Flow tube and theoretical study of proton transfer reactions of $C_3H_5^+$ ions

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Abstract

The allyl, $CH_2CHCH_2^+$, and 2-propenyl, $CH_3CCH_2^+$, ions have been observed as distinct isomeric species in a flowing afterglow/selected ion flow drift tube (FA/SIFDT). Reaction with methanol is used as a diagnostic for distinguishing the two isomers. The isomeric ratio of allyl:2-propenyl formed via protonation of allene or propyne by a protonated base BH^+, is shown to be dependent on the proton affinity of the base B. Proton transfer from H_3O^+ to allene produces the 2-propenyl cation only, whereas proton transfer from SO_2H^+ to allene generates a mixture of allyl and 2-propenyl cations, enabling us to estimate the barrier height for the rearrangement allyl $\rightarrow$ 2-propenyl as 110 ± 30 kJ mol^{-1}. This is in accord with ab initio calculations performed at the G2(MP2) level of theory. The $C_3H_5^+$ product of the reaction between $C_2H_4^+$ and C_2H_4 was identified as the 2-propenyl cation. Rate coefficients are also reported for reactions of the allyl and 2-propenyl cations with several neutrals. (Int J Mass Spectrom 185/186/187 (1999) 253–261) © 1999 Elsevier Science B.V.

Keywords: Selected ion flow tube, SIFT; Proton transfer; Allyl ion; 2-propenyl ion; Isomeric structures

1. Introduction

Some of the most studied carbocations in the gas phase are those carbocations designated $C_3H_5^+$. Many studies, both theoretical and experimental, have been reported [1–21]. Quite early on it was recognized that different isomeric structures of $C_3H_5^+$ exist. This was based on the existence of several minima on the $C_3H_5^+$ potential surface [2]. Two of the structures identified in theoretical investigations [2–5], the allyl and 2-pro-

penyl cations, were also characterized in the laboratory [6,9,10].

Aue et al. [6], in an ion cyclotron resonance (ICR) equilibrium study, in which they examined the equilibrium system

$$H_3S^+ + C_3H_4 \rightleftharpoons C_3H_5^+ + H_2S \qquad (1)$$

reported a proton affinity for propyne of 728 kJ mol^{-1} assuming $PA(H_2S) = 720$ kJ mol^{-1}. Further, the $C_3H_5^+$ structure arising from the protonation of propyne was found to have the 2-propenyl structure (2, Fig. 1). Proton transfer from H_3S^+ to allene was also found to produce the 2-propenyl structure [6]. Other measurements based on ionization energies [1], pho-

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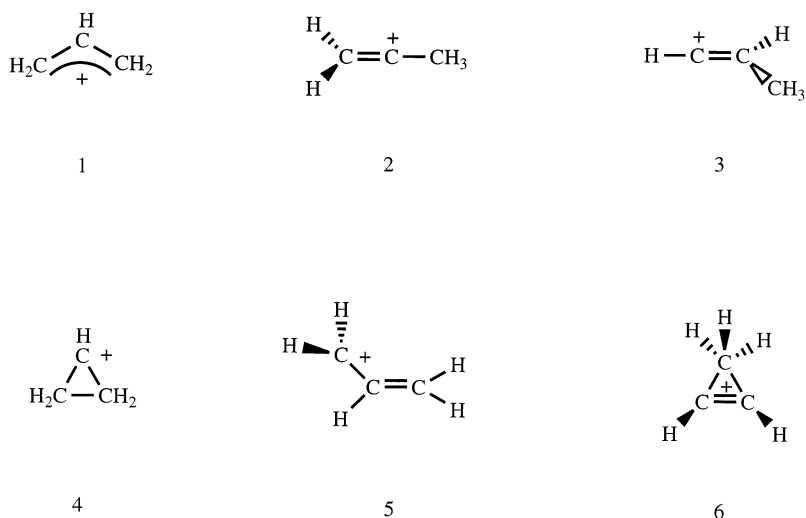Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

Fig. 1. Possible $C_3H_5^+$ ion structures: allyl cation (1), 2-propenyl cation (2), 1-propenyl cation (3), cyclopropyl cation (4), perpendicular allyl ion (5), corner protonated cyclopropene (6).

toelectron spectroscopy [22], and photoionization mass spectrometry [23] in combination with contributions from theory [3] have clearly identified the allyl structure (1, Fig. 1) as the lowest energy structure and global minimum on the $C_3H_5^+$ surface [3,8,11,18]. Collision-induced dissociation studies [9,10, 12] and proton transfer reactions [6,13,17] have also distinguished between the allyl and 2-propenyl structures.

