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# STUDIES OF REACTIONS OF $C_3H^+$ IONS IN THE GAS PHASE AT 296 ± 2 K

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## ABSTRACT

Rate constants and product distributions have been determined for ion–molecule reactions between $C_3H^+$ and $H_2$, $D_2$, CO, $N_2$, $O_2$, $CO_2$, OCS, $H_2O$, $H_2S$, $CH_3OH$, NO, $N_2O$, $NH_3$, $ND_3$, $CH_4$, HCN, $CH_3CN$, $C_2N_2$, $C_2H_2$, $C_2D_2$ and $C_2H_4$. The measurements were done using the Selected-Ion Flow Tube or SIFT technique at 296 ± 2 K. The observed reactions exhibit a wide range in reactivity and a large variety of pathways including proton transfer, charge transfer, hydride abstraction, complex formation and association. Many of these reactions provide routes for C–H, C–C, C–O, C–N or C–S bond formation in the ion and/or neutral product which are of relevance in molecular synthesis by ion chemistry.

## INTRODUCTION

The mass-spectrometric observation of $C_3H^+$ has a long history and there has been a long-standing interest in the experimental determination of its energy [1,2]. Nevertheless, very little information has been forthcoming about the chemical reactivity of this species. A need for such information has recently become apparent, especially in connection with interstellar ion chemistry [3–5], which has provided the motivation for the experiments reported here. We have chosen a large variety of molecules containing C, O, N and S as neutral substrates to explore fully the many pathways of the reactions of this interesting ion at room temperature. Molecular orbital theory has shown the most stable structure of $C_3H^+$ to be linear and stabilized by resonance [4,6] as in

$$H{-}C^+{=}C{=}C{:} \leftrightarrow H{-}C{\equiv}C{-}C^+{:} \qquad (1)$$

Both cationic and carbene character are indicated by this structure. These properties, together with the high energy and low acidity of $C_3H^+$ [7] and its low electron-recombination energy, also make this ion a most attractive candidate for providing further insight into the more chemical aspects of ion–molecule reactions in general.

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## EXPERIMENTAL

The measurements were done with the Selected-Ion Flow Tube, SIFT, apparatus at York University. An early version of this apparatus has been described in detail elsewhere [8]. A number of important modifications have been made for most of the measurements reported here. These are incorporated in the schematic diagram which appears in Fig. 1. The miniature flowing afterglow source can now be replaced with an axial electron impact ionizer (Extranuclear, Model 041-3). The Bendix magnetic electron multiplier can be replaced with a high current CEM Channeltron multiplier (Galileo Electro-Optics Corp., Model 4830). Also the mass range of the analysis quadrupole has been extended up to $m/z = 425$ with the use of a new combination of a high-$Q$ head (Extranuclear, Model 13) and quadrupole mass filter (Extranuclear, Model 4-162-8).

The $C_3H^+$ was produced from propylene either in the miniature flowing afterglow source in a He buffer at total pressures of ca. 0.3 Torr, or from the pure gas at much lower pressures in the axial electron impact ionizer at 45–60 eV. The results were found to be independent of the ion source employed. After formation, the $C_3H^+$ was selected and injected at ca. 80 V

