The Formation of $C_3H_3^+$ from the Reaction of CH_3^+ with Acetylene

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A triple quadrupole mass spectrometer has been used to study the reactions of simple even-electron ions (*e.g.* CH_3^+, CH_2F^+, *etc.*) with acetylene and substituted acetylenes; CH_3^+ reacts with C_2H_2 to give $C_3H_3^+$ in very high yield.

The present studies were made using a triple quadrupole mass spectrometer which consisted of a conventional electron-impact ion source attached in series to the first quadrupole (mass filter); the second radio frequency-only quadrupole (collision chamber); the third quadrupole (mass filter); and to an electron multiplier.[1,2] Methyl cations formed by electron impact on methane in the ion source were mass-analysed by the first quadrupole. The selected CH_3^+ ions passed on into the second quadrupole which held the ions in stable trajectories and into which the acetylene gas was admitted at relatively high pressure. Differential pumping between the ion source and the collision region prevented mixing of the neutral gases. Ions formed in the collision zone were mass-analysed by the third quadrupole and detected by the electron multiplier.[3,4]

The base peaks for the reactions of methyl cations and the three fluoromethyl cations with acetylene, propyne, and 3,3,3-trifluoropropyne are listed in Table 1.

The secondary ion formed in by far the largest yield was $C_3H_3^+$ from acetylene and the methyl cation. It seems probable that $C_3H_3^+$ is the cyclopropenium cation. Evidence supporting this conclusion comes from the observation that when at low pressure CH_3^+ ions are replaced by CD_3^+, $C_3H_2D^+$ (*m/z* 40) and $C_3HD_2^+$ (*m/z* 41) are formed in the proportions 1:2; this suggests that the thermally excited addition complex $(C_3H_5)^{*+}$ is symmetrical; this in turn suggests that $C_3H_3^+$ is not the cation $CH_2{=}C{=}\overset{+}{C}H$ but cyclopropenium [reaction (1)].[5]

$$CH_3^+ + CH{\equiv}CH \rightarrow (C_3H_5)^{*+} \rightarrow \text{cyclo-}C_3H_3^+ + H_2 \quad (1)$$

When CD_3^+ was the primary ion and the acetylene pressure was increased the proportions of the ions *m/z* 39 and *m/z* 40 increased substantially until at the highest pressure *m/z* 39 became the major peak. Thus exchange must occur between the propenium ion and acetylene [reaction (2)].

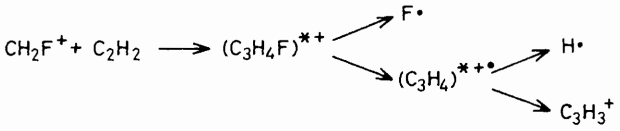
Table 1. The base peaks in the reactions of CH_3^+ and fluoromethyl cations with acetylene, propyne, and 3,3,3-trifluoropropyne.[a]

$R^+ + CH{\equiv}CH$			$R^+ + CH_3C{\equiv}CH$			$R^+ + CF_3C{\equiv}CH$		
Primary ion	Base peak		Primary ion	Base peak		Primary ion	Base peak	
CH_3^+	$C_3H_3^+$	(717)	CH_3^+	$C_2H_3^+$	(6)	CH_3^+	$C_3HF_2^+$	(2)
CH_2F^+	$C_3H_3^+$	(19)	CH_2F^+	$C_2H_3^+$	(12)	CH_2F^+	$C_3HF_2^+$	(36)
CHF_2^+	$C_3H_4F^+$	(4)	CHF_2^+	$C_3H_5^+$	(9)	CHF_2^+	$C_3HF_2^+$	(11)
CF_3^+	CHF_2^+	(3)	CF_3^+	$C_3H_4F^+$	(8)	CF_3^+	$C_3HF_2^+$	(34)

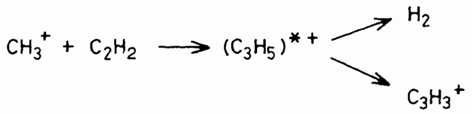
[a] Figures in parentheses represent $[\text{secondary ions}]_{\text{final}}/[\text{primary ions}]_{\text{initial}} \times 10^3$.

$$C_3HD_2^+ + C_2H_2 \rightarrow C_3H_2D^+(C_2HD^+) \xrightarrow{C_2H_2} C_3H_3^+(C_2HD^+) \quad (2)$$

The reactions with propyne yield $C_3X_5^+$ ($C_3H_5^+$ and $C_3H_4F^+$) as the most abundant secondary ions with the di- and tri-fluoromethyl ions, in contrast to the reactions with 3,3,3-trifluoropropyne which all yield $C_3X_3^+$ ($C_3HF_2^+$) as the predominant secondary ion.



(3)



(4)

The relatively low yield of $C_3H_3^+$ from the reaction of $CH_2F^+ + C_2H_2$ compared with $CH_3^+ + C_2H_2$ may be due to the loss of a fluorine atom from the initial adduct cluster [reaction (3)]. In contrast no such predissociation is likely with methyl cations [reaction (4)].

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