International Journal of Mass Spectrometry and Ion Processes, 84 (1988) 69–87
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ACETONITRILE IN GAS-PHASE ION/MOLECULE CHEMISTRY

H. WINCEL

Polish Academy of Science, Institute of Physical Chemistry, 01-224 Warsaw (Poland)

S. WŁODEK and D.K. BOHME

Department of Chemistry and Centre for Research in Experimental Space Science,
York University, North York, Ont. M3J 1P3 (Canada)

(First received 20 August 1987; in final form 18 January 1988)

ABSTRACT

Rate coefficients and branching ratios have been determined for the reactions of N_2^+, CO^+, and CO_2^+ with CH_3CN utilizing the selected-ion flow tube (SIFT) technique. The ion/molecule reactions following the electron-beam irradiation of the gas mixtures CH_3CN–M (where M = Ar, H_2, N_2, CO, CO_2, and CH_4) have been examined in a high-pressure mass spectrometer (HPMS). Pathways are presented for reactions of cations produced from acetonitrile with acetonitrile. The reactions of CH_3CN^+ with CO and CO_2 are also reported, as are the reactions of CH_3^+, $C_2H_5^+$. $C_3H_7^+$, and $C_4H_9^+$ with CH_3CN.

INTRODUCTION

The gas-phase chemistry of acetonitrile (CH_3CN) is of considerable interest, not only from the chemical point of view, but also in such fields as geophysics and astrophysics. In recent years, CH_3CN has been discovered in the stratosphere by detection of the ion clusters $H^+ \cdot (H_2O)_m(CH_3CN)_n$ [1]. Also acetonitrile has been detected in the troposphere [2] and in interstellar space [3], including cold dust clouds [4].

The possible role of cyano compounds in the ion chemistry of the terrestrial atmosphere has been discussed extensively [5] and the importance of their ionic reactions in interstellar molecular synthesis has been demonstrated [6]. However, little attention has been devoted to the experimental investigation of sequential ion/molecule reactions in systems containing cyano compounds. Although a number of studies of the ion/molecule reactions of acetronitrile have been made [7–15], so far there is little information concerning such ionic reactions at high pressures. Gray has examined acetronitrile at low pressures using the ion cyclotron resonance

0168-1176/88/$03.50

(ICR) technique and observed a number of positive and negative ion/molecule reactions [8]. At low pressures, such as those present in ICR studies ($\approx 10^{-5}$ torr), the adduct ions which require collisional stabilization are rarely observed. In the work reported here, the experimental pressure regime is extended toward higher pressures (10^{-2} to 4 torr) in an attempt to search for ion/molecule complexes in gas mixtures containing acetonitrile and to identify reaction channels leading to ionic products.

EXPERIMENTAL

The experimental results reported here were obtained in two laboratories. The experiments in the Institute of Physical Chemistry at the Polish Academy of Science were performed with a high-pressure mass spectrometer (HPMS) which has been described previously [16,17]. Two different reaction chambers have been used: the high-pressure reaction chamber previously described [17,18], designated here as chamber 1 (15 mm in diameter with a reaction path length of 4 mm), and the chamber used in ref. 19, designated here as chamber 2 (8 mm in diameter with a reaction path length of 2 mm).

The general technique was similar to that employed in previous work [17–21]. The ion-accelerating voltage was 2 or 3 kV and the electron-accelerating voltages were 1000 V (chamber 1) and 500 V (chamber 2). The repeller and electron-collector electrodes were maintained at the ionization chamber potential. The total pressure inside the reaction chambers was measured directly with a diaphragm-capacitance micromanometer [22].

The reactant ions were produced by bombardment with an electron beam of the gas mixtures CH_3CN–M with M = Ar, H_2, N_2, CO, CO_2 and CH_4 at pressures ranging from 0.01 to 0.4 torr and temperatures between 305 and 345 K. The concentartion of CH_3CN in these mixtures was in the range 0.8–3.5 mol %.

Under these conditions, the production of reactant ions from CH_3CN was initiated either by charge-transfer reactions

$$M^+ + CH_3CN \rightarrow CH_3CN^+ + M \qquad (1)$$

$$\text{decomposition products} \qquad (2)$$

for M = Ar, N_2, CO, and CO_2 or by proton-transfer to CH_3CN

$$XH^+ + CH_3CN \rightarrow CH_3CNH^+ + X \qquad (3)$$

where $X = H_2$ when H_2 was used as bath gas and $X = CH_4$, C_2H_4, and C_3H_6 for CH_4 as bath gas.

The measurements in the Ion Chemistry Laboratory at York University, Canada, were done with the selected-ion flow tube (SIFT) apparatus [23,24] at room temperature with helium (at 0.34 torr) as the buffer gas. The reactant ions were generated by electron impact with 70 eV electrons at low pressures. An axial electron-impact ionizer [25] was used as the ion source.

Acetonitrile was obtained from Fluka [26] and purified by the usual freeze–thaw cycle before use (in the HPMS experiments) or obtained from Matheson, Coleman and Bell (spectroquality) [27] and used without further purification (in the SIFT experiments). All bath gases were commercially available products. Traces of water in these gases were significantly reduced by passing them through a copper coil immersed in different cooling agents (in the HPMS experiments) or through zeolite traps (a 50:50 mixture of molecule sieves 4A and 13X [28]) cooled to liquid-nitrogen temperature (in the SIFT experiments).

RESULTS AND DISCUSSION

Acetonitrile gives a number of primary and secondary ionic products when it undergoes ion/molecule collisions in the gas phase.

Table 1 presents the rate constants and product distributions measured with the SIFT apparatus for reactions of CH_3CN with three charge-transfer ions. A number of the observed product channels correspond to dissociative charge transfer. The channels leading to $CHCN^+$ in the reaction of N_2^+ and CH_2CN^+ in the reaction of CO^+ are interesting since they may be endothermic by as much as 8 or 9 kcal mol^{-1}. If endothermicity applies, then the occurrence of these two channels implies that excited N_2^+ and CO^+ species are involved. Long-lived ($\approx 10^{-2}$ s) electronically excited ions of N_2^+ and CO^+ and vibrationally excited ions of N_2^+ have been observed previously in several laboratories and their participation in ion/molecule reactions is

TABLE 1

Summary of rate constants and product distributions measured for the ion/molecule reactions with the SIFT technique at 298±2 K in helium at a total pressure of 0.34 torr and helium concentration of 1.1×10^{16} atoms cm^{-3}

Reaction		Branching ratios	k_{total} [a] (cm^3 $molecule^{-1}$ s^{-1})	ΔH_r (kcal mol^{-1})
$N_2^+ + CH_3CN$	$\rightarrow CH_3CN^+ + N_2$	0.15	2.1×10^{-9}	−73.5
	$\rightarrow CH_2CN^+ + H + N_2$	0.65		−27.4
	$\rightarrow CHCN^+ + H_2 + N_2$	0.20		+7.7
$CO^+ + CH_3CN$	$\rightarrow CH_3CN^+ + CO$	0.75	3.0×10^{-9}	−36.7
	$\rightarrow CH_2CN^+ + H + CO$	0.25		+9.4
$+ CH_3CN$	$\rightarrow CH_3CN^+ + CO_2$	1.0	2.5×10^{-9}	−31.8

[a] The accuracy of the rate constants is estimated to be better than ±30%.

