

# Solvation of the Proton by HCN and CH<sub>3</sub>CN. Condensation of HCN with Ions in the Gas Phase

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**Abstract:** Temperature studies on the reactions  $(\text{HCN})_n\text{H}^+ + \text{HCN} \rightleftharpoons (\text{HCN})_{n+1}\text{H}^+$  ( $n = 1-4$ ), yielded the values  $\Delta H^\circ = -30.0, -13.8, -11.8,$  and  $-9.2$  kcal/mol for the (1,2), (2,3), (3,4), and (4,5) equilibria, respectively. Decrease in the heat of solvation of  $\text{HCNH}^+$  in going from the (1,2) to the (2,3) equilibrium is significantly larger than the analogous change in the hydration of  $\text{H}_3\text{O}^+$ , as in  $\text{HCNH}^+$  only one site is available for hydrogen bonding of a solvent molecule to the protonated center. This observation and a discontinuity observed in the change of the heat of solvation with  $n$  in going from the (3,4) to the (4,5) equilibrium are consistent with a linear structure  $\text{HCN}\cdots\text{HCN}\cdots\text{HCN}\cdots\text{H}^+\cdots\text{NCH}\cdots\text{NCH}\cdots\text{NCH}$ , where each one-dimensional analogue of a solvent shell contains two HCN molecules. For the reactions  $(\text{CH}_3\text{CN})_n\text{H}^+ + \text{CH}_3\text{CN} \rightleftharpoons (\text{CH}_3\text{CN})_{n+1}\text{H}^+$  ( $n = 1$  and  $2$ )  $\Delta H^\circ$  was measured as  $-30.2$  and  $-9.3$  kcal/mol, respectively. Comparison of the solvation of the proton by  $\text{CH}_3\text{CN}$  with the solvation of alkali metal ions by  $\text{CH}_3\text{CN}$  indicates that, like in HCN, the first solvent "shell" about  $\text{H}^+$  in  $\text{CH}_3\text{CN}$  clusters is also completed by two solvent molecules.  $\Delta H^\circ$  for the association of  $s\text{-C}_3\text{H}_7^+$  and  $t\text{-C}_4\text{H}_9^+$  with HCN was measured as  $-30.8$  and  $-16.3$  kcal/mol, respectively. Heats of formation of the product ions indicate that the products of the condensation reactions are protonated isocyanides,  $\text{RNCH}^+$ . Pressure and temperature studies show that the association reactions between  $\text{R}^+$  and HCN are three-body processes at low temperatures but become two-body processes, possibly with an activation energy, at high temperatures.

## Introduction

Equilibrium measurements that yield the enthalpy and entropy for the solvation of the proton in the gas phase have become a valuable tool in the investigation of bonding and solvation in ionic systems. For example, in comparing the bonding between  $n$ -donor bases and protonated ions in the formation of symmetric dimer ions  $\text{BH}^+\text{B}$ , where  $\text{B} = \text{H}_2\text{O}, \text{NH}_3, \text{H}_2\text{S},$  and  $\text{PH}_4$ , we observed recently that about 10 kcal/mol of ion-solvent interaction enthalpy can be ascribed to electrostatic forces, while hydrogen bonding may contribute up to 23 kcal/mol (in the case of  $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ ) to the solvation of the protonated ion.<sup>1</sup> The significance of hydrogen bonding was also demonstrated by Kebarle and co-workers in several cases. Thus it was found that in the hydration of  $\text{H}_3\text{O}^+$ , hydrogen bonding of  $\text{H}_2\text{O}$  to the hydrogens of the central  $\text{H}_3\text{O}^+$  ion causes an observable difference between inner-shell and outer-shell solvation.<sup>2</sup> Grimsrud and Kebarle also showed that the solvation of protonated  $\text{H}_3\text{O}^+$ ,  $\text{CH}_3\text{OH}_2^+$ , and  $(\text{CH}_3)_2\text{OH}^+$  by the respective neutrals exhibited marked differences that could be assigned to the blocking of hydrogen bonding sites by methyl groups in  $\text{CH}_3\text{OH}_2^+$  and  $(\text{CH}_3)_2\text{OH}^+$ .<sup>2</sup>