Two other structures, 1-propenyl and cyclopropyl (3, 4, respectively, Fig. 1) have not been unequivocally identified and some doubt remains as to whether they retain their identity under the conditions existing in most mass spectrometer systems, or whether they collapse to the more stable 2-propenyl and allyl structures. Some evidence has been found for a stable cyclopropyl ion (4, Fig. 1). Aue et al. [6] proposed that proton transfer from $(CH_3)_2OH^+$ to cyclopropene produces the cyclopropyl structure. Further, bands arising from photoionization of the c-C_3H_5 radical have been attributed to the cyclopropyl cation structure [24].

We report here a study of proton transfer reactions of $C_3H_5^+$ made from propyne, allene, ethylene, and cyclopropane using a flowing afterglow/selected ion flow drift tube (FA/SIFDT). We have also undertaken self consistent ab initio calculations of the proton affinities of propyne and allene.

2. Experimental

The measurements reported here were carried out using the SIFT apparatus at Canterbury University, operating at room temperature (295 ± 10 K). The original version of the SIFT at Canterbury has been described elsewhere [25]. The instrument has been modified recently with the addition of a flowing afterglow (FA) ion source and a drift tube. Most of the reactions reported here were examined using the new instrument. The new FA source is similar in design to that used by Van Doren et al. [26]. Further details of the modified instrument will be described elsewhere [27].

Two techniques were used to form $C_3H_5^+$ ions. In the first method, $C_3H_5^+$ was generated in the FA source region by addition of cyclopropane or ethylene to a helium carrier subjected to microwave discharge. The $C_3H_5^+$ was mass selected from the ions in the afterglow and injected into the flow tube. In the second method, a suitable base, B, was protonated, mass selected, and then injected into the flow tube. Proton transfer then occurred from HB^+ to propyne or allene added at the first inlet port of the flow reactor tube. Under the experimental conditions, complete conversion of BH^+ to $C_3H_5^+$ will occur with ~5 cm:

a distance that is much less than the separation between inlet ports (40 cm). The structure of the resultant $C_3H_5^+$ ions was then probed using a diagnostic reagent added at the second inlet port. Reagents tried in the present study include HCN, BrCN, CH_3OH, C_2H_5I, C_4H_2, C_6H_6, C_6F_6, and C_7H_7F (4-fluorotoluene).

All reagents were obtained commercially with the exception of propyne, HCN, BrCN, and C_4H_2. Propyne and C_4H_2 were prepared according to the methods of Brandsma [28,29] while HCN was prepared by the action of phosphoric acid on KCN and CNBr was prepared by reacting bromine with excess mercuric cyanide under vacuum.

The rate coefficients reported here are considered accurate to $\pm 15\%$ and the product distributions to $\pm 10\%$ unless stated otherwise.

3. Results and discussion

3.1. Theoretical calculations

All calculations were performed using the GAUSSIAN 94 programs [30]. The calculations follow the prescription detailed in the original description of the $G2(MP2)$ procedure [31].

Although many calculations at various levels of theory have examined the $C_3H_5^+$ potential surface and that of the unprotonated C_3H_4 species [3,4,8,11,15, 16,18,19] an internally consistent set of calculations at a high level of theory such as the G2(MP2) level of theory does not exist. The geometries of the various species have been reported elsewhere [19].

Theory has also shown that protonation directly at the C_2 position of allene cannot occur in a direct mechanism. Originally it was proposed that protonation and CH_2 rotation occurred in a concerted fashion [6] but Foresman et al. [19] found that the necessary perpendicular allyl structure (5, Fig. 1) did not represent a true saddle point on the potential surface. Instead, low energy protonation of allene occurs via the terminal C atom forming the 2-propenyl structure and not the allyl structure. In the present work we found a structure corresponding to the perpendicular