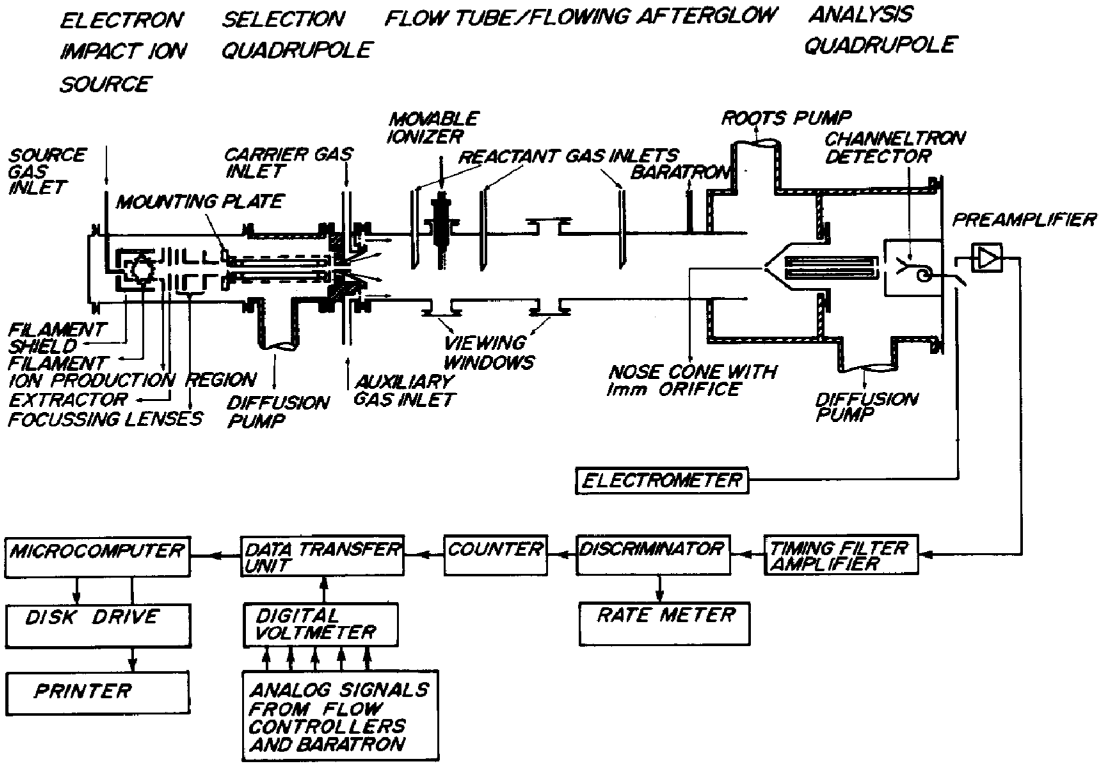


Fig. 1. Schematic diagram of the selected-ion flow tube and flowing afterglow apparatus.

or 8–20 V, respectively, into a helium carrier gas at a total pressure of ca. 0.35 Torr unless indicated otherwise. The ions were allowed to thermalize by collisions with the carrier gas prior to their entry into the reaction region. However, in the process, the selected ions may undergo collisional dissociation and reaction with impurities in the buffer gas and with any propylene which may "leak" through the aspirator. For example, at the high ion injection energy which was required with the flowing afterglow source, $C_3H^+$ was observed to be dissociated to $C^+$, giving rise to a $C_3H^+/C^+$ ion signal ratio at the downstream detector of only about 10/1. At the much lower injection energies of the electron impact source, this ratio was much higher, $\sim 10^4/1$, but reactions with impurities gave rise to small signals, especially at $m/z$ 27, 29, 39, 53 and 54. Nevertheless, the selected $C_3H^+$ signal was always at least 200 times as large as any of these impurity peaks. As a consequence, the assignment of product ions could be made with confidence to levels as low as about 1%. Optimum operation of the electron impact source with the off-axis Channeltron detector provided currents for $C_3H^+$ in excess of $10^{-8}$ A and count rates in excess of $5 \times 10^4$ counts $s^{-1}$.

As has been the case in our previous studies, all of the reagent gases and vapours as well as the helium buffer gas were of high purity. This was especially true for the three least reactive gases, viz. $O_2$, $N_2$ and $CO_2$, for which low rate constants are reported. These gases had a minimum purity of 99.99 mol %. All measurements were made at an ambient temperature of $296 \pm 2$ K.

## RESULTS AND DISCUSSION

Table 1 summarizes the rate constants and product distributions obtained in this study. Both bimolecular and termolecular products were observed. Rate constants were derived as before [8] and product distributions were determined using the method described by Adams and Smith [9]. The results are discussed in the following section in groups of neutral reagents, in part to emphasize common features in their chemistry.

### *Reactions with $H_2$, $D_2$, CO, and $N_2$*

Hydrogen, deuterium and carbon monoxide were observed to add to $C_3H^+$ in helium buffer gas to form $C_3H_3^+$, $C_3HD_2^+$ and $HC_4O^+$, respectively. The effective two-body rate constants for these three association reactions were measured at total pressures in the range from 0.33 to 0.75 Torr. Their observed dependences on pressure are shown in Fig. 2 and lead to three-body rate constants of $(1.9 \pm 0.8) \times 10^{-27}$, $(7.7 \pm 3.1) \times 10^{-28}$ and $(2.9 \pm 1.2) \times 10^{-27}$ $cm^6$ $molecule^{-2}$ $s^{-1}$, respectively. No adduct was ob-

TABLE 1

Summary of the rate constants and product distributions measured at 296 ± 2 K for reactions of $C_3H^+$

