

**C<sub>m</sub>H<sub>n</sub><sup>+</sup> Reactions with H and H<sub>2</sub>: An Experimental Study****Graham B. I. Scott, David A. Fairley, Colin G. Freeman, and Murray J. McEwan\****Department of Chemistry, University of Canterbury, Christchurch, New Zealand***Nigel G. Adams and Lucia M. Babcock***Department of Chemistry, University of Georgia, Athens, Georgia 30602**Received: February 25, 1997; In Final Form: May 1, 1997*<sup>⊗</sup>

We report measurements of the reactions of a number of hydrocarbon ions with atomic and molecular hydrogen made using a selected ion flow tube (SIFT) operating at room temperature. Results, including branching ratios and rate coefficients, are reported for C<sub>m</sub>H<sub>n</sub><sup>+</sup> ions ( $m = 2-6$ ,  $n = 0-9$ ). Highly unsaturated hydrocarbon ions undergo mainly H atom abstraction reactions with H<sub>2</sub> forming C<sub>m</sub>H<sub>n+1</sub><sup>+</sup> + H products. More saturated ions are unreactive. Two types of reactions occur for H atoms: H atom transfer to give C<sub>m</sub>H<sub>n-1</sub><sup>+</sup> + H<sub>2</sub> (if exothermic) and association (to give C<sub>m</sub>H<sub>n+1</sub><sup>+</sup>).

**Introduction**

The most ubiquitous and abundant species in the universe are molecular and atomic hydrogen. The enormous clouds of gas and dust that exist in the interstellar medium are composed largely of H<sub>2</sub> and H. Radioastronomy techniques have discovered significant densities of hydrocarbon molecules and ions in these interstellar clouds,<sup>1</sup> and models have been constructed showing how the chemistry taking place within the clouds can lead to the various hydrocarbon species observed.<sup>2</sup> Moreover, the precursor ion in many synthetic schemes, H<sub>3</sub><sup>+</sup>, has recently been detected for the first time.<sup>3</sup> The physical conditions existing within a typical dense cloud (viz. low temperatures 10–50 K) and low densities (10<sup>3</sup>–10<sup>6</sup> particles cm<sup>-3</sup>) mean that conventional chemical processes are very slow.<sup>2</sup> Chemical models, involving a mixture of ion–molecule, radical–radical, and some heterogeneous reactions occurring on grain surfaces have been developed, and these provide reasonable estimates of the observed abundances for many species.<sup>2,4</sup> These models use results from experimental studies as input. Although many laboratory investigations of ions reacting with molecular hydrogen relevant to interstellar cloud chemistry have been made, the same is not true for ion–H atom processes. Atomic hydrogen is not an easy reactant to monitor in the laboratory, and this is the main reason reported ion reactions with H<sub>2</sub> outnumber those with H by about a factor of 20.<sup>5</sup>

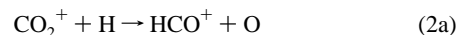
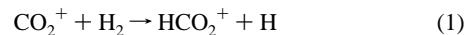
In addition to the relevance of ion–H<sub>2</sub>, H chemistry to interstellar clouds, there is a more fundamental aspect. Reactions of hydrocarbon ions with H atoms and H<sub>2</sub> provide information on ion stabilities and on the mode of hydrogen addition to hydrocarbon species.

Efforts have been made in the past by different groups to overcome the problems of monitoring H-atom densities with by far the majority of attempts using flow-tube techniques.<sup>6</sup> Early ion–H atom studies applied conventional methods from neutral–H atom studies,<sup>7,8</sup> but later, methods unique to ion–H atom reactions were developed. One such technique utilizes the reaction of CO<sub>2</sub><sup>+</sup> with a mixture of H<sub>2</sub> and H.<sup>9,10</sup> We recently compared this method for determining H atom concentrations with those using other systems (e.g., CO<sup>+</sup>, H<sub>2</sub>/H; C<sub>2</sub>N<sub>2</sub><sup>+</sup>, H<sub>2</sub>/H; CN<sup>+</sup>, H<sub>2</sub>/H) and obtained good agreement between the different systems.<sup>10</sup> In the present study, we apply

the CO<sub>2</sub><sup>+</sup>, H<sub>2</sub>/H technique to examine the reactions of a series of hydrocarbon ions, C<sub>m</sub>H<sub>n</sub><sup>+</sup> ( $m = 2-6$ ;  $n = 0-9$ ) with H atoms. As part of the study we have also measured the reactions of the same ions with H<sub>2</sub>. The ions were chosen on the basis of their importance to gas-phase molecular synthesis in interstellar clouds. Primarily, although not exclusively, we have concentrated on reactions that have not been previously studied. In several cases we have repeated work performed in other laboratories to verify the accuracy of our methods.