Table 1
G2(MP2) energies of $C_3H_5^+$ species

	Species[a]	E(G2(MP2)) (Hartree)	ΔE(0 K) (kJ mol^{-1})
I	H_2CCCH_2	−116.41565	
II	H_3CCCH	−116.41506	
III	$H_2CCHCH_2^+$	−116.70624	0.0
IV	$H_3CCCH_2^+$	−116.69354	+33.4
V	c-$H_2CCHCH_2^+$(TS)	−116.65260	+140.9
VI	TS(III→IV)	−116.66478	+108.9
VII	TS ($H_2CCHCH_2^+$)		
	Twist – HF geometry	−116.65377	+137.8
VIII	c-$C_3H_4^b$	−116.37906	

[a] The species listed here correspond to structures shown in Fig. 1 as follows: III = 1; IV = 2; V = 4, and VII = 5.
[b] Cyclopropene.

allyl cation (5, Fig. 1) at the HF/6-31G* level of theory, which collapses at the higher MP2/6-31G* level to the 2-propenyl species, in accordance with the calculations of Foresman et al. [19]. We also find that the cyclopropyl ion (4, Fig. 1) represents a transition state for the disrotatory stereomutation of the allyl cation, again in accord with earlier calculations [3, 8].

The G2(MP2) energies and relative energies from the calculations are given in Table 1. The calculated proton affinities of both allene and propyne are given in Table 2. It is interesting to note that the 2-propenyl structure may give rise to either propyne or allene on deprotonation. A diagram of a section of the $C_3H_5^+$ potential surface is illustrated in Fig. 2.

3.2. Measurements

A knowledge of the structure of $C_3H_5^+$ is crucial to an understanding of what reaction is occurring with

Table 2
Proton affinities of C_3H_4 species from G2(MP2) calculations

		Proton affinity (298 K) (kJ mol^{-1})	Expt [32]
H_2CCCH_2	C1	733.6	–
H_2CCCH_2	C2	769.1	775
H_3CCCH	C1	735.4	747.6
c-$C_3H_4^a$		828.5[b]	818.5

[a] Cyclopropene.
[b] Calculated with respect to the 2-propenyl cation, $CH_3CCH_2^+$ (see text for discussion).
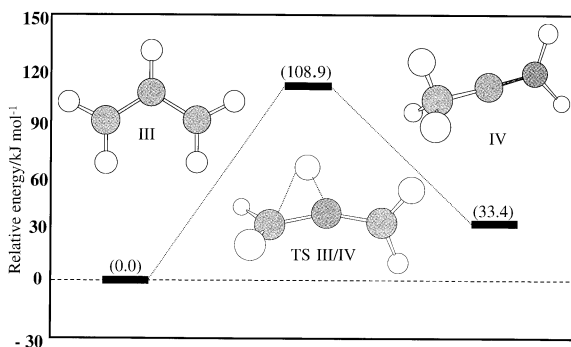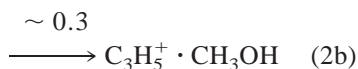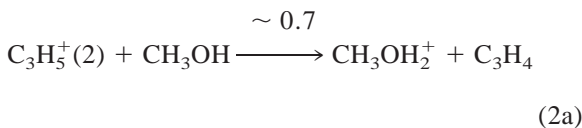
Fig. 2. Diagram of a section of the $C_3H_5^+$ potential energy surface showing the allyl and 2-propenyl structures and the transition state between them (bridge protonated allene). The energies are expressed in kJ mol^{-1} relative to the allyl cation at 0 K.

what isomer. It was therefore necessary to develop a method for distinguishing between the allyl (1, Fig. 1) and 2-propenyl (2, Fig. 1) isomers. Of all the reactions examined in this work, the only reagent found that distinguished clearly between the structures was the reaction with methanol.

3.2.1. CH₃OH reactions (PA = 754 kJ mol⁻¹)

The 2-propenyl $C_3H_5^+$ structure was formed by injecting H_3O^+ from the source region into the flow tube and adding propyne at the first inlet port as discussed in the experimental section. As the difference in PA (propyne − H_2O) is small (57 kJ mol^{-1}) [32] and the barrier calculated for rearrangement to the more stable allyl structure is larger than this (see Table 1) then the resulting $C_3H_5^+$ should have the 2-propenyl structure designated $C_3H_5^+$ (2)