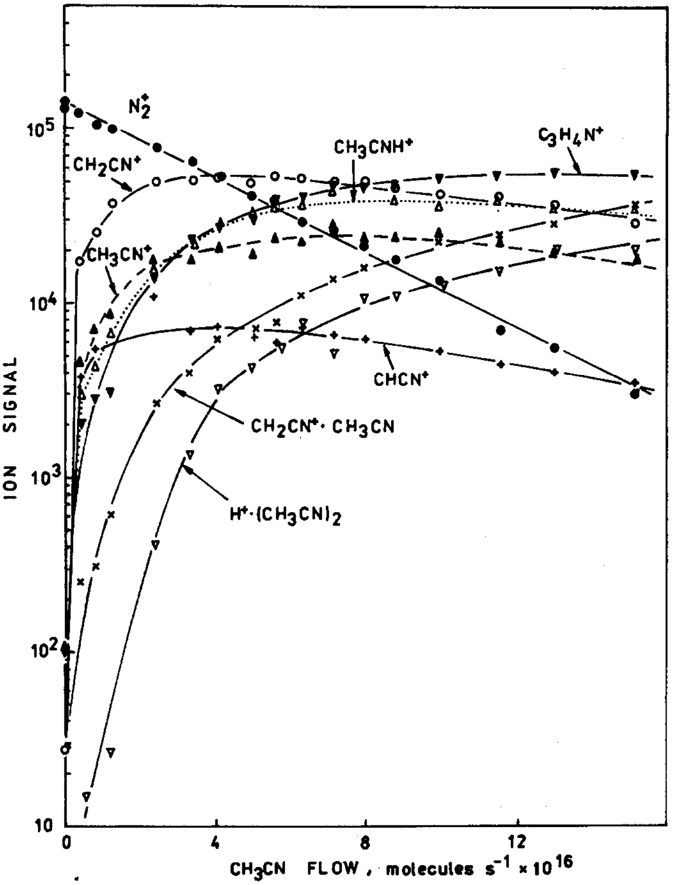


Fig. 1. The observed variation in ion signals for the addition of acetonitrile into a reaction region in which the presence of N_2^+ has been established with the SIFT technique. $P = 0.34$ torr; reactant velocity $\bar{v} = 6.3 \times 10^3$ cm s^{-1}; reaction path $L = 46$ cm; $T = 298$ K; concentration of carrier gas (He) $= 1.14 \times 10^{16}$ molecules cm^{-3}.

documented (see, for example, ref. 29). This is also qualitatively consistent with our HPMS study of the 1.9% CH_3CN/CO mixture in which a significant amount ($\approx$ 8% of the total ionization) of the ionic products arises from CH_2CN^+. The possibility of the formation of CH_2CN^+ in this mixture by loss of H_2 from excited CH_3CNH^+, produced by the reaction of CH_3CN^+ with CH_3CN, has been ruled out because such a reaction is not observed in the CH_3CN/H_2 and CH_3CN/CH_4 mixtures where the excited CH_3CNH^+ species are formed by highly exothermic proton transfer reactions of type (3).

Figure 1 shows the variation of the ionic products resulting from the addition of N_2^+ into a helium carrier gas containing CH_3CN as observed in

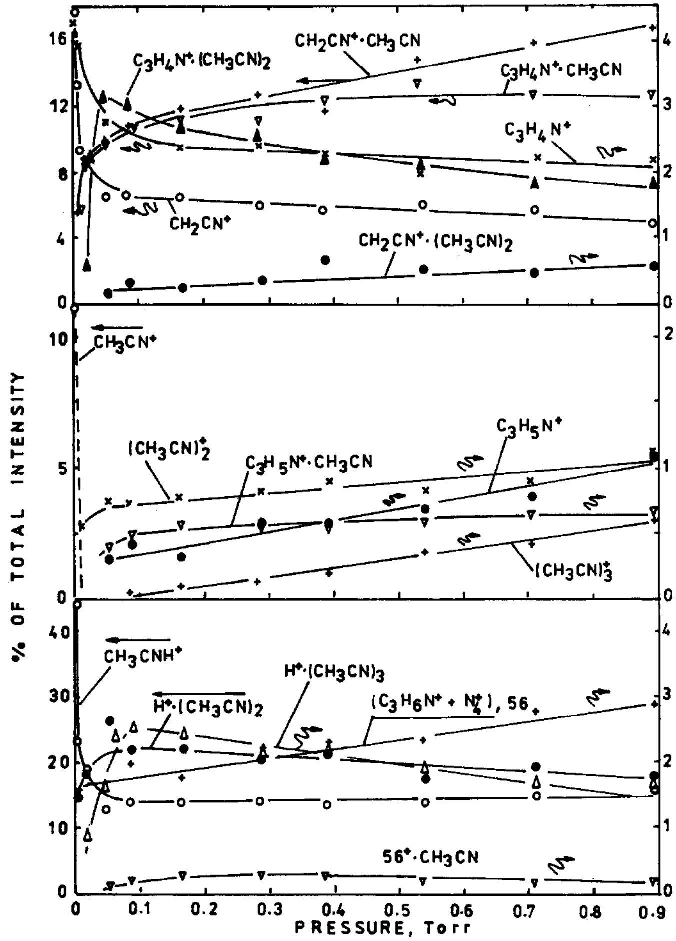


Fig. 2. Relative abundances of the major ions observed with HPMS in 1% CH_3CN/N_2 gas mixture as a function of the total pressure at 342 K (chamber 2).

the SIFT experiments. One can see the exponential decrease in the N_2^+ count rate with increasing concentration of CH_3CN (by increasing the flow rate) and the appearance of the primary products CH_3CN^+, CH_2CN^+, and $CHCN^+$ as well as the secondary products CH_3CNH^+, $CH_3CNH^+ \cdot CH_3CN$, $CH_2CN^+ \cdot CH_3CN$, and $C_3H_4N^+$. These ions were also observed in the HPMS experiments but, in this case, additional products were found (see Fig. 2). The ions observed in the latter study may be described by the following groups: $H^+ \cdot (CH_3CN)_n$, $(CH_3CN)_n^+$, $CH_2CN^+ \cdot (CH_3CN)_n$, $C_3H_3N^+ \cdot (CH_3CN)_n$, $C_3H_4N^+ \cdot (CH_3CN)_n$, $C_3H_5N^+ \cdot (CH_3CN)_n$, and $C_3H_6N^+ \cdot (CH_3CN)_n$. The clusters with $n \leqslant 4$ have been detected for the major ions at the highest pressures applied in this study. Rather good

TABLE 2

Heats of formation used in the work. Unless stated otherwise, all values are taken from ref. 44.