**Experimental Section**

The details of the selected ion flow tube (SIFT) at the University of Canterbury that was used in this work have been described elsewhere.<sup>11</sup> Only a brief summary of that part of the equipment pertinent to the present study will be given here. The C<sub>m</sub>H<sub>n</sub><sup>+</sup> reactant ions are generated by electron impact on an appropriate hydrocarbon gas and, after mass selection by the upstream quadrupole mass filter, are injected into the flow tube. H atoms are generated in a quartz side tube by a microwave discharge of either a 10% mixture of hydrogen in helium or, alternatively, pure hydrogen as is discussed elsewhere.<sup>10</sup> A typical degree of dissociation of the He/H<sub>2</sub> mixture is 25–40%. The reactions of CO<sub>2</sub><sup>+</sup> with H<sub>2</sub> and H



are used to calibrate the H atom number density within the flow tube as described by Tosi et al.<sup>9</sup> and also in our earlier paper.<sup>10</sup> As the extent of dissociation of H<sub>2</sub> in the microwave discharge is always less than 100%, a mixture of H<sub>2</sub> and H enters the flow tube. It is therefore necessary in each case to establish the outcome of the reaction of the C<sub>m</sub>H<sub>n</sub><sup>+</sup> ion with H<sub>2</sub> first (microwave discharge off) before examining its reactivity with H atoms (microwave discharge on). Small fluxes of minor species formed in the discharge (e.g. H<sup>+</sup>, H<sub>2</sub><sup>+</sup>, H<sub>3</sub><sup>+</sup>), metastable atoms (e.g., He 2<sup>3</sup>S), and electrons are produced concomitantly with H atoms. Ion–electron recombination and surface neutralization reduce the concentration of charged species to an insignificant level compared with the reacting molecular and

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, June 15, 1997.

**TABLE 1: Reaction of the Designated  $C_mH_n^+$  Ion with  $H_2$** 

reactant ion	products	branching ratio	$k^a$	$k_{\text{prev}}^b$	$-\Delta H^\circ/(\text{kJ mol}^{-1})^c$
$C_2^+$	$C_2H^+ + H$	1.0	11	11, <sup>d</sup> 14, <sup>e</sup> 12 <sup>f</sup>	88
$C_2H^+$	$C_2H_2^+ + H$	1.0	11	7.8, <sup>d</sup> 17 <sup>e</sup>	149
$C_3H_3^+$	NR		<0.05	<0.01, <sup>g</sup> <0.001 <sup>h</sup>	
$HCCCH_2^+$	NR		<0.05	<0.05 <sup>i</sup>	
$c\text{-}C_3H_3^+$	NR		<0.05	<0.05 <sup>i</sup>	
$H_2CCCH_2^+$	NR		<0.05	<0.001 <sup>j</sup>	
$HCCCH_3^+$	NR		<0.005	<0.001 <sup>j</sup>	
$C_3H_5^+$	NR		<0.005	NR <sup>k</sup>	
$C_3H_7^+$	NR		<0.05	NR <sup>k</sup>	
$C_4H^+$	$C_4H_2^+ + H$	1.0	1.8	<0.001, <sup>k</sup> 1.5, <sup>l</sup> 1.8 <sup>f</sup>	$\sim 137^m$
$C_4H_2^+$	NR		<0.04		
$C_4H_3^+$	NR		<0.02		
$C_4H_4^+$	NR		<0.03		
$C_4H_5^+$	NR		<0.03		
$C_4H_6^+$	NR		<0.04		
$C_4H_8^+$	NR		<0.005		
$C_4H_9^+$	NR		<0.005		
$ac\text{-}C_6H_4^+$	NR		<0.005		
$c\text{-}C_6H_4^+$	NR		<0.03		
$ac\text{-}C_6H_5^+$	NR		<0.01	<0.01 <sup>n</sup>	
$c\text{-}C_6H_5^+$	$C_6H_7^+$	1.0	0.38 <sup>o</sup>	0.15, <sup>p</sup> 0.5 <sup>l,n</sup>	273
$c\text{-}C_6H_6^+$	NR		<0.05	<0.01 <sup>n</sup>	

<sup>a</sup> Observed rate coefficient in units of  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . The Langevin capture rate coefficient for all reactions in this table is  $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ .

<sup>b</sup> Rate coefficients determined in other laboratories in units of  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . <sup>c</sup> The listed exothermicities are taken from ref 12. <sup>d</sup> Reference 13 <sup>e</sup> Reference 14. <sup>f</sup> Reference 15. <sup>g</sup> Reference 16. <sup>h</sup> Reference 17. No bimolecular reaction was observed, but a limit to termolecular association of  $k \leq 1 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$  at 80 K was reported. <sup>i</sup> Reference 18. <sup>j</sup> Reference 17. Results are measured at 80 K. Isomeric form of  $C_3H_4^+$  not specified. No bimolecular reaction was observed, but a limit to termolecular association of  $k < 1 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$  was reported. <sup>k</sup> Reference 17. A limit to termolecular association of  $k < 1 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$  at 80 K was reported. <sup>l</sup> Reference 19. <sup>m</sup> Exothermicity from refs 12 and 20. <sup>n</sup> Reference 21. <sup>o</sup> Pseudobimolecular reaction. The rate constant shown is for a flow tube pressure of 0.30 Torr. The termolecular rate for the three body association process is estimated as  $\geq 3.9 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$ . <sup>p</sup> Reference 22.

