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Structures of Product Ions $C_6H_7^+$ and $C_6H_9^+$ of Ion–Molecule Reactions with Allyl Bromide†

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The ion–molecule reactions of allyl bromide with the molecular ion of allyl bromide and with its major fragment, the allyl ion, yield the $C_6H_7^+$ and $C_6H_9^+$ ions. The structure of these product ions was explored by means of photofragmentation with laser light in the 10 μm region and by proton transfer reaction to selected reagents. These product ions were also formed by other reactions and their reactivities compared. In both cases the presence of at least two populations is demonstrated. For $C_6H_9^+$ these two populations are initially present, whereas for $C_6H_7^+$ an isomer is formed by the infrared light before the loss of H_2. When this ion is produced by photofragmentation of $C_6H_9^+$, at least one third, stable isomer is formed. Two isomers of $C_6H_5^+$ are formed in the photofragmentation of $C_6H_7^+$, but only one form photofragments further by loss of C_2H_2. The use of non-linear least-squares fitting does not allow definite conclusions to be drawn concerning the kinetics of the consecutive photofragmentations.

INTRODUCTION

In ion–molecule reactions of gas-phase cations there is frequently the possibility of different isomeric structures of the ionic reaction products. The structures of interest here are $C_6H_7^+$ and $C_6H_9^+$ ions formed in ion–molecule reactions (1) of the fragment ion $C_3H_5^+$ with allyl bromide, and the $C_6H_9^+$ formed in reaction (2) of the allyl bromide molecular ion with its precursor.[1]

$$C_3H_5^+ + CH_2{=}CHCH_2Br \rightarrow C^6H_7^+ + HBr + H_2 \quad (1a)$$

$$\rightarrow C_6H_9^+ + HBr \quad (1b)$$

$$C_3H_5Br^{+\cdot} + CH_2{=}CHCH_2Br \rightarrow C_6H_9^+ + HBr + Br^\cdot \quad (2)$$

It has been shown that the reacting species of $C_3H_5^+$ has an allyl structure.[1]

Although numerous structures are possible for $C_6H_7^+$ entities, most studies have assumed, or presented evidence, that $C_6H_7^+$ formed in gas-phase systems has predominantly the structure of a protonated benzene, i.e. the benzenium ion (*a*) (see Table 1) with a heat of formation of 854 kJ mol^{-1}.[2–6] In the work of Franklin and Carroll,[7] the possible structures of the fragment $C_6H_7^+$ ions from several isomers were discussed with emphasis on rearrangements. The most plausible non-benzenium structures corresponding to a low heat of formation and the two protonated fulvenes (*b*) and (*c*);[8] their heat of formations was estimated to be in the range 891–954 kJ mol^{-1}.[9] In addition, a heat of formation ranging from 1046 to 1088 kJ mol^{-1} for a linear structure of $C_6H_7^+$ ion was determined by a method developed by Franklin[10] and confirmed experimentally by Harrison *et al.*[11] In an earlier ion cyclotron resonance (ICR) study, Lias and Ausloos[9] determined the non-benzenium fractions formed in a variety of reaction systems by monitoring the deprotonation of $C_6H_7^+$ ions, and concluded that the most likely structures are the ions (*b*) and (*c*).

The other ion structure of interest is the $C_6H_9^+$ ion. The experimental evidence based on collision-induced dissociation (CID) spectra[12] and semi-empirical and *ab initio* theoretical calculations[13] predict that 1-methylcyclopentenyl (*d*) and cyclohexenyl (*e*) are the most stable species. In kinetic energy release (KER) determinations,[14] two different structures of $C_6H_9^+$ (*d*) and (*e*) were postulated following methyl loss from ionized hept-2-yne and hept-3-yne and ethyl loss from oct-2-yne and oct-3-yne. The estimated heats of formation for both ions (*d*) and (*e*) are identical, whereas it has been shown that a linear structure of $C_6H_9^+$ corresponds to a heat of formation higher than that of these cyclic structures in the gas phase.[15] Table 1 summarizes the estimated or experimental heats of formation of certain $C_6H_7^+$ and $C_6H_9^+$ isomers, and also gives the proton affinities of their conjugate bases.

The formation of ions through the ion–molecule condensation–dissociation processes (1) and (2) may correspond to a cyclic structure, i.e. cycloaddition occurs in the gas phase. In this work the structure of these adduct ions, $C_6H_7^+$ and $C_6H_9^+$, was studied by using IR multiphoton dissociation and proton transfer reaction techniques. The efficiency of the proton transfer reaction as a diagnostic tool for structure determination of gas phase ions is well established.[9,18] This is due to the fact that an ion MH^+ only transfers a proton to the molecule with a proton affinity higher than that of the conjugate M base. Hence the choice of neutral compounds was dictated by their known proton affinities, with reference to those of the conjugate bases of

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† Dedicated to John Holmes in recognition of his work as Editor and mass spectrometrist.