$$C_3H_5^+(2) + CH_3OH \xrightarrow{\sim 0.7} CH_3OH_2^+ + C_3H_4$$

$$(2a)$$

$$\xrightarrow{\sim 0.3} C_3H_5^+ \cdot CH_3OH \quad (2b)$$

$$k = 1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

The semilogarithmic decay for this reaction is shown in Fig. 3(a).
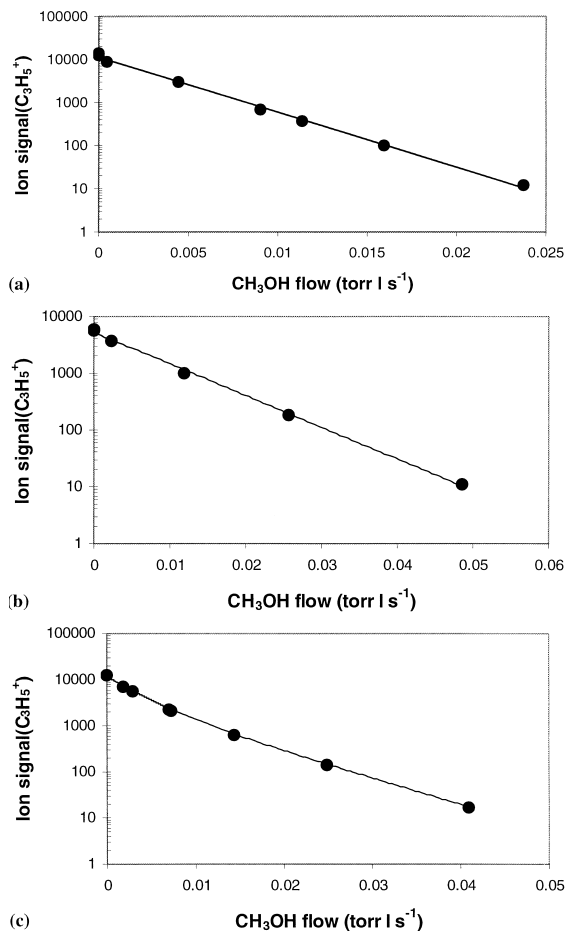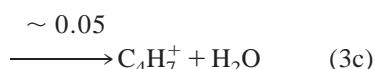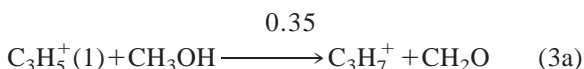
The allyl structure, designated hereafter as $C_3H_5^+$

Fig. 3. (a) Semilogarithmic decay of the 2-propenyl $C_3H_5^+$ ion signal vs. CH₃OH flow. The linear fit yields a rate coefficient of $k = 1.7 \times 10^{-9} \text{ s}^{-1}$. (b) Semilogarithmic decay of the allyl $C_3H_5^+$ ion signal vs. CH₃OH flow. The linear fit yields a rate coefficient of $k = 7.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. (c) Semilogarithmic decay of the $C_3H_5^+$ ion signal, formed via the reaction of SO_2H^+ with allene, vs. CH₃OH flow. The curve is a double-exponential fit with $k_1 = 1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and $k_2 = 7.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and yields an allyl:2-propenyl ratio of 65:35.

(1), was prepared by injecting any $C_3H_5^+$ ion formed in the FA source section into the flow tube. All sources of $C_3H_5^+$ (proton transfer and fragmentation) produced a common $C_3H_5^+$ structure after injection into the flow tube. Even though the injection energies were relatively small (ion energies were typically 20 eV, or < 2 eV in the centre of mass frame) the very process of injecting the ion into the helium

carrier gas flow of the reactor tube was sufficient to cause rearrangement to the allyl structure, $C_3H_5^+$ (1)

$$C_3H_5^+(1) + CH_3OH \xrightarrow{\quad 0.35 \quad} C_3H_7^+ + CH_2O \qquad (3a)$$