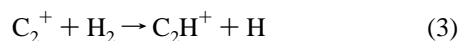
atomic hydrogen. He 2 <sup>3</sup>S atoms are not so easily removed, and although the flux of such metastables is several orders of magnitude below that of H and H<sub>2</sub>, they can be effectively excluded only by discharging pure hydrogen.

All reactions reported here were carried out at  $300 \pm 5 \text{ K}$  and at a flow tube pressure of 0.30–0.35 Torr. We estimate the uncertainty in the rate coefficients reported in this work for H atoms as  $\pm 30\%$  (unless specified otherwise) where the increase in uncertainty over the  $\pm 15\%$  usually specified for SIFT measurements arises from the uncertainties associated with the determination of H-atom densities.

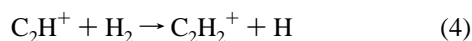
## Results and Discussion

A summary of all the results obtained in this work for  $C_mH_n^+$  reactions are presented in Table 1 for H<sub>2</sub> and Table 2 for H atoms. Previous measurements, where they exist, are indicated in column 5 of each table.

**$C_2^+$  and  $C_2H^+$ .** Each of these ions was generated by electron impact on a He/C<sub>2</sub>H<sub>2</sub> mixture. In both cases the determination of the rate coefficient with H was hampered by a rapid reaction with H<sub>2</sub>:



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

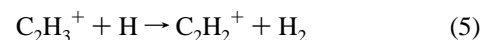


$$k = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

The apparent rate coefficients for reactions 3 and 4 decreased with the discharge on, to rate coefficient values equivalent to that expected for diluting H<sub>2</sub> with a nonreacting gas in the reaction mixture at the same level as H atoms. No new products appeared, and we thus conclude that no reaction with H occurs at measurable rates for either ion. These results are consistent

with the fact that no exothermic binary channels are available for either reaction.

**$C_2H_3^+$ .** The  $C_2H_3^+$  ion in this study was generated by a sequential process from  $C_2H_5^+$  which was produced by electron impact on C<sub>2</sub>H<sub>5</sub>Br.  $C_2H_5^+$  was mass selected and injected into the flow tube at just sufficient energy for fragmentation to  $C_2H_3^+$  to occur by collision-induced dissociation with the helium bath gas during injection. No reaction was found with H<sub>2</sub> but  $C_2H_3^+$  does undergo reaction with H:



$$k = 6.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

The significance of this measurement to establishing the endothermicity of the reverse of reaction 5 has been commented on elsewhere.<sup>10,24,25</sup>

**$C_3H_3^+$ .** There are two low-energy forms of  $C_3H_3^+$ : the acyclic propargyl ion,  $HCCCH_2^+$ , and the cyclopropenylum ion,  $c\text{-}C_3H_3^+$ . Mixtures of these ions (typically 60% acyclic, 40% cyclic) are readily made from reactions ensuing after initial electron impact on C<sub>2</sub>H<sub>4</sub>. The primary ion,  $C_2H_4^+$ , reacts with C<sub>2</sub>H<sub>4</sub> in a high-pressure ion source producing  $C_3H_5^+$ , which fragments after mass selection into the two isomeric forms of  $C_3H_3^+$  during the injection process. We have discussed previously methods based on differing reactivities for distinguishing between the two isomers of  $C_3H_3^+$ :<sup>18</sup> in all cases  $HCCCH_2^+$  is more reactive than  $c\text{-}C_3H_3^+$ . In the present study neither ion was found to be reactive with H<sub>2</sub>. Similarly, no reaction was found with H atoms despite each isomeric ion having an apparent exothermic binary reaction channel available<sup>12</sup> leading to their respective cyclic and acyclic  $C_3H_2^+$  isomers (+H<sub>2</sub>). However extensive ab initio calculations of the  $C_3H_2^+$  and  $C_3H_3^+$  surface<sup>26,27</sup> have shown both H-atom-transfer reactions to be endothermic which is in keeping with our observations. The endothermicity of the  $ac\text{-}C_3H_3^+/H$  atom-transfer reaction is calculated as only 8 kJ mol<sup>-1</sup>.<sup>26</sup>

TABLE 2: Reactions of the Designated C<sub>m</sub>H<sub>n</sub><sup>+</sup> Ion with H

