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Proton affinity of cyanogen and association reactions of $C_2N_2H^+$ and $C_2N_2CH_3^+$

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Abstract

The proton affinity (PA) of cyanogen (C_2N_2) was redetermined through selected ion flow tube (SIFT) measurement of the rate coefficients of the reaction $C_2H_3^+ + C_2N_2 = C_2N_2H^+ + C_2H_2$ in both directions. The observed $\Delta G^o{}_{300} = -6.1$ kJ mol^{-1} and derived $\Delta H^o = -10.6$ kJ mol^{-1}, and previous equilibrium results with CH_3Cl, give PA(C_2N_2) = 651.2 ± 2 kJ mol^{-1}. The results are consistent with the recently revised PA(CH_3Cl) = 647.3 kJ mol^{-1}, and in good agreement with recent high-level theoretical values of PA(C_2N_2) = 655–657 kJ mol^{-1}. We also observed that SO_2H^+ transfers a proton to C_2N_2 as well as to C_2H_2, and that in the reverse direction, the new reaction $C_2H_3^+ + SO_2 \rightarrow CH_2SOH^+ + CO$ occurs but no proton transfer, indicating that PA(SO_2) < 641.1 kJ mol^{-1}. The methylated species $C_2N_2CH_3^+$ does not transfer a methyl cation to HCN, CH_3CN, $(CH_3)_2CO$ and $(CH_3)_3N$. However, association is observed in these systems and in the reactions of $C_2N_2H^+$ with C_2H_2 and SO_2. These processes can contribute to the astrochemical synthesis of complex heteroatom containing organics. In particular, we observe the apparently covalent $C_2N_2H^+ \cdot C_2H_2$ adduct, an isomer of deprotonated 1,4-diazine, which suggests that similar reactions of other C_2N_2 containing ions and acetylenes can yield pyrimidine nucleic bases by simple ion-molecule processes. (Int J Mass Spectrom 179/180 (1998) 285–291) © 1998 Elsevier Science B.V.

Keywords: Proton affinity; Methyl cation affinity; Ion-molecule condensation; Interstellar synthesis

1. Introduction

The proton affinity and ion chemistry of cyanogen were subject to several investigations, motivated by the roles of cyanides in astrochemistry [1–8]. Previous studies of cyanogen (NCCN, denoted hereafter as C_2N_2) ion chemistry concern the reactions of $C_2N_2^{\cdot+}$ [4] and proton transfer reactions applied for proton affinity measurements [2–4].

The current tabulated proton affinity of C_2N_2 is 674.7 kJ mol^{-1} [9], based on published bracketing and equilibrium measurements [2–4]. However, recent theoretical calculations by Botschwina and Sebald using CEPA-1 calculations yielded PA(C_2N_2) = 657 ± 5 kJ mol^{-1} [10], and G2, G2Q, CNS-Q and CBS-APNO calculations by Petrie yielded PA(C_2N_2) = 655 kJ mol^{-1} [11]. Petrie pointed out that these values and new PA determinations of one of the reference compounds, CH_3Cl [12], indicate

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Dedicated to Professor Fulvio Cacace in recognition of his outstanding contributions for many decades to gas-phase ion chemistry and physics.

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inconsistencies in several reported proton transfer reactions.

The literature measurements included proton transfer equilibrium with CH_3Cl and apparent equilibrium with C_2H_4 [4]. These results appeared consistent because the PAs of CH_3Cl and C_2H_4 were believed to be similar. However, the proton affinity of CH_3Cl has been revised recently [12] and the new tabulated value is 647.3 kJ mol^{-1} [9]. The published equilibrium reactions of CH_3Cl with C_2N_2 [4], combined with our new results below, lead to PA(C_2N_2) of 651.2 ± 2 kJ mol^{-1}, a value that is also supported by new high level theoretical calculations [10,11]. This value is substantially lower than PA(C_2H_4) = 680.5 kJ mol^{-1} [9], and the reported proton transfer reaction from $C_2H_5^+$ to C_2N_2 [4] is then endothermic by 29.3 kJ mol^{-1}. An endothermicity of this magnitude leads to a rate coefficient of about $k_{\text{collision}}\exp(-\Delta H/RT) = 6.9 \times 10^{-15}$ $cm^3\ s^{-1}$ which is too slow to be observed by the ion cyclotron resonance (ICR) and SIFT techniques. In fact, there are two conflicting reports on this reaction. An ICR measurement showed no reaction [3], which would be consistent with the endothermicity. However, a SIFT report showed slow but observable proton transfer with $k = 8.4 \times 10^{-11}$ $cm^3\ s^{-1}$ [4], which is much faster than predicted from a revised low PA(C_2N_2).