$$\xrightarrow{\quad 0.55 \quad} CH_3OH_2^+ + C_3H_4 \qquad (3b)$$

$$\xrightarrow{\quad \sim 0.05 \quad} C_4H_7^+ + H_2O \qquad (3c)$$

$$\xrightarrow{\quad \sim 0.05 \quad} C_3H_5^+ \cdot CH_3OH \qquad (3d)$$

$$k = 7.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

The semilogarithmic decay for this reaction is shown in Fig. 3(b). The rate coefficients and product distributions observed for the two isomers, $C_3H_5^+$ (1) and $C_3H_5^+$ (2) are thus sufficiently different to enable ready characterization of the ion structure. Recently, Riveros and Zhu [17] also noted a difference in reactivity with CH_3OH for each structure using the Fourier transform ion cyclotron resonance (FTICR) technique. However, they concluded that $C_3H_5^+$ (2) reacted seven times faster than $C_3H_5^+$ (1) with CH_3OH although our results show a difference of a factor of 2.3. They also did not report product channels. Proton transfer from $C_3H_5^+$ (1), reaction (3b), was not reported by Aue et al. in their study [6]. The fact that it occurs at all, although being apparently endothermic ($\Delta H° = +21$ kJ mol^{-1} for the allene structure), may indicate that the tabulated PA's are slightly in error.
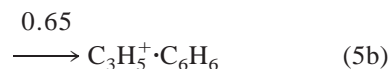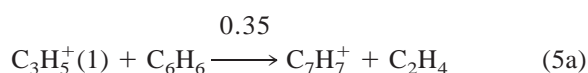
3.2.2. C_6H_6 reactions (PA = 750 kJ mol^{-1})

Both $C_3H_5^+$ (1) and $C_3H_5^+$ (2) reactions with C_6H_6 were examined

$$C_3H_5^+(2) + C_6H_6 \rightarrow \text{products} \qquad (4)$$

$$k = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

The products of the reaction could not be determined because of mass overlaps arising from other ions also present in the flow tube

$$C_3H_5^+(1) + C_6H_6 \xrightarrow{\quad 0.35 \quad} C_7H_7^+ + C_2H_4 \qquad (5a)$$

$$\xrightarrow{\quad 0.65 \quad} C_3H_5^+ \cdot C_6H_6 \qquad (5b)$$

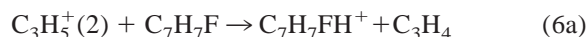$$k = 1.35 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

There is a small difference in the rate coefficients for the two structures but it is not large enough to be definitive.

3.2.3. C_6F_6 reactions (PA = 648 kJ mol^{-1})

Both structures, $C_3H_5^+$ (1 and 2) exhibited identical rate coefficients ($k = 2.0 \times 10^{-11}$ cm^3 s^{-1}) with C_6F_6. The products were not determined but there is some evidence for the cluster ion.

3.2.4. 4-fluorotoluene reactions (PA = 764 kJ mol^{-1})

Both $C_3H_5^+$ (1 and 2) exhibited collision-rate reactions with C_7H_7F. Proton transfer was a major product of reaction from $C_3H_5^+$ (2)

$$C_3H_5^+(2) + C_7H_7F \rightarrow C_7H_7FH^+ + C_3H_4 \qquad (6a)$$

$$\rightarrow C_3H_5^+ \cdot C_7H_7F \qquad (6b)$$

$$k = 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

It is worth noting that proton transfer and association commonly occur together when the PA's of the two bases differ by less than $\sim$20 kJ mol^{-1} [33–35]. No proton transfer was observed from $C_3H_5^+$ (1)

$$C_3H_5^+(1) + C_7H_7F \rightarrow C_3H_5^+ \cdot C_7H_7F \qquad (7)$$

$$k = 1.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

3.2.5. Other allyl cation reactions

In addition to these reactions in which the reactivity of both structures 1 and 2 was examined, a number of reactions of the allyl ion only were investigated. The allyl $C_3H_5^+$ ion was formed via electron impact on cyclopropane in the FA source and injected, following mass selection, into the flow tube. The structure of this ion was confirmed as the allyl structure by examining its reactivity with CH_3OH

$$C_3H_5^+(1) + CNBr \xrightarrow{0.5} CNBrH^+ + C_3H_4 \quad (8a)$$

$$\xrightarrow{0.5} C_3H_5^+ \cdot CNBr \quad (8b)$$

$$k = 6.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

Both proton transfer and adduct formation were observed in the reaction with CNBr. The measured rate coefficient for proton transfer, $k = 3.3 \times 10^{-10}$ cm^3 s^{-1}, suggests a reaction endothermicity for reaction (8a) of 5 kJ mol^{-1} (calculated by assuming Arrhenius behaviour and a pre-exponential factor equal to the collision rate). This is apparently at odds with the tabulated thermochemical data [32] that predicts reaction (8a) to be endothermic by 25 kJ mol^{-1}. Again, this may indicate that the tabulated proton affinities are slightly in error

$$C_3H_5^+(1) + HCN \xrightarrow{1.0} C_3H_5^+ \cdot HCN \quad (9)$$

$$k = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

The allyl cation was observed to react with HCN via a termolecular association channel only. The effective bimolecular rate coefficient for reaction (9) was measured at 0.34 Torr

$$C_3H_5^+(1) + C_2H_5I \xrightarrow{1.0} C_3H_5^+ \cdot C_2H_5I \quad (10)$$
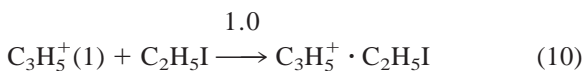
$$k = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

