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Short Communication

THE PROTON AFFINITY OF C_3 AND HEAT OF FORMATION OF C_3H^+

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The energy and structure of C_3H^+ have been the subject of numerous studies for more than 25 years. Recent theoretical treatments have provided a reasonable structure for the most stable form of this ion [1,2]. The determination of its heat of formation has been attempted in the past, primarily through appearance energy measurements. Early measurements of the electron impact appearance energies of C_3H^+ from various unsaturated hydrocarbon molecules have led to reported heats of formation for this ion in the range from 280 to 418 kcal mol^{-1} [3,4]. More recently Stockdale and coworkers [5] made a series of careful photoionization appearance energy measurements which led to values ranging only from 381 to 390 kcal mol^{-1} with allene, propyne and cyclopropene as parent molecules. Here we report the results of experimental measurements of the heat of formation of C_3H^+ based on an entirely different approach; namely on measurements of its reactivity in ion/molecule reactions. Specifically, we have used a series of reactions chosen to explore the tendency of C_3H^+ to loose a proton. The resulting value for the proton affinity of C_3, $PA(C_3)$, leads to a heat of formation for C_3H^+ since it is related to $PA(C_3)$ by eqn. (1)

$$PA(C_3) = \Delta H_f^0(C_3) + \Delta H_f^0(H^+) - \Delta H_f^0(C_3H^+) \quad (1)$$

Our own investigations of the energetics of this ion have been motivated primarily by an interest in its role as a reactive intermediate in interstellar ion chemistry [2,6].

The experiments were done in the selected ion flow tube apparatus at York University which has been described previously [7]. The C_3H^+ was produced from propylene at low pressures in an axial electron impact ionizer (Extranuclear Laboratories, Model 041-3) at an electron energy of 45 V. After formation it was injected into a helium carrier gas in the flow tube at a low energy of ca. 8 eV. The total pressure in the flow tube was held at ca.

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TABLE 1

Summary of reactions observed at 296±2 K between C_3H^+ and molecules with adjacent proton affinities

Reaction		Product distribution [a]	PA [b]	k [c]
$C_3H^+ + ND_3$	$\rightarrow ND_3H^+ + C_3$	0.4	200	1.7±0.34
	$\rightarrow ND_3^+ + C_3H$	0.25		
	$\rightarrow D_2CN^+ + HC_2D$	0.2		
	$\rightarrow HC_3ND_2^+ + D$	0.15		
$C_3H^+ + CH_3CN$	$\rightarrow C_2H_3^+(HCN^+) + HCN_3(C_4H_3)$	0.4	187	2.5±0.6
	$\rightarrow C_3NH_2^+ + C_2H_2$	0.3		
	$\rightarrow CH_3CNH^+ + C_3$	0.2		
	$\rightarrow C_3H^+ \cdot CH_3CN$	0.1		
$C_3H^+ + CH_3OH$	$\rightarrow HC_3O^+ + CH_4$	0.7	181	2.2±0.6
	$\rightarrow CH_3O^+ + C_3H_2$	0.2		
	$\rightarrow CH_3^+ + C_3H_2O$	0.1		
	$\rightarrow CH_3OH_2^+ + C_3$	≤0.01		
$C_3H^+ + HCN$	$\rightarrow C_3H^+ \cdot HCN$	1.0	171	1.1±0.2
	$\rightarrow H_2CN^+ + C_3$	≤0.01		

[a] Product distributions were determined with the method described in ref. [8].
[b] Proton affinity of the neutral reactant in kcal mol^{-1} as reported in ref. [9].
[c] Rate constant for the disappearance of C_3H^+ in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}.

0.35 torr. The neutral reagents were chosen to cover a range of proton affinities and included, in order of increasing proton affinity, the molecules N_2, CO_2, CO, H_2O, HCN, CH_3OH, CH_3CN and ND_3. These molecules provide a range in proton affinity from 117 to 200 kcal mol^{-1}

Proton transfer was observed to be a product channel only with CH_3CN and NH_3, the two molecules with the highest proton affinities. The observed reactions are shown in Table 1. There was no evidence for the occurrence of proton transfer with CH_3OH and HCN or any of the other molecules with lower proton affinity. These results therefore bracket the proton affinity of C_3 between those of CH_3OH and CH_3CN, viz. $PA(CH_3OH) < PA(C_3) < PA(CH_3CN)$. The recent compilation of proton affinities by Walder and Franklin [9] indicates values for $PA(CH_3OH)$ and $PA(CH_3CN)$ of 181 or 182 and 186 to 188 kcal mol^{-1}, respectively. Consequently our results indicate a value for $PA(C_3)$ of 184 ± 4 kcal mol^{-1}. With the heats of formation at 298 K reported for H^+ and C_3 in the JANAF tables [10], viz. 367.2 ± 0.01 and 196 ± 4 kcal mol^{-1}, respectively, this result implies a heat of formation for C_3H^+ of 379 ± 8 kcal mol^{-1}. Current revisions of the JANAF tables appear to favour a value of 200 ± 4 kcal mol^{-1} for the heat of formation of C_3 [11].

This latter value leads to a higher heat of formation for C_3H^+ of 383 ± 8 kcal mol^{-1} which is in good agreement with the more recent range of values reported by Stockdale and coworkers [5].

The high proton affinity of C_3 arises from resonance stabilization in the carbene cation (2) produced on protonation. Ab initio molecular orbital theory has shown that $C_{\infty v}$ symmetry is the most stable [1]. A second, non-linear structure with C_{2v} symmetry has been found to have an energy 45.9 kcal mol^{-1} greater than the structure below.

$$H-\overset{+}{C}=C=C: \leftrightarrow H-C\equiv C-\overset{+}{C}: \qquad (2)$$

In spite of the high proton affinity of C_3, the C_3H^+ ion is a very reactive species. We have observed fast reactions other than proton transfer with all of the molecules studied except N_2. The results of these investigations will be reported separately.

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