Further inconsistencies in the literature pointed out by Petrie [11] are the previous SIFT report of proton transfer from $C_2H_5{}^+$ to CH_3Cl [4], which is incompatible with the new low PA of CH_3Cl. In addition, fast proton transfer from SO_2H^+ to C_2N_2 was reported [2], which would be inconsistent with the recent tabulated value of PA(SO_2) = 672.3 kJ mol^{-1} [9], if this value and the low PA(C_2N_2) are both correct. The present article aims to resolve these inconsistencies.

In addition to $C_2N_2{}^{\cdot+}$ and $C_2N_2H^+$, another ionized form of C_2N_2, the methylated species CH_3NCCN^+ is likely to be found in space environments. In fact, this ion can form readily through the association of the common interstellar ion CH_3^+ with C_2N_2 [4,13]. In turn, CH_3NCCN^+ may methylate many organic molecules that have a higher PA than C_2N_2, and are therefore also expected to have a higher methyl cation affinity (MCA) than C_2N_2. These reactions would constitute low-energy alternatives to direct alkylation reactions of the type studied both by the JPL/McEwan [14,15] and the Cacace groups [16–18], and would be similar to methyl cation transfer from $CH_3OH_2^+$ to H_2CO and CH_3OH [19,20]. On the other hand, CH_3NCCN^+ may be strongly covalently bonded and may not transfer methyl cations. In this case, this ion, as well as the protonated analogue $NCCNH^+$, may be available for nucleophilic condensation with unsaturated compounds leading to complex molecules. We shall examine the association reactions of $NCCNH^+$ and CH_3NCCN^+ in these respects.

2. Experimental

The measurements reported here were performed at room temperature (295 ± 10) K using the new flowing afterglow–selected ion flow drift tube (FA/SIFDT) apparatus at Canterbury University. The original version of the selected ion flow tube (SIFT) at the University of Canterbury has been described in detail elsewhere [21]. This instrument has been modified recently with the addition of a drift tube and flowing afterglow ion source. This new source is similar in design to that used by Van Doren et al. [22]. Further details of the modified instrument will be described elsewhere [23]. The protonated ions (e.g. $C_2H_5^+$, $C_2N_2H^+$ and $CH_3\ ClH^+$), along with other ions were formed in the flowing afterglow flow tube and injected into the upstream mass spectrometer section where they were mass selected before injection into the flow reactor section of the instrument. When a protonated ion was studied, a moveable electron impact ioniser in conjunction with a moveable gas inlet was used. The electron impact source generated the ion H_3^+ from hydrogen added through the movable inlet in a Helium carrier gas. The $H_3{}^+$ then transferred its proton to the reactant gas requiring protonation. When the methyl cation transfer reactions were studied, we usually reverted to a microwave discharge source and methylated the ion of interest before injection. In many cases, ions produced from CH_3Br were used as the methylating reactants.