The observed reaction between the allyl cation and ethyl iodide also proceeded via termolecular association. The measured effective bimolecular rate coefficient suggests that this reaction is close to pressure saturation at 0.34 Torr

$$C_3H_5^+(1) + C_4H_2 \xrightarrow{0.7} C_3H_5^+ \cdot C_4H_2 \quad (11a)$$

$$\xrightarrow{0.3} C_5H_5^+ + C_2H_2 \quad (11b)$$
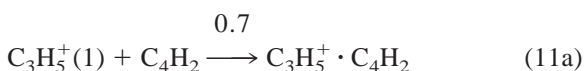
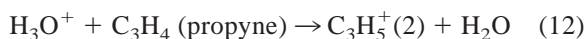$$k = 1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

The allyl cation also undergoes rapid termolecular association with diacetylene. $C_5H_5^+$ was also identified as a reaction product.

Most of the reactions of $C_3H_5^+$ (1) and $C_3H_5^+$ (2) studied in this work are summarized in Table 3 which also includes the thermochemistry data.
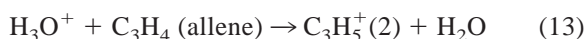
3.2.6. Proton transfer reactions

The reactions of several protonated bases, HB$^+$, with propyne and allene were examined. The bases, B, were selected on the basis of their known proton affinities, viz H$_2$O (PA = 691 kJ mol^{-1}), SO$_2$ (PA = 636 kJ mol^{-1}) [36], and CO (PA = 594 kJ mol^{-1}). The HB$^+$ ions were produced in the FA source region of the SIFT instrument, mass selected, and injected into the flow reactor tube. Propyne and allene were added at the upstream inlet of the flow tube and the resulting $C_3H_5^+$ product ions were then identified via subsequent reaction with methanol at the downstream reactant neutral inlet.

(a) H_3O^+ reactions

$$H_3O^+ + C_3H_4 \text{ (propyne)} \rightarrow C_3H_5^+(2) + H_2O \quad (12)$$

$$(\Delta H^\cdot = -57 \text{ kJ mol}^{-1}, \text{ 2-propenyl})$$

$$H_3O^+ + C_3H_4 \text{ (allene)} \rightarrow C_3H_5^+(2) + H_2O \quad (13)$$

$$(\Delta H^\circ = -84 \text{ kJ mol}^{-1}, \text{ allyl})$$

Note that protonating allene via low energy proton transfer produces the 2-propenyl structure exclusively. This result is consistent with the earlier studies of Aue et al. [6] who also found that proton transfer from H$_3$O$^+$ to allene produced the 2-propenyl structure. We note, however, that Aue et al. reported that the allyl cation (1, Fig. 1) does not transfer a proton to methanol whereas the 2-propenyl cation (2, Fig. 1) does. We have found that *both ions* proton transfer to methanol [reactions (2) and (3)], although the 2-propenyl ion undergoes much faster, apparently exothermic, proton transfer than the allyl cation. We deduce proton transfer from the allyl cation to be endothermic, from its slow reaction with methanol.