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Table 1. Thermochemistry of $C_6H_7^+$ and $C_6H_9^+$ ions and their conjugate bases[9,15,16]

Ion	Structure	ΔH_f (298 K) (kJ mol^{-1})	Conjugate base	ΔH_f (298 K) (kJ mol^{-1})	Proton affinity (kJ mol^{-1})
$C_6H_7^+$	Benzenium (*a*)	854	Benzene	82.8	758.6
	3-Methylcyclopentadienyl (*b*)	891–954	3-Methylenecyclopenta-1,4-diene	225.1	799–862
	3-Methylenecyclopentenyl (*c*)	895	3-Methylenecyclopenta-1,4-diene	225.1	799–862
$C_6H_9^+$	1-Methylcyclopentenyl (d)	808	Methylcyclopenta-1,3-diene	96.2	~833[b]
	Cyclohexenyl (*e*)	812	Cyclohexa-1,4-diene, cyclohexa-1,3-diene	106.7 ± 2.1[a]	837
	1,3-Dimethylcyclobutenyl (*f*)	845	1-Methyl-3-methylenecyclobutene	202.1	887

[a] The difference between these two isomers is indicated in Ref. 17.

[b] See text for this estimated value.

the reactant ions. The ions of $C_6H_7^+$ and $C_6H_9^+$ were compared with ions of different origins; three ion systems were selected.

EXPERIMENTAL

The ion–molecule reactions and photodissociation experiments were carried out in a Fourier transform ICR spectrometer that has been described previously[1,19,20] and equipped with a system of pulsed valves. The different preparations of $C_6H_7^+$ and $C_6H_9^+$ are described below, referring to the experimental sequence shown in Fig. 1.

Protonated benzene

Protonated benzene was prepared by proton transfer reaction from CH_5^+ to benzene. Gaseous methane was admitted to the cell and ionized by electron impact at a pressure of 8.5×10^{-9} mbar (1 mbar = 100 Pa). The pulse S1 was used to isolate the molecular ions of $CH_4^{+\bullet}$, and a reaction delay of 2 s was added between S1 and S2 to allow reaction of $CH_4^{+\bullet}$ with neutral methane. The product ion CH_5^+ was selected by pulse S2, and gaseous benzene was then introduced through a pulsed valve to a maximum pressure of $\sim 3 \times 10^{-7}$ mbar. The gas pulse shown in Fig. 1 corresponded to a valve opening time of 20 ms followed by 3 s of pumping time. Then the ion $C_6H_7^+$ generated by proton transfer reaction was selectively isolated by pulse S3.

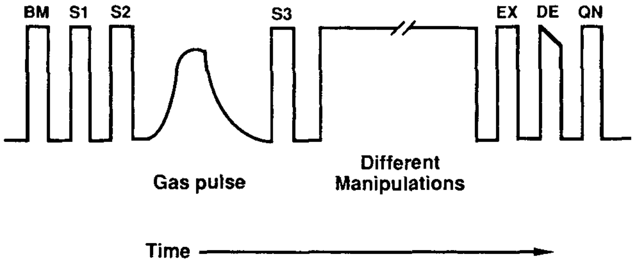

Figure 1. Pulse sequence employed for the investigation of $C_6H_7^+$ and $C_6H_9^+$. BM, electron impact, 70 eV; EX and DE, excitation and detection pulses; S1, S2, S3, SWIFT pulses; QN, quench pulse.

Product ion of the condensation reaction (1)

Isolation of fragment ion $C_3H_5^+$ was achieved by pulses S1 and S2 after electron impact ionization of allyl bromide at a pressure of 8.5×10^{-9} mbar. The pressure was then increased by introducing neutral allyl bromide through a pulsed valve to a maximum pressure of 3.5×10^{-7} mbar. The gas pulse shown in Fig. 1 had a valve opening time of 50 ms followed by 6 s of pumping time. Once the $C_6H_7^+$ had been formed, it was selectively isolated by pulse S3.

Fragment ion of cyclohexa-1,4-diene

The pulses S1, S2 and S3 were used for ejecting all primary ions in the spectrum of cyclohexa-1,4-diene, except the ion $C_6H_7^+$. The pressure of the cyclohexa-1,4-diene was maintained at about 8.5×10^{-9} mbar. No gas pulse was used in this ion preparation.

The three different ion preparations for $C_6H_9^+$ ions were similar to the process mentioned above: (i) protonated cyclohexa-1,4-diene was prepared according to Eqn (3) with $C_6H_7^+$ originating from the fragmentation of cyclohexa-1,4-diene by electron impact, and its neutral precursor introduced through a pulsed valve under conditions similar to those of protonated benzene:

$$C_6H_7^+ + \text{1,4-c-}C_6H_8 \rightarrow C_6H_9^+ + C_6H_6 \qquad \Delta H = -24.2\ \text{kcal/mol} \qquad (3)$$

(ii) the product ion of ion–molecule reaction (2) between the molecular ion of allyl bromide and its neutral precursor; (iii) the fragment ion in a spectrum of hept-2-yne.

Usually, the event labelled 'different manipulations' in Fig. 1 consists of a pulse of a collision gas, SF_6, before starting the laser pulse for photodissociation; or a reagent gas pulse in proton transfer reaction studies. The buffer gas, SF_6, was introduced through a pulsed valve with 50 ms of open time, at a maximum pressure of $\sim 5 \times 10^{-7}$ mbar in order to allow relaxation of the inernal energy of the ions. After 3 s of pumping it was assumed that the pressure was low enough for irradiation without collisions. A focused continuous-wave (cw) CO_2 laser of about 10 W total power was used to carry out infrared multiphoton dissociation at the selected wavelength. The diameter of the laser beam in the cell was 0.6 mm. The kinetics of the proton transfer reaction were measured by varying the opening time of the pulsed valve.

