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$C_mH_n^+$ Reactions with H and H_2: 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

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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 $C_mH_n^+$ ions ($m = 2-6$, $n = 0-9$). Highly unsaturated hydrocarbon ions undergo mainly H atom abstraction reactions with H_2 forming $C_mH_{n+1}^+ + H$ products. More saturated ions are unreactive. Two types of reactions occur for H atoms: H atom transfer to give $C_mH_{n-1}^+ + H_2$ (if exothermic) and association (to give $C_mH_{n+1}^+$).

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_2 and H. Radioastronomy techniques have discovered significant densities of hydrocarbon molecules and ions in these interstellar clouds,[1] and models have been constructed showing how the chemistry taking place within the clouds can lead to the various hydrocarbon species observed.[2] Moreover, the precursor ion in many synthetic schemes, H_3^+, has recently been detected for the first time.[3] The physical conditions existing within a typical dense cloud (viz. low temperatures 10−50 K) and low densities (10^3-10^6 particles cm^{-3}) mean that conventional chemical processes are very slow.[2] 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.[2,4] 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_2 outnumber those with H by about a factor of 20.[5]

In addition to the relevance of ion−H_2, H chemistry to interstellar clouds, there is a more fundamental aspect. Reactions of hydrocarbon ions with H atoms and H_2 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.[6] Early ion−H atom studies applied conventional methods from neutral−H atom studies,[7,8] but later, methods unique to ion−H atom reactions were developed. One such technique utilizes the reaction of CO_2^+ with a mixture of H_2 and H.[9,10] We recently compared this method for determining H atom concentrations with those using other systems (e.g., CO^+, H_2/H; $C_2N_2^+$, H_2/H; CN^+, H_2/H) and obtained good agreement between the different systems.[10] In the present study, we apply the CO_2^+, H_2/H technique to examine the reactions of a series of hydrocarbon ions, $C_mH_n^+$ ($m = 2-6$; $n = 0-9$) with H atoms. As part of the study we have also measured the reactions of the same ions with H_2. 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.[11] Only a brief summary of that part of the equipment pertinent to the present study will be given here. The $C_mH_n^+$ 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.[10] A typical degree of dissociation of the He/H_2 mixture is 25− 40%. The reactions of CO_2^+ with H_2 and H

$$CO_2^+ + H_2 \rightarrow HCO_2^+ + H \tag{1}$$

$$CO_2^+ + H \rightarrow HCO^+ + O \tag{2a}$$

$$\rightarrow H^+ + CO_2 \tag{2b}$$

are used to calibrate the H atom number density within the flow tube as described by Tosi et al.[9] and also in our earlier paper.[10] As the extent of dissociation of H_2 in the microwave discharge is always less than 100%, a mixture of H_2 and H enters the flow tube. It is therefore necessary in each case to establish the outcome of the reaction of the $C_mH_n^+$ ion with H_2 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^+, H_2^+, H_3^+), metastable atoms (e.g., He 2 ^{3}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

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

reactant ion	products	branching ratio	k^a	$k_{prev}{}^b$	$-\Delta H°/(\text{kJ mol}^{-1})^c$
C_2^+	$C_2H^+ + H$	1.0	11	11,[d] 14,[e] 12[f]	88
C_2H^+	$C_2H_2^+ + H$	1.0	11	7.8,[d] 17[e]	149
$C_2H_3^+$	NR		<0.05	<0.01,[g] <0.001[h]	
$HCCCH_2^+$	NR		<0.05	<0.05[i]	
c-$C_3H_3^+$	NR		<0.05	<0.05[i]	
$H_2CCCH_2^+$	NR		<0.05	<0.001[j]	
$HCCCH_3^+$	NR		<0.005	<0.001[j]	
$C_3H_5^+$	NR		<0.005	NR[k]	
$C_3H_7^+$	NR		<0.05	NR[k]	
C_4H^+	$C_4H_2^+ + H$	1.0	1.8	<0.001,[k] 1.5,[l] 1.8[f]	~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-$C_6H_4^+$	NR		<0.005		
c-$C_6H_4^+$	NR		<0.03		
ac-$C_6H_5^+$	NR		<0.01	<0.01[n]	
c-$C_6H_5^+$	$C_6H_7^+$	1.0	0.38[o]	0.15,[p] 0.5[l,n]	273
c-$C_6H_6^+$	NR		<0.05	<0.01[n]	