| Neutral reactant [a] | Products [b] | Product distribution [c] | $k$ [d] |
|---|---|---|---|
| $H_2$ (He) | $C_3H_3^+$ | 1.0 | 1.9 (−27) [e] |
| $D_2$ (He) | $C_3HD_2^+$ | 1.0 | 7.7 (−28) [e] |
| CO (He) | $HC_4O^+$ | 1.0 | 2.9 (−27) [e] |
| $N_2$ | | | ≤1(−13) |
| $O_2$ | $HCO^+ + C_2O$ | 0.6 | 2.5 (−11) |
| | $HC_3O^+ + O$ | 0.3 | |
| | $HC_2O^+ + CO$ | 0.1 | |
| $CO_2$ | $HC_3O^+ + CO$ | 1.0 | 2.0 (−12) |
| COS | $CS^+ + HC_3O$ | 0.7 | 6.1 (−10) |
| | $HC_3O^+ + CS$ | 0.2 | |
| | $HC_3S^+ + CO$ | 0.1 | |
| $H_2O$ | $CHO^+ + C_2H_2$ | 0.55 | 4.5 (−10) |
| | $C_2H_3^+ + CO$ | 0.40 | |
| | $HC_3O^+ + H_2$ | 0.05 | |
| $H_2S$ | $CHS^+ + C_2H_2$ | 0.63 | 1.2 (−9) |
| | $C_2H_3^+ + CS$ | 0.30 | |
| | $HC_3S^+ + H_2$ | 0.07 | |
| $CH_3OH$ | $HC_3O^+ + CH_4$ | 0.8 | 2.2 (−9) |
| | $CH_3O^+ + C_3H_2$ | 0.1 | |
| | $CH_3^+ + H_2C_3O$ | 0.1 | |
| NO | $HC_2N^+ + CO$ | 0.75 | 5.5 (−10) |
| | $NO^+ + C_3H$ | 0.25 | |
| $N_2O$ | $NO^+ + HC_3N$ | 0.55 | |
| | $HC_3O^+ + N_2$ | 0.4 | |
| | $HCN^+ + C_2NO$ | 0.05 | |
| $NH_3$ | $NH_4^+ + C_3$ | 0.5 | 1.6 (−9) |
| | $H_2CN^+ + C_2H_2$ | 0.3 | |
| | $NH_3^+ + C_3H$ | 0.15 | |
| | $HC_3NH_2^+ + H$ | 0.05 | |
| $ND_3$ | $ND_3H^+ + C_3$ | 0.5 | 1.7 (−9) |
| | $D_2CN^+ + C_2HD$ | 0.2 | |
| | $ND_3^+ + C_3H$ | 0.2 | |
| | $HC_3ND_2^+ + D$ | 0.1 | |
| $CH_4$ | $C_2H_3^+ + C_2H_2$ | 0.7 | 5.5 (−10) |
| | $C_3H_3^+ + CH_2$ | 0.2 | |
| | $C_4H_3^+ + H_2$ | 0.1 | |
| HCN (He) | $C_4H_2N^+$ | 1.0 | 1.0 (−9) |
| $CH_3CN$ | $C_3NH_2^+ + C_2H_2$ | 0.35 | 3.0 (−9) |
| | $C_3H^+ \cdot CH_3CN$ | 0.3 | |
| | $C_2H_3^+ + HC_3N$ | 0.2 | |
| | $CH_3CNH^+ + C_3$ | 0.15 | |
| $CD_3CN$ | $C_3NHD^+ + C_2D_2$ | 0.3 | 3.0 (−9) |
| | $C_3H^+ \cdot CD_3CN$ | 0.3 | |
| | $C_2D_3^+ + HC_3N$ | 0.15 | |
| | $CD_3CNH^+ + C_3$ | 0.15 | |
| | $C_2ND_2^+ + C_2D_2$ | 0.1 | |

TABLE 1 (continued)

| Neutral reactant [a] | Products [b] | Product distribution [c] | $k$ [d] |
|---|---|---|---|
| $C_2N_2$ (He) | $C_5HN_2^+$ | 1.0 | ≥ 4.4 (−10) |
| $C_2H_2$ (He) | $C_5H_3^+$ | 0.7 | 1.0 (−9) |
| | $C_5H_2^+ + H$ | 0.3 | |
| $C_2D_2$ (He) | $C_5HD_2^+$ | 0.7 | 9.3 (−10) |
| | $C_5HD^+ + D$ | 0.3 | |
| $C_2H_4$ | $C_3H_3^+ + C_2H_2$ | 0.95 | 9.5 (−10) |
| | $C_5H_3^+ + H_2$ | 0.05 | |

[a] For termolecular reactions, the third body is indicated in parentheses.

[b] The neutral products were not detected in the present experiments. In writing the neutral products, only the most exothermic channel is indicated.

[c] We estimate that the absolute branching ratio may be in error by as much as ±30% due to the possible mass discrimination effects in the mass spectrometer. For ionic products over a narrow mass range ( ≲ 5 u) these effects are negligible.

[d] Unless otherwise indicated, $k$ is the effective bimolecular rate constant for the disappearance of $C_3H^+$ in units of $cm^3$ $molecule^{-1}$ $s^{-1}$ in helium buffer gas at a total pressure of ca. 0.35 Torr. The accuracy is estimated to be better than ±30%. Rate constants are expressed as $a(-b)$ to represent $a \times 10^{-b}$.

[e] Termolecular rate constant in units of $cm^6$ $molecule^{-2}$ $s^{-1}$.

served to be formed between $C_3H^+$ and $N_2$: the $C_3H^+$ failed to react altogether with $N_2$ at 0.36 Torr, $k \leqslant 1 \times 10^{-13}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. Insofar as the magnitude of a three-body rate constant correlates with the stability of the association complex [10,11], the relatively high values of the three-body rate constants for the reactions with $H_2$, $D_2$ and CO, as well as the failure of $C_3H^+$ to form an adduct with $N_2$, are indicative of the formation with $H_2$, $D_2$ and CO of "tight" adducts through chemical bonding rather than "loose" adducts through electrostatic interaction. Thus the $C_3H_3^+$ and $C_3HD_2^+$ ions formed by association of $C_3H^+$ with $H_2$ and $D_2$, respectively, are likely to be cyclopropenium or propargyl cations, while the $HC_4O^+$ formed from $C_3H^+$ and CO is likely to have the linear structure $H{-}\overset{+}{C}{=}C{=}C{=}C{=}O$. The isotope effect observed for the termolecular association reactions with $H_2$ and $D_2$ is quite large, $k_{H_2}/k_{D_2} = 2.5$. An isotope effect of 1.38 can be attributed to the difference in the reduced mass of the reacting species in the first step of the two-step mechanism for such reactions.

