form, the vinylcyclopropenylium ion, provided that the $C_5H_3^+$ ion product was in its $\Delta H_f(C_5H_3^+) \leqslant 11.22$ eV lowest energy form.

$C_4H_5^+$: There are similarities in the apparent $\Delta H_f(C_4H_5^+)$ values for the respective pairs, cycloheptatriene and norbornadiene, toluene and spiro[2,4]hepta-4,6-diene and for quadricyclane and heptadiyne (Table 3). Standard values of $\Delta H_f(C_4H_5^+) = 10.66$, 11.13, 10.94 and 10.28 eV exist respectively for three linear and one cyclic isomer of $C_4H_5^+$ [8]. Comparison with our experimental apparent heats of formation enables us to exclude loss of c-C_3H_3 as the channel for formation of $C_4H_5^+$ from cycloheptatriene and at the first PIMS onset energy for norbornadiene.

$C_4H_4^+$: The $C_4H_4^+$ ions coming from cycloheptatriene and norbornadiene have similar ΔH_f values, as do those formed from quadricyclane and spiro[2,4]hepta-4,6-diene. Standard values of $\Delta H_f(C_4H_4^+)$ are, respectively, 12.64 eV for 1-buten-3-yne (= vinylacetylene), 12.77 eV for butatriene, 12.54 eV for methylene cyclopropene and 12.83 eV for cyclobutadiene [8,49]. Methylene cyclopropene is the $C_4H_4^+$ isomer of lowest energy. From the apparent heats of formation $\Delta H_f(C_4H_4^+)$ in Table 3, we can eliminate the two $H + C_3H_3$ neutral product channels for all six isomers. We can also eliminate the cyclopropene form of C_3H_4 as the neutral product in the formation of $C_4H_4^+$ from toluene.

$C_4H_3^+$: The apparent $\Delta H_f(C_4H_5^+)$ values are similar for all six $C_7H_8^+$ isomers, including spiro[2,4]hepta-4,6-diene if one considers the second onset energy for the latter (Table 3). The C_1-protonated linear form of C_4H_2 is calculated to be the lowest energy isomer of $C_4H_3^+$ [50,51], and it is this structure which is assumed in the following thermochemical considerations.

We consider eight possible routes, including variants as to isomeric form of neutral loss species, in the formation of this fragment ion. An experimental value of $\Delta H_f(C_4H_3^+) = 12.49$ eV can be deduced from the relation $\Delta H_f(C_4H_3^+) = \Delta H_f(C_4H_2) + \mathrm{PA}\ (C_4H_2)$, where $\Delta H_f(C_4H_2) = 4.81$ eV [52] and the proton affinity of diacetylene $\mathrm{PA}(C_4H_2) = 7.68$ eV [50]. A semi-empirical value is $\Delta H_f(C_4H_3^+) = 12.61$ eV [39]).

Using $\Delta H_f(C_4H_3^+) = 12.49$ eV as the standard value, the incompatibilities of particular routes with the apparent heats of formation of $C_4H_3^+$ given in Table 3 are as follows: (i) $C_2H_2 + CH_3$ loss cannot be the route for formation of $C_4H_3^+$ at its first PIMS onset energy in the case of spiro[2,4]hepta-4,6-diene for which the apparent $\Delta H_f(C_4H_3^+) = 11.29$ eV; (ii) the $H + c$-C_3H_3 and $H + l$-C_3H_3 loss routes are unacceptable for spiro[2,4]hepta-4,6-diene at its PIMS first onset energy; (iii) the C_3H_5 allyl isomer loss route is compatible with our measured apparent $\Delta H_f(C_4H_3^+)$ values for all six C_7H_8 isomers but the C_3H_5 cyclopropyl isomer loss route is not compatible with spiro[2,4]hepta-4,6-diene at its PIMS first onset energy although it is possible for the other C_7H_8 isomers; (iv) for the $H + C_3H_4$ loss route, where three isomeric forms of the C_3H_4 species are considered, the loss of the highest ΔH_f form of C_3H_4, i.e. cyclopropene, is excluded for all isomers, except possibly at the second onset energy for spiro[2,4]hepta-4,6-diene, whereas for the other two isomeric forms of neutral C_3H_4 (allene and propyne), only spiro[2,4]hepta-4,6-diene at its PIMS first onset energy would be excluded as a parent molecular ion.