In the present work we examined the solvation of  $\text{HCNH}^+$  by HCN. In this case, unlike in  $\text{H}_3\text{O}^+$ , there is only one site for hydrogen bonding at the protonated center, i.e., at  $\equiv\text{NH}^+$ . If hydrogen bonding is important in building up the first solvent shell, there should be therefore significant differences between the solvation of  $\text{HCNH}^+$  and  $\text{H}_3\text{O}^+$ . Comparison of the thermodynamics of solvation of  $\text{HCNH}^+$  and  $\text{H}_3\text{O}^+$  should be an instructive further test of the significance of hydrogen bonding in ion-solvent interactions.

Another interesting aspect of the gaseous ionic chemistry of HCN is the condensation reactions of this molecule with carbonium ions. The possible significance of this class of reactions in reducing planetary atmospheres was recently pointed out by Hiraoka and Kebarle, who observed the formation of protonated alcohols in reactions between carbonium ions and water,<sup>3</sup> and the synthesis of protonated propionic acid by the condensation of  $\text{C}_2\text{H}_5^+$ , CO, and  $\text{H}_2\text{O}$ .<sup>4</sup> Further syntheses by gaseous ion-molecule condensation were observed in our laboratory in the reactions of  $\text{C}_2\text{H}_5^+$ ,  $s\text{-C}_3\text{H}_7^+$  and  $t\text{-C}_4\text{H}_9^+$  with ammonia and primary and secondary alkylamines to form protonated ethyl, *sec*-propyl, and *tert*-butylamine, and secondary and tertiary alkylamines, respectively.<sup>5</sup> In the present

work we investigated the condensation of  $s\text{-C}_3\text{H}_7^+$  and  $t\text{-C}_4\text{H}_9^+$  with HCN. In these reactions, the condensation products may be the respective protonated alkyl cyanides, alkyl isocyanides, or possibly electrostatically bonded cluster ions. We use the thermodynamic results for the condensation reactions to infer the structure of the reaction products. In addition, we present some novel and unusual kinetic phenomena in these condensation processes.

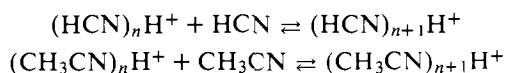
## Experimental Section

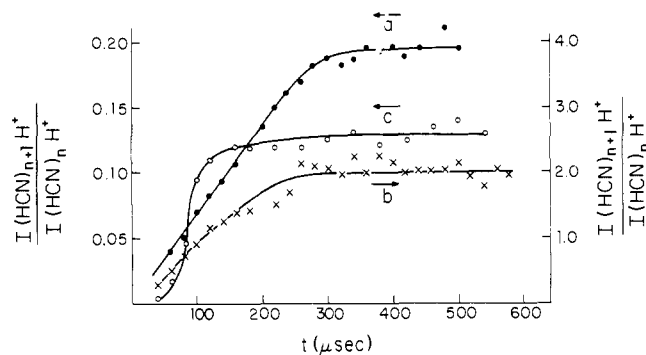
The present investigations were carried out using the Rockefeller University Chemical Physics Mass Spectrometer. The pulsed high-pressure mass spectrometric technique was employed as described in earlier publications.<sup>1,6</sup> Gas mixtures of HCN or  $\text{CH}_3\text{CN}$  (1%) plus, when applicable,  $\text{C}_3\text{H}_8$  or  $t\text{-C}_4\text{H}_{10}$  (10%) in  $\text{CH}_4$  were prepared in 5-L bulbs and allowed to flow to the ionization chamber. Pulses (10–15  $\mu\text{s}$ ) of 600 V electrons were used to ionize the gas mixture in the mass spectrometer ion source. The intensities of ion signals due to ions exiting from the reaction chamber were integrated by a multichannel analyzer.