[a] Observed rate coefficient in units of 10^{-10} cm^3 s^{-1}. The Langevin capture rate coefficient for all reactions in this table is 1.5×10^{-9} cm^3 s^{-1}. [b] Rate coefficients determined in other laboratories in units of 10^{-10} cm^3 s^{-1}. [c] The listed exothermicities are taken from ref 12. [d] Reference 13 [e] Reference 14. [f] Reference 15. [g] Reference 16. [h] Reference 17. No bimolecular reaction was observed, but a limit to termolecular association of $k \lesssim 1 \times 10^{-30}$ cm^6 s^{-1} at 80 K was reported. [i] Reference 18. [j] 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 $k < 1 \times 10^{-30}$ cm^6 s^{-1} was reported. [k] Reference 17. A limit to termolecular association of $k < 1 \times 10^{-30}$ cm^6 s^{-1} at 80 K was reported. [l] Reference 19. [m] Exothermicity from refs 12 and 20. [n] Reference 21. [o] 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 $\geq 3.9 \times 10^{-27}$ cm^6 s^{-1}. [p] Reference 22.

atomic hydrogen. He 2 ^3S atoms are not so easily removed, and although the flux of such metastables is several orders of magnitude below that of H and H_2, they can be effectively excluded only by discharging pure hydrogen.

All reactions reported here were carried out at 300 ± 5 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 ±30% (unless specified otherwise) where the increase in uncertainty over the ±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_2 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_2H_2 mixture. In both cases the determination of the rate coefficient with H was hampered by a rapid reaction with H_2:

$$C_2^+ + H_2 \rightarrow C_2H^+ + H \tag{3}$$

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

$$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H \tag{4}$$

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

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_2 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_2H_5Br. $C_2H_5^+$ 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_2 but $C_2H_3^+$ does undergo reaction with H:

$$C_2H_3^+ + H \rightarrow C_2H_2^+ + H_2 \tag{5}$$

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

The significance of this measurement to establishing the endothermicity of the reverse of reaction 5 has been commented on elsewhere.[10,24,25]

$C_3H_3^+$. There are two low-energy forms of $C_3H_3^+$: the acyclic propargyl ion, $HCCCH_2^+$, and the cyclopropenylium ion, c-$C_3H_3^+$. Mixtures of these ions (typically 60% acyclic, 40% cyclic) are readily made from reactions ensuing after initial electron impact on C_2H_4. The primary ion, $C_2H_4^+$, reacts with C_2H_4 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 $C_3H_3^+$:[18] in all cases $HCCCH_2^+$ is more reactive than c-$C_3H_3^+$. In the present study neither ion was found to be reactive with H_2. Similarly, no reaction was found with H atoms despite each isomeric ion having an apparent exothermic binary reaction channel available[12] leading to their respective cyclic and acyclic $C_3H_2^+$ isomers (+H_2). However extensive ab initio calculations of the $C_3H_2^+$ and $C_3H_3^+$ surface[26,27] have shown both H-atom-transfer reactions to be endothermic which is in keeping with our observations. The endothermicity of the ac-$C_3H_3^+$/H atom-transfer reaction is calculated as only 8 kJ mol^{-1}.[26]