Species	ΔH°_{298} (kcal mol^{-1})	Species	ΔH°_{298} (kcal mol^{-1})
H	52.1	CO_2^+	223.3
CN	109 [a]	N_2^+	358.8
CO	−26.4	CH_3CO^+	157 [e]
CO_2	−93.8	$CH_3N_2^+$	223 [f]
HCN	32.3 [b]	$CHCN^+$	387.4 [d]
NCO	48 [c]	CH_2CN^+	300.2 [d]
C_2N	123 [a]	CH_3CN^+	306.2 [d]
CH_4	−17.8	CH_2CNH^+	240.8 [g]
CH_2CN	55 [a]	CH_3CNH^+	194.9 [h]
CH_3CN	20.9 [d]	$H_2C{=}\overset{+}{C}{-}N{=}CH_2$	240.8 [i]
CH_3^+	258	$C_3H_5N^+$	284.7 [j]
CO^+	295.6	$H_3C{-}\overset{+}{C}{=}N{-}CH_3$	185.2 [k]

[a] Ref. 8. [b] Ref. 45. [c] Ref. 46. [d] Ref. 34. [e] Ref. 47. [f] Ref. 48. [g] Ref. 49. [h] Ref. 14. [i] Ref. 36. [j] Ref. 50. [k] Ref. 40.

consistency exists between our HPMS data and previous ICR observations [8]. The significant difference in the product ions and their distibutions between the HPMS and SIFT results, which can be seen from Figs. 1 and 2, can also be reconciled. Analysis of the HPMS data indicates that the fragmentation produced in the collisions of N_2^+ with CH_3CN proceeds to a lesser extent (≈ 0.50 compared with 0.85 in the SIFT experiments, see Table 1) and the clustering of the product ions is more effective than in the SIFT experiments. This apparent discrepancy can be attributed to differences in the collisional stabilization efficiency of the buffer gases which is expected to be considerably higher (1.5–4 times) for N_2 than for He [30], as well as to differences in the N_2^{+*} quenching efficiency of the buffer gases which is known to be many orders of magnitude higher for N_2 than for He [31], in part because of the importance of symmetric charge transfer which is known to be fast [32].

An examination of Figs. 1 and 2, together with other data presented in this study, suggests the mechanistic pathways of ions derived from acetonitrile which are described below. The heats of formation used in this work are listed in Table 2.

Reactions of $CHCN^+$

The earlier ICR study showed that the reaction of $CHCN^+$ with CH_3CN has three channels which lead to the products CH_3CNH^+, $C_3H_3N^+$, and

$C_4H_3N_2^+$ [8]. The reaction pathway

$$\mathrm{CHCN^+ + CH_3CN \rightarrow CH_3CNH^+ + C_2N} \quad \Delta H_r = -90\ \mathrm{kcal\ mol^{-1}} \tag{4}$$

proposed in that work probably accounts for most of the decay in the $CHCN^+$ ion intensity observed in Fig. 1. Neither the cluster ion $CHCN^+ \cdot CH_3CN$ nor the $C_4H_3N_2^+$ species is observed as a product in the HPMS study. Small amounts of ions were detected at m/z 53 ($C_3H_3N^+$) and 94 ($C_3H_3N^+ \cdot CH_3CN$) and these support the occurrence of the reaction channel [8]

$$\mathrm{CHCN^+ + CH_3CN \rightarrow C_3H_3N^+ + HCN} \tag{5}$$

Reactions of CH_2CN^+

Analysis of the ionic products observed in the HPMS shows that the abundances of the $CH_2CN^+ \cdot (CH_3CN)_n$ and $C_3H_4N^+ \cdot (CH_3CN)_n$ ion groups are coupled. In the previous ICR study [8], the formation of $C_3H_4N^+$ is attributed to the reaction of $C_2H_2N^+$ with CH_3CN. Both our HPMS and SIFT results confirm that this channel occurs in competition with collisional stabilization of the intermediate complex ($CH_2CN^+ \cdots CH_3CN$). This is especially evident from the SIFT results shown in Fig. 1.

$$\mathrm{CH_2CN^+CH_3CN} \rightleftharpoons (\mathrm{CH_2CN^+}\ldots\mathrm{CH_3CN})^* - \begin{cases} \xrightarrow{\mathrm{M}} \mathrm{CH_2CN^+ \cdot CH_3CN} & (6) \\ \rightarrow \mathrm{C_3H_4N^+ + HCN} & (7) \end{cases}$$

However, we cannot confirm the reaction pathway ($CH_2CN^+ \cdots CH_3CN$) $\rightarrow C_5H_6N^+ \rightarrow C_3H_4N^+$ as suggested by Gray [8] for the production of $C_3H_4N^+$ from $C_2H_3N^+$ by the two-step mechanism involving the formation of the ($CH_2CN^+ \cdots CH_3CN$) and $C_5H_6N^+$ intermediates. In contrast to that work, we did not detect species at m/z 80 which could be assigned to the $C_5H_6N^+$ ion. We found that the product ratio $R = [CH_2CN^+ \cdot CH_3CN)_n]/[C_3H_4N^+ \cdot (CH_3CN)_n]$ increases with pressure (Fig. 3). This means that the collision of (CH_2CN^+–CH_3CN) with CH_3CN leads preferentially to the stabilization of this complex rather than to the production of the $C_3H_4N^+$ species. At relatively high pressures, both ions, CH_2CN^+ and $C_3H_4N^+$, undergo clustering reactions (Fig. 2)

$$\mathrm{CH_2CN^+ \cdot (CH_3CN)_{n-1} + CH_3CN \rightleftharpoons CH_2CN^+ \cdot (CH_3CN)_n} \tag{8}$$

$$\mathrm{C_3H_4N^+ \cdot (CH_3CN)_{n-1} + CH_3CN \rightleftharpoons C_3H_4N^+ \cdot (CH_3CN)_n} \tag{9}$$

Theoretical studies suggest that CH_2CN^+ can exist in different isomeric structures, such as the linear resonance forms [33] $H_2C^+{-}C{\equiv}N$ (44%),

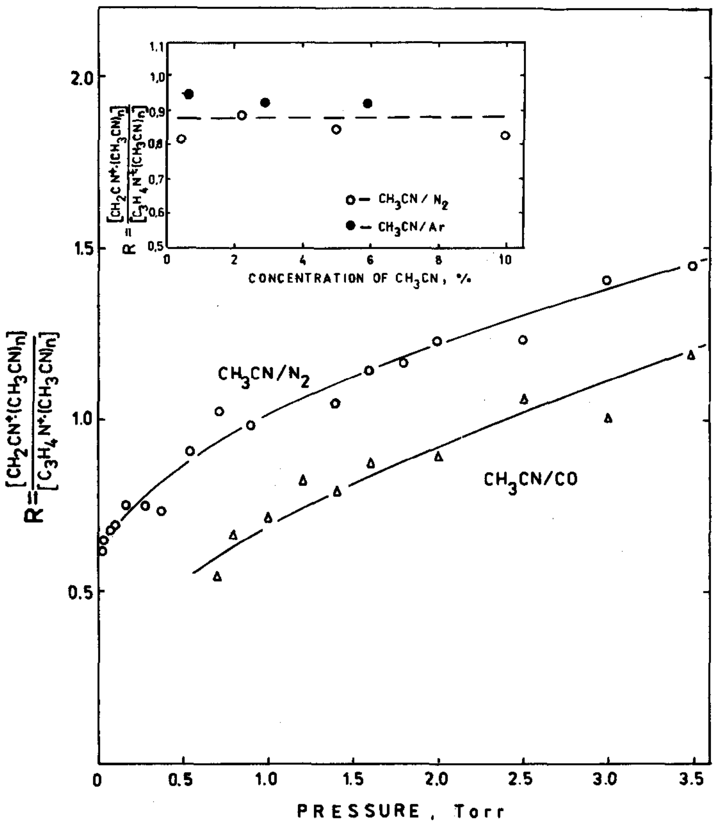
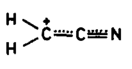
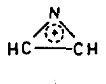


Fig. 3. Variations of the ion current ratio $R = [CH_2CN^+ \cdot (CH_3CN)_n]/[C_3H_4N^+ \cdot (CH_3CN)_n]$ with pressure in the gas mixtures 2% CH_3CN/N_2 and 3% CH_3CN/CO at 342 K. The insert shows the plot of the ratio $R = [CH_2CN^+ \cdot (CH_3CN)_n]/[C_3H_4N^+ \cdot (CH_3CN)_n]$ against concentration of CH_3CN for the CH_3CN/N_2 and CH_3CN/Ar mixtures at a total pressure of 1 torr and a gas temperature of 323 K. (HPMS; chamber 1.)