We estimate that the rate coefficients measured in the present work are accurate to ±15% and the branching ratios to ±10%. The reactant species (with

Table 1
Proton transfer kinetics and thermochemistry

Reactants	Products	Branching ratio	k_{obs}[a]	k_{PT}[a]	k_{col}[a]	ΔG°_{300}[b,c]	ΔH^0[b,d]	PA(C_2N_2)[b,e]
Reactions involving C_2N_2 and $C_2N_2H^+$								
$C_2H_3^+ + C_2N_2$	$C_2N_2H^+ + C_2H_2$	0.75	1.1	0.83[f]	1.6	−6.1	−10.6	651.7
	Adduct	0.25						
$C_2N_2H^+ + C_2H_2$	$C_2H_3^+ + C_2N_2$	0.15	0.48	0.072	1.1			
	Adduct	0.85						
$CH_3ClH^+ + C_2N_2$	$C_2N_2H^+ + CH_3Cl$	1.0[g]	0.20[g]	0.20[g]	1.0	−0.6	−3.3	650.6
$C_2N_2H^+ + CH_3Cl$	$CH_3ClH^+ + C_2N_2$	1.0	0.16[h]	0.16	2.1			
$SO_2H^+ + C_2N_2$	$C_2N_2H^+ + SO_2$	1.0	1.20	1.20	1.0			
$C_2N_2H^+ + SO_2$	Adduct	1.0	0.030		1.7			
$C_2H_5^+$ C_2N_2	Adduct	1.0	0.31		1.5			
$C_2N_2H^+ + C_2H_4$	$C_2H_5^+ + C_2N_2$	1.0	0.88	0.88	1.1			
$CH_3OH_2^+ + C_2N_2$	Adduct	1.0	0.023		1.5			
$HNCCN^+ \cdot C_2H_2 + H_2O$		1.0	NR		2.3			
$HNCCN^+ \cdot C_2H_2 + C_3H_8$			NR		1.1			
Reactions of reference bases								
$C_2H_3^+ + CH_3Cl$	$CH_3ClH^+ + C_2H_2$	0.75	1.1	0.83	2.5			
	Adduct	0.15						
	$C_3H_5^+ + HCl$	0.10						
$C_2H_5^+ + CH_3Cl$	Adduct	1.0	0.16		2.4			
$C_2H_3^+ + SO_2$	$CH_2SOH^+ + CO$	1.0	1.2		2.0		−193[i]	
$SO_2H^+ + C_2H_4$	$C_2H_5^+ + SO_2$	1.0	0.96	0.96	1.2			
$C_2H_5^+ + SO_2$	Adduct	1.0	0.0088		2.0			
$SO_2H^+ + C_2H_2$	$C_2H_3^+ + SO_2$	0.4	1.1	0.44	1.2			
	$CH_2SOH^+ + CO$	0.6			1.2			

[a] All rate coefficients (k) are in units of 10^{-9} cm^3 s^{-1} measured at a temperature of 300 K and a helium buffer gas pressure of 0.48 Torr. k_{obs} is the observed total rate coefficient. The absolute uncertainty of the reported rate coefficients is estimated as ±15%. k_{PT} is the rate coefficient for proton transfer only. k_{col} is the calculated collision rate coefficient according to the trajectory theory [26].

[b] ΔG°_{300}, ΔH^0 and PA are in kJ mol^{-1}.

[c] $\Delta G^0 = k_{PT\ (forward)}/k_{PT\ (reverse).}$

[d] ΔH^0 obtained from $\Delta G^0 + T\Delta S^0$. The enthalpy change is calculated from $\Delta H^0 = \Delta G^0 + T\Delta S^0$, where $T\Delta S^0$ is obtained from the difference between PA(B) = $-\Delta H^0$ ((B + H^+) → BH^+) and GB = $-\Delta G^0$(B + H^+) → BH^+ for B = C_3H_2, CH_3Cl and C_2H_2 [9], which gives ΔS°_{300} ($C_2H_2 + H^+ \rightarrow C_2H_3{}^+$) = −8.1 J mol^{-1} K, ΔS°_{300} ($CH_3Cl + H^+ \rightarrow CH_3ClH^+$) = −8.7 J mol^{-1} K and ΔS°_{300} ($C_2N_2 + H^+ \rightarrow C_2N_2H^+$) = −9.6 J mol^{-1} K^{-2}.

[e] PA(C_2N_2) as obtained from the present results, using PA(C_2H_2) = 641.1 kJ mol^{-1} and PA(CH_3Cl) = 647.3 kJ mol^{-1} [9].