TABLE 2: Reactions of the Designated $C_mH_n^+$ Ion with H

reactant ion	products	branching ratio	k[a]	k_{prev}[b]	$-\Delta H°$/(kJ mol^{-1})[c]
C_2^+	NR		<1.0		
C_2H^+	NR		<1.0		
$C_2H_3^+$	$C_2H_2^+ + H_2$	1.0	0.68	<0.1;[d] 1.0[e]	5.8[f]
$HCCCH_2^+$	NR		<0.03		
c-$C_3H_3^+$	NR		<0.03		
$H_2CCCH_2^+$	$C_3H_3^+ + H_2$	1.0	1.7		164[g]
$HCCCH_3^+$	$C_3H_3^+ + H_2$	1.0	3.0		224[g]
$C_3H_5^+$	$C_3H_6^+$	1.0	1.6[h,i]		206[j]
$C_3H_7^+$	$C_3H_6^+ + H_2$	1.0	0.32		59[k]
C_4H^+	$C_4H_2^+$	1.0	~5.8[h,l]		~574[m]
$C_4H_2^+$	$C_4H_3^+$	1.0	2.6[h,n]		~420
$C_4H_3^+$	$C_4H_4^+$	1.0	~0.5[h,o]		~206[g]
$C_4H_5^+$	NR		<0.4		
$C_4H_6^+$	$C_2H_3^+ + C_2H_4$	~0.15			38[p]
	$C_2H_5^+ + C_2H_2$	~0.65	1.9		73[p]
	$C_4H_5^+ + H_2$	~0.20			174[q]
$C_4H_8^+$	$C_4H_7^+ + H_2$	1.0	1.1		193[r]
$C_4H_9^+$	NR		<0.2		
ac-$C_6H_4^+$	NR		<0.05		
c-$C_6H_4^+$	$C_6H_5^+$	1.0	0.33[h,s]		400[t]
ac-$C_6H_5^+$	NR		<0.05	0.05[u]	
c-$C_6H_5^+$	NR		<0.1	0.01[u]	
c-$C_6H_6^+$	$C_6H_5^+ + H_2$	~0.35			67[v]
			2.1[w]	2.5[u]	
	$C_6H_7^+$	~0.65			340[x]

[a] Observed rate coefficient in units of 10^{-10} cm^3 s^{-1}. The Langevin capture rate coefficient for all reactions in this table is 19×10^{-10} cm^3 s^{-1}. [b] Rate coefficients determined in other laboratories in units of 10^{-10} cm^3 s^{-1}. [c] Unless specified otherwise, the listed exothermicities are taken from ref 12. [d] Reference 23. [e] Reference 24. [f] See reference 10. [g] Thermochemistry for acyclic isomers. [h] Pseudobimolecular reaction. The rate coefficient shown is for a flow tube pressure of 0.30 Torr. [i] The termolecular rate for the three body association process is estimated as $\geq 1.6 \times 10^{-26}$ cm^6 s^{-1}. [j] Thermochemistry for lowest energy acyclic isomers. [k] This value corresponds to the iso $C_3H_7^+$ structure converted to the acyclic $C_3H_6^+$ species. [l] The termolecular rate for the three-body association process is estimated as $\gtrsim 6 \times 10^{-26}$ cm^6 s^{-1}. [m] References 12 and 20. [n] The termolecular rate for the three-body association process is estimated as $\geq 2.7 \times 10^{-26}$ cm^6 s^{-1}. [o] The termolecular rate for the three body association process is estimated as $\geq 5.1 \times 10^{-27}$ cm^6 s^{-1}. [p] Thermochemistry based on (*E*)-1,3-butadiene ion. [q] Thermochemistry as for (*p*) and $CH_2{=}CCH{=}CH_2^+$. [r] Thermochemistry based on (*E*)-2-$C_4H_8^+$ and $CH_3CCHCH_3^+$. [s] The termolecular rate for the three body association process is estimated as $\geq 3.4 \times 10^{-27}$ cm^6 s^{-1}. [t] Thermochemistry based on benzyne ion and phenyl radical ion. [u] Reference 21. [v] Thermochemistry based on benzene ion and phenyl radical ion. [w] The termolecular rate for the three body association channel between c-$C_6H_6^+$ + H is estimated as $\geq 1.4 \times 10^{-26}$ cm^6 s^{-1}. [x] Thermochemistry based on benzene ion and protonated benzene ion.

$H_2CCCH_2^+$ and $HCCCH_3^+$. The ions $H_2CCCH_2^+$ and $HCCCH_3^+$ were made by electron impact on their parent precursors, allene and propyne, respectively. No reaction was observed with H_2 for either ion. Both ions underwent efficient H atom transfer with H:

$$H_2CCCH_2^+ + H \rightarrow \text{ac-}C_3H_3^+ + H_2 \tag{6}$$

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

$$HCCCH_3^+ + H \rightarrow \text{ac-}C_3H_3^+ + H_2 \tag{7}$$

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

The $C_3H_3^+$ products of reactions 6 and 7 are shown as ac-$C_3H_3^+$ (acyclic $C_3H_3^+$) on the basis that the precursor ions are acyclic, although this was not confirmed by experiment.