$H_2C^+{-}C^- = N^+$ (22.9%), $H_2C{=}C{=}N^+$ (15.8%), $H_2C{-}C^+{=}N$ (15.5%), and $H_2C^+{-}C^+{=}N^-$ (1.9%), represented here by the general structure **1** or the cyclic structure [34] denoted by **2**



1

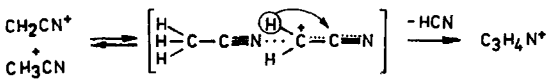


2

We presume that CH_2CN^+ produced in this study by reaction (2) has the linear structure given by **1**. The experiments performed with different CH_3CN concentrations at a constant total pressure of the gas mixture (see insert in Fig. 3) indicate that the product ratio R is independent of the

CH_3CN concentration. This suggests that the reactivity of the CH_2CN^+ species does not vary with the number of stabilizing collisions. These observations seem to provide an indirect argument against the structural conversion of the CH_2CN^+ reactant ion under the conditions of our experiments.

It appears plausible that the relative orientation of CH_2CN^+ and CH_3CN is important in the formation of the initial cofigurations of the ($CH_2CN^+ \cdots CH_3CN$) collision complex and determines the relative probabilities of the reaction channels (6) and (7). Since the main portion of the positive charge in structure **1** is localized at the CH_2– group [33], one may expect that the negatively charged cyano group of CH_3CN [35] will attack predominantly at this position. It seems likely that the intermediate complex formed in such an interaction will have the form **3** which leads to favourable production of $C_3H_4N^+$.



3

This scheme is consistent with the ICR study of $CH_3C^{14}N/CH_3C^{15}N$ and CH_3CN/CD_3CN systems which showed that HCN is eliminated only from the ionic reactant, i.e. CH_2CN^+ [8]. The third-body collision may, of course, change the energetic state and rearrange the particular collision complex configurations which determine the product ratio.

A recent collisional activation study indicates that the most probable structure of the $C_3H_4N^+$ species should be $H_2C{=}C^+{-}N{=}CH_2$ [36]. The conversion of this structure into those of lower energy is separated by an energy barrier of at least 27 kcal mol^{-1}.

Reactions of CH_3CN^+

When charge-transfer reagent gases were used in the HPMS experiments, the major primary ion was CH_3CN^+, which is produced by reaction (1). It is well known that this ion rapidly protonates the acetonitrile molecule, $k = 2 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} [9] to produce CH_3CNH^+ which reacts further with parent neutrals to yield higher clustered species, $H^+ \cdot (CH_3CN)_n$. This is displayed in Figs. 1 and 2.

Two other groups of ions, $(CH_3CN)_n^+$ and $C_3H_5N^+ . (CH_3CN)_n$, were detected in the HPMS (Fig. 2) when the primary ion CH_3CN^+ was generated by charge transfer. These groups of ions were not observed in the CH_3CN/CH_4 and CH_3CN/H_2 mixtures in which the proton-transfer reaction (3) produces CH_3CNH^+ as the primary ion from CH_3CN. We conclude from this that the CH_3CN^+ ion is the precursor for both groups, $(CH_3CN)_n^+$ and $C_3H_5N^+ \cdot (CH_3CN)_n$.

The formation of the $(CH_3CN)_n^+$ species can be attributed to the stabilized ionic products which arise from the reaction sequence starting from the collision complex $(CH_3CN^+ \cdots CH_3CN)$. On the basis of the data from ref. 37, one can expect that the contribution of the neutral dimer $(CH_3CN)_2$ to the production of the ionic species $(CH_3CN)_2^+$ is negligible under the conditions of our HPMS experiments.

For the reduction $C_3H_5N^+$, we considered the reactions

$$\mathrm{CH_3CN^+ + CH_3CN \rightarrow C_3H_5N^+ + HCN} \qquad \Delta H_r = -10 \text{ kcal mol}^{-1} \tag{10}$$

$$\mathrm{CH_2CN^+ + CH_3CN \rightarrow C_3H_5N^+ + CN} \qquad \Delta H_r = 73 \text{ kcal mol} \tag{11}$$

$$\mathrm{CH_2CN^+ + CH_3CN \rightarrow CH_2CNH^+ + CH_2CN} \qquad \Delta H_r = -25 \text{ kcal mol}^{-1} \tag{12}$$

$$\mathrm{CH_2CNH^+ + CH_3CN \rightarrow C_3H_5N^+ + HCN} \qquad \Delta H_r = 56 \text{ kcal mol}^{-1} \tag{13}$$

While reaction (10) is exothermic, the pathways leading to $C_3H_5N^+$ either directly from CH_2CN^+ [reaction (11)] or via the ketenimine ion, CH_2CNH^+, [reactions (12) and (13)] are highly endothermic and seem to be very improbable. Therefore we may suggest that the reaction of CH_3CN^+ with its parent neutral proceeds by the channels

$$\mathrm{CH_3CN^+ + CH_3CN}$$

$$\rightleftharpoons (\mathrm{CH_3CN^+ \ldots CH_3CN})^* \begin{cases} \xrightarrow{\mathrm{M}} (\mathrm{CH_3CN})_2^+ & (14) \\ \rightarrow \mathrm{CH_3CNH^+ + CH_2CN} & (15) \\ \rightarrow \mathrm{C_3H_5N^+ + HCN} & (10) \end{cases}$$

Channel (15) is exothermic by 77 kcal mol^{-1}. Reaction channel (10) has been proposed recently to describe the two-step mechanism of $C_3H_4N^+$ production from acetonitrile [36]

$$\mathrm{CH_3CN^+ + CH_3CN} \xrightarrow{-\mathrm{HCN}} \mathrm{C_3H_5N^+} \xrightarrow{-\mathrm{H}} \mathrm{C_3H_4N^+}$$

At relatively high pressures, as in our HPMS experiments, the $C_3H_5N^+$ ion is probably collisionally stabilized and udergoes clustering reactions with CH_3CN in a manner similar to the other two species, CH_3CNH^+ and $(CH_3CN)_2^+$, produced in the reaction of CH_3CN^+ with CH_3CN. This is seen

