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REACTIONS OF $^{12}C^+$ WITH HYDROCARBONS AT 296 K: CARBON–CARBON BOND FORMATION

D.K. BOHME, A.B. RAKSHIT and H.I. SCHIFF
Department of Chemistry and Centre for Research in Experimental Space Science, York University,
Downsview, Ontario, Canada M3J 1P3

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Rate constants and product distributions have been determined for the ion–molecule reactions between $^{12}C^+$ and methane, ethane, propane, ethylene, propylene, allene, acetylene, propyne and benzene. The measurements were carried out with the SIFT technique at a temperature of 296 ± 2 K. The results provide insight into the build-up of carbon skeletons to form C_{n+1}^+ ions and other competing modes of reaction at room temperature.

1. Introduction

There has been a continuing interest in the chemistry of the carbon cation primarily because of its proposed role in the build-up of hydrocarbon molecules in dense interstellar clouds [1]. Earlier measurements of the reactions of this ion with hydrocarbon molecules were made in part because of the fundamental importance of atomic ion reactions, but also to explore analogies with corresponding reactions of C atoms [2–5]. They were carried out at elevated translational energies with a tandem mass spectrometer. Previous measurements of the reaction of C^+ with benzene were motivated in part by ion-accelerator studies of $^{14}C^+$ bombardment of solid benzene targets which led to the synthesis of an interesting variety of complex organic compounds [5]. Here we explore the hydrocarbon chemistry of $^{12}C^+$ thermalized by collisions at 300 K. A variety of saturated and unsaturated hydrocarbons and benzene were chosen as substrates. The main intent was to establish the degree to which build-up of the carbon skeleton of the neutral substrate was reflected in the observed product ion distributions at room temperature. Various mechanisms of reaction are also discussed. These have been based primarily on the interpretations reported earlier in connection with tandem mass spectrometer experiments carried out with $^{12}C^+$ and $^{13}C^+$ down to 0.1 eV of translational energy [2,5].

2. Experimental

The measurements were carried out with the SIFT technique [6]. The SIFT apparatus at York University has been described in detail elsewhere [7]. One modification has been made for the experiments reported here. The miniature flowing afterglow source has been replaced with an axial electron impact ionizer (Extranuclear Laboratories, model 041-3). The C^+ ions were produced at low pressures from cyanogen at an electron energy of 45 V. $^{12}C^+$ ions were selected and injected into the He carrier gas in the flow tube at a low energy of ≈8 eV. The total pressure in the flow tube was held at ≈0.35 Torr. Collisions with the carrier gas were allowed to thermalize the ions before they entered the reaction region further downstream. All measurements were carried out at a temperature of 296 ± 2 K.

3. Results and discussion

Table 1 summarizes the rate constants and product distributions obtained in this study. Multiple ionic products were observed for all of the reactions except that with acetylene. Product distributions were determined using the method described by Adams and Smith [8]. We estimate that the absolute branching ratios may be in error by as much as 30% due to possible mass discrimination effects in the quadrupole mass spectrometer.

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Table 1
Summary of the rate constants and product distributions measured at 296 ± 2 K for reactions between $^{12}C^+$ and a variety of hydrocarbon molecules