### *Reactions with $O_2$, $CO_2$ and OCS*

The reaction with $O_2$ was observed to be quite slow, $k = 2.5 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, but a number of interesting product channels appeared. The

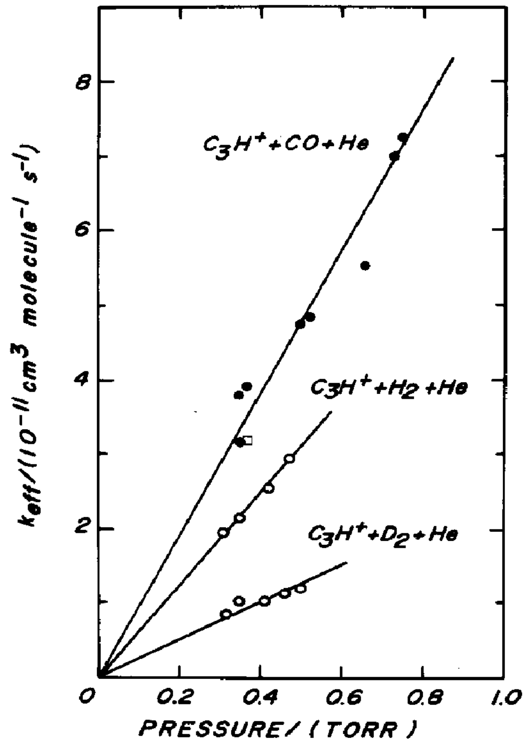


Fig. 2. Observed dependence of the effective two-body rate constant on the total pressure for the associations of $C_3H^+$ with $H_2$, $D_2$ and CO at 296±2 K. In the $H_2$ and $D_2$ experiments, the $C_3H^+$ ions were produced from pure propylene with the axial electron impact ionizer at ca. 60 eV. In the CO experiments, the $C_3H^+$ ions were derived from a propylene/helium mixture at 0.4 Torr and 50 eV in the miniature flowing afterglow source (solid points). The open square refers to selection of $C_3H_3^+$ from the same mixture with subsequent collisional dissociation with He to $C_3H^+$ prior to the reaction region.

$HCO^+$ and $HC_2O^+$ ions are likely to arise from side-on attack by $O_2$ and subsequent proton transfer before the products separate. The $HC_3O^+$ channel can arise directly by O atom abstraction.

The reaction with $CO_2$ was observed to occur even less rapidly, $k = 2.0 \times 10^{-12}$ $cm^3$ molecule$^{-1}$ $s^{-1}$, and in this case in only one fashion: by O atom abstraction to produce $HC_3O^+$.

Substitution of a sulphur atom for one of the oxygen atoms in $CO_2$ was observed to give rise to a very substantial enhancement in the specific rate of reaction with $C_3H^+$. Carbonyl sulfide, OCS, reacts at close to the collision rate and gives rise to three product ions which can be accounted for by a mechanism which involves attack at either end of the molecule. The $HC_3O^+$ ion may arise as before with $CO_2$ by O atom abstraction to leave CS. The CS has a low ionization energy (IE = 11.8 eV) and so may be ionized by charge transfer before the products separate. Attack at the opposite end of COS will yield $HC_3S^+$ and CO. The CO has a much higher ionization energy (IE = 14.1 eV) than CS and this may account for the failure to observe production of $CO^+$, the analogue of $CS^+$.

### *Reaction with $H_2O$, $H_2S$ and $CH_3OH$*

As anticipated, $C_3H^+$ was observed to react with $H_2O$ and $H_2S$ in a very similar fashion. Figure 3 shows the raw data obtained for the reaction with $H_2S$. Rearrangement to eliminate $C_2H_2$ was the major reaction channel. The $CHS^+$ (or $CHO^+$ in the case of $H_2O$) may transfer a proton to $C_2H_2$ before the products completely separate and so account for the observed $C_2H_3^+$ product. The eventual decline in the $C_2H_3^+$ seen in Fig. 3 is due to the