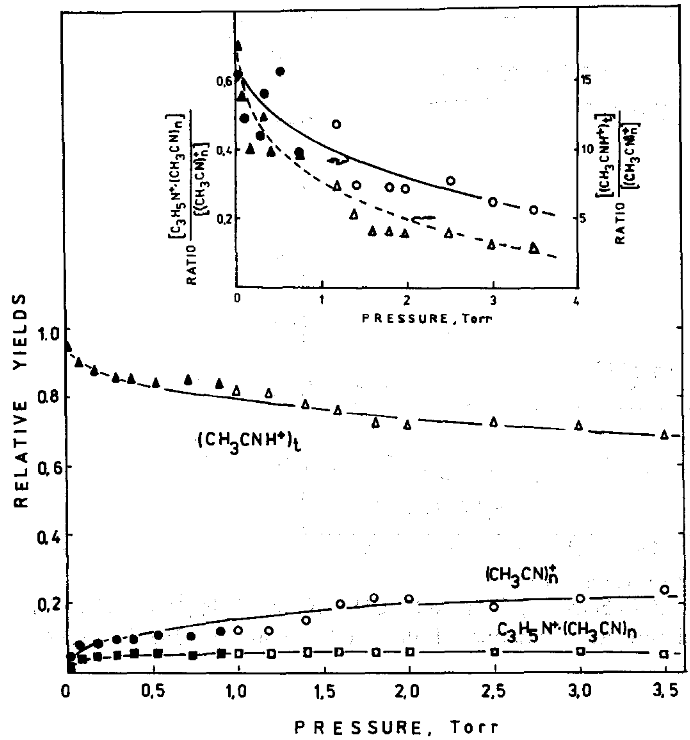


Fig. 4. Variation with pressure of the relative yields of ions (expressed as a fraction of the sum of the ion concentrations $[(CH_3CN)_n^+]+[C_3H_5N^+\cdot(CH_3CN)_n]+[(CH_3CNH^+)_t]$, where $[(CH_3CNH^+)_t]$ is the initial concentration of CH_3CNH^+) in 2% CH_3CN/N_2 mixture at 342 K. The insert shows the plot of ion concentration ratios $[C_3H_5N^+\cdot(CH_3CN)_n]/[(CH_3CN)_n^+]$ and $[(CH_3CNH^+)_t]/[(CH_3CN)_n^+]$ against pressure for the 2% CH_3CN/N_2 mixture. (HPMS; open symbols, chamber 1; solid symbols, chamber 2.)

in Fig. 2 and the interpretation correlates well with the data given in Fig. 4, which shows that, while the amount of $(CH_3CN)_n^+$ increases, the sum of ionic products derived from CH_3CNH^+, denoted here as $[(CH_3CNH^+)_t]$, decreases with pressure in what may be ascribed to collisional stabilization of the collision complex ($CH_3CN^+ \cdots CH_3CN$). A decrease with pressure of the ionic product ratios $[(CH_3CNH^+)_t]/(CH_3CN)_n^+]$ and $[C_3H_5N^+\cdot(CH_3CN)_n]/[(CH_3CN)_n^+]$ is observed as a result (see insert in Fig. 4). At the same time, the $C_3H_5N^+\cdot(CH_3CN)_n$ species, which represents only a minor portion of the product distribution, shows a small increase in the abundance when the pressure rises. This indicates that collisional stabilization of the $C_3H_5N^+$ species produced by reaction channel (10) occurs and that the probability of its decomposition into $C_3H_4N^+$ decreases.

It follows from the collisional activation spectra reported in ref. 36 that $C_3H_5N^+$ is likely to have a linear structure of the type $H_3C{-}C^+{=}N{-}C^{\cdot}H_2$.

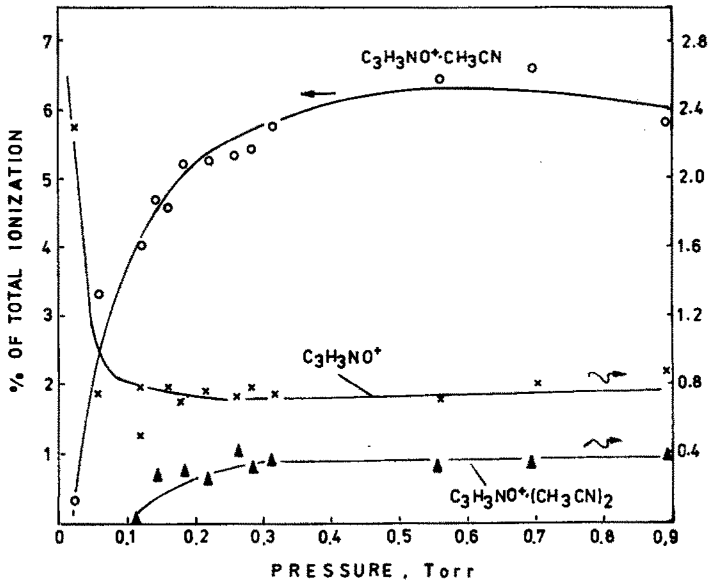


Fig. 5. Relative abundances of $C_3H_3NO^+$, $C_3H_3NO^+ \cdot CH_3CN$ and $C_3H_3NO^+ \cdot (CH_3CN)_2$ in the 2% CH_3CN/CO mixture as a function of the total pressure at 342 K. (HPMS; chamber 2.)

Initially, the ionic product in channel (15) is likely to have the protonated acetonitrile structure $H_3C{-}C^+{=}NH$. However, since this channel is highly exothermic, the question arises as to whether this species, perhaps being excited, can rearrange to other possible isomers [38]. On the basis of the experimental data obtained by the collision-induced dissociation technique [11] and by proton affinity tests for the $C_2H_4N^+$ ions generated by proton transfer to CH_3CN and CH_3NC, as well as the highly exothermic (95 kcal mol^{-1}) association reaction of CH_3^+ with HCN [14], one may presume that the structural conversion of $CH_3{-}C^+{=}N{-}H$ is not very probable in this case.

In the CH_3CN/CO mixture, significant quantities of ions at *m/z* 69 [$C_3H_3NO^+$], 110 [$C_3H_3NO^+ \cdot CH_3CN$], and 151 [$C_3H_3NO^+ \cdot (CH_3CN)_2$] were found (Fig. 5). The observation of these species suggests the sequence of reactions (16)–(18), which is likely to begin with the formation in reaction (16) of the adduct $H_3C{-}C^+{=}N{-}CO$

$$CH_3CN^+ + CO \rightarrow C_3H_3NO^+ \qquad (16)$$

$$C_3H_3NO^+ + CH_3CN \rightarrow C_3H_3NO^+ \cdot CH_3CN \qquad (17)$$

$$C_3H_3NO^+ \cdot CH_3CN + CH_3CN \rightarrow C_3H_3NO^+ \cdot (CH_3CN)_2 \qquad (18)$$

The observation in the HPMS experiments with the CH_3CN/CO and CH_3CN/CO_2 mixtures of considerable amounts of ions at *m/z* 43, 84, and

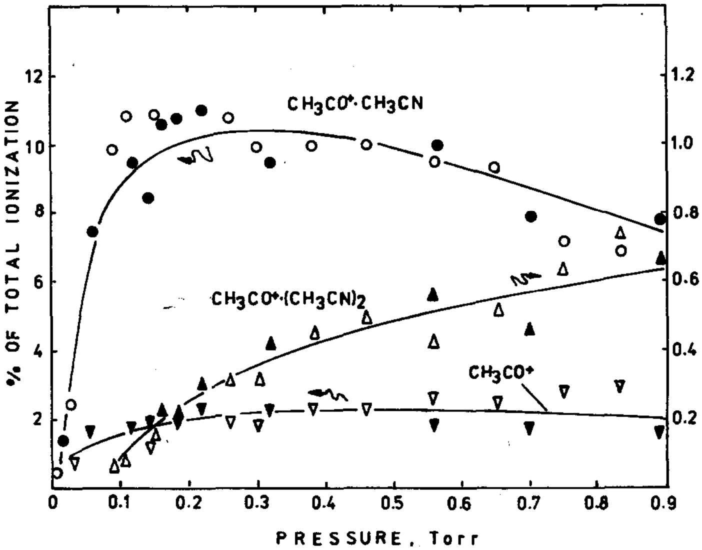


Fig. 6. Relative abundances of ions at *m/z* 43 [CH_3CO^+], 84 [$CH_3CO^+ \cdot CH_3CN$], and 125 [$CH_3CO^+ \cdot (CH_3CN)_2$] in the 2% CH_3CN/CO (solid symbols) and 1% CH_3CN/CO_2 (open symbols) mixtures as a function of the total pressure at 342 K. (HPMS; chamber 2.)