Reaction [a]		Product distribution	k [b]
$C^+ + CH_4$	$\rightarrow C_2H_3^+ + H$	0.75	1.3 ± 0.4
	$\rightarrow C_2H_2^+ + H_2$	0.25	
$C^+ + C_2H_6$	$\rightarrow C_3H_3^+ + H_2 + H$	0.3	1.6 ± 0.4
	$\rightarrow C_2H_3^+ + CH_3$	0.3	
	$\rightarrow C_2H_4^+ + CH_2$	0.2	
	$\rightarrow C_2H_5^+ + CH$	0.2	
$C^+ + C_3H_8$	$\rightarrow C_2H_5^+ + C_2H_3$	0.35	1.9 ± 0.5
	$\rightarrow C_2H_3^+ + C_2H_5$	0.25	
	$\rightarrow C_2H_2^+ + C_2H_6$	0.2	
	$\rightarrow C_3H_3^+ + CH_3 + H_2$	0.2	
$C^+ + C_2H_4$	$\rightarrow C_3H_2^+ + H_2$	0.4	1.3 ± 0.3
	$\rightarrow C_3H_3^+ + H$	0.3	
	$\rightarrow C_2H_4^+ + C$	0.15	
	$\rightarrow C_2H_3^+ + CH$	0.15	
$C^+ + CH_3CHCH_2$	$\rightarrow C_2H_3^+ + C_2H_3$	0.3	2.0 ± 0.5
	$\rightarrow C_3H_5^+ + CH$	0.2	
	$\rightarrow C_3H_3^+ + CH_3$	0.15	
	$\rightarrow C_2H_2^+ + C_2H_4$	0.15	
	$\rightarrow C_3H_6^+ + C$	0.1	
	$\rightarrow C_4H_3^+ + H_2 + H$	0.1	
$C^+ + CH_2CCH_2$	$\rightarrow C_4H_2^+ + H_2$	0.4	1.4 ± 0.3
	$\rightarrow C_3H_3^+ + CH$	0.25	
	$\rightarrow C_2H_2^+ + C_2H_2$	0.2	
	$\rightarrow C_3H_4^+ + C$	0.15	
$C^+ + C_2H_2$	$\rightarrow C_3H^+ + H$	1.0	2.2 ± 0.7
$C^+ + CH_3C_2H$	$\rightarrow C_4H_2^+ + H_2$	0.3	1.9 ± 0.5
	$\rightarrow C_3H_4^+ + C$	0.3	
	$\rightarrow C_3H_3^+ + CH$	0.2	
	$\rightarrow C_2H_2^+ + C_2H_2$	0.1	
	$\rightarrow C_2H_3^+ + C_2H$	0.1	
$C^+ + C_6H_6$	$\rightarrow C_6H_6^+ + C$	0.67	2.4 ± 0.6
	$\rightarrow C_5H_3^+ + C_2H_3$	0.17	
	$\rightarrow C_7H_5^+ + H$	0.10	
	$\rightarrow C_3H_3^+ + C_4H_3$	0.06	

[a] The neutral products were not detected in the present experiments. Only the most exothermic channel is indicated.
[b] Rate constant for the disappearance of C^+ in units of 10^{-9} cm^3 molecule^{-1} s^{-1} along with its estimated uncertainty.

For ionic products over a narrow mass range (≲ 5 amu) these effects are negligible.

The product distributions in table 1 may be compared with those obtained by Smith and Futrell [2] in a detailed study of $^{12}C^+$ and $^{13}C^+$ reactions with saturated hydrocarbons, ethylene and propylene at near thermal energies (0.1 eV) using a tandem Dempster–ICR mass spectrometer. Although obtained at higher energies and at much lower total pressures in the absence of stabilizing collisions of the product ions, the results obtained by these workers for the most part compare favourably with those reported here. Detailed comparisons are provided in the following text. Other measurements have been reported for the much higher translational energies of 3, 6 and 100 eV [3,4]. Smith and DeCorpo [5] have investigated in detail the reaction of $^{12}C^+$ and $^{13}C^+$ with benzene at ≈0.1 and 1 0–12 eV. Only the reactions with CH_4 and C_2H_2 have been investigated previously in a thermalized system at 300 K [9,10]

All of the reactions investigated in this study were observed to proceed rapidly, $k \geqslant 1\ 3 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} This amounts to essentially unit reaction efficiency when comparisons are made with collision rate constants calculated with currently available theories [11]

3 1. *Reactions with saturated hydrocarbons*

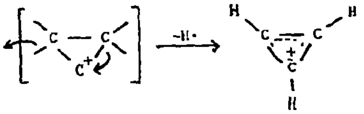
The measurements with CH_4 reproduced earlier room-temperature observations of this reaction [9,11]. Both of the channels which were observed lead to C–C bond formation in the product ion Formation of CH_3^+ by direct hydride abstraction was not apparent (<3%) Previous measurements have shown that CH_3^+ becomes the dominant product at high translational energies where it may also be formed by dissociative charge transfer [3] C–C bond formation can be envisaged to proceed by insertion at a C–H bond accompanied by loss of H· or H_2 to form the vinyl cation, $CHCH_2^+$, and the radical cation, $\cdot CHCH^+$, respectively

Insertion at a C–H bond may also be a major pathway in the reaction with ethane [2]. The $C_3H_3^+$ may be formed through this pathway by elimination of ·H and H_2 and $C_2H_3^+$ may be formed through insertion at the C–H bond [2], but in this case formation of the new C–C bond is accompanied by cleavage of the old C–C bond with elimination of the $\cdot CH_3$ radical Formation of the cyclopropenyl isomer of $C_3H_3^+$ is most exothermic but formation of the linear propargyl and non-linear carbene cation is also allowed on energetic and probably mechanistic grounds. $C_3H_3^+$ is also a major product ion at 0.1 eV but is totally absent at 100 eV of C^+ translational energy [2,3] The $C_2H_5^+$ has been shown to be produced by direct hydride abstraction [2] and $C_2H_4^+$ presumably arises from H_2^- abstraction to produce the radical cation, $^{\dot{+}}CHCH_3$, and methylene. The latter channel was not observed at 0.1 eV [2] but it increases in relative abundance at higher energies [3] The $C_3H_2^+$ and $C_2H_2^+$ ions observed as minor products at 0.1 eV were not noticed in measurements reported here (≲3%). There was no evidence for charge transfer which is endothermic in this case.