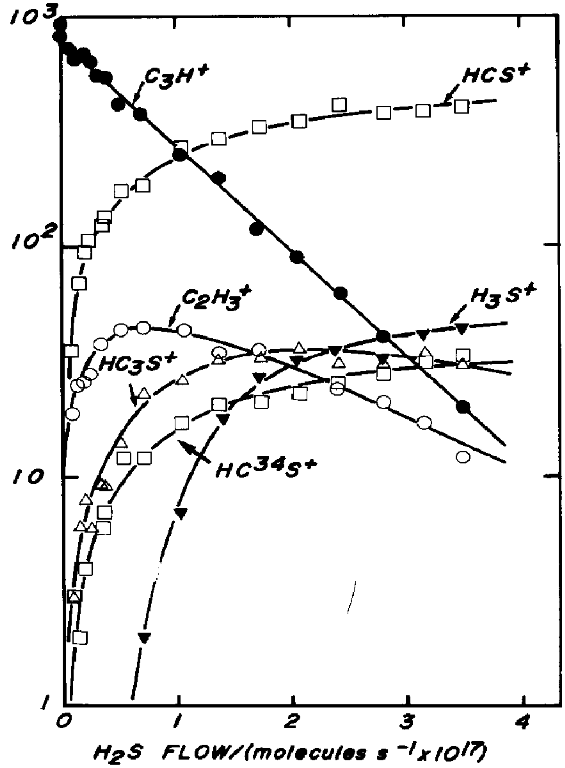


Fig. 3. The observed variation in ion signals detected upon the addition of $H_2S$ into the reaction region of the SIFT apparatus in which $C_3H^+$ is initially established in helium buffer gas. The $C_3H^+$ ions were generated in the electron impact ionizer from propylene at low pressures with 45 eV electrons. The conditions in the reaction region were $P = 0.358$ Torr, $\bar{v} = 7.6 \times 10^3$ cm $s^{-1}$, $L = 46$ cm and $T = 298$ K.

further reaction with $H_2S$ by proton transfer. A small fraction of the reactions of $C_3H^+$ with $H_2O$ and $H_2S$ led to the elimination of $H_2$ to produce $HC_3O^+$ and the sulphur analogue $HC_3S^+$, respectively. The failure to observe charge transfer is noteworthy in the case of $H_2S$. This molecule has a relatively low ionization energy ($IE = 10.47$ eV) and so failure to observe charge transfer in this case may provide an upper limit to the ionization energy of $C_3H$.

Many channels are exothermic for the reaction of $C_3H^+$ with $CH_3OH$ but only a few are actually selected by these reactants. The analogues of the main channels with $H_2O$, viz. production of $HCO^+ + CH_3CCH$ or $CH_3CO^+ + C_2H_2$ and $CH_3CCH_2^+ + CO$ or $C_2H_3^+ + CH_2CO$, were not observed even though they are all exothermic. Instead, the analogue of the minor channel observed with $H_2O$, viz. production of $HC_3O^+ + CH_4$, becomes the preferred channel with $CH_3OH$. The $CH_3^+$ product can arise from hydride transfer to produce $H_2C{=}C{=}C{=}O$ before the $HC_3O^+$ and $CH_4$ completely separate. The observed $CH_3O^+$ product ion likely arises by direct hydride abstraction from $CH_3OH$. Protonated methanol was observed in the product spectrum, but the product analysis showed that it was not produced directly from $C_3H^+$. Instead, it could be attributed entirely to the secondary proton-transfer reactions of $CH_3O^+$ and $HC_3O^+$ with $CH_3OH$. The $CH_3^+$ product was observed to undergo the known secondary reaction with $CH_3OH$ which produces $CH_3O^+$.

### *Reactions with NO and $N_2O$*

Nitric and nitrous oxides were observed to react with $C_3H^+$ in very different ways. Nitric oxide, NO, the most stable oxide of nitrogen, reacts by rearrangement to eliminate CO and by charge transfer. Rearrangement is the major channel. The $HC_2N^+$ ion produced along with the CO may have the resonance-stabilized structure $\mathrm{H}-\overline{\mathrm{C}=\overset{+}{\mathrm{C}}-\mathrm{N}}\,\overset{\cdot}{\cdot}$. In contrast, $N_2O$ reacts primarily by $N^{(-)}$ abstraction to form $NO^+$ and a neutral species, which is probably cyanoacetylene, as well as by oxygen-atom abstraction to produce $HC_3O^+$ and $N_2$. These two reaction paths can be envisaged to result from attack at either of the two negative ends of the $N_2O$ molecule.

### *Reactions with $NH_3$, $ND_3$ and $CH_4$*

Multiple products were observed for all three of these reactions. $NH_3$ and $ND_3$ were observed to react predominantly by the direct processes of proton transfer and charge transfer and by C–N bond formation while $CH_4$ reacted exclusively by C–C and C–H bond formation.