[f] Rate coefficient for proton transfer from ICR results [3] 0.4 × 10^{-9} cm^3 s^{-1}.

[g] [4], ICR results.

[h] [4]. We obtained 0.20 × 10^{-9} cm^3 s^{-1} in the present measurements of $C_2N_2H^+ + CH_3Cl$, and also observed adduct formation with k = 0.02 × 10^{-9} cm^3 s^{-1}.

[i] [27,28].

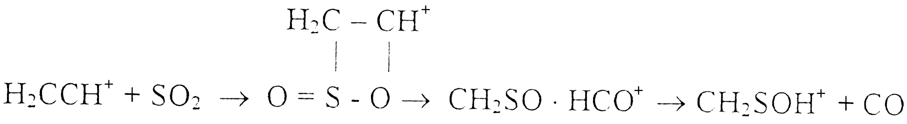
the exception of cyanogen) were all obtained from commercial sources and purified by repeated freeze–pump–thaw cycles. Cyanogen was prepared according to the method of Janz [24].

3. Results and discussion

3.1. Proton transfer reactions

The rate coefficients of proton transfer reactions are summarized in Table 1. Based on the present results and considering the uncertainties in the measurements and in the PAs of the reference compounds, PA(C_2N_2) can be assigned to 651.2 ± 2 kJ mol^{-1}. This result is in good agreement with the theoretical values of 657 and 655 kJ mol^{-1} [10,11]. As the PA(C_2N_2) values derived from the equilibrium with C_2H_2 and with CH_3Cl are in excellent agreement, the cycle of these reactions ties CH_3Cl to C_2H_2 and supports the revised value of PA(CH_3Cl) [9,12].

We rechecked, in our new FA/SIFDT apparatus,



$$H_2CCH^+ + SO_2 \rightarrow \begin{array}{c} H_2C - CH^+ \\ | \quad\quad | \\ O = S - O \end{array} \rightarrow CH_2SO \cdot HCO^+ \rightarrow CH_2SOH^+ + CO \qquad (1)$$

Scheme 1.

the two reported slow reactions upon which the anomalous results are based. The reactions that are inconsistent with the new PA values, namely, the apparent slow proton transfer reactions from $C_2H_5^+$ to C_2N_2 and CH_3Cl were found not to occur in the new measurements. The apparent proton transfer reported in the earlier measurements were based on the $C_2H_5^+ + C_2N_2$ and $C_2H_5^+ + CH_3Cl$ systems by attributing the very small signals observed of $C_2N_2H^+$ and CH_3ClH^+ ions to products of the reactions of the $C_2H_5^+$ ion. The small concentrations of these protonated ions in the earlier measurements is evidenced by the apparent low rate coefficients of 0.084×10^{-9} and 0.063×10^{-9} cm^3 s^{-1}, respectively, reported for proton transfer. With the new more sensitive instrument, small concentrations of these products are still observed, but they are completely accounted for by reactions of trace amounts of the $C_2H_3^+$ breakup ion formed in the injection of $C_2H_5^+$. Similarly, breakup ions were almost certainly the source of the protonated species in the previous study [4]. We note also that the overall rate coefficients measured in the previous and present studies are in fair agreement. For the reaction of $C_2H_5^+$ with C_2N_2, the overall rate coefficient is 0.31×10^{-9} in the present measurements and 0.21×10^{-9} cm^3 s^{-1} previously [4], and with CH_3Cl, 0.16×10^{-9} in the present measurements and 0.079×10^{-9} cm^3 s^{-1} previously [4]. The mass selection and injection capabilities of the new FA/SIFDT system are substantially improved over the earlier SIFT system in which the experiments were first done [4]. In the new instrument the problem of injecting small amounts of ions adjacent in mass to the ion of interest is entirely eliminated. Consequently, the assignment of product ion identities has become a much simpler process.