The data were treated by a non-linear least-squares calculation. This is a reasonable procedure as Fourier-transformed spectra, obtained under identical conditions, are very reproducible. Models with the smallest number of parameters were chosen; an increase of the number of adjustable parameters usually had no influence on the quality of the distribution of the residuals that amounted to about 1% or less of the total current as long as they were randomly distributed. The experiments were reproducible within these limits. As is usual in kinetics, this is no proof that the proposed mechanism is correct. It simply means that the model chosen explains the results within the precision of our data. However, the distribution of the residuals allowed a distinction between different possible models because a systematic deviation of the random distribution can easily be seen. It is very difficult to estimate the accuracy of these parameters, since they are not orthogonal to each other and the minima are often rather flat. We think a value of ±15% to be a fair estimation. A non-linear least-squares calculation may depend on the starting values of the parameters to be estimated and the step size chosen for the Marquardt–Levenberg algorithm. This is particularly true when many parameters have to be adjusted. In such a case it may be useful to keep some parameters constant and to study their influence separately. In all calculations this did not turn out to be necessary; all results given were obtained after a few iterations and did not seem to depend on the initial choice of the parameters; we did not obtain any indications of other minima.

RESULTS AND DISCUSSION

$C_6H_7^+$

Multiphoton dissociation of $C_6H_7^+$ ions. In related work, Freiser and Beauchamp[21] investigated the photodissociation spectrum of $C_6H_7^+$ ions formed by the proton transfer reaction of HCN^+ with benzene in the gas phase at UV wavelengths ranging from 225 to 400 nm. Two peaks at 245 ± 10 and 330 ± 10 nm were observed to result in a high photodissociation probability for H_2 loss from $C_6H_7^+$. In comparison, we could not observe any detectable photodissociation with the visible wavelengths of an argon ion laser in the range 454.5–514.5 nm. However, under infrared laser irradiation, the $C_6H_7^+$ ion dissociates by loss of H_2, with different rates at the different wavelengths used:

$$C_6H_7^+ \xrightarrow{nh\nu} C_6H_5^+ + H_2 \quad \Delta H = 273.2 \text{ kJ mol}^{-1} \tag{4}$$

Based on the protonated benzene and the phenyl, the endothermicity of this dissociation reaction is estimated to be 273.2 kJ mol^{-1}; hence, on average, the absorption of at least 24 photons at 10.25 μm is required for the dissociation of $C_6H_7^+$, assuming no activation energy in excess of the reaction endothermicity.[21]

At 10.25 μm, the irradiation of $C_6H_7^+$ formed from the different sources described above had a maximum rate of photodissciation according to reaction (5):

$$[C_6H_7^+]_a + nh\nu \rightarrow [C_6H_5^+]_a + H_2 \tag{5a}$$

$$[C_6H_7^+]_b + nh\nu \rightarrow [C_6H_5^+]_b + H_2 \tag{5b}$$

$$[C_6H_5^+]_b + nh\nu \rightarrow C_4H_3^+ + C_2H_2 \tag{5c}$$

This pathway was confirmed by continuous ejection of the intermediate product ion $C_6H_5^+$ during the irradiation pulse, indicating that the $C_6H_5^+$ ion is at the origin of $C_4H_3^+$ ion. A typical plot of photodissociation reaction (5) with $C_6H_7^+$ ion originating from protonated benzene is shown in Fig. 2. The fact that the appearance of product ions $C_6H_5^+$ attains a plateau value may signify that two different structures are present: one of them (b) photodissociates by loss of a C_2H_2 at a fast rate; the other one (a) is stable, or dissociates slowly. When studying the reactivity of phenylium ions, Ausloos *et al.*[22] came to the conclusion that two populations must exist. This situation may be described by two reaction channels from the $C_6H_7^+$ for formation of the $C_6H_5^+$ ions. The equations shown in Fig. 2 are obtained by assuming a double exponential decay for the $C_6H_7^+$ and one consecutive reaction leading to $C_4H_3^+$. The results show that a very good approximation of the experimental data is obtained by assuming that the slow photofragmentation of the $[C_6H_7^+]_b$ ion fragments further with a rate constant $k_{5c} = 8.0 \text{ s}^{-1}$ by losing an acetylene. The $[C_6H_5^+]_a$ ion formed in the fast fragmentation does not seem to decompose further within the time-scale of the experiment. Table 2 gives the results for the photodissociation of $C_6H_7^+$ ions generated from different precursors at 10.25 μm and 3540 W cm^{-2}. In this study, both the relative contributions and the corresponding rate constants are nearly identical. The rate constants k_{5c} for cyclohexa-1, 4-diene and 3-bromopropene as precursor are 12.8 and 12.6 s^{-1}, respectively, but are subject to a large uncertainty.

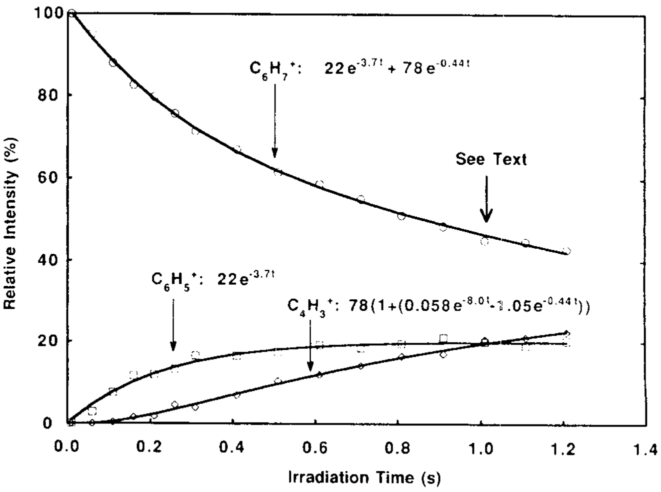

Figure 2. Plot of the normalized relative intensity of the peak of the $C_6H_7^+$ ion originating from protonated benzene as a function of irradiation time. Laser intensity, 3540 W cm^{-2} at 10.25 μm. The continuous lines correspond to a nonlinear regression yielding the equations given.