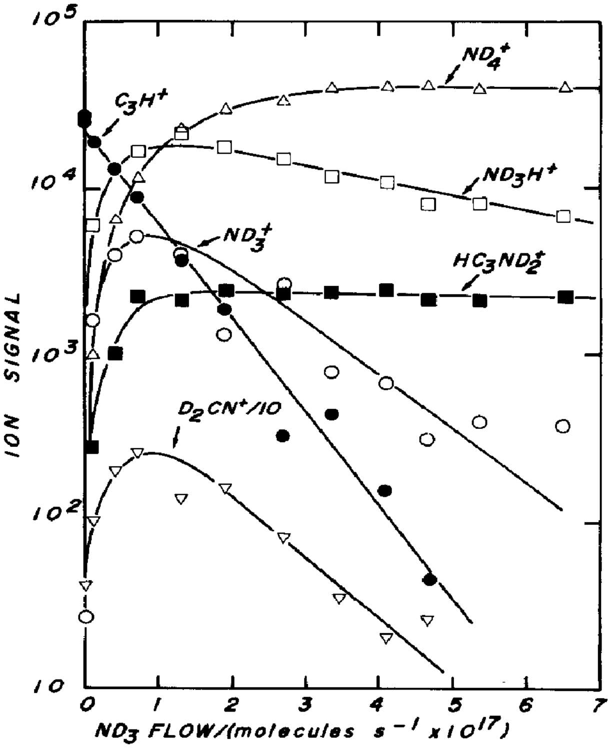


Fig. 4. The observed variation in ion signals detected upon the addition of $ND_3$ into the reaction region in which $C_3H^+$ has been established with the SIFT technique using the electron impact ionizer at 60 eV. $P = 0.349$ Torr, $\bar{v} = 7.5 \times 10^3$ cm $s^{-1}$, $L = 46$ cm and $T = 296$ K.

Figure 4 shows data recorded for the reaction of $C_3H^+$ with $ND_3$. The product analysis indicated that the major channel was proton transfer to produce $ND_3H^+$ which appears to react further with $ND_3$ by H/D exchange to form $ND_4^+$. The latter ion is also generated by secondary reactions of the charge-transfer product $ND_3^+$ and the product ion at $m/z = 30$. Experiments with $NH_3$ indicated a shift of the product ion at $m/z = 30$ to $m/z = 28$, which is consistent with the formation of $D_2CN^+$ rather than $C_2D_3^+$. A minor fraction of the reaction of $C_3H^+$ with $ND_3$ appears to proceed by condensation with elimination of a deterium atom to form a radical cation which may have the structure $H\overset{+}{\overline{C{=}C{-}\dot{C}}}{-}ND_2$. Also, there was some indication of the formation of an ion at $m/z$ 41 ($HC_3D_2^+$, $HC_2ND^+$?) with a branching ratio of $\leq 0.02$, but the corresponding ions at $m/z = 39$ or 40 did not appear to be produced with $NH_3$.

The products observed for the reaction of $C_3H^+$ with $CH_4$ were of the type $C_nH_3^+$ with $n = 2$, 3 and 4 and correspond to the elimination from the intermediate complex of acetylene, methylene and hydrogen, respectively. As

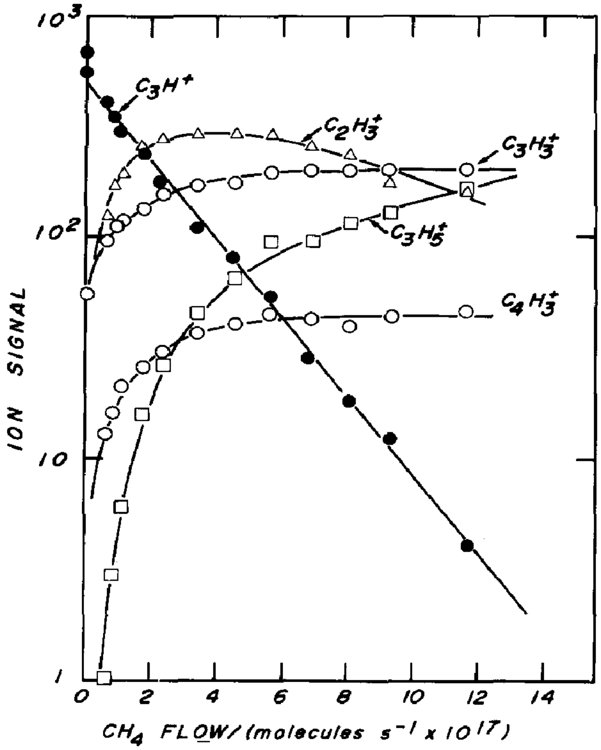


Fig. 5. The observed variation in ion signals detected with the addition of $CH_4$ into the reaction region in which $C_3H^+$ has been established with the SIFT technique using the electron impact ionizer at 45 eV. $P = 0.353$ Torr, $\bar{v} = 7.4 \times 10^3$ cm $s^{-1}$, $L = 46$ cm and $T = 297$ K.

regards the production of $C_3H_3^+$, it is interesting to note that currently available heats of formation for $C_3H^+$ and $C_3H_3^+$ [1,2] indicate that only the formation of the cyclopropenium ion (and not, for example, the propargyl cation) is exothermic in this case. The $C_4H_3^+$ ion may arise from insertion at a C–H bond with concomitant elimination of $H_2$, in which case $H\overset{+}{C}{=}C{-}C{=}CH_2$ would be a reasonable structure for this ion.