We also checked a further reaction that seems to be in conflict with the present results and the tabulated PA data [9]: proton transfer between SO_2H^+ and C_2N_2. We confirm that proton transfer from SO_2H^+ to C_2N_2 is fast [2], and in the reverse direction, $C_2N_2H^+$ does not protonate SO_2. This result shows that $PA(SO_2) < PA(C_2N_2) = 651.2$ kJ mol^{-1}. To further check $PA(SO_2)$, we examined its reactions with C_2H_2. Table 1 shows that SO_2H^+ transfers a proton efficiently to C_2H_2, and in the reverse direction, proton transfer from $C_2H_3^+$ to SO_2 does not occur. These results show that $PA(SO_2) < PA(C_2H_2) = 641.1$ kJ mol^{-1} [9]. The observations are consistent with previous results [2], but they show that the currently tabulated value for $PA(SO_2)$ as 672.3 kJ mol^{-1} should be lowered substantially to match theoretical calculations by Fairley et al. that gave $PA(SO_2) = 627$ kJ mol^{-1} for trans $OSOH^+$ at 0 K [25].

While no proton transfer was observed from $C_2H_3^+$ to SO_2, we observed the formation of $CH_2SOH^+ + CO$, which is exothermic by 193 kJ mol^{-1} [using $\Delta H_f^o(CH_2SOH^+) = 736$ kJ mol] [27,28]. A possible mechanism in reaction (1) proceeds through cycloaddition, complex formation, and intracomplex proton transfer.

This mechanism produces the stable CH_2SOH^+ isomer [27,28]. While this complex reaction occurs near collision efficiency, proton transfer is not observed, suggesting that proton transfer would be endothermic. Interestingly, we observe a CH_2SOH^+ product also in the reverse reaction $SO_2H^+ + C_2H_2$, possibly through intra-complex proton transfer followed by dissociation to yield $C_2H_3^+$, in competition with the complex mediated highly exothermic reaction in Scheme 1. Reactions similar to (1) may of course occur also between SO_2 and other hydrocarbon ions, and they would warrant further studies because they may be significant in planetary atmospheres.

Table 2
Reactants of CH_3NCCN^+ with bases BA and further association reactions

Reactants	Products	$k_{obs}{}^{+a}$	$k_{col}{}^{+a}$	PA(B)[b]
$CH_3NCCN^+ + C_2H_2$		NR	0.99	641.1
$+ HCN$	$CH_3NCCNNCH^+$	0.0062	3.2	712.9
$+ (CH_3)_2O$	$CH_3NCCNO(CH_3)_2^+$	0.025[c]	1.6	792.0
$+ CH_3CN$	$CH_3NCCNNCCH_3^+$	0.27	3.6	779.2
$+ (CH_3)_2CO$	$CH_3NCCNOC(CH_3)_2^+$	0.40	2.6	812.0
$+ (CH_3)_3N$	$CH_3NCCNN(CH_3)_3^+$	1.2	1.3	948.9
$CH_3OH_2^+ + C_2N_2$	$CH_3OH_2^+ \cdot C_2N_2$	0.08	1.5	
$CH_3BrCH_3^+ + C_2N_2$		NR	1.1	
$(CH_3)_3O^+ + CH_3CN$	$(CH_3)_3O^+ \cdot CH_3CN$	0.012[d]	3.7	
$(CH_3)_3^+O + (CH_3)_2CO$	$(CH_3)_3O^+ \cdot (CH_3)_2CO$	0.016[d]	2.7	

[a] All rate coefficients in units of 10^{-9} cm^3 s^{-1}. See footnote a, Table 1.

[b] In kJ mol^{-1} [9].

[c] A possible methyl cation transfer product $(CH_3)_3O^+$ of <10, probably from reactions of breakup ions is observed.

[d] Low ion signals of $CH_3CNCH_3^+$ and $(CH_3)_2COCH_3^+$ products, respectively, $<1\%$ of ΣI are observed, corresponding to k(methyl cation transfer) $<10^{-13}$ cm^3 s^{-1}, or from breakup ions.

3.2. Tests of methyl cation transfer reactions

Several of the reactions in Table 1 show association channels. If the products are covalent adducts, these reactions may provide mechanisms for interstellar and planetary synthesis of molecular containing multiple heteroatoms, and if cyclised, complex heterocyclics.