Table 2. Photodissociation kinetics of $C_6H_7^+$ ions at 10.25 μm and 3540 W cm^{-2} fitted with a double exponetial decay: $[C_6H_7^+]_t = [C_6H_7^+]_0$ $(A_{5a} e^{-k_{5a}t} + A_{5b} e^{-k_{5b}t})$ ($[C_6H_7^+]_0 = 100\%$)

$C_6H_7^+$ precursor	A_{5a} (%)	A_{5b} (%)	k_{5a} (s^{-1})	k_{5b} (s^{-1})
c-$C_6H_6 + CH_5^+$	22	78	3.7	0.44
3-$C_3H_5Br + C_3H_5^+$	22	78	4.1	0.33
1,4-c-C_6H_8	26	74	4.4	0.44

The question arises of the interpretation of experimental results in terms of a two-component decay when a photon-induced ion isomerization cannot be easily ruled out owing to a high-energy threshold for ion fragmentation. It is known that there are several situations which give rise to two-component decay rates. One explanation might be that there are in fact two initial isomers which photodissociate at different rates. Another explanation is that an isomerization step competes with dissociation. For a large number of ions, the energy barrier for isomerization is below the dissociation limit. The slow inrease of internal energy by the successive absorption of infrared photons may then lead to isomerization before the dissociation limit is reached (see Fig. 3).[23,24] A similar explanation has been proposed and similar problems in finding a structural rearrangement were encountered for the dissociation of the $C_5H_{10}^+$ ions.[25] In particular, the energy threshold of 273.2 kJ mol^{-1} for fragmentation of benzenium $C_6H_7^+$ to a stable phenyl $C_6H_5^+$ is extremely high, so that an energy barrier for converting to other non-benzenium isomers may be lower. If this is the case, isomerization of a considerable proportion of $C_6H_7^+$ ion could accompany photodissociation. Based on this suggestion and the observations in the photodissociation of $C_6H_7^+$, the overall complicated dissociation process may be speculated to be as shown in Fig. 3, which can be determined by the following reaction sequence:

$$P_1 \xleftarrow{k_a} M_1 \xrightarrow{k_b} M_2 \xrightarrow{k_c} P_2 \qquad (6)$$

Here it is assumed that the ion M_1 decomposes directly to the product ion P_1 at a rate k_a. However, in competition with this direct dissociation, M_1 can also rearrange to ion M_2 with a rate k_b. This ion will dissociate with a rate k_c to give the product P_2, which probably corresponds to a slowly photodissociating fraction of $C_6H_5^+$.

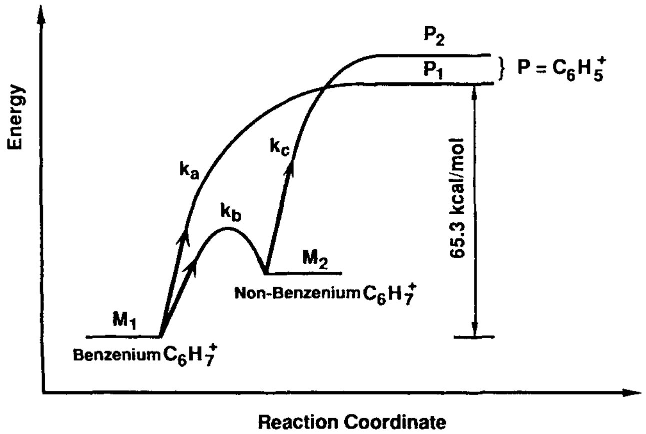

Figure 3. Proposed model for a competitive photodissociation–isomerization reaction of the $C_6H_7^+$ ions. 273.2 kJ/mol^{-1} ≡ 65.3 kcal/mol.

An exact solution of the kinetic equations for the reaction sequence (6) leads to the double exponential expression (7) for the proton-induced dissociation–isomerization decay of ions $[C_6H_7^+]_t = [M_1]_t + [M_2]_t$, assuming that initially the $C_6H_7^+$ ions are a mixture of two structures ($[C_6H_7^+]_0 = [M_1]_0 + [M_2]_0 = 100\%$):

$$[M_1]_t + [M_2]_t = [M_1]_0((k_a - k_c)/(k_a + k_b - k_c)) \times \exp(-(k_a + k_b)t) + ([M_1]_0(k_b/(k_a + k_b - k_c)) + [M_2]_0 \exp(-k_c t)) \qquad (7)$$