reactant ion	products	branching ratio	k <sup>a</sup>	k <sub>prev</sub> <sup>b</sup>	-ΔH <sup>o</sup> /(kJ mol <sup>-1</sup> ) <sup>c</sup>
C <sub>2</sub> <sup>+</sup>	NR		<1.0		
C <sub>2</sub> H <sup>+</sup>	NR		<1.0		
C <sub>2</sub> H <sub>3</sub> <sup>+</sup>	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> + H <sub>2</sub>	1.0	0.68	<0.1; <sup>d</sup> 1.0 <sup>e</sup>	5.8 <sup>f</sup>
HCCCH <sub>2</sub> <sup>+</sup>	NR		<0.03		
c-C <sub>3</sub> H <sub>3</sub> <sup>+</sup>	NR		<0.03		
H <sub>2</sub> CCCH <sub>2</sub> <sup>+</sup>	C <sub>3</sub> H <sub>3</sub> <sup>+</sup> + H <sub>2</sub>	1.0	1.7		164 <sup>g</sup>
HCCCH <sub>3</sub> <sup>+</sup>	C <sub>3</sub> H <sub>3</sub> <sup>+</sup> + H <sub>2</sub>	1.0	3.0		224 <sup>g</sup>
C <sub>3</sub> H <sub>5</sub> <sup>+</sup>	C <sub>3</sub> H <sub>6</sub> <sup>+</sup>	1.0	1.6 <sup>h,i</sup>		206 <sup>j</sup>
C <sub>3</sub> H <sub>7</sub> <sup>+</sup>	C <sub>3</sub> H <sub>6</sub> <sup>+</sup> + H <sub>2</sub>	1.0	0.32		59 <sup>k</sup>
C <sub>4</sub> H <sup>+</sup>	C <sub>4</sub> H <sub>2</sub> <sup>+</sup>	1.0	~5.8 <sup>h,l</sup>		~574 <sup>m</sup>
C <sub>4</sub> H <sub>2</sub> <sup>+</sup>	C <sub>4</sub> H <sub>3</sub> <sup>+</sup>	1.0	2.6 <sup>h,n</sup>		~420
C <sub>4</sub> H <sub>3</sub> <sup>+</sup>	C <sub>4</sub> H <sub>4</sub> <sup>+</sup>	1.0	~0.5 <sup>h,o</sup>		~206 <sup>g</sup>
C <sub>4</sub> H <sub>5</sub> <sup>+</sup>	NR		<0.4		
C <sub>4</sub> H <sub>6</sub> <sup>+</sup>	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> + C <sub>2</sub> H <sub>4</sub>	~0.15			38 <sup>p</sup>
	C <sub>2</sub> H <sub>5</sub> <sup>+</sup> + C <sub>2</sub> H <sub>2</sub>	~0.65	1.9		73 <sup>p</sup>
	C <sub>4</sub> H <sub>5</sub> <sup>+</sup> + H <sub>2</sub>	~0.20			174 <sup>q</sup>
C <sub>4</sub> H <sub>8</sub> <sup>+</sup>	C <sub>4</sub> H <sub>7</sub> <sup>+</sup> + H <sub>2</sub>	1.0	1.1		193 <sup>r</sup>
C <sub>4</sub> H <sub>9</sub> <sup>+</sup>	NR		<0.2		
ac-C <sub>6</sub> H <sub>4</sub> <sup>+</sup>	NR		<0.05		
c-C <sub>6</sub> H <sub>4</sub> <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> <sup>+</sup>	1.0	0.33 <sup>h,s</sup>		400 <sup>t</sup>
ac-C <sub>6</sub> H <sub>5</sub> <sup>+</sup>	NR		<0.05	0.05 <sup>u</sup>	
c-C <sub>6</sub> H <sub>5</sub> <sup>+</sup>	NR		<0.1	0.01 <sup>u</sup>	
c-C <sub>6</sub> H <sub>6</sub> <sup>+</sup>	C <sub>6</sub> H <sub>5</sub> <sup>+</sup> + H <sub>2</sub>	~0.35			67 <sup>v</sup>
	C <sub>6</sub> H <sub>7</sub> <sup>+</sup>	~0.65	2.1 <sup>w</sup>	2.5 <sup>u</sup>	340 <sup>x</sup>

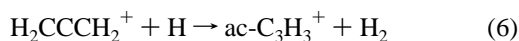
<sup>a</sup> Observed rate coefficient in units of 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup>. The Langevin capture rate coefficient for all reactions in this table is 19 × 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup>.

<sup>b</sup> Rate coefficients determined in other laboratories in units of 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup>. <sup>c</sup> Unless specified otherwise, the listed exothermicities are taken from ref 12. <sup>d</sup> Reference 23. <sup>e</sup> Reference 24. <sup>f</sup> See reference 10. <sup>g</sup> Thermochemistry for acyclic isomers. <sup>h</sup> Pseudobimolecular reaction. The rate coefficient shown is for a flow tube pressure of 0.30 Torr. <sup>i</sup> The termolecular rate for the three body association process is estimated as ≥ 1.6 × 10<sup>-26</sup> cm<sup>6</sup> s<sup>-1</sup>.