Table 3
Reaction rate coefficients and product ratios with the specified reagent for the $C_3H_5^+$ ions: allyl, $CH_2CHCH_2^+$, and 2-propenyl, $CH_3CCH_2^+$

Reactant	Products	Branching ratio	k_{obs} 10^{-9} cm^3 s^{-1}	k_{coll}[a] 10^{-9} cm^3 s^{-1}	$-\Delta H^{\circ b}$/(kJ mol^{-1})
		$CH_2CHCH_2^+$ (1)			
CH_3OH	$C_3H_7^+ + CH_2O$	0.35	0.73	2.2	53.7[c]
	$CH_3OH_2^+ + C_3H_4$	0.55			−21.0
	$C_4H_7^+ + H_2O$	~0.05			140.7[d]
	$C_3H_5^+ \cdot CH_3OH$	~0.05			
C_6H_6	$C_7H_7^+ + C_2H_4$	0.35	1.35	1.4	76.5[e]
	$C_3H_5^+ \cdot C_6H_6$	0.65			
C_7H_7F[f]	$C_3H_5^+ \cdot C_7H_7F$	1.0	1.8	2.3	
CNBr	$CNBrH^+ + C_3H_4$	0.5	0.66	2.0	−25.5
	$C_3H_5^+ \cdot CNBr$	0.5			
HCN	$C_3H_5^+ \cdot HCN$	1.0	0.11	3.4	
C_2H_5I	$C_3H_5^+ \cdot C_2H_5I$	1.0	1.2	2.1	
C_4H_2	$C_5H_5^+ + C_2H_2$	0.3	1.3	1.2	144.0[g]
	$C_3H_5^+ \cdot C_4H_2$	0.7			
		$CH_3CCH_2^+$ (2)			
CH_3OH	$CH_3OH_2^+ + C_3H_4$	~0.7	1.7	2.2	6.3
	$C_3H_5^+ \cdot CH_3OH$	~0.3			
C_6H_6			1.1	1.4	
C_7H_7F[f]	$C_7H_7FH^+ + C_3H_4$		1.5	2.3	15.8
	$C_3H_5^+ \cdot C_7H_7F$				

[a] Calculated using the method of Su and Chesnavich [38].
[b] Based on ΔH°'s presented in [32].
[c] Calculated assuming the iso-$C_3H_7^+$ structure.
[d] Calculated assuming the $CH_3CHCH = CH_2^+$ structure.
[e] Calculated assuming the benzyl $C_7H_7^+$ structure.
[f] 4-fluorotoluene.
[g] Calculated assuming the vinyl cyclopropenyl structure.

(b) SO_2H^+ reactions

SO_2 was protonated via addition of SO_2 to a hydrogen carrier gas subjected to microwave discharge in the FA source. The resultant SO_2H^+ ion was mass selected, injected into the flow tube, and allowed to undergo proton transfer to propyne or allene, added at the first neutral inlet

$$HSO_2^+ + C_3H_4 \rightarrow C_3H_5^+ + SO_2 \qquad (14)$$
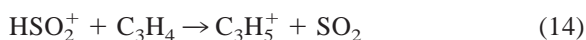
$$\Delta H^{\circ} = -112 \text{ kJ mol}^{-1} \text{ (2-propenyl)};$$

$$\Delta H^{\circ} = -139 \text{ kJ mol}^{-1} \text{ (allyl)}$$

The $C_3H_5^+$ ion formed in reaction (14) from propyne was examined for structure by measuring its reaction with CH_3OH

$$C_3H_5^+ + CH_3OH \rightarrow \text{products} \qquad (15)$$
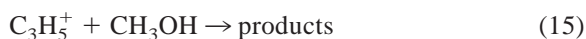
The resulting semilogarithmic plot of $C_3H_5^+$ signal against CH_3OH flow is *curved* indicating that two $C_3H_5^+$ structures are present. The curve was fitted using a double exponential expression [25] that showed ~20% of the $C_3H_5^+$ had the 2-propenyl structure and ~80% the allyl structure.

The $C_3H_5^+$ ion formed in reaction (14) from allene was examined for structure by its reaction with CH_3OH as above. The resulting semilogarithmic decay of $C_3H_5^+$ ion signal versus CH_3OH flow is also curved [Fig. 3(c)] and indicates a 2-propenyl to allyl ratio of 35:65.

(c) HCO^+ reactions

Protonated CO, HCO^+, was made by adding CO to a hydrogen carrier in the FA source. After mass selection and injection into the flow tube, the resultant

HCO^+ ion underwent proton transfer to propyne or allene at the first inlet.