The reagents used were isobutane, Instrument Grade (purity 99.5%); propane, Research Grade (purity 99.99%); and methane, Ultra High Purity (purity 99.97%), all purchased from Matheson. Acetonitrile, 99.99% purity, was purchased from Eastman. HCN was prepared by dripping 75%  $\text{H}_2\text{SO}_4$  on NaCN. Water was removed from HCN by vacuum distillation through a  $\text{P}_2\text{O}_5$  trap. In some experiments the reaction mixture flowed through an additional  $\text{P}_2\text{O}_5$  trap upstream from the ion source. It was observed that  $\text{H}_2\text{O}$  impurities were effectively diminished below detection levels by this technique. HCN concentrations were not affected by the presence of the  $\text{P}_2\text{O}_5$  trap. This was demonstrated by the constancy of the measured rate or equilibrium constants of reactions involving HCN in control experiments with or without the trap.

## Results

**Equilibrium Studies: Clustering and Condensation Reactions of HCN and  $\text{CH}_3\text{CN}$ .** The protonated ions  $\text{HCNH}^+$  and  $\text{CH}_3\text{CNH}^+$  are formed in reaction systems of 1% HCN or  $\text{CH}_3\text{CN}$  in methane by proton transfer from  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$ . These reactions are completed under our conditions in 20  $\mu\text{s}$ . The  $\text{HCNH}^+$  and  $\text{CH}_3\text{CNH}^+$  ions then react with HCN or  $\text{CH}_3\text{CN}$  molecules, respectively, until equilibrium is established in the reactions:





**Figure 1.** Approach to equilibrium in the formation of protonated HCN clusters: (a) for the reaction  $\text{HCNH}^+ + \text{HCN} \rightleftharpoons (\text{HCN})_2\text{H}^+$  in a mixture of 1.14% HCN in  $\text{CH}_4$ , at  $T = 619 \text{ K}$ ,  $P = 3.84 \text{ Torr}$ ; (b) for the reaction  $(\text{HCN})_2\text{H}^+ + \text{HCN} \rightleftharpoons (\text{HCN})_3\text{H}^+$ , in the same reaction mixture at  $T = 296 \text{ K}$ ,  $P = 1.52 \text{ Torr}$ ; (c) for the reaction  $(\text{HCN})_4\text{H}^+ + \text{HCN} \rightleftharpoons (\text{HCN})_5\text{H}^+$ , in a mixture of 8.99% HCN in  $\text{CH}_4$  at  $T = 228 \text{ K}$ ,  $P = 1.25 \text{ Torr}$ . Left hand side ordinate applies to plots a and c and right hand side ordinate to plot b. The complex form of plot c may be due to the necessary formation of lower order clusters prior to the formation of the  $(\text{HCN})_4\text{H}^+$  cluster.

**Table I.** Thermochemical Values for Ion-Molecule Association Reactions of HCN and CH<sub>3</sub>CN

reaction	$-\Delta H^\circ$ , kcal/mol	$-\Delta S^\circ$ , cal/(mol K)
1. $\text{HCNH}^+ + \text{HCN} \rightleftharpoons (\text{HCN})_2\text{H}^+$	30.0	32
2. $(\text{HCN})_2\text{H}^+ + \text{HCN} \rightleftharpoons (\text{HCN})_3\text{H}^+$	13.8	23
3. $(\text{HCN})_3\text{H}^+ + \text{HCN} \rightleftharpoons (\text{HCN})_4\text{H}^+$	11.8	25
4. $(\text{HCN})_4\text{H}^+ + \text{HCN} \rightleftharpoons (\text{HCN})_5\text{H}^+$	9.2	26
5. $\text{CH}_3\text{CNH}^+ + \text{CH}_3\text{CN} \rightleftharpoons (\text{CH}_3\text{CN})_2\text{H}^+$	30.2	29
6. $(\text{CH}_3\text{CN})_2\text{H}^+ + \text{CH}_3\text{CN} \rightleftharpoons (\text{CH}_3\text{CN})_3\text{H}^+$	9.3	19
7. $s\text{-C}_3\text{H}_7^+ + \text{HCN} \rightleftharpoons s\text{-C}_3\text{H}_7\text{NCH}^+$	30.8	32
8. $t\text{-C}_4\text{H}_9^+ + \text{HCN} \rightleftharpoons t\text{-C}_4\text{H}_9\text{NCH}^+$	16.3	25