Comparing Eqn (7) with the double exponential Eqn (8) used to fit the experimental data by a non-linear last-squares calculation:

$$[C_6H_7^+]_t = A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) \qquad (8)$$

the parameters in the two-component decay are given by

$$A_1 = \frac{k_a - k_c}{k_a + k_b - k_c}[M_1]_0$$

$$A_2 = \frac{k_b[M_1]_0}{k_a + k_b - k_c} + [M_2]_0$$

$$k_1 = k_a + k_b$$

$$k_2 = k_c$$

It can be seen that these parameters depend on combinations of rate constants. However, the fitting procedure yields only three experimental values, k_1, k_2 and A_1 ($A_2 = 100\% - A_1$), as listed in Table 2, for the four unknown quantities k_a, k_b, k_c and $[M_1]_0$ ($[M_2]_0 = 100\% - [M_1]_0$). The systems is underdetermined, i.e. the ratio k_a/k_b and $[M_1]_0$ cannot be obtained separately. Consequently, in the case when dissociation and isomerization are in competition, it is not possible to determine from a two-component decay whether already initially a mixture of structures is present or if the second form is formed only by photoisomerization. Such a reaction is easily possible, since the relatively slow absorption of IR photons corresponds in essence to increase in the equilibrium temperature of the isolated ion.[26] As an isomerization results in a loss of all information about the original ion structures, the data shown in Table 2 indicate only that both photodissociation and isomerization of $C_6H_7^+$ ions could take place in an IR light field. In order to confirm further this assumption and the identity of $C_6H_7^+$ ions, proton transfer reactions were performed as a 'bracketing experiment'.

Proton transfer reactions of $C_6H_7^+$ ions with neutral compounds. It is reasonable to assume that the identical results of photodissociation for $C_6H_7^+$ ions originating from different sources are caused by isomerization of the $C_6H_7^+$ ion. From this point of view, it is interesting to study whether a single structure is intially present for the $C_6H_7^+$ ion.

A proton transfer reaction used for ion structural identification is based on the difference in proton affinity of the neutrals M and C_6H_6 involved:

$$C_6H_7^+ + M \rightarrow C_6H_6 + MH^+ \qquad (9)$$

The $C_6H_7^+$ species will react with neutral bases in proton transfer processes only if their proton affinities (*PA*) are higher than that of the conjugate bases of the reactant ions, i.e. $PA_{(M)} > PA_{(C_6H_6)}$. The proton affinities of several conjugate C_6H_6 bases are listed in Table 1.[9,15] Some experiments were performed with various compounds having a known proton affinity in order to determine the identities of isomeric $C_6H_7^+$.

Table 3 gives the results of the bracketing experiments performed with $C_6H_7^+$ ions of different origins. The $C_6H_7^+$ ions formed both from protonated benzene and from the ion–molecule reaction (1) transfer their proton to nitroethane and methanol but not to cyclopropane, demonstrating that their conjugate C_6H_6 bases have a proton affinity between 752.3 and 761.1 kJ mol^{-1}. This corresponds to the benzene base (*PA* = 758.6 kJ mol^{-1}) which indicates that the $C_6H_7^+$ ions generated in both systems have the benzenium structure (*a*).

Data obtained from the fragment of cyclohexa-1,4-diene show that the observed abundance of $C_6H_7^+$ as a function of reaction time reaches an unreactive plateau of about 20 ± 2% when it reacts with a neutral reactant habint a proton affinity in the range 752.3–852.3 kJ mol^{-1}, but it only disappears completely when reacting with *N*-methylformamide (*PA* = 861.1 kJ mol^{-1}). A typical plot of disappearance of $C_6H_7^+$ by transferring a proton to molecule of different proton affinity is shown in Fig. 4. The interpretation of this result is that there are initially at last two distinct populations of $C_6H_7^+$ ions present. One, corresponding to a C_6H_6 base with a lower *PA* value, has the benzenium structure (*a*). The most likely structures of the other $C_6H_7^+$ ions are the protonated fulvenes (*b*) or/and (*c*), with conjugate C_6H_6 bases having a *PA* value approaching that of fulvenes. Unfortunately, these two non-benzenium structures (*b*) and (*c*) cannot be distinguished.

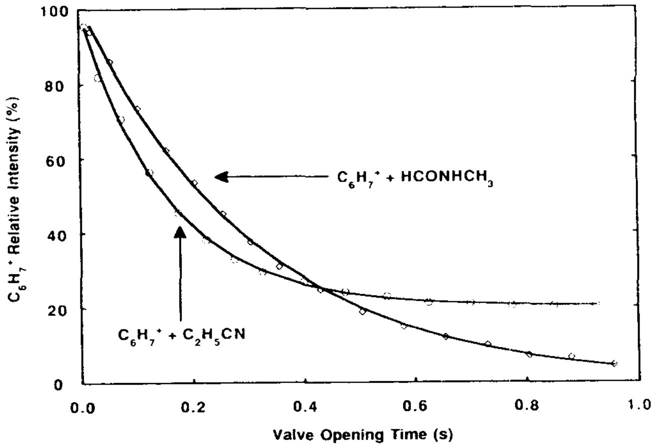

Figure 4. Plot of the proton transfer reaction of the $C_6H_7^+$ ion originating from cyclohexa-1,4-diene with different reactants.