Following subsequent reaction with methanol it was found that proton transfer from HCO^+ to both allene and propyne produces predominantly the allyl structure

$$HCO^+ + C_3H_4 \rightarrow C_3H_5^+ + CO \tag{16}$$
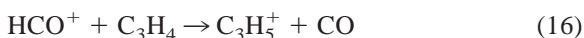
$\Delta H° = -154$ kJ mol^{-1} (propyne);

$\Delta H° = -181$ kJ mol^{-1} (allene)

These results indicate that in the proton transfer reactions of HCO^+ and SO_2H^+ sufficient energy is available within the complex to overcome the transition barrier between the 2-propenyl and allyl structures, whereas this energy is not available in the proton transfer reaction of H_3O^+ with allene. From these results we estimate the height of the transition state barrier between the 2-propenyl and allyl structures as 110 ± 30 kJ mol^{-1} (1.2 ± 0.3 eV). This is in excellent agreement with our calculated value of 109 kJ mol^{-1}.

3.2.7. $C_2H_4^{\cdot+} + C_2H_4$ reaction

$C_2H_4^{\cdot+}$ was formed in the FA source from ethylene, mass selected at $m/z = 28$ and injected into the flow tube. Addition of C_2H_4 at the first neutral inlet produced $C_3H_5^+$ via reaction (17)

$$C_2H_4^{\cdot+} + C_2H_4 \rightarrow C_3H_5^+ + CH_3 \tag{17}$$
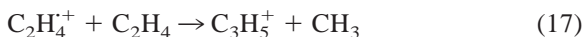
$$k = 7.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} [39]$$

$\Delta H° = -6$ kJ mol^{-1} (2-propenyl);

$\Delta H° = -27$ kJ mol^{-1} (allyl)

Subsequent reaction with CH_3OH at the second neutral inlet identified the product of reaction (17) as the 2-propenyl cation only. This is in conflict with the findings of Bowers et al. who, on the basis of collisionally-induced dissociation (CID) experiments, identified the $C_3H_5^+$ structure of reaction (17) as the allyl cation only [10]. Interestingly, formation of both the allyl and 2-propenyl ions in (17) is close to thermoneutral. It is possible, although improbable,

that the allyl cation is formed in reaction (17) and isomerises to the 2-propenyl structure under the conditions of our flow tube experiment (i.e. in the presence of excess C_2H_4).

3.2.8. Cyclopropyl cation

Attempts to generate the cyclopropyl ion, c-$C_3H_5^+$ (4, Fig. 1), via Penning ionization of cyclopropane by metastable excited helium in our FA source, resulted in only the allyl structure after injection into the flow tube. Using ion cyclotron double resonance techniques Aue et al. [6] found that cyclopropene forms a $C_3H_5^+$ ion by proton transfer from $(CH_3)_2OH^+$ but not $(C_2H_5)_2OH^+$. From this they deduced a heat of formation for the $C_3H_5^+$ ion formed of 238 kcal mol^{-1} that is not consistent with the allyl cation. They suggested that either a cyclopropyl structure is formed or that there is a barrier associated with concerted protonation and rearrangement to the allyl structure. Köhler and Lischka [8] offered an alternative explanation of the experimental results of Aue et al. based on MINDO/3 and CEPA calculations of the $C_3H_5^+$ hypersurface. They proposed that the most favourable approach of a proton towards cyclopropene will be towards the CH_2 group producing corner-protonated cyclopropene (6, Fig. 1). The resulting structure undergoes facile ring opening and rearranges to the 2-propenyl cation. Their calculated proton affinity of cyclopropene with respect to the 2-propenyl cation, and calculated $\Delta H_f°$ for the 2-propenyl cation were in excellent agreement with the values determined for the $C_3H_5^+$ species observed experimentally by Aue et al. [6]. Similarly, our calculated proton affinity of cyclopropene, with respect to the 2-propenyl cation (Table 2), is in good agreement with the revised PA (cyclopropene) listed in [32], lending credence to the conclusions of Köhler and Lischka [8].

4. Conclusions

The present work, together with experimental and theoretical work performed during the last 30 years, demonstrates conclusively that the allyl cation and the 2-propenyl cation are distinct isomeric species in the

gas phase and that they are separated by a sizeable barrier to isomerization. Proton transfer from a protonated base, BH^+, to both allene and propyne produces the 2-propenyl cation exclusively unless the difference in proton affinities is sufficiently large to overcome the barrier to isomerization. Beyond this point, as the proton affinity of B decreases, the ratio of allyl:2-propenyl increases. CH_3OH has been found to be a suitable reagent to distinguish between the allyl and 2-propenyl structures, the allyl cation reacting more than two times slower than the 2-propenyl cation.

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