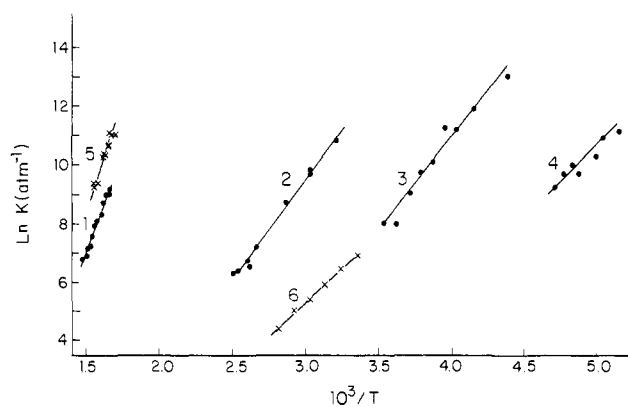
<sup>a</sup> Precision is estimated as  $\pm 1 \text{ kcal/mol}$  for  $\Delta H^\circ$  and  $\pm 2.5 \text{ cal/(mol K)}$  for  $\Delta S^\circ$ .

Approach to equilibrium is observed as the ion intensity ratios  $I((\text{HCN})_{n+1}\text{H}^+)/I((\text{HCN})_n\text{H}^+)$  increase with reaction time until a constant value is reached. Examples of approach to equilibrium in the formation of protonated HCN clusters are shown in Figure 1. Equilibrium constants are obtained using ion intensity ratios obtained from the horizontal portions of the approach to equilibrium plots. Temperature studies on the association reactions yield the van't Hoff plots shown in Figure 2. The thermochemical values are presented in Table I.

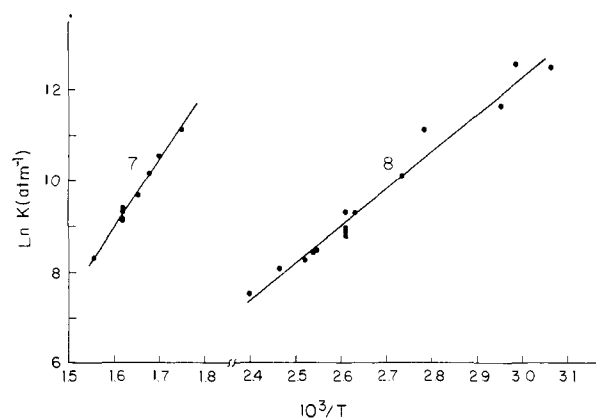
In the association reactions of  $s\text{-C}_3\text{H}_7^+$  and  $t\text{-C}_4\text{H}_9^+$  with HCN, the reactant ions were produced in reaction mixtures of 0.3–0.8% HCN + 5–10%  $\text{C}_3\text{H}_8$  or  $i\text{-C}_4\text{H}_{10}$  in  $\text{CH}_4$ . In these systems the  $\text{CH}_5^+$  ion reacts with  $\text{C}_3\text{H}_8$  and  $i\text{-C}_4\text{H}_{10}$  by dissociative  $\text{H}^+$  transfer, and the  $\text{C}_2\text{H}_5^+$  ion reacts with  $\text{C}_3\text{H}_8$  and  $i\text{-C}_4\text{H}_{10}$  via  $\text{H}^-$  abstraction to form  $s\text{-C}_3\text{H}_7^+$  and  $t\text{-C}_4\text{H}_9^+$ , respectively. These reactions are completed in 10  $\mu\text{s}$ . The carbonium ions then associate with HCN. van't Hoff plots for the association reactions are shown in Figure 3. Thermochemical data are summarized in Table I, rows 7 and 8.