The $C_6H_7^+$ isomerization during irradiation may be further confirmed by a photodissociation experiment using protonated benzene, $C_6H_7^+$. The remaining 40% of the $C_6H_7^+$ ions after 1 s of irradiation time with a CO_2 laser were isolated again (see Fig. 2; the moment of isolating pulse is indicated by an arrow) and allowed to react with neutral $C_2H_5NO_2$ introduced through a pulsed valve. This resulted in the formation of an unreactive $C_6H_7^+$ plateau of about 30% of the remaining $C_6H_7^+$ ion after irradiation. Comparing this result with that for the same reaction carried out in the absence of irradiation, in which no plateau was observed (results shown in Table 3), it has to be concluded that the proportion which does not react with neutral $C_2H_5NO_2$ has arisen from intramolecular rearrangement processes during laser irradiation. This means that an isomerization of the protonated benzene ions takes place. It cannot be proved that the new isomer formed has the same structure as the non-decomposing isomer formed in the $C_6H_7^+$ ion formed from cyclohexadiene.

Table 3. Proton transfer reactions between $C_6H_7^+$ and reactant molecules with different proton affinity (*PA*)[a]

	$C_6H_7^+$ precursor		
Reactant molecule	CH_5^+ + c-C_6H_6	$C_3H_5^+$ + 3-C_3H_5Br	1,4-c-C_6H_8
Cyclopropane (*PA* = 752.3 kJ mol^{-1})	0%	0%	0%
Methanol (*PA* = 761.1 kJ mol^{-1})	100% PT	100% PT	81% PT
Nitroethane (*PA* = 773.2 kJ mol^{-1})	100% PT	100% PT	79% PT
3-Fluorotoluene (*PA* = 792.9 kJ mol^{-1})			81% PT
Propionitrile (*PA* = 852.3 kJ mol^{-1})			80% PT
N-Methylformamide (*PA* = 861.1 kJ mol^{-1})			100% PT

[a] 0% = No reaction was observed. PT = proton transfer from a fraction of $C_6H_7^+$ to M was observed; 100% indicates that all of $C_6H_7^+$ ions participate in the proton transfer reaction.

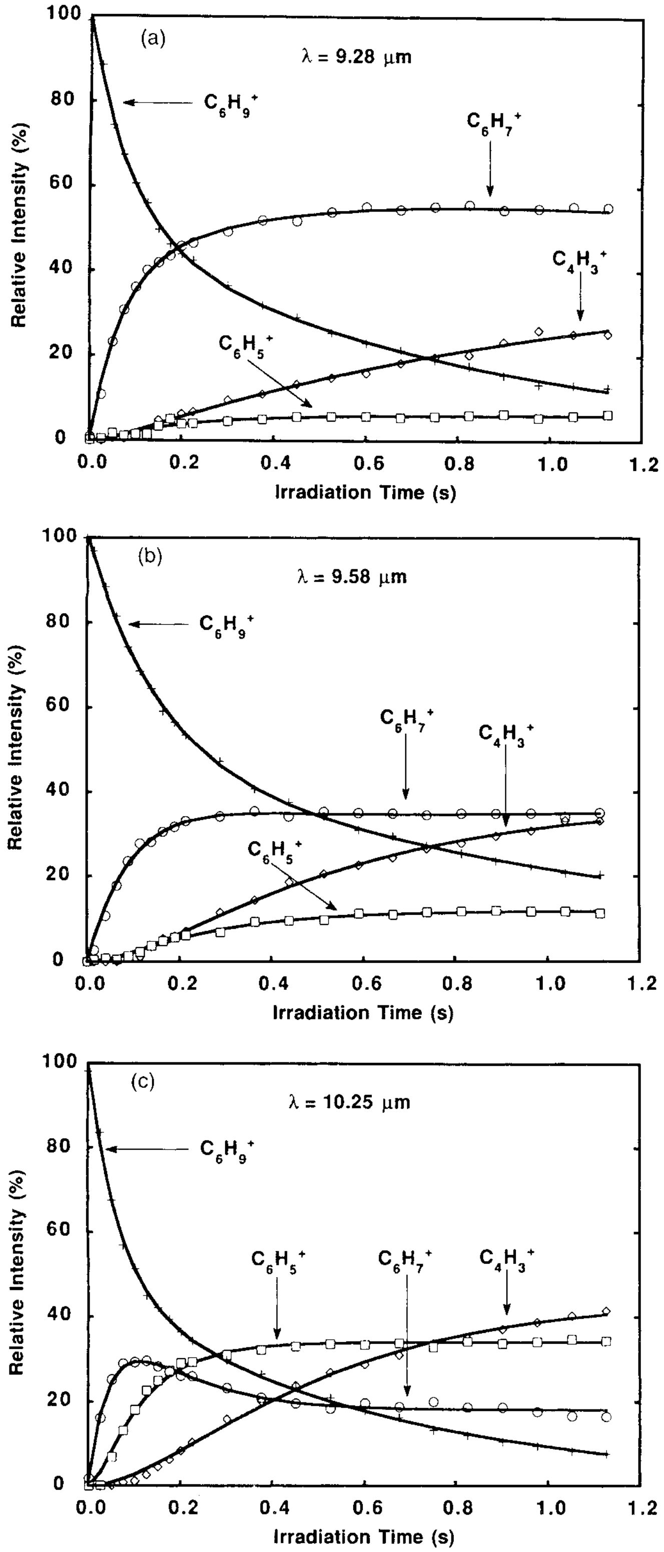

Figure 5. Photodissociation of $C_6H_9^+$ originating from cyclohexa-1,4-diene at different wavelengths. The products of further photofragmentation are also given. The solid lines correspond to the least-squares approximation described in the text. Laser intensity, 3540 W cm^{-2}.