$C_3H_3^+$: The apparent $\Delta H_f(C_3H_3^+)$ values for the two fragmentation routes considered are similar for cycloheptatriene, norbornadiene, quadricyclane (first PIMS onset energy), spiro[2,4]hepta-4,6-diene and 1,6-heptadiyne (Table 3). The standard values of $\Delta H_f(C_3H_3^+)$ are 11.14 and 12.22 eV respectively for the cyclic (c-$C_3H_3^+$) and linear (l-$C_3H_3^+$) forms of this fragment ion. For the fragmentation pathway in which the two neutral products are C_2H_3 and C_2H_2, the apparent heats of formation of $C_3H_3^+$ are compatible with the

standard values of $\Delta H_f(c\text{-}C_3H_3^+)$ and $\Delta H_f(l\text{-}C_3H_3^+)$ for all isomers. The second pathway envisaged in Table 3, in which the neutral products are H and two C_2H_2 molecules, is only compatible with the second onset energy of $C_3H_3^+$ for quadricyclane and not with the other observed fragmentation onsets for the various C_7H_8 isomers. These results are consistent with our conclusions concerning the formation of the $C_5H_5^+$ ion, the probable precusor of $C_3H_3^+$.

$C_2H_3^+$: The apparent heats of formation ΔH_f $(C_2H_3^+)$ are very similar for all isomers except spiro[2,4]hepta-4,6-diene (Table 3). The standard value of $\Delta H_f(C_2H_3^+) = 11.53$ eV [8] is for the non-classical, bridged hydrogen form of the vinyl radical cation [53,54]. The classical $H_2C{=}C{-}H^+$ radical cation is estimated to be about 0.26 eV higher in energy $(\Delta H_f(C_2H_3^+) = 11.79$ eV) [55]. We note that these values of $\Delta H_f(C_2H_3^+)$ are based on the value of $\mathrm{IE}(C_2H_3) = 8.59$ eV of Berkowitz et al. [56]. A lower value of $\mathrm{IE}(C_2H_3) = 8.25$ eV is given in the photoelectron spectroscopy study of Blush and Chen [57]; this value, which is controversial [55], would lead to lowering of the $\Delta H_f(C_2H_3^+)$ values to 11.19 and 11.45 eV. Furthermore, there is some controversy concerning the heat of formation $\Delta H_f(C_2H_3)$ of the neutral radical [55], which adds to the uncertainty concerning $\Delta H_f(C_2H_3^+)$.

A very recent PIMS study of ethylene oxide by Liu et al. [58] provides another possibility to determine $\Delta H_f(C_2H_3^+)$ for the classical $H_2C{=}C{-}H^+$ radical cation. This $C_2H_3^+$ isomer is considered to be the product, in their experiment, whose $\mathrm{AE}(C_2H_3^+) = 12.78 \pm 0.02$ eV and whose calculated transition barrier E_b is about 0.2 eV above the products. We can determine a value of the heat of formation of $C_2H_3^+$ from the relation ΔH_f $(C_2H_3^+) = \mathrm{AE}(C_2H_3^+) - \Delta H_f(OH) + \Delta H_f(C_2H_4O)$ $-E_b$. Using the known thermodynamic quantities $\Delta H_f(OH) = 0.4$ eV and $\Delta H_f(C_2H_4O) = -0.55$ eV [8], we obtain a value of $\Delta H_f(C_2H_3^+) = 11.63$ eV, which is in reasonable agreement with the two possible values given above for the classical cation, $\Delta H_f(C_2H_3^+) = 11.79$ eV and $\Delta H_f(C_2H_3^+) = 11.45$ eV. Therefore, from this alone, it is not possible to choose between the two proposed values for $\mathrm{IE}(C_2H_3)$.

In spite of the uncertainties in the exact values of $\Delta H_f(C_2H_3^+)$ for the classical as well as the non-classical form of the $C_2H_3^+$ ion that we presume to be our product, we can conclude that the whole set of controversial $\Delta H_f(C_2H_3^+)$ values are smaller than the apparent heats of formation for all six isomers of $C_7H_8^+$, except for the l-C_5H_5 loss channel in spiro[2,4]hepta-4,6-diene, while the cyclopentadienyl (c-C_5H_5) loss route (Table 3) is compatible with the apparent heats of formation of $C_2H_3^+$ for all six isomers. The low value of $\Delta H_f(C_2H_3^+)$ for spiro[2,4]hepta-4,6-diene indicates that the loss of C_5H_5 is facilitated in this case with respect to the other C_7H_8 isomers.