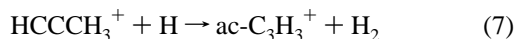
<sup>j</sup> Thermochemistry for lowest energy acyclic isomers. <sup>k</sup> This value corresponds to the iso C<sub>3</sub>H<sub>7</sub><sup>+</sup> structure converted to the acyclic C<sub>3</sub>H<sub>6</sub><sup>+</sup> species. <sup>l</sup> The termolecular rate for the three-body association process is estimated as ≥ 6 × 10<sup>-26</sup> cm<sup>6</sup> s<sup>-1</sup>. <sup>m</sup> References 12 and 20. <sup>n</sup> The termolecular rate for the three-body association process is estimated as ≥ 2.7 × 10<sup>-26</sup> cm<sup>6</sup> s<sup>-1</sup>. <sup>o</sup> The termolecular rate for the three body association process is estimated as ≥ 5.1 × 10<sup>-27</sup> cm<sup>6</sup> s<sup>-1</sup>. <sup>p</sup> Thermochemistry based on (E)-2-C<sub>4</sub>H<sub>8</sub><sup>+</sup> and CH<sub>3</sub>CCHCH<sub>3</sub><sup>+</sup>. <sup>q</sup> The termolecular rate for the three body association process is estimated as ≥ 3.4 × 10<sup>-27</sup> cm<sup>6</sup> s<sup>-1</sup>. <sup>r</sup> Thermochemistry based on benzyne ion and phenyl radical ion. <sup>s</sup> Reference 21. <sup>t</sup> Thermochemistry based on benzene ion and phenyl radical ion. <sup>u</sup> The termolecular rate for the three body association channel between c-C<sub>6</sub>H<sub>6</sub><sup>+</sup> + H is estimated as ≥ 1.4 × 10<sup>-26</sup> cm<sup>6</sup> s<sup>-1</sup>. <sup>v</sup> Thermochemistry based on benzene ion and protonated benzene ion.

<sup>w</sup> Thermochemistry based on benzene ion and protonated benzene ion.

**H<sub>2</sub>CCCH<sub>2</sub><sup>+</sup> and HCCCH<sub>3</sub><sup>+</sup>.** The ions H<sub>2</sub>CCCH<sub>2</sub><sup>+</sup> and HCCCH<sub>3</sub><sup>+</sup> were made by electron impact on their parent precursors, allene and propyne, respectively. No reaction was observed with H<sub>2</sub> for either ion. Both ions underwent efficient H atom transfer with H:



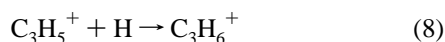
$$k = 1.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$



$$k = 3.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

The C<sub>3</sub>H<sub>3</sub><sup>+</sup> products of reactions 6 and 7 are shown as ac-C<sub>3</sub>H<sub>3</sub><sup>+</sup> (acyclic C<sub>3</sub>H<sub>3</sub><sup>+</sup>) on the basis that the precursor ions are acyclic, although this was not confirmed by experiment.

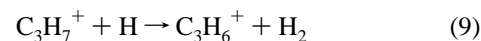
**C<sub>3</sub>H<sub>5</sub><sup>+</sup>.** The C<sub>3</sub>H<sub>5</sub><sup>+</sup> ion was generated by electron impact on C<sub>2</sub>H<sub>4</sub> in a high pressure ion source. C<sub>3</sub>H<sub>5</sub><sup>+</sup> is also the major product ion from the reaction between C<sub>2</sub>H<sub>4</sub><sup>+</sup> and C<sub>2</sub>H<sub>4</sub> as discussed previously for C<sub>3</sub>H<sub>3</sub><sup>+</sup>. After mass selection, C<sub>3</sub>H<sub>5</sub><sup>+</sup> was injected into the flow tube (using sufficiently low energies to prevent fragmentation into C<sub>3</sub>H<sub>3</sub><sup>+</sup>). No reaction was observed with H<sub>2</sub> (k < 5 × 10<sup>-13</sup> cm<sup>3</sup> s<sup>-1</sup>), but an observable reaction did occur with H atoms, the major channel resulting from an association reaction:



$$k = 1.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

A curved semilogarithmic decay of Ln(C<sub>3</sub>H<sub>5</sub><sup>+</sup>) count versus H-atom flow indicates at least two C<sub>3</sub>H<sub>5</sub><sup>+</sup> isomers may be present. The rate coefficient shown here is that for the more reactive isomer. No reaction was observed for the less reactive isomers.

**C<sub>3</sub>H<sub>7</sub><sup>+</sup>.** This ion was generated by electron impact on either 1-bromopropane or 2-bromopropane, C<sub>3</sub>H<sub>7</sub>Br. There was no difference in the behavior of the C<sub>3</sub>H<sub>7</sub><sup>+</sup> arising from either precursor with H<sub>2</sub> and H. No reaction was found between C<sub>3</sub>H<sub>7</sub><sup>+</sup> and H<sub>2</sub>, which is consistent with the lack of a bimolecular exothermic channel. The slow reaction with H atoms proceeded via H atom transfer:



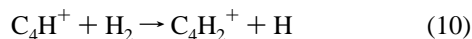
$$k = 3.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

The fact that the H-atom-transfer reaction appears independent of ion structure is an interesting result. If the C<sub>3</sub>H<sub>7</sub><sup>+</sup> ions generated from 1- and 2-bromopropane retain the structural distinction of their precursor, then the slow rate coefficient observed for each ion may suggest a similar kinetic barrier. Alternatively, the C<sub>3</sub>H<sub>7</sub><sup>+</sup> ions from the two precursors may have the same structure. Energies and geometries of the C<sub>3</sub>H<sub>6</sub><sup>+</sup>, C<sub>3</sub>H<sub>7</sub><sup>+</sup> and C<sub>3</sub>H<sub>8</sub><sup>+</sup> ions have been characterized using quantum chemistry ab initio methods.<sup>28-30</sup> A study of the [C<sub>3</sub>H<sub>7</sub><sup>+</sup>···H] transition states has not to our knowledge been undertaken and would be valuable in clarifying the details of reaction 9.