125 (Fig. 6), which can be assigned to CH_3CO^+, $CH_3CO^+ \cdot CH_3CN$, and $CH_3CO^+ \cdot (CH_3CN)_2$, respectively, may indicate the occurrence of the reactions

$$CH_3CN^+ + CO \rightarrow CH_3CO^+ + CN \qquad \Delta H_r = -13 \text{ kcal mol}^{-1} \qquad (19)$$

$$CH_3CN^+ + CO_2 \rightarrow CH_3CO^+ + NCO \qquad \Delta H_r = -7 \text{ kcal mol}^{-1} \qquad (20)$$

$$CH_3CO^+ + CH_3CN \rightleftharpoons CH_3CO^+ \cdot CH_3CN \qquad (21)$$

$$CH_3CO^+ \cdot CH_3CN + CH_3CN \rightleftharpoons CH_3CO^+ \cdot (CH_3CN)_2 \qquad (22)$$

The SIFT technique was used to measure the reactions of CH_3CN^+ with CO and CO_2 in helium buffer gas at 0.34 torr and 1.1×10^{16} atoms cm^{-3} at 296 K. No reaction was observed with CO_2, $k \leqslant 1.5 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. The reaction with CO was slow, $k = (2.1 \pm 0.5) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, but the products of both reactions (16) and (19) were observed in the proportion of 2 to 3.

Reactions of CH_3CNH^+

The reaction (23) of CH_3CNH^+ with its parent molecule initiates the reaction sequence (24), producing the proton-bound acetonitrile clusters,

$H^+ \cdot (CH_3CN)_n$, which are the most abundant species in all systems studied with the HPMS.

$$CH_3CNH^+ + CH_3CN \rightleftharpoons H^+ \cdot (CH_3CN)_2 \qquad (23)$$

$$H^+ \cdot (CH_3CN)_{n-1} + CH_3CN \rightleftharpoons H^+ \cdot (CH_3CN)_n \qquad (24)$$

The HMPS results also suggest that CH_3CNH^+ leads to the production of small amounts of the $C_3H_6H^+$ ion by the reaction

$$CH_3CNH^+ + CH_3CN \rightarrow C_3H_6N^+ + HCN \quad \Delta H_r = +2 \text{ kcal mol}^{-1} \qquad (25)$$

This ion also clusters with CH_3CN

$$C_3H_6N^+ \cdot (CH_3CN)_{n-1} + CH_3CN \rightleftharpoons C_3H_6N^+ \cdot (CH_3CN)_n \qquad (26)$$

The suggestion of reaction (25) is based on the observation of the ionic species at m/z 56 and the clustered products $[56^+ \cdot (CH_3CN)_n]$ in all the

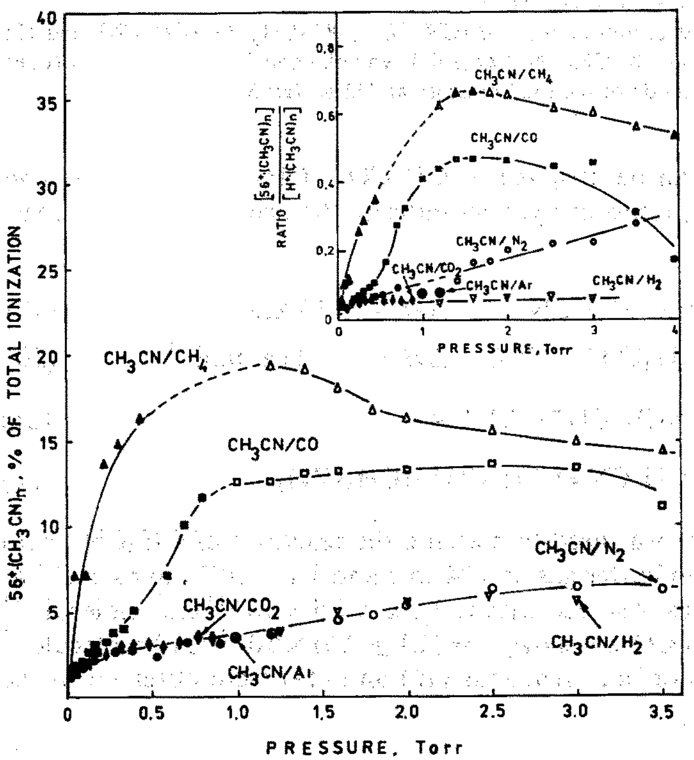


Fig. 7. Relative abundances of the $[56^+ \cdot (CH_3CN)_n]$ ions observed with HPMS as a function of the total pressure at 342 K in the mixtures 2% CH_3CN/CH_4, 2% CH_3CN/CO, 1% CH_3CN/CO_2, 2% CH_3CN/N_2, 1% CH_3CH/H_2, and 2% CH_3CN/Ar. The insert shows the plot of the ion current ratio $[56^+ \cdot (CH_3CN)_n]/[H^+ \cdot (CH_3CN)_n]$ against pressure for different gas mixtures. (Open symbols, chamber 1; solid symbols, chamber 2.)

mixtures studied (Fig. 7). The considerably higher abundances of these species found in the CH_3CN/CH_4 and CH_3CN/CO mixtures, and also the higher product ratio $[56^+\cdot(CH_3CN)_n]/[H^+\cdot(CH_3CN)_n]$ obtained for these mixtures and for the CH_3CN/N_2 mixture, in comparison with those for the CH_3CN/H_2, CH_3CN/CO_2, and CH_3CN/Ar mixtures (see insert of Fig. 7), is assigned to the contribution of ionic products arising from sources other than the reaction pathway (25).

In the CH_3CN/CO and CH_3CN/N_2 mixtures, the well-known association reactions

$$CO^+ + CO \rightarrow (CO)_2^{+*} \xrightarrow{M} (CO)_2^+ \qquad (27)$$

$$N_2^+ + N_2 \rightarrow (N_2)_2^{+*} \xrightarrow{M} (N_2)_2^+ \qquad (28)$$

may be important in the production of the ions at m/z 56 [39].

In the CH_3CN/CH_4 mixture, the reaction

$$CH_3^+ + CH_3CN \rightarrow C_3H_6N^+ \quad \Delta H_r = -94 \text{ kcal mol}^{-1} \qquad (29)$$

is believed to lead to the ion with m/z 56.