One of the adducts in Table 1 is the species $C_2N_2 \cdot C_2H_5^+$, probably the alkylated ion $CH_3CH_2NCCN^+$. Similarly, we previously observed the formation of CH_3NCCN^+ in the association of $CH_3{}^+ + C_2N_2$ [5,13]. These species may serve as alkylating agents by alkyl cation transfer to lone pair donor bases. In fact, according to the general correlation between PAs and MCAs [29], the low PA(C_2N_2) suggests that it may also have a low MCA and therefore CH_3NCCN^+ may be an efficient alkylating agent. On the other hand, CH_3NCCN^+ may be strongly covalently bonded, having a bond strength similar to the bond strength in the analogous covalent ion CH_3NCH^+. In this case, rather than transferring methyl cations, CH_3NCCN^+ may form covalent adducts with lone pair donor bases, contributing to astrochemical synthesis of larger molecules.

To examine these possibilities, we investigated the reactions of CH_3NCCN^+ with several bases. As observed in Table 2, all the reactions yield the respective adducts and no methyl cation transfer is observed in any reaction. One possible exception is $(CH_3)_2O$ in which a small $(CH_3)_3O^+$ signal was present because of the reaction $(CH_3)_2OH^+ + (CH_3)_2O \rightarrow (CH_3)_3O^+ + CH_3OH$ [20], from the $(CH_3)_2OH^+$ ion present in the flow tube because of stray photoionization of the reactant $(CH_3)_2O$. We attribute all the observed $(CH_3)_3O^+$ ions to this reaction and not methyl cation transfer from CH_3NCCN^+. No transfer reaction is observed to $(CH_3)_3N$, although this compound has a high MCA of 528 kJ mol^{-1} [30].

For comparison, we checked methyl cation transfer from $(CH_3)_3O^+$, the methylated ion of CH_3OCH_3 (a base with a relatively high MCA of 390 kJ mol^{-1}) [22]. Similar to CH_3NCCN^+, this ion showed no transfer reactions to bases that have comparable or higher MCA such as CH_3CN [30] and CH_3COCH_3, with k (methyl cation transfer) $<10^{-13}$ s^{-1} at 298 K. However, it transfers a methyl cation near the collision rate at 300 K to $(CH_3)_3N$ [29], and is therefore more reactive than CH_3NCCN^+, which does not.

The lack of methyl cation transfer from CH_3NCCN^+ suggests that C_2N_2 may have a high MCA, and therefore alkylating cations would be expected to transfer methyl cations to it. To test this, we tried to observe reactions of $(CH_3)_2Br^+$ and $CH_3OH_2^+$ with C_2N_2, because CH_3OH_2 can transfer a methyl cation to compounds with relatively low PAs and MCAs such as H_2CO and CH_3OH [20]. However, no methyl cation transfer to C_2N_2 was observed. The lack of reactivity in either direction suggests that methyl cation transfer both to and from C_2N_2 may have a high energy barrier.

3.3. Association reactions

Although CH_3NCCN^+ shows no reactivity through methyl cation transfer, it associates with lone pair donor bases, as observed in Table 2. An interesting trend in these reactions is that the rate coefficients for association correlate with the PAs of the bases. It is likely that PA(B) is correlated with the CH_3NCCN^+–B bond strengths. The reaction complexes formed in the additions would be in a deeper well with increasing PA(B). This can lead to decreasing back-dissociation to reactants according to the Rice–Ramsperger–Kassell–Marcus (RRKM) theory, and would account for the observed trend.

Association products (those in Table 2 are examples) may exist as noncovalent cluster ions in which the two entities retain much of their identity, hydrogen-bonded complexes, or linear or cyclic covalent condensation products. If the adducts were $CH^+ \cdot X$ type cluster ions they might be expected to have bond strengths less than $\sim$60 kJ mol^{-1} without significant correlation of the bond strengths and association rates to PA(B)—contrary to the strong correlation in Table 2. Evidence that most of the adduct ions in Table 2 are strongly bonded also comes from their behaviour under a potential gradient in the drift tube. When a drift field of 250 V was applied at 0.48 Torr (10.5 V cm^{-1} Torr^{-1}) no fragmentation of the association ions $HNCCN^+ \cdot C_2H_2$ and $CH_3NCCN^+ \cdot HCN$ was apparent. Weakly bonded cluster ions will often break up under less drastic experimental conditions.