**C<sub>4</sub>H<sup>+</sup>, C<sub>4</sub>H<sub>2</sub><sup>+</sup>, C<sub>4</sub>H<sub>3</sub><sup>+</sup>.** All three ions were produced by

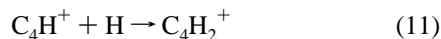
electron impact on acetylene in a high-pressure ion source.  $C_4H_2^+$  and  $C_4H_3^+$  are the primary product ions from the reaction of  $C_2H_2^+$  on  $C_2H_2$ , and  $C_4H^+$  is the product ion of the reaction between  $C_2^+$  and  $C_2H_2$ .

$C_4H^+$  undergoes an H-atom abstraction with  $H_2$  at about 10% of the collision rate:



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

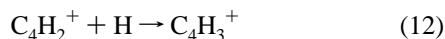
and also exhibits an efficient association reaction with H atoms:



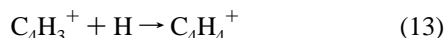
$$k \sim 5.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

The higher uncertainty in the rate coefficient for reaction 11 ( $\pm 50\%$ ) is a consequence of the presence of both  $H_2$  and H atoms together in the reaction mixture when the microwave discharge is on.  $C_4H^+$  produces the same product ion with  $H_2$  (H-atom abstraction) as with H (association). The observation of reaction 10 allows us to place an estimate for  $\Delta H_f^\circ(C_4H^+) \geq 1640 \text{ kJ mol}^{-1}$  which is consistent with the best theoretical estimate of  $\Delta H_f^\circ(C_4H^+) = 1779 \text{ kJ mol}^{-1}$ .<sup>20</sup> To separate the  $C_4H^+$  loss via  $H_2$  from the H atom loss, it was necessary to computer-model the observed total decay of  $C_4H^+$  using the rate coefficient for reaction 10 (measured with the microwave discharge off) as input.

$C_4H_2^+$  and  $C_4H_3^+$  do not undergo reaction with  $H_2$  but in both cases show association with H atoms (reactions 12 and 13) with pseudobimolecular rate coefficients of  $2.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , respectively:



$$k = 2.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

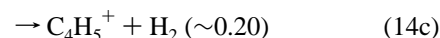
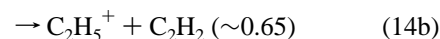
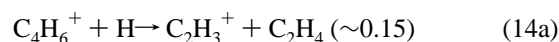


$$k = (5 \pm 3) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

The higher uncertainty in the rate coefficient for reaction 13 stems from a small contribution to  $C_4H_3^+$  from reaction 12. The decrease in association rate with number of H atoms in the series  $C_4H_n^+$  ( $n = 1-3$ ) is possibly a consequence of the decreasing well depth of the  $(C_4H_{n+1})^*$  collision complex as  $n$  increases. If this occurs, the complex lifetime is shortened thus allowing less time for complex stabilization. Assuming the most stable structures for the acyclic ions  $C_4H_n^+$  ( $n = 1-4$ ) the well depths are<sup>12,20</sup> reaction 11 ( $\geq 574 \text{ kJ mol}^{-1}$ ); reaction 12;  $\sim 420 \text{ kJ mol}^{-1}$ , and reaction 13 ( $\sim 205 \text{ kJ mol}^{-1}$ ).

$C_4H_5^+$ ,  $C_4H_6^+$ . These ions were generated by electron impact on 1,3-butadiene and injected into the flow tube after mass selection, in company with lesser amounts of  $C_4H_7^+$ . Neither  $C_4H_5^+$  nor  $C_4H_6^+$  undergo reaction with  $H_2$ . Although  $C_4H_5^+$  is produced in the fast reaction of  $C_4H_6^+ + H$ , it does not appear to react with atomic hydrogen, and we assess an upper limit for its reaction as  $k < 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . The fast reaction of  $C_4H_6^+$  with H atoms yields three products including

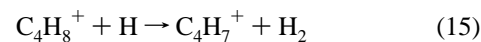
a 20% H-atom-transfer channel:



$$k = 1.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

The fact that this reaction is substantially different in terms of dissociative reaction pathways, from all other  $C_mH_n^+/H$  reactions studied thus far indicates a different reaction mechanism is in operation. Insertion of H into  $C_4H_6^+$  to form the  $(C_4H_7^+)^*$  collision complex results in rapid dissociation of the complex before stabilization can occur. The  $\sim 360 \text{ kJ mol}^{-1}$  of available excitation energy above the  $C_4H_7^+$  well is sufficient to cause fragmentation at the C2 position of a protonated 1,3-butadiene type ion,  $CH_3CHCH=CH_2^+$ , giving rise to the two fragmentation channels observed.