Because reaction (25) is slightly endothermic (or thermoneutral), one may expect that the nitrilium ion, $H_3C{-}C^+{=}N{-}CH_3$, is its stable final product. The heat of formation of the nitrilium ion, $\Delta H_f(CH_3C^+NCH_3) = 185.2$ kcal mol^{-1} [40], is lower than that of protonated ethyl cyanide, $\Delta H_f(C_2H_5CNH^+) = 201$ kcal mol^{-1} [41]. It should be mentioned that reactions similar to (25) have been observed recently in methyl, ethyl, and *tert*-butyl isocyanides [40]. Presumably, the reaction of CH_3NCH^+ with CH_3NC also yields the nitrilium ion.

Reactions of alkyl ions with CH_3CN

The rapid association reaction (29) of CH_3^+ with CH_3CN was observed in the SIFT and HPMS studies. The rate constant at 0.34 torr was measured with the SIFT technique to be 4.0×10^{-9} cm^3 molecule^{-1} s^{-1}, which corresponds to that reported recently by Knight et al. [14].

It is likely that the collision of CH_3^+ with CH_3CN leads initially to the formation of the nitrilium ion which, in this case, is expected to be highly excited (94 kcal mol^{-1}) due to the large exothermicity of reaction (29). The final structure of the resultant $C_3H_6H^+$ ion depends on the barriers to isomerization and the process of relaxation.

The HPMS experiments indicate that the association of higher alkyl ions, i.e. $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$, also occurs with the neutral CH_3CN molecule (Fig. 8), presumably by the reaction

$$R^+ + CH_3CN \rightarrow RNC^+CH_3 \qquad (30)$$

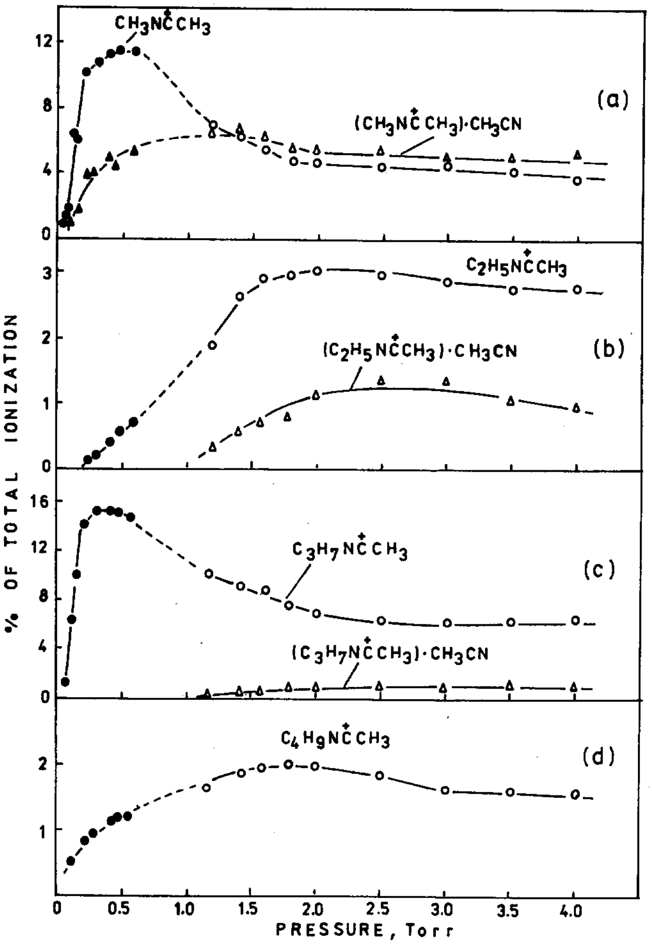


Fig. 8. Relative abundances of ions observed with HPMS in the 2% CH_3CN/CH_4 mixture as a function of the total pressure at 342 K. (Open symbols, chamber 1; solid symbols, chamber 2.) The alkyl ions CH_3^+, $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ are produced from methane by the reaction sequence [42] $CH_5^+ \xrightarrow{-H_2} CH_3^+ \xrightarrow{CH_4} C_2H_5^+ \xrightarrow{CH_4} C_3H_7^+ \xrightarrow{CH_4} C_4H_9^+$. Some amounts of $C_3H_7^+$ are also produced by the reactions of CH_5^+ and $C_2H_5^+$ with propane [43] present in the system as an impurity ($CH_5^+ + C_3H_8 \rightarrow C_3H_7^+ + CH_4$ and $C_2H_5^+ + C_3H_8 \rightarrow C_3H_7^+ + C_2H_6$).

where $R^+ = CH_3^+$, $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$, which is analogous to reaction (29).

The possibility of formation of the nitrilium ions, RNC^+CH_3, in the sequential reactions given by

$$CH_3NC^+CH_3 + CH_3CN \rightarrow C_2H_5NC^+CH_3 + HCN \tag{31}$$

$$C_2H_5NC^+CH_3 + CH_3CN \rightarrow C_3H_7NC^+CH + HCN \tag{32}$$

has been eliminated by the SIFT study which showed that reaction (31) involving thermalized $CH_3NC^+CH_3$ ions does not occur.

Finally, the HPMS experiments show (Fig. 8) that the RNC^+CH_3 ions produced in the CH_3CN/CH_4 mixture react further with CH_3CN to yield $RNC^+CH_3 \cdot CH_3CN$.

$$RNC^+CH_3 + CH_3CN \rightarrow RNC^+CH_3 \cdot CH_3CN \tag{33}$$

CONCLUSIONS

The results presented here indicate that the reactions of N_2^+, CO^+, and CO_2^+ observed in this study proceed exclusively by charge transfer and that electronically excited N_2^+ and CO^+ are involved.

The reaction of CH_2CN^+ with CH_3CN has been established to proceed by two primary competing pathways, collisional stabilization and fragmentation of the collision complex, under the high-pressure conditions employed in this study. Ionized acetonitrile reacts with its neutral parent mainly by proton transfer along with two other pathways of reaction: collisional stabilization of the intermediate complex ($CH_3CN^+ \cdots CH_3CN$) and loss from it of HCN. Formation of the cluster ion, $H^+ \cdot (CH_3CN)_2$, is the major pathway for the reaction of protonated acetonitrile with acetonitrile, but a minor channel leading to the nitrilium ion, $H_3CNC^+CH_3$, is also observed. The latter ion is also produced at near the collision limit in the reaction of CH_3^+ with acetonitrile. Adduct formation is also observed in the reactions of the higher alkyl ions $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ with acetonitrile as well as in the reaction of CH_3CN^+ with CO. Both the alkylation and carbonylation reactions may be important channels for converting acetonitrile in the terrestrial atmosphere.

ACKNOWLEDGEMENTS

The research at the Polish Academy of Sciences was supported by the Central Program for Fundamental Research CPBP-01.19. At York University, the research was supported by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

1 (a) F. Arnold, H. Böhringer and G. Henschen, Geophys. Res. Lett., 5 91978) 653. (b) E. Arijs, D. Nevejans and J. Ingels, Nature (London), 288 (1980) 684. (c) F. Arnold, G. Henschen and E.E. Ferguson, Planet. Space Sci., 29 (1981) 185.