## Discussion

For the reasons noted in the Introduction, it is of interest to compare the bonding involved in building up the solvent sphere of HCN molecules around the protonated ion  $\text{HCNH}^+$  with the bonding involved in the solvation of  $\text{H}_3\text{O}^+$  by  $\text{H}_2\text{O}$ .  $\Delta H^\circ_{1,2}$  for the hydration of  $\text{H}_3\text{O}^+$  was measured as  $-33.0 \text{ kcal/mol}$



**Figure 2.** van't Hoff plots for the formation of protonated HCN and  $\text{CH}_3\text{CN}$  clusters. Numbers indicate reactions as listed in Table I.



**Figure 3.** van't Hoff plots for the reactions: (7)  $s\text{-C}_3\text{H}_7^+ + \text{HCN} \rightleftharpoons s\text{-C}_3\text{H}_7\text{NCH}^+$ ; (8)  $t\text{-C}_4\text{H}_9^+ + \text{HCN} \rightleftharpoons t\text{-C}_4\text{H}_9\text{NCH}^+$ . (Numbers correspond to reactions as listed in Table I.)

in our laboratory<sup>1</sup> and as  $-31.6 \text{ kcal/mol}$  by Kebarle and coworkers;<sup>2</sup> we consider the average of these results,  $-32.3 \pm 1 \text{ kcal/mol}$ , as the best available value. This enthalpy is similar to the value of  $-30.0 \text{ kcal/mol}$  for the solvation of  $\text{HCNH}^+$  by HCN. However, a major difference is observed upon adding the next solvent molecule to the two  $\text{B}\cdots\text{H}^+\cdots\text{B}$  ions. This difference is illustrated in Figure 4, which shows the decreasing strength of ion-solvent bonding in the solvation of  $\text{H}_3\text{O}^+$ ,  $\text{CH}_3\text{OH}^+$ ,  $(\text{CH}_3)_2\text{OH}^+$ ,  $\text{HCNH}^+$ , and  $\text{CH}_3\text{CNH}^+$  with increasing solvation. We note that the difference  $\Delta\Delta H^\circ = \Delta H^\circ_{1,2} - \Delta H^\circ_{2,3}$  is  $-12.1 \text{ kcal/mol}$  for  $\text{H}_2\text{O}$  and  $-11.8 \text{ kcal/mol}$  for  $\text{CH}_3\text{OH}$ , while it is  $-16.4 \text{ kcal/mol}$  for HCN. The larger drop in HCN must be due to the absence of hydrogen bonding to the third HCN molecule since in  $\text{HCNH}^+$ , unlike in  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{OH}_2^+$ , unoccupied hydrogen sites are not available for the third solvent molecule.

Figure 4 also shows the large drop in  $\Delta H^\circ$  for the addition of a third solvent molecule to  $(\text{CH}_3\text{CN})_2\text{H}^+$ . This drop between  $\Delta H^\circ_{1,2}$  and  $\Delta H^\circ_{2,3}$  is very similar to that observed in the solvation of  $\text{H}^+$  by  $(\text{CH}_3)_2\text{O}$  (Figure 4). The sharp decrease in  $\Delta H^\circ$  in bonding to the third solvent molecule in  $(\text{CH}_3)_2\text{O}$  as compared with bonding to the third solvent molecule in water and methanol was used by Grimsrud and Kebarle<sup>2</sup> as an elegant demonstration of the blocking of hydrogen bonding sites in the ion-solvent clusters. In a similar manner, we compare  $-\Delta H^\circ$  for reactions 2 and 6 in Table I and observe that methyl substitution causes a decrease by 4.5 kcal/mol for bonding the third solvent molecule in  $\text{CH}_3\text{CN}$  clusters as compared with bonding the third solvent molecule in HCN. In analogy with the difference between solvation of the proton by  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , or  $(\text{CH}_3)_2\text{O}$ , the difference between bonding the third solvent molecule in HCN or  $\text{CH}_3\text{CN}$  clusters may