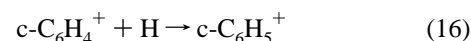
$C_4H_8^+$ ,  $C_4H_9^+$ . These ions were each generated by electron impact on 2-butene. Neither ion was reactive with  $H_2$ .  $C_4H_9^+$  was also unreactive with H atoms ( $k < 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ), but  $C_4H_8^+$  exhibited H-atom transfer:



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

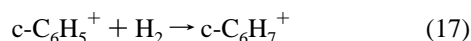
$C_6H_4^+$ ,  $C_6H_5^+$ ,  $C_6H_6^+$ . These  $C_6H_n^+$  ions were generated either by electron impact on benzene or following electron impact on  $C_2H_2$  in a high-pressure source ( $C_6H_4^+$ ,  $C_6H_5^+$ ). With the latter method,  $C_4H_2^+$  and  $C_4H_3^+$  are produced from  $C_2H_2$  as described previously and injected into the flow tube.  $C_2H_2$  is then added at the first inlet port, forming  $C_6H_4^+$  and  $C_6H_5^+$  as the primary products of the reactions of  $C_4H_2^+$  and  $C_4H_3^+$ , respectively, with  $C_2H_2$ .<sup>31</sup> Two stable isomeric structures are known to exist for  $C_6H_4^+$  and  $C_6H_5^+$  when prepared from  $C_2H_2^+$ . These two structures are thought to be the cyclic and acyclic isomers which are readily distinguished by their different reactivities. The more reactive isomer of  $C_6H_5^+$  was originally attributed to acyclic  $C_6H_5^+$ ,<sup>32,33</sup> but later work has shown that the lower energy phenylium ion is more reactive than the acyclic isomer.<sup>22</sup> Accordingly, we attribute the  $C_6H_5^+$  isomer which is more reactive with  $H_2$ , to c- $C_6H_5^+$  as also did Petrie et al.<sup>21</sup> Similarly the  $C_6H_4^+$  ion derived from benzene was found to have a higher reactivity with  $C_2H_2$  than did the  $C_6H_4^+$  isomer produced in the reaction between  $C_4H_2^+$  and  $C_2H_2$ .<sup>32</sup> We therefore also attribute the more reactive  $C_6H_4^+$  isomer, derived from benzene, to c- $C_6H_4^+$ .

No reaction of either isomer of  $C_6H_4^+$  with  $H_2$  was observed. An association reaction (almost certainly three-body) with H atoms was observed for the cyclic isomer, c- $C_6H_4^+$ , only:



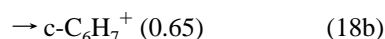
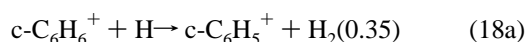
$$k = 3.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

Acyclic  $C_6H_5^+$  did not react with either  $H_2$  or H atoms. c- $C_6H_5^+$  did not react with H, but a reaction with  $H_2$  was observed. Again this is almost certainly a three-body process, resulting from the collisional stabilization of the  $(c-C_6H_7^+)^*$  complex by the bath gas:



$$k = 3.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

c-C<sub>6</sub>H<sub>6</sub><sup>+</sup> did not react with H<sub>2</sub> but underwent a comparatively fast two-channel reaction with H atoms. Association is the major channel (65%), but a significant amount of H-atom transfer also occurred:



$$k = 2.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

These results are in good accord with Petrie et al.<sup>21</sup> except that they did not report the 35% H-atom-transfer channel. Petrie et al. have argued that the efficiency of association of the c-C<sub>6</sub>H<sub>5</sub><sup>+</sup> isomer with H<sub>2</sub> stems from H<sub>2</sub> bond insertion into the vacant sp<sup>2</sup> orbital on the ipso carbon of the phenylium ion.<sup>21</sup> This orbital is not vacant for the c-C<sub>6</sub>H<sub>6</sub><sup>+</sup> ion, and there is no observable association of c-C<sub>6</sub>H<sub>6</sub><sup>+</sup> with H<sub>2</sub>. They also argued that the absence of association of c-C<sub>6</sub>H<sub>5</sub><sup>+</sup> with atomic H might be explained by the formation of an excited electronic state of (c-C<sub>6</sub>H<sub>6</sub><sup>+</sup>)\*. This excited state lowers the well depth of the (c-C<sub>6</sub>H<sub>6</sub><sup>+</sup>)\* complex to ≤130 kJ mol<sup>-1</sup>, thereby reducing the complex lifetime.<sup>21</sup> It is interesting to note that both c-C<sub>6</sub>H<sub>4</sub><sup>+</sup> and c-C<sub>6</sub>H<sub>6</sub><sup>+</sup> show the same behavior: neither associate with H<sub>2</sub>, yet both associate with H atoms. The potential surface of C<sub>6</sub>H<sub>4</sub><sup>+</sup> is not well characterized, and a more detailed comparison must wait until this has been done.