2 (a) K.H. Becker and A. Jonescu, Geophys. Res. Lett., 9 (1982) 1349. (b) J.R. Snider and G.A. Dawson, Geophys. Res. Lett., 11 (1984) 241.

3 (a) P.M. Solomon, K.B. Jefferts, A.A. Penzias and R.W. Wilson, Astrophys. J. Lett., 168 (1971) 107. (b) P.M. Solomon, A.A. Penzias, K.B. Jefferts and R.W. Wilson, Astrophys. J. Lett., 185 (1973) 63. (c) F.J. Lovas, D.R. Johnson, D. Buhl and L.E. Snyder, Astrophys. J., 209 (1976) 770. (d) B.L. Ulich and E.K. Conklin, Nature (London), 240 (1974) 121. (e) R.A. Linke, S.E. Cummins, S. Green and P. Thaddeus, in R.S. Roger and P.E. Dewdney (Eds.), Regions of Recent Star Formation, Reidel, Dortrecth, 1982, p. 391.

4 H.E. Matthews and T.J. Sears, Astrophys. J. Lett., 267 (1983) 53.

5 (a) H. Böhringer and F. Arnold, Nature (London), 290 (1981) 321. (b) G. Brasseur and A. Chatel, Ann. Geophys., 1 (1983) 173. (c) G. Brasseur, E. Arijs, A. De Rudder, D. Nevejaus and J. Ingels, Geophys. Res. Lett., 10 (1983) 725. (d) G. Brasseur, R. Zellner, A. De Rudder and E. Arijs, Geophys. Res. Lett., 12 (1985) 117. (e) A. Arijs and G. Brasseur, J. Geophys. Res., 91 (1986) 4003.

6 (a) E. Herbst and W. Klemperer, Astrophys. J., 185 (1973) 505. (b) W.T. Huntress, Jr. and V.G. Anicich, Astrophys. J., 208 (1976) 237. (c) H.J. Schiff and D.K. Bohme, Astrophys. J., 232 (1979) 740. (d) D.J. De Frees, A.D. McLean and E. Herbst, Astrophys. J., 293 (1985) 236.

7 J.L. Franklin, Y. Wada, P. Natalis and P.M. Nierl, J. Phys. Chem., 70 (1966) 2353.

8 G.A. Gray, J. Am. Chem. Soc., 90 (1968) 6002.

9 J. Vogt and J.L. Beauchamp, J. Am. Chem. Soc., 97 (1975) 6682.

10 M. Meot-Ner, J. Am. Chem. Soc., 100 (1978) 4694.

11 A.J. Illies, S. Liu and M.T. Bowers, J. Am. Chem. Soc., 103 (1981) 5674.

12 A.B. Raksit, H.J. Schiff and D.K. Bohme, Int. J. Mass Spectrom. Ion Processes, 56 (1984) 321.

13 P. Ausloos and S.G. Lias, Int. J. Mass Spectrom. Ion Processes, 58 (1984) 165.

14 J.S. Knight, C.G. Freeman and M.J. McEwan, J. Am. Chem. Soc., 108 (1986) 1404.

15 M. Meot-Ner, Z. Karpas and C.A. Deakyne, J. Am. Chem. Soc., 108 (1986) 3918.

16 H. Wincel, Int. J. Mass Spectrom. Ion Phys., 9 (1972) 267.

17 S. Włodek, Z. Łuczyński and H. Wincel, Int. J. Mass Spectrom. Ion Phys., 35 (1980) 39.

18 Z. Łuczyński, S. Włodek and H. Wincel, Radiat. Phys. Chem., 11 (1978) 55.

19 Z. Łuczyński, W. Malicki and H. Wincel, Int. J. Mass Spectrom. Ion Phys., 15 (1974) 321.

20 S. Włodek, Z. Łuczyński and H. Wincel, Int. J. Mass Spectrom Ion Processes, 67 (1982) 221.

21 Z. Łuczyński and H. Wincel, Int. J. Mass Spectrom. Ion Phys., 14 (1974) 29.

22 MCT Atlas Werke, Bremen, F.R.G.

23 G.J. Mackay, G.D. Vlachos, D.K. Bohme and H.J. Schiff, Int. J. Mass Spectrom. Ion Phys., 36 (1980) 259.

24 A.B. Raksit and D.K. Bohme, Int. J. Mass Spectrom Ion Processes, 55 (1983) 69.

25 Extranuclear Laboratories, Pittsburgh, PA 15238, U.S.A., Model 041-3.

26 Fluka AG, CH-9470 Buchs, Switzerland.

27 Matheson, Coleman and Bell, Norwood, OH 45212, U.S.A.

28 Union Carbide, Danbury, CT 06817, U.S.A.

29 (a) K.R. Ryan and H.M. Stock, Int. J. Mass Spectrom. Ion Phys., 21 (1976) 389. (b) E. Alge and W. Lindinger, J. Geophys. Res., 86 (1981) 871.

30 L.M. Babcock and G.E. Streit, J. Phys. Chem., 88 (1984) 5025.

31 M. Tichy, A.B. Raksit, D.G. Lister, N.D. Twiddy, N.G. Adams and D. Smith, Int. J. Mass Spectrom Ion Phys., 29 (1979) 231.

32 N.G. Adams and D. Smith, Astrophys. J. Lett., 247 (1981) L123.

33 F. Delbecq, J. Org. Chem., 49 (1984) 4838.

34 P.W. Harland and B.J. McIntosh, Int. J. Mass Spectrom. Ion Processes, 67 (1985) 29.

35 J.B. Moffat, Int. J. Quantum Chem., 19 (1981) 771.

36 W. Heerma, M.M. Sarneel and G. Gijkstra, Org. Mass Spectrom., 21 (1986) 681.

37 S.V. Olesik and J.W. Taylor, Int. J. Mass Spectrom. Ion Processes, 57 (1984) 299.

38 E.U. Würthwein, J. Org. Chem., 49 (1984) 2971.

39 M.S.B. Munson, F.H. Field and J.L. Franklin, J. Chem. Phys., 37 (1962) 1790.

40 N. Meot-Ner and Z. Karpas, J. Phys. Chem., 90 (1986) 2206.

41 F.H. Field and J.L. Franklin, Electron Impact Phenomena, Academic Press, New York, 1957.

42 E. Heckel and R.J. Hanrahan, J. Chem. Phys., 62 (1975) 1027.

43 M.S.B. Munson and F.H. Field, J. Am. Chem. Soc., 87 (1965) 3294.

44 R.R. Bernecker and F.A. Long, J. Phys. Chem., 65 (1961) 1565.

45 V.G. Anicich, W.T. Huntress, Jr. and M. J. McEwan, J. Phys. Chem. 90 (1986) 2446.

46 B.J. Sullivan, G.P. Smith and D.R. Crosley, Chem. Phys. Lett., 96 (1983) 307.

47 J.C. Traeger, R.G. McLaughlin and A.J.C. Nicholson, J. Am. Chem. Soc., 104 (1982) 5318.

48 M.S. Foster and J.L. Beauchamp, J. Am. Chem. Soc. 94 (1972) 2425.

49 G.D. Willett and T. Baer, J. Am. Chem. Soc., 102 (1980) 6774.

50 E.K. Chess, R.L. Lapp and M.L. Gross, Org. Mass Spectrom., 17 (1982) 475.