$C_6H_9^+$

Multiphoton dissociation of $C_6H_9^+$ ions. For all $C_6H_9^+$ ions studied, the observed decomposition pathway of H_2 loss does not depend on the wavelength of the infrared laser:

$$C_6H_9^+ \xrightarrow{nh\nu} C_6H_7^+ + H_2 \quad \Delta H = 46 \text{ kJ mol}^{-1} \tag{10}$$

As demonstrated in Fig. 5, the disappearance of the $C_6H_9^+$ ion as a function of irradiation time can be adequately characterized by a double exponential decay with two components whose concentrations are independent of wavelength. The multiphoton dissociations of all $C_6H_9^+$ species from different systems are summarized in Table 4. The dependence of the rate constants on the wavelength used reflects the difference in the absorption coefficients.

From these data two features are noticeable: for all $C_6H_9^+$ ions studied, a double exponential decay with identical rate constants (i.e. absorption coefficients) at the same wavelength was found; and the relative concentrations of the two components are independent of laser wavelength within experimental error. A straightforward explanation of these differences between the two components of the photodissociation rate for different $C_6H_9^+$ souces might be the presence of two ion populations differing in structure. If this is the case, it is not surprising that the ion populations are independent of laser wavelength. Further, SF_6 as buffer gas, introduced for relaxing collisions before irradiation, does not affect substantially this behaviour and these values. It seems reasonable to preclude the existence of ions with high internal energy, because of a low energy threshold (46 kJ mol^{-1}) for $C_6H_9^+$ dissociation. In order to confirm further the identity of the $C_6H_9^+$ species, a series of proton transfer reactions were performed with selected neutral compounds.

In Fig. 5, the products of further decomposition are also shown as a function of the wavelength for cyclohexa-1,4-diene as precursor for $C_6H_9^+$. It is evident that at least one form of the $C_6H_7^+$ does not decompose within the time-scale of the experiment. This was not the case for $C_6H_7^+$ that was directly formed. Hence at least three different isomers of $C_6H_7^+$ can coexist. In Fig. 5 the solid lines for $m/z = 79$ correspond to a least-squares approximation for a model that takes into account two forms of $C_6H_7^+$: one is stable at the wavelength used and the other decomposes further. The fit seems fairly good, but the plateau value decreases with increasing wavelength from 40 to 18% with rate constants identical with those for the fast decay of $C_6H_9^+$. The concentration of the intermediate form of $C_6H_7^+$ changes from 24 to 46%, the estimation of these latter values being very inaccurate. In spite of the fact that this approximation seems fairly good, this simple model cannot explain the wavelength dependence.

Part of this ion does lose H_2 to form $C_6H_5^+$, which again has two isomers, one of them stable against infrared irradiation and the other losing acetylene to form $C_4H_3^+$. In Fig. 5, the non-linear least-squares approximation is given, where $C_6H_5^+$ and $C_4H_3^+$ are treated as stable products, each resulting from a consecutive reaction. Although the fit is fairly good and no systematic deviation of the residuals can be seen, it is evident that the kinetic behaviour must be more complex, since a strong wavelength dependence is observed, in contrast to the photofragmentation of $C_6H_9^+$. The average

Table 4. Photodissociations of $C_6H_9^+$ at different wavelengths and 3540 W cm^{-2} laser power, fitted with a double exponential decay: $[C_6H_9^+]_t = [C_6H_9^+]_0\,(A_1 e^{-k_1 t} + A_2\, e^{-k_2 t})$ ($[C_6H_9^+]_0$ = 100%)

$C_6H_9^+$ precursor	Wavelength (μm)	A_1 (%)	A_2 (%)	k_1 (s^{-1})	k_2 (s^{-1})
Hept-2-yne	9.28	69	31	11.9	1.7
	9.58	66	34	5.9	0.6
	10.25	67	33	13.8	1.7
$3\text{-}C_3H_5Br^{+\cdot} + 3\text{-}C_3H_5Br$	9.28	71	29	12.6	2.0
	9.58	69	31	6.4	0.8
	10.25	71	29	15.4	1.8
$C_6H_7^+ + 1{,}4\text{-}c\text{-}C_6H_8$	9.28	50	50	11.0	1.3
	9.58	52	48	6.6	0.8
	10.25	54	46	15.5	1.6

values of the residuals is in all cases below 1%, i.e. within the experimental scatter. Since no systematic deviation of the residuals can be seen (with the exception of $C_4H_3^+$ in Fig. 5(c), we are at the limit that can be achieved by such approximations. Several models will probably reproduce the results equally well, but there is no justification to try to increase the number of the parameters.

Proton transfer reactions of $C_6H_9^+$ ions with neutral compounds.

The proton transfer reactions were examined by monitoring the disappearance of $C_6H_9^+$ ion as a function of time:

$$C_6H_9^+ + M \rightarrow C_6H_8 + MH^+ \qquad (11)$$

As shown in Table 5, these experiments agree with what was observed in $C_6H_9^+$ photodissociations, i.e. the existence of two ion populations is indeed confirmed.