Carbon insertion to form a C_4 cation does not prevail in the reaction with propane (≲3%, $C_4H_5^+$ appears primarily as a secondary product ion). Apparently the decomposition of the adduct results in insertion at a C–H and a C–C bond to form $CHCH_2^+$ and $\cdot CHCH^+$ by loss of $\cdot C_2H_5$ and C_2H_6 as well as $C_3H_3^+$ by loss of CH_3 and H_2 (although other neutral products are thermodynamically allowed). These results are consistent with the ^{13}C retention observed by Smith and Futrell and 0 1 eV [2]. $C_2H_5^+$ can then be formed by electron transfer from C_2H_5 to $CHCH_2^+$ as the products separate, rather than CH_3^- of CH_2^- abstraction as has been proposed [2]. The $C_2H_2^+$ channel was not reported by Smith and Futrell Instead these authors observed 54% of the reaction at 0 1 eV to proceed by the direct mechanisms of charge transfer, hydride abstraction (with and without dissociation) and H_2^- pickup. None of these channels were observed in our experiments at 300 K. Instead all of our observed products can be accounted for by complex formation

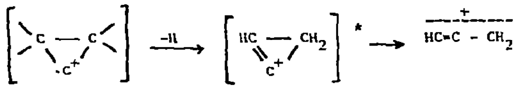
3 2. *Reactions with unsaturated hydrocarbons*

Our room-temperature studies indicate predominant formation of C_3 cations for the reaction of C^+ with ethylene. ≈30% of the reaction apparently proceeds by charge and hydride transfer. These results are comparable to the earlier tandem mass spectrometer experiments at 0.1 eV [2]. For $C_3H_3^+$, formation of the cyclopropenyl action isomer is again the most exothermic and may arise via the concerted mechanism



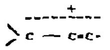
(1a)

Formation of the linear propargyl cation may arise via the mechanism.



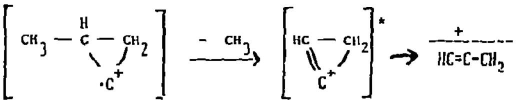
(1b)

Calculations by Radom et al. [12] indicate that the unsaturated cyclic intermediate in mechanism (1b) collapses without activation energy to the propargyl cation. The loss of H· in the first step is extremely exothermic and the calculations indicate that the less stable carbene and dicarbene cationic isomers may also be energetically allowed. Loss of H_2 (loss of 2H· is endothermic) may result in the formation of the resonance-stabilized radical cation


(2)

We did not detect the further breakup to C_3H^+ which was observed by Smith and Futrell [2].

As might be expected, the reaction of C^+ with propylene appears to combine the modes of reaction observed with the saturated hydrocarbons and those observed with ethylene. Direct charge transfer and H^- transfer appear to account for ≈30% of the reaction. Insertion at a saturated C–H bond can lead to formation of $CHCH_2^+$ with elimination of $\cdot C_2H_3$ and formation of $\cdot CHCH^+$ with elimination of C_2H_6. A cyclic intermediate can give rise to the formation of $C_3H_3^+$, e.g.


(3)

Elimination of H and H_2 instead of $\cdot CH_3$ can lead to the formation of the resonance-stabilized C_4 cation

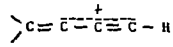

(4)

Table 1 shows that formation of a C_4 cation by the reaction of C^+ with propylene is only a minor channel.

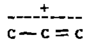
Allene, somewhat less saturated than propylene, showed a major production of a C_4 cation in its reaction with C^+. The intermediate $C_4H_4^+$ ion may eliminate either H_2 or two H· atoms exothermically. A radical cation is produced in either case as is shown in:

$$C^+ + CH_2CCH_2 \rightarrow [C_4H_4^+] \xrightarrow{-H_2} \cdot C^+{=}C{=}C{=}CH_2 \quad (5a)$$

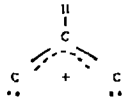
$$\xrightarrow{-2H} HC^+{=}C{=}C{=}CH \quad (5b)$$

Resonance structures may be drawn for both of the product ions. The observed $C_2H_2^+$ may be produced if the intermediate $C_4H_4^+$ eliminates C_2H_2. Again, the direct processes of H atom transfer and charge compete with the formation and breakup of the $C_4H_4^+$ intermediate.