4.3. Interconversion between toluene, cycloheptatriene and norbornadiene ions

We examine further some of the results concerning the three isomers, toluene, cycloheptatriene and norbornadiene which have been much discussed in the literature in connection with possible interconversion processes in these isomers during the formation of the $C_7H_7^+$ fragment ion [6,59]. The data in Table 3 indicate that the apparent heats of formation $\Delta H_f(m_1^+)$ for each respective m_1^+ ion are equal, to within 0.3 eV, for the following fragment ions formed from both cycloheptatriene and norbornadiene, $C_7H_7^+$, $C_7H_5^+$, $C_6H_5^+$, $C_5H_5^+$, $C_4H_5^+$, $C_4H_4^+$, $C_4H_3^+$, $C_3H_3^+$ and $C_2H_3^+$, whereas the apparent heats of formation of only four of these ions, $C_7H_7^+$, $C_5H_5^+$ (second onset, where the latter is considered to be formed by C_2H_2 loss from $C_7H_7^+$ [1,2]), $C_4H_3^+$ and $C_2H_3^+$ have approximately common values for the three isomers, toluene, cycloheptatriene and norbornadiene.

The latter observations support the suggestion of Lifshitz et al. [6,59] that the formation of the tropylium ion $C_7H_7^+$ by dissociative photoionization of toluene requires prior isomerization of toluene to the cycloheptatriene ion. The results also suggest that interconversion of the norbornadiene and cycloheptatriene ions occurs prior to the formation not only of $C_7H_7^+$ but also of several other product ions formed by dissociative ionization of these two isomers. In the case of toluene,

Table 5
Energy differences[a] $E_{max}(i) - E_{max}(heptadiyne^+)$ and $\Delta H_f(heptadiyne^+) - \Delta H_f(i)$

Ion i	$E_{max}(i) - E_{max}(heptadiyne^+)$ (eV)			$\Delta H_f(heptadiyne^+) - \Delta H_f(i)$ (eV)
	$C_4H_3^+$	$C_3H_3^+$	$C_2H_3^+$	
1,6-Heptadiyne	0	0	0	0
Quadricyclane	2.78	2.88	2.18	2.50
Norbornadiene	3.40	3.30	2.60	2.97
Spiro[2,4]hepta-4,6-diene	3.99	3.89	0.89	3.39
Cycloheptatriene	3.85	4.15	3.85	3.81
Toluene	4.90	5.60	4.70	4.60

[a] E_{max} is the maximum amount of internal energy of the parent ion at the AEs of the $C_4H_3^+$, $C_3H_3^+$ and $C_2H_3^+$ fragment ions (see text).

isomerization is not necessary for the formation of most low-energy product ions (see below), but is required for formation of the tropylium form of $C_7H_7^+$ and its sequential product $C_5H_5^+$. This behaviour is probably related to the amount of internal energy and the time scale of fragmentation. In toluene, the $C_7H_7^+$ ion has the lowest appearance energy of the fragment ions produced by dissociative photoionization, so that it is formed from the parent toluene ion containing a smaller amount of internal energy as compared to the internal energy necessary for the formation of other ions having higher AEs. Thus the formation of $C_7H_7^+$ in toluene corresponds to the favoured situation of isomerization at low internal energies [6,59].

4.4. Interconversion between all six C_7H_8 ions

Data is available for all six C_7H_8 parent species on the ion apparent heats of formation for the following fragment ions: $C_7H_7^+$, $C_5H_5^+$, $C_5H_3^+$, $C_4H_5^+$, $C_4H_4^+$, $C_4H_3^+$, $C_3H_3^+$ and $C_2H_3^+$ (Table 3). The only case where the apparent heats of formation of a fragment ion are approximately equal for all six $C_7H_8^+$ isomers is for $C_4H_3^+$, taking into account the second PIMS onset energy for spiro[2,4]hepta-4,6-diene. For the fragment ions $C_3H_3^+$ and $C_2H_3^+$, the apparent heats of formation are approximately equal for five of the six parent isomers. It is noteworthy that the three fragment ions $C_4H_3^+$, $C_3H_3^+$ and $C_2H_3^+$ have AEs in the higher energy ranges for the six C_7H_8 isomers (Table 1). At the onset energy for the appearance of $C_4H_3^+$, E_{max}, the maximum amount of internal energy of the parent ion is 8.25, 7.2, 6.75, 6.13, 7.34 and 3.35 eV, as can be established from Table 1. The values of E_{max} in the case of the fragment ions $C_3H_3^+$ and $C_2H_3^+$ are similar to the respective $C_4H_3^+$ values for the six isomers. Furthermore, in Table 5, in which we list for each isomer ion i the differences $E_{max}(i) - E_{max}(heptadiyne^+)$ and $\Delta H_f(heptadiyne^+) - \Delta H_f(i)$, we see that these two parameters are similar in value and that they vary in quasi-parallel fashion. The spiro[2,4]hepta-4,6-diene value of $E_{max}(i) - E_{max}(heptadiyne^+)$ for $C_2H_3^+$ is anomalous, in accord with our earlier discussion.