From the data in Table 5, the fact that only a fraction of $C_6H_9^+$ species react with propionitrile by proton transfer may reflect that the corresponding ion has the stucture of cyclohexenyl (*e*). This ion structure associates with the conjugate C_6H_8 base of the isomeric cyclohexadienes, which have a proton affinity of 837 kJ mol^{-1} (see Table 1). It is reasonable to assume that the protonation of cyclohexa-1,4-diene favours the formation of structure (*e*), resulting in enhancement of the fraction of cyclohexenyl ion (*e*) to 51%. Another fraction of the $C_6H_9^+$ ions, which cannot transfer a proton to propionitrile, was observed to react completely with molecules having a higher proton affinity such as *n*-propylamine. The question arises of which structure corresponds to a conjugate C_6H_8 base with a higher proton affinity than propionitrile. The proton affinity of methylcyclopenta-1,3-diene is estimated to be ~833 kJ mol^{-1} from the known heats of formation $\Delta H_f(C_6H_8)$, $\Delta H_f(H^+)$ and $\Delta H_f(C_6H_9^+)$:[27,28]

$$PA = \Delta H_f(C_6H_8) + \Delta H_f(H^+) - \Delta H_f(C_6H_9^+) \quad (12)$$

It becomes clear that the 1-methylcyclopentenyl structure (*d*) can be ruled out on the basis of a calculated proton affinity of methylcyclopenta-1,3-diene. However, it may exist in an equilibrium with cyclohexenyl (*e*).

In order to elucidate this $C_6H_9^+$ ion structure, it is necessary to consider the possible isomers corresponding to both a low heat of formation and a conjugate C_6H_8 base having a proton affinity higher than 852.3 kJ mol^{-1}. The thermochemical data[28,29] indicate the two ethyl-substituted cyclobutenyls have a higher heat of formation ranging from 879 to 1079 kJ mol^{-1}. This implies that these ions do not have a stable minimum of the potential energy. Nevertheless, 1,3-dimethylcyclobutenyl shows a relative low heat of formation of 845 kJ mol^{-1}.[15] It is particularly interesting that the corresponding neutral 1-methyl-3-methylenecyclobutene has a proton affinity of 887 kJ mol^{-1}. It is reasonable to suggest that the $C_6H_9^+$ identified with the

Table 5. Proton transfer reactions between $C_6H_9^+$ and reactant molecules with different proton affinity (*PA*)[a]

Reactant molecule	$C_6H_9^+$ precursor Hept-2-yne	 $C_3H_5Br^{+\cdot} + 3\text{-}C_3H_5Br$	 $C_6H_7^+ + 1{,}4\text{-}c\text{-}C_6H_8$
Cyclopentene (*PA* = 767.3 kJ mol^{-1})	0%	0%	0%
Propionitrile (*PA* = 852.3 kJ mol^{-1})	35% PT	30% PT	51% PT
n-Propylamine (*PA* = 911.7 kJ mol^{-1})	100% PT	100% PT	100% PT

[a] 0% = No reaction was observed. PT = proton transfer from a fraction of $C_6H_9^+$ ions to M was observed; 100% indicates that all of $C_6H_9^+$ ions participate in the proton transfer reaction.

conjugate C_6H_8 base of proton affinity in the range 852.3–911.7 kJ mol^{-1} would most likely be 1,3-dimethylcyclobutenyl (*f*).

The fact that similar ion populations can be derived from photofragmentation kinetics and proton transfer reactions clearly indicates that a mixture of structures is initially present in all $C_6H_9{}^+$ systems. Based on this comparison, it can be concluded that the initial $C_6H_9{}^+$ species appears to involve at least two isomers: the rapidly photodissociating fraction has the 1,3-dimethylcyclobutenyl structure (*f*), which only transfers a proton to a molecule having a proton affinity higher than that of 1-methy-3-methylenecyclobutene ($PA = 887$ kJ mol^{-1}); the slowly photodissociating fraction probably corresponds to a structural mixture of both 1-methylcyclopentenyl (*d*) and cyclohexenyl (*e*), both of which could transfer a proton to a molecule having a proton affinity higher than that of the cyclohexadienes ($PA = 837$ kJ mol^{-1}). It may be noted that Wolfschütz and Schwarz[30] provided evidence that the facile rearrangement from cyclohexenyl (*e*) to the 1-methylcyclopentenyl (*d*) cation was observed.

CONCLUSIONS

The IR multiphoton dissociation of $C_6H_7{}^+$ species in the three systems is characterized by a two-component decay rate, which can be explained as the initial presence of isomeric ions or the occurrence of isomerization from original iond during the irradiation pulse. Some information about the identities of the ion structures can be obtained from proton transfer reactions. This is an efficient technique when the conjugate bases corresponding to the ions have a large difference in proton affinities. The studies of proton transfer reactions show evidence that the $C_6H_7{}^+$ species formed from protonated benzene and in the 3-bromopropene system have only the benzenium structure (*a*) that can be isomerized during irradiation. In contrast, the $C_6H_7{}^+$ ions in cyclohexa-1,4-diene exhibit a mixture of $20 \pm 2\%$ non-benzenium structures. It is concluded that the most likely non-benzenium structures are the two protonated fulvenes.

Unlike the $C_6H_7{}^+$ ions, the photodissociations of $C_6H_9{}^+$ species are in good agreement with the data obtained from proton transfer reactions. The relative abundances of different isomers are estimated from the promoted fitting parameters for the double exponential decay in photodissociation and the differences observed in proton transfer reactions. Conclusions concerning the structures of $C_6H_9{}^+$ ions may be drawn from these experiments, which show that the $C_6H_9{}^+$ species in the three systems divide into two groups, one containing the 1-methylcyclopentenyl (*d*) or/and cyclohexenyl, (*e*) and the other probably including the 1,3-dimethylcyclobutenyl (*f*).

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