Only one channel was observed in the reaction of C^+ with acetylene as we have reported previously [10]. The C_3H^+ which is produced very likely arises from insertion at the C–H bond accompanied by elimination of H· and has the linear and resonance-stabilized structure


$$C{-}C{=}C{-}H \quad (6a)$$

A second non-linear structure

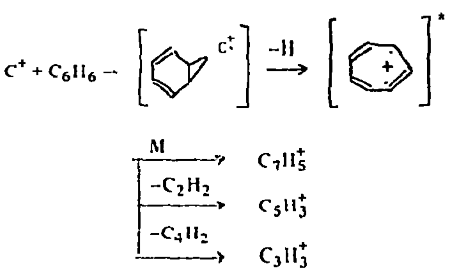

(6b)

also stabilized by charge delocalization, has been calculated to have an energy 46 kcal mole^{-1} higher [12]. Available heats of formation indicate that the formation of this isomer is ≈8 kcal mole^{-1} exothermic. Charge transfer and hydride transfer are both endothermic in this case and cannot compete at room temperature.

The products observed for the reaction of C^+ with propyne are consistent with the pattern of reactivity exhibited by the previous reactions with saturated and unsaturated hydrocarbons. Insertion at a saturated C–H bond can lead to formation of $CHCH_2^+$ with elimination of C_2H and formation of $\cdot CHCH^+$ with elimination of C_2H_2. This would account for the formation of the two minor products which contribute 20% to the reaction. Direct charge transfer and hydride transfer accounts for ≈50% of the reaction. The remaining 30% of the reaction leads to a carbon–carbon bond formation which can arise from insertion at either a saturated C–H bond or the acetylenic C–H bond. Elimination by the $C_4H_4^+$ intermediate of H_2 or two H atoms can lead to the same products as observed with allene, viz. the radical cations produced in (5a) and (5b).

3.3. Reactions with benzene

The most significant result of our measurements at room temperature of the reaction of C^+ with benzene is the observation of the $C_7H_5^+$ product ion which proved to be so elusive in the low-pressure tandem mass spectrometer experiments of Smith and DeCorpo [5] even at their lowest energy of 0.1 eV. Our observation of this ion provides direct evidence of a C_7 intermediate species which may result from C^+ attack at a C=C double bond in analogy with the previous reactions with olefins. According to the scheme proposed by Smith and DeCorpo we may write as a possible reaction mechanism.



(7)

However, direct charge transfer is still the dominant reaction channel at room temperature accounting for 67% of the products. The tandem mass spectrometer results at 0.1 eV showed an even larger proportion of $C_6H_6^+$ formation (83%) [5].

4. Conclusions

We have shown that $^{12}C^+$ reacts at room temperature with a variety of saturated and unsaturated hydrocarbons, $k \geqslant 1.3 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. The high heat of formation of C^+ provides many exothermic routes for reaction. Indeed, multiple ionic products were observed for all of the reactions except for that with acetylene. Build-up of the carbon skeleton was reflected in the observation of C_{n+1}^+ ions for all of the hydrocarbons except propane. Build-up was observed to compete successfully with other modes of reaction, particularly with lower members of homologous series

(a) CH_4 (100%), C_2H_6 (30%), C_3H_8 ($\lesssim$3%),

(b) C_2H_4 (70%), CH_2CCH_2 (40%), CH_3CHCH_2 (10%),

(c) C_2H_2 (100%), CH_3C_2H (30%),

(d) C_6H_6 (10%).

Our observations indicate that dissociative channels compete more effectively as the length of the carbon skeleton increases.

The insight provided by previous ^{13}C retention experiments carried out at suprathermal energies [2,5] has proven to be very useful for understanding the possible mechanisms of the reactions which were investigated. All of the observed product ions can be rationalized in terms of five modes of reaction: the direct processes of charge transfer, hydride transfer and H_2^- transfer, and complex formation with insertion at a C–H or C–C bond both of which result in the formation of new C–C bonds. Consideration of the mechanisms of reaction provides some insight into the structure of the product ions. As expected, all of the observed product ions except the charge-transfer products, were less saturated than the hydrocarbon reactant. The mechanisms of insertion at a C–H or C–C bond may favour the formation of linear unsaturated hydrocarbon ions of the type $C_nH_3^+$ and $C_nH_2^+$ where n = 2, 3 or 4 but this has not been established unequivocally by the measurements reported here. Charge delocalization provides a means of stabilization for these ions with n = 3 and 4. In the case of acetylene the C_3H^+ product ion appears to have carbene character. We have explored extensively the reactions of this latter ion with a variety of C, O, N and S containing molecules. The results of these investigations will be reported separately.

Acknowledgement

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