### *Reactions with HCN, $CH_3CN$, $CD_3CN$, and $C_2N_2$*

Four product ions were observed for the reaction of $C_3H^+$ with $CH_3CN$. Experiments with $CD_3CN$ confirmed that the product at $m/z = 27$ was $C_2H_3^+$ rather than $HCN^+$ and that the product at $m/z = 52$ was $C_3NH_2^+$ rather than $C_4H_4^+$. The $C_3H_3^+$ may arise through complex formation with the elimination of cyanoacetylene. Transfer of a proton to the developing cyanoacetylene molecule can account for the observation of $C_3NH_2^+$. The observation with $CD_3CN$ of $C_3ND_2^+$ as well as $C_3NHD^+$ suggests that some

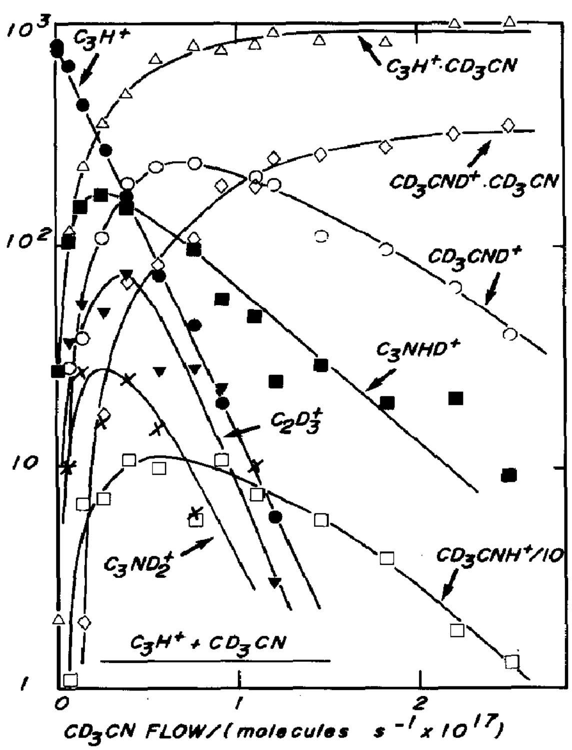
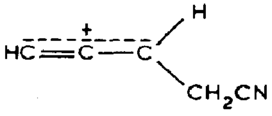


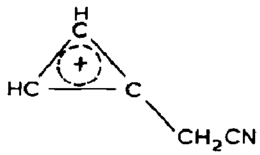
Fig. 6. The observed variation in ion signals detected with the addition of $CD_3CN$ into the reaction region in which $C_3H^+$ has been established with the SIFT technique using the electron impact ionizer at 60 eV. $P = 0.345$ Torr, $\bar{v} = 7.5 \times 10^3$ cm $s^{-1}$, $L = 46$ cm and $T = 296$ K.

H/D exchange may also occur in the complex before the products separate. Both $C_2H_3^+$ and $C_3NH_2^+$ were observed to react further with $CH_3CN$ apparently by proton transfer. Figure 5 shows the corresponding results with $CD_3CN$. The reaction of $C_2H_3^+$ is expected since the proton affinity of $C_2H_2$ is known to be less than that of $CH_3CN$. The secondary reaction of $C_3NH_2^+$ also places the proton affinity of cyanoacetylene below that of $CH_3CN$.

The observation of a primary proton-transfer channel places an upper limit on the proton affinity of $C_3$ [7]. The nature of the adduct formed between $C_3H^+$ and $CH_3CN$ (or $CD_3CN$) is uncertain; insertion at a C–H bond could result in a linear resonance-stabilized ion of type (2a) or, upon isomerization, the cyclic structure (2b).

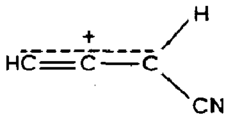


( 2a )

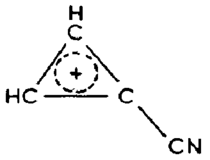


( 2b )

Only the adduct was observed to be formed with HCN and $C_2N_2$. The high values of the effective two-body rate constants which were measured suggest that these associations proceed at the saturated rate. With HCN, insertion at the C–H bond may proceed again to form the linear or cyclic resonance-stabilized ions (3a) or (3b). With $C_2H_2$, insertion at the C–C bond may lead to an ion of the type $HC_2\text{–}\overset{+}{C}(CN)_2$.



(3a)



(3b)

### *Reactions with $C_2H_2$, $C_2D_2$ and $C_2H_4$*

$C_5H_3^+$ and $C_5H_2^+$ were both observed as product ions for the reaction of $C_3H^+$ with $C_2H_2$ in helium buffer gas at 0.35 Torr. The former product corresponds to formation of the adduct while the latter involves the elimination of a hydrogen atom. Both ions may arise from insertion at a C–H bond and so have structures of the type $H\overline{C{=}C{-}\overset{+}{C}}H{-}C{\equiv}CH$ and $H\overline{C{=}C{-}\overset{+}{C}}{-}C{\equiv}CH$, respectively. Further isomerization could lead to cyclic structures of the type (2b) and (3b). Experiments with $C_2D_2$ indicated that the hydrogen atom is eliminated from $C_2H_2$ rather than $C_3H^+$. Previous flowing afterglow measurements failed to reveal the formation of the adduct, apparently because of insufficient resolution of the mass spectrometer [3].

$C_3H^+$ was observed to react rapidly with $C_2H_4$ to produce $C_3H_3^+$ with elimination of $C_2H_2$. In this case, formation of either the cyclopropenium or the propargyl isomer is exothermic. Formation of $C_5H_3^+$ with elimination of $H_2$ was indicated by the product analysis to account for about 5% of the reaction.