$C_3H_5^+$. The $C_3H_5^+$ ion was generated by electron impact on C_2H_4 in a high pressure ion source. $C_3H_5^+$ is also the major product ion from the reaction between $C_2H_4^+$ and C_2H_4 as discussed previously for $C_3H_3^+$. After mass selection, $C_3H_5^+$ was injected into the flow tube (using sufficiently low energies to prevent fragmentation into $C_3H_3^+$). No reaction was observed with H_2 ($k < 5 \times 10^{-13}$ cm^3 s^{-1}), but an observable reaction did occur with H atoms, the major channel resulting from an association reaction:

$$C_3H_5^+ + H \rightarrow C_3H_6^+ \tag{8}$$

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

A curved semilogarithmic decay of Ln($C_3H_5^+$) count versus H-atom flow indicates at least two $C_3H_5^+$ 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.

$C_3H_7^+$. This ion was generated by electron impact on either 1-bromopropane or 2-bromopropane, C_3H_7Br. There was no difference in the behavior of the $C_3H_7^+$ arising from either precursor with H_2 and H. No reaction was found between $C_3H_7^+$ and H_2, which is consistent with the lack of a bimolecular exothermic channel. The slow reaction with H atoms proceeded via H atom transfer:

$$C_3H_7^+ + H \rightarrow C_3H_6^+ + H_2 \tag{9}$$

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

The fact that the H-atom-transfer reaction appears independent of ion structure is an interesting result. If the $C_3H_7^+$ 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 $C_3H_7^+$ ions from the two precursors may have the same structure. Energies and geometries of the $C_3H_6^+$, $C_3H_7^+$ and $C_3H_8^+$ ions have been characterized using quantum chemistry ab initio methods.[28-30] A study of the [$C_3H_7^+$ ···H] transition states has not to our knowledge been undertaken and would be valuable in clarifying the details of reaction 9.

C_4H^+, $C_4H_2^+$, $C_4H_3^+$. 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:

$$C_4H^+ + H_2 \rightarrow C_4H_2^+ + H \qquad (10)$$

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

and also exhibits an efficient association reaction with H atoms:

$$C_4H^+ + H \rightarrow C_4H_2^+ \qquad (11)$$

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

The higher uncertainty in the rate coefficient for reaction 11 (±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 $\Delta H°_f(C_4H^+) \geq 1640$ kJ mol^{-1} which is consistent with the best theoretical estimate of $\Delta H°_f(C_4H^+) = 1779$ kJ mol^{-1}.[20] 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 2.6×10^{-10} $cm^3\ s^{-1}$ and 5×10^{-11} $cm^3\ s^{-1}$, respectively:

$$C_4H_2^+ + H \rightarrow C_4H_3^+ \qquad (12)$$

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

$$C_4H_3^+ + H \rightarrow C_4H_4^+ \qquad (13)$$

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

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[12,20] reaction 11 (≥574 kJ mol^{-1}); reaction 12; ~420 kJ mol^{-1}, and reaction 13 (~205 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 $k < 4 \times 10^{-11}$ $cm^3\ s^{-1}$. The fast reaction of $C_4H_6^+$ with H atoms yields three products including a 20% H-atom-transfer channel:

$$C_4H_6^+ + H \rightarrow C_2H_3^+ + C_2H_4\ (\sim 0.15) \qquad (14a)$$

$$\rightarrow C_2H_5^+ + C_2H_2\ (\sim 0.65) \qquad (14b)$$

$$\rightarrow C_4H_5^+ + H_2\ (\sim 0.20) \qquad (14c)$$

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

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 ~360 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 ($k < 2 \times 10^{-11}$ $cm^3\ s^{-1}$), but $C_4H_8^+$ exhibited H-atom transfer:

$$C_4H_8^+ + H \rightarrow C_4H_7^+ + H_2 \qquad (15)$$

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

$C_6H_4^+$, $C_6H_5^+$, $C_6H_6^+$. 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.[31] 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 $C_6H_5^+$,[32,33] but later work has shown that the lower energy phenylium ion is more reactive than the acylic isomer.[22] 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.[21] 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.[32] 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:

$$\text{c-}C_6H_4^+ + H \rightarrow \text{c-}C_6H_5^+ \qquad (16)$$

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

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:

$$\text{c-}C_6H_5^+ + H_2 \rightarrow \text{c-}C_6H_7^+ \quad (17)$$

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

c-$C_6H_6^+$ did not react with H_2 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:

$$\text{c-}C_6H_6^+ + H \rightarrow \text{c-}C_6H_5^+ + H_2 (0.35) \quad (18a)$$

$$\rightarrow \text{c-}C_6H_7^+ \ (0.65) \quad (18b)$$

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

These results are in good accord with Petrie et al.[21] 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-$C_6H_5^+$ isomer with H_2 stems from H_2 bond insertion into the vacant sp^2 orbital on the ipso carbon of the phenylium ion.[21] This orbital is not vacant for the c-$C_6H_6^+$ ion, and there is no observable association of c-$C_6H_6^+$ with H_2. They also argued that the absence of association of c-$C_6H_5^+$ with atomic H might be explained by the formation of an excited electronic state of $(\text{c-}C_6H_6^+)^*$. This excited state lowers the well depth of the $(\text{c-}C_6H_6^+)^*$ complex to $\leq$130 kJ mol^{-1}, thereby reducing the complex lifetime.[21] It is interesting to note that both c-$C_6H_4^+$ and c-$C_6H_6^+$ show the same behavior: neither associate with H_2, yet both associate with H atoms. The potential surface of $C_6H_4^+$ is not well characterized, and a more detailed comparison must wait until this has been done.

Concluding Remarks

Sufficient reactions of $C_mH_n^+$ with H_2 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[5,13,15] shows that highly unsaturated ions ($C_mH_n^+$, $m = 1-4$, $n = 0-1$) undergo largely H atom abstraction reactions with H_2. As m approaches 4, the rate coefficient decreases to $\leq$10% of the capture rate. More saturated hydrocarbon ions ($n \geq 2$) do not undergo reactions with H_2, which is largely a consequence of the lack of exothermic channels available for H atom abstraction. The only option for reaction other than H atom abstraction, is association—when H_2 inserts into the hydrocarbon ion. However, as Table 1 shows, these association reactions are rare, occurring only for c-$C_6H_5^+$, although association also occurs with C_3H^+,[34] which is not included in the ions in this study. Association with H_2 generally leads to a product ion that is more stable by at least 100 kJ mol^{-1}. Why then does it not occur for a wider range of $C_mH_n^+$ ions? The association reaction $C_3H^+ + H_2$ has been studied in some detail using ab initio techniques.[27] The conclusion of that study was that the reaction proceeds because $C_3H^+ + H_2$ can access the deep potential well of ac-$HCCCH_2^+$.[27] 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 $(C_mH_n^+\cdots H_2)^*$ complex is not surviving long enough for stabilization to take place. When association does occur (e.g., $C_3H^+ + H_2$, c-$C_6H_5^+ + H_2$), the products are new covalently bound $C_mH_{n+2}^+$ ions.

H atom reactions of $C_mH_n^+$ behave very differently from the corresponding reactions with H_2. 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_2, results in an increase in hydrogenation. Highly unsaturated ions, such as C_2^+ and C_2H^+, are unreactive with H atoms but larger unsaturated ions, such as C_4H^+ and $C_4H_2^+$, 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 $C_mH_n^+$ with H atoms as compared with H_2 is a consequence of the greater complex stability. It appears that H atom/$C_mH_n^+$ reactions form complexes that can access the region of the $(C_mH_{n+1}^+)^*$ potential surface above the deepest wells and which may be the result of H tunneling through barriers.

The structures of the $C_mH_n^+$ 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-$C_3H_3^+$ from C_2H_4) and acyclic ions from cyclic precursors (ac-$C_6H_5^+$ from C_6H_6). There has been some debate about the structures of many of these ions and distonic configurations of some $C_mH_n^+$ ions forming radical cations have been suggested for some radical hydrocarbon ions.[35,36]

Finally we note that whereas saturated $C_mH_n^+$ ions are unreactive with H_2, they are more reactive with H. The implication of this observation to interstellar cloud chemistry is that reactions of $C_mH_n^+$ with H_2 occur only for very unsaturated ions and quickly reach a level of saturation from which no further addition of H_2 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_2 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_2.[37]

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