### Concluding Remarks

Sufficient reactions of C<sub>m</sub>H<sub>n</sub><sup>+</sup> with H<sub>2</sub> and H atoms have now been measured in the laboratory for some interesting trends to appear. A comparison of the present results with those already known<sup>5,13,15</sup> shows that highly unsaturated ions (C<sub>m</sub>H<sub>n</sub><sup>+</sup>, *m* = 1–4, *n* = 0–1) undergo largely H atom abstraction reactions with H<sub>2</sub>. As *m* approaches 4, the rate coefficient decreases to ≤10% of the capture rate. More saturated hydrocarbon ions (*n* ≥ 2) do not undergo reactions with H<sub>2</sub>, which is largely a consequence of the lack of exothermic channels available for H atom abstraction. The only option for reaction other than H atom abstraction, is association—when H<sub>2</sub> inserts into the hydrocarbon ion. However, as Table 1 shows, these association reactions are rare, occurring only for c-C<sub>6</sub>H<sub>5</sub><sup>+</sup>, although association also occurs with C<sub>3</sub>H<sup>+</sup>,<sup>34</sup> which is not included in the ions in this study. Association with H<sub>2</sub> generally leads to a product ion that is more stable by at least 100 kJ mol<sup>-1</sup>. Why then does it not occur for a wider range of C<sub>m</sub>H<sub>n</sub><sup>+</sup> ions? The association reaction C<sub>3</sub>H<sup>+</sup> + H<sub>2</sub> has been studied in some detail using ab initio techniques.<sup>27</sup> The conclusion of that study was that the reaction proceeds because C<sub>3</sub>H<sup>+</sup> + H<sub>2</sub> can access the deep potential well of ac-HCCCH<sub>2</sub><sup>+</sup>.<sup>27</sup> For an association ion to be observed in a flow tube, the association complex must first be stabilized by collision with the bath gas. Access to deep wells on the potential surface lengthens the lifetime of the complex so that collisional stabilization can occur. The time between collisions in the flow tube is typically ~70 ns. It is evident then that for most ions, the (C<sub>m</sub>H<sub>n</sub><sup>+</sup>···H<sub>2</sub>)<sup>\*</sup> complex is not surviving long enough for stabilization to take place. When association does occur (e.g., C<sub>3</sub>H<sup>+</sup> + H<sub>2</sub>, c-C<sub>6</sub>H<sub>5</sub><sup>+</sup> + H<sub>2</sub>), the products are new covalently bound C<sub>m</sub>H<sub>n+2</sub><sup>+</sup> ions.

H atom reactions of C<sub>m</sub>H<sub>n</sub><sup>+</sup> behave very differently from the corresponding reactions with H<sub>2</sub>. Two types of reaction are

common; H-atom transfer and association. If an exothermic pathway is available for H-atom transfer, it usually occurs. H-atom transfer results in a decrease in hydrogenation of the ion, whereas H-atom abstraction, which occurs with H<sub>2</sub>, results in an increase in hydrogenation. Highly unsaturated ions, such as C<sub>2</sub><sup>+</sup> and C<sub>2</sub>H<sup>+</sup>, are unreactive with H atoms but larger unsaturated ions, such as C<sub>4</sub>H<sup>+</sup> and C<sub>4</sub>H<sub>2</sub><sup>+</sup>, which are intermediate in size, undergo association reactions. The larger number of atoms increases the number of modes among which the energy of the complex can be dissipated. The much greater propensity for association of C<sub>m</sub>H<sub>n</sub><sup>+</sup> with H atoms as compared with H<sub>2</sub> is a consequence of the greater complex stability. It appears that H atom/C<sub>m</sub>H<sub>n</sub><sup>+</sup> reactions form complexes that can access the region of the (C<sub>m</sub>H<sub>n+1</sub><sup>+</sup>)<sup>\*</sup> potential surface above the deepest wells and which may be the result of H tunneling through barriers.

The structures of the C<sub>m</sub>H<sub>n</sub><sup>+</sup> ions examined in this study were not always identified from experiment. In some cases it was loosely assumed that the structure of the ion formed by electron impact from the neutral precursor was the structure most closely resembling the precursor configuration. However, as previously noticed, sometimes cyclic ions can be made from acyclic precursors (e.g., c-C<sub>3</sub>H<sub>3</sub><sup>+</sup> from C<sub>2</sub>H<sub>4</sub>) and acyclic ions from cyclic precursors (ac-C<sub>6</sub>H<sub>5</sub><sup>+</sup> from C<sub>6</sub>H<sub>6</sub>). There has been some debate about the structures of many of these ions and distonic configurations of some C<sub>m</sub>H<sub>n</sub><sup>+</sup> ions forming radical cations have been suggested for some radical hydrocarbon ions.<sup>35,36</sup>

Finally we note that whereas saturated C<sub>m</sub>H<sub>n</sub><sup>+</sup> ions are unreactive with H<sub>2</sub>, they are more reactive with H. The implication of this observation to interstellar cloud chemistry is that reactions of C<sub>m</sub>H<sub>n</sub><sup>+</sup> with H<sub>2</sub> occur only for very unsaturated ions and quickly reach a level of saturation from which no further addition of H<sub>2</sub> occurs. Where regions of significant H-atom densities exist, then the termination steps for molecular hydrogen are bypassed by H-atom reactions which lead ultimately to even more saturated hydrocarbons. This has great significance to interstellar chemistry, since the H to H<sub>2</sub> ratio is very variable in the interstellar gas clouds. Observations of hydrocarbons might be a monitor of that ratio. Indeed, CH has been used as a monitor for H<sub>2</sub>.<sup>37</sup>

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