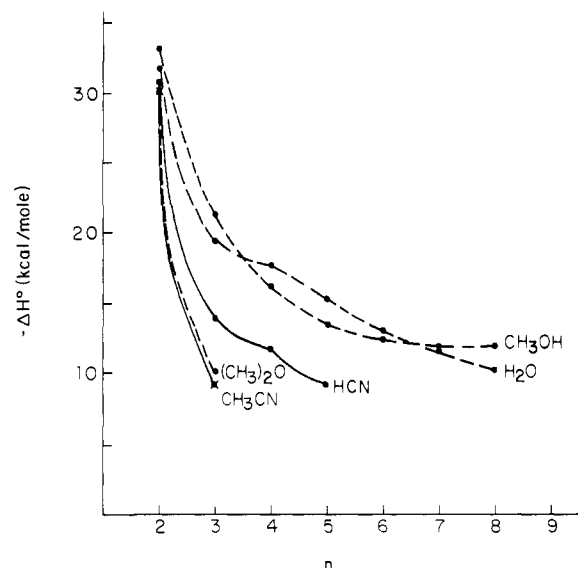


Figure 4. Comparison of  $-\Delta H^\circ_{n,n+1}$  vs.  $n$  for the reactions  $B_{n-1}H^+ + B \rightleftharpoons B_nH^+$ , where  $B$  is the base indicated on the plot.

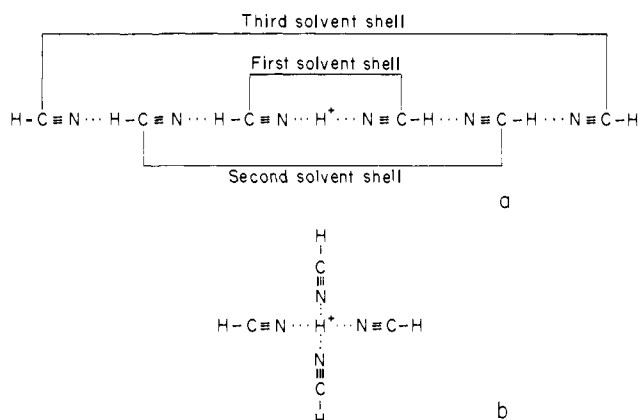


Figure 5. Hypothetical structures of cluster ions  $(HCN)_nH^+$ .

be assigned to blocking hydrogen bonding in  $HCN \cdots H^+ \cdots NCH \cdots NCH$  by methyl substitution in  $CH_3CN$ . Indeed, the experimental difference of 4.5 kcal/mol between  $\Delta H^\circ_{2,3}$  for the  $(HCN)_nH^+$  and  $(CH_3CN)_nH^+$  clusters is surprisingly similar to the theoretical value of 4.6 kcal/mol assigned to hydrogen bonding in liquid  $HCN$ ,<sup>7</sup> or the value 3.3 kcal/mol found for the formation of the  $HCN \cdots HCN$  dimer in gaseous  $HCN$ .<sup>8</sup> The linear structures in Figure 5 would also be similar to the formation of chains of  $HCN$  molecules by hydrogen bonding, which gives rise to the high dipole moment of liquid  $HCN$ .<sup>9</sup> Another possible explanation for the difference between  $-\Delta H^\circ_{2,3}$  of  $HCN$  and  $CH_3CN$  could be the additional delocalization of the positive charge on the central  $H^+$  ion in the  $(CH_3CN)_2H^+$  dimer, as compared with  $(HCN)_2H^+$ . However, such a delocalization effect is not in evidence in the relative  $-\Delta H^\circ_{1,2}$  values, which are similar in  $HCN$  and  $CH_3CN$ . Thus the effect of methyl substitution in going from  $HCN$  to  $CH_3CN$  constitutes indirect evidence in favor of hydrogen bonding leading to the linear structure a in  $(HCN)_nH^+$  clusters, rather than a symmetric structure such as b in Figure 5. Also, the large drop between  $-\Delta H^\circ_{1,2}$  and  $-\Delta H^\circ_{2,3}$  for  $HCN$  would be compatible with a linear structure, since the third  $HCN$  molecule would be adding to an outer layer in the one-dimensional analogue of a solvent shell around  $H^+$ . Moreover, the slight drop observed in Figure 4 between  $-\Delta H^\circ_{3,4}$  and  $-\Delta H^\circ_{4,5}$  for  $HCN$  would also be compatible with the starting of a new, second removed "layer" in the sol-