Further evidence supporting a covalent structure for the adduct ions came from their reactivity. We observed that $HNCCN^+ \cdot C_2H_2$ did not react with H_2O at 298 K. Since the PA of H_2O is substantially higher than that of C_2N_2, proton transfer would be expected from a weakly bonded cluster ion. Alternatively, the weak ligand C_2H_2 would be expected to switch with H_2O, and further switching reactions would lead to $(H_2O)_nH^+$ cluster ions.

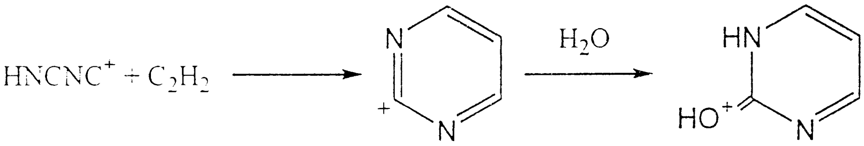
It is therefore likely that the adducts ions $CH_3NCCN^+ \cdot HCN$ and $HNCCN^+ \cdot C_2H_2$ are covalently bonded ions, and consequently, the other adducts are the covalent ions suggested in Table 2. The products are examples of the synthesis of complex organic species with unsaturated chains that include multiple heteroatoms. Through ion-molecule chemistry, C_2N_2 therefore constitutes a facile starting compound for complex organic synthesis in astrochemical environments.

An interesting adduct is $HNCCN^+ \cdot C_2H_2$, which as we observed, appears to be a strongly bonded covalent $C_4N_2H_3^+$ isomer. A possible structure is the $N{\equiv}C{-}CH{=}N{-}C^+{=}CH_2$ carbonium ion, produced by end-to-end addition and hydrogen shift. The charge on the carbon in this ion would be well stabilised by the adjacent double bond and heteroatom. This possible structure is supported by the lack of reaction with C_3H_8, which shows that the carbon center is stabilised and has a lower hydride affinity than the *s*-$C_3H_7^+$ ion.

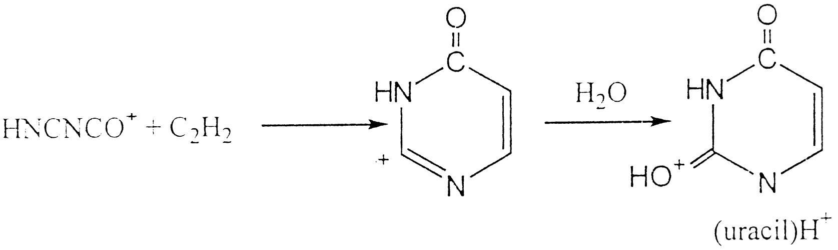
A particularly interesting possibility is that the adduct is a cyclic $C_4N_2H_3^+$ ion, specifically, deprotonated 1,4-diazine, which can lead to protonated substituted diazines through further addition reactions (Scheme 2). Similar reactions can constitute ion-molecule pathways to pyrimidine nucleic base isomers or precursors from similar interstellar cyano compounds. For example, a cyclic $HNCNC^+ \cdot C_2H_2$ isomer from the protonated suspected interstellar species NCNC would be deprotonated pyrimidine, and association with H_2O molecules at low temperatures can yield protonated hydroxypyrimidine, a possible ionic precursor of uracil.

An even more likely reaction would involve similar condensation with C_2H_2 by the $HNCNCO^+$ ion, followed by H_2O addition (Scheme 3).

These reactions illustrate the potential of condensation reactions of the type observed between $C_2N_2H^+$ and C_2H_2 to form heterocyclics, including pyrimidine nucleic base isomers or precursors, through simple ion-molecule reactions.



Scheme 2.



Scheme 3.

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