These results thus suggest that interconversion to an isomer common to all six species occurs and that this isomer fragments give rise to the $C_4H_3^+$, $C_3H_3^+$ and $C_2H_3^+$ ions when the internal energy of the parent ion is of the order of 6 eV or more, the exact value depending on the particular isomer, with 1,6-heptadiyne being a less stable exception. Since markedly less internal energy is required to reach the onset for formation of these three fragment ions from 1,6-heptadiyne as compared with the other C_7H_8 species, it is not unreasonable to suggest that the common isomer has an acyclic heptadiyne structure and that the higher internal energies at the dissociation limit in the other isomers reflects activation energies in isomerization to the acyclic form.

There are some similarities here to the case of the dissociative photoionization of naphthalene and azulene. Their ions undergo isomerization processes prior to dissociation leading to a series of fragmentations occurring at low internal energies ($AE < 16$ eV) via rupture of one ring of common bicyclic precursors. In addition, there are a series of high energy dissociations (AE $>$ 18 eV) in which both rings are broken, to give an open chain precursor [35].

5. Conclusion

A monochromatized synchrotron radiation source (BESSY I) and a quadrupole mass spectrometer were used to measure the photoion yield curves, in the 7–22 eV excitation energy range, of six isomers of C_7H_8. A total of 18 fragment cations were measured, of which 15 for toluene, 13 for cycloheptatriene, 14 for norbornadiene, 11 for quadricyclane and 12 each for spiro[2,4]hepta-4,6-diene and 1,6-heptadiyne. The appearance energies of the photoions were used to determine the apparent heats of formation of the various fragment ions. A comparison of the apparent and the standard thermochemical values of the heats of formation of the fragment ions permitted assignment of energetically allowed fragmentation channels. In the case of the ions $C_7H_5^+$, $C_5H_3^+$ and $C_4H_3^+$, standard or improved standard heats of formation are required for confirmation of the proposed fragmentation channels leading to the formation of these ions.

The PEPICO mass spectra of the isomers, measured at LURE-Orsay at a photon excitation energy of 20 eV, and the respective apparent heats of formation of the observed fragment ions were used to discuss the question of the formation of common isomers during dissociative ionization. The results support the suggestion of Lifshitz et al. [6,59] that the formation of the tropylium ion $C_7H_7^+$ by dissociative photoionization of toluene occurs via initial isomerization of the parent ion to cycloheptatriene$^+$. Interconversion of norbornadiene$^+$ and cycloheptatriene$^+$ ions is suggested by our results to occur prior to the formation of $C_7H_7^+$ and of several other fragment ions in the case of these two isomers. For toluene, isomerization does not appear to be necessary for the formation of low-energy fragment ions except for the tropylium form of $C_7H_7^+$ and its sequential product $C_5H_5^+$.

Apparent heats of formation for each of the six $C_7H_8^+$ parent species were determined for eight of the eleven fragment ions detected in these experiments. The results suggest that interconversion to an isomer common to all six species occurs in the formation of $C_4H_3^+$, $C_3H_3^+$ and $C_2H_3^+$, whose AEs are in the higher excitation energy ranges. It is suggested that this interconversion occurs when the internal energy of the parent ion is of the order of 6 eV or more, although 1,6-heptadiyne$^+$ is evidently less stable. The structure of the common isomeric ion is not known but it is probably acyclic and possibly heptadiyne$^+$. Further theoretical studies on the energies and structures of C_7H_8 cation isomers are needed to confirm this conjecture as well as for other aspects concerning the formation of common isomers during dissociative ionization of C_7H_8 species.

Finally, we remark that the appearance energies determined for the fragment ions discussed here have been important for the interpretation of dissociative ionization processes of isotopomers of toluene [1] and isomeric [2] $C_7H_8^+$ species in the 20–100 eV photon excitation range. In association with other information, in particular, energy propensity rules involving product ionization potentials and proton affinities, the fragment ion formation threshold energies made it possible to propose favoured dissociation pathways of the toluene cations [1]. These fragmentation channels have been used in the determination of the apparent heats of formation given in Table 3 and discussed in Section 4.2. Calculations of transition state energies should be carried out in order to refine the choice of fragmentation pathways.

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