## CONCLUSIONS

The measurements reported here show that $C_3H^+$ reacts with simple inorganic and organic molecules in the gas phase at room temperature in a variety of different ways with a large range in reactivity. The observed pathways of reaction were proton transfer, charge transfer, hydride abstraction, complex formation and association.

Proton transfer was observed with molecules having proton affinities greater than 187 kcal $mol^{-1}$ but not with molecules having proton affinities less than 181 kcal $mol^{-1}$. These observations have provided values for the proton affinity of $C_3$, $PA(C_3) = 184 \pm 4$ kcal $mol^{-1}$, and for the heat of formation of $C_3H^+$, $\Delta H^{\circ}_{f,298}(C_3H^+) = 383 \pm 8$ kcal $mol^{-1}$ [7].

Charge transfer was observed with molecules having ionization potentials less than 10.21 eV but not with molecules having ionization potentials greater than 10.47 eV. These observations suggest values for the adiabatic ionization energy of $C_3H$, $IE(C_3H) = 10.35 \pm 0.15$ eV, and for the heat of formation of $C_3H$, $\Delta H^{\circ}_{f,298}(C_3H) = 144 \pm 12$ kcal $mol^{-1}$.

Many of the observed reaction channels are in accord with a carbenoid character associated with $C_3H^+$ [12]. Coordination with a non-bonded electron pair on oxygen in $H_2O$, $CO_2$, OCS, $N_2O$ and $CH_3OH$ can account for the common product ion $HC_3O^+$ observed with these reagents. Likewise, coordination with a non-bonded electron pair on sulphur in $H_2S$ and OCS and on carbon in CO can account for the product ions $HC_3S^+$ and $HC_4O^+$, respectively.

Insertion can account for several of the product channels observed with the molecules containing C–H, N–H, O–H or S–H sigma bonds, in particular the channels leading to formation of $C_2H_2$ or $C_2H_3^+$. Also, it appears from the high rates of association that the adducts which have been observed with $H_2$, HCN, $CH_3CN$ and $C_2H_2$ may have structures corresponding to strongly bound chemical species which may be formed by sigma bond C–H insertion.

Several of the observed reactions are of relevance to molecular synthesis by means of ion chemistry as, for example, in astrochemical environments: the $C_3H^+$ ion has been implicated in the chemistry of dense interstellar clouds where it may be formed by reaction of $C^+$ with $C_2H_2$ [3] or $C_3^+$ with $H_2$ [5]. In the present study, members of a homologous series of product ions of the type $HC_nO^+$, with possible structures which may be represented by $\overset{+}{H}C{=}C_n{=}O$, have been observed in the reactions with CO, $O_2$, $CO_2$, OCS, $H_2O$, $CH_3OH$ and $N_2O$. Neutralization of these ions by proton transfer, electron–ion recombination or hydride transfer may lead to the formation of molecules of the type $:C{=}C_n{=}O$ or ketene-like molecules of the type $H_2C{=}C_n{=}O$. The reactions of $C_3H^+$ with $N_2O$ and $CH_3CN$ are potential sources of cyanoacetylene. The reactions with $CH_4$, $C_2H_2$ and $C_2H_4$ can lead to the build-up of carbon skeletons. The nature of the adducts observed with HCN, $CH_3CN$ and $C_2H_2$ is uncertain, but they appear to allow the formation of larger organonitrogen molecules, particularly at elevated pressures.

Clearly, $C_3H^+$ is a very aggressive chemical species in the gas phase. Its reactivity has only been sampled in the present study, but it is evident from the results obtained that this ion can be an important intermediate in molecular growth by ion chemistry.

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## REFERENCES

1 J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron, K. Draxl and F.H. Field, Natl. Stand. Ref. Data, Ser. Natl. Bur. Stand., 26 (1969).
2 H.M. Rosenstock, K. Draxl, B.W. Steiner and J.T. Herron, J. Phys. Chem. Ref. Data, Suppl. 1, 6 (1977).
3 H.I. Schiff and D.K. Bohme, Astrophys. J., 232 (1979) 740.
4 S. Wilson and S. Green, Astrophys. J., 240 (1980) 968.
5 G.F. Mitchell, J.L. Ginsburg and P.J. Kuntz, Astrophys. J., Suppl. Ser., 38 (1978) 39.
6 K. Raghavachari, R.A. Whiteside, J.A. Pople and P.V.R. Schleyer, J. Am. Chem. Soc., 103 (1981) 5649.
7 A.B. Raksit and D.K. Bohme, Int. J. Mass Spectrom. Ion Phys., 49 (1983) 275.
8 G.I. Mackay, G.D. Vlachos, D.K. Bohme and H.I. Schiff, Int. J. Mass Spectrom. Ion Phys., 36 (1980) 259.
9 N.G. Adams and D. Smith, J. Phys. B, 9 (1976) 1439.
10 E. Herbst, J. Chem. Phys., 70 (1979) 2201.
11 A. Good, Trans. Faraday Soc., 67 (1971) 3495.
12 D.K. Bohme, A.B. Raksit and A. Fox, J. Am. Chem. Soc., 105 (1983) 5481.