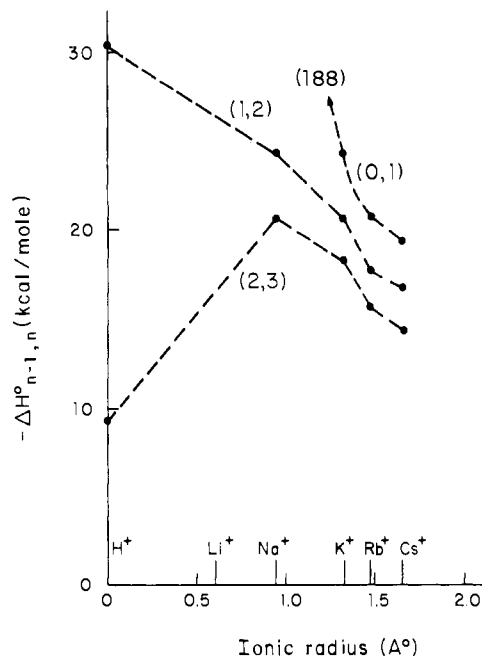


Figure 6. Enthalpies of solvation of  $H^+$  and alkali ions by  $CH_3CN$  as a function of ionic radius. The number in parentheses above the arrow on the plot for the (0,1) equilibrium indicates the proton affinity of  $CH_3CN$ .

vent "shell" about  $H^+$  with the addition of the fifth solvent molecule.

The solvation of  $H^+$  by  $CH_3CN$ , which was observed in this work, may be compared with the solvation of alkali ions by  $CH_3CN$  as was measured recently by Davidson and Kebarle.<sup>10</sup> In Figure 6 we plot the enthalpies of solvation of interest as a function of ionic radii. Both for the (0,1) and (1,2) equilibria, the solvation enthalpies increase monotonically as the ionic radius decreases, as might be expected, and  $H^+$  fits into this trend. However, the (2,3) equilibrium is qualitatively different, in that the bonding of the third solvent molecule is much weaker when  $H^+$  is the central ion than in the case of any of the alkali ions. This phenomenon may be interpreted to indicate that the first solvation shell about  $H^+$  is completed with the addition of two  $CH_3CN$  molecules to  $H^+$ , unlike the alkali ions such as  $Na^+$  where up to 5  $CH_3CN$  molecules may be in the first shell.<sup>10</sup> Thus the solvation of  $H^+$  is also consistent with the concept of linear solvent "shells", where each "shell" is completed by the addition of two solvent molecules (Figure 5a).

In addition to association reactions where  $HCN$  served as a solvent molecule, we observed in the present study equilibria where  $HCN$  served as a reactant in ion-molecule condensation processes. The obvious question in these processes, i.e., in the association of  $HCN$  WITH  $S-C_3H_7^+$  and  $t-C_4H_9^+$ , is the nature of the reaction product. Two prime candidates for the reaction products would be protonated cyanides,  $s-(CH_3)_2CHCNH^+$  and  $t-(CH_3)_3CCNH^+$ , or the protonated isocyanides,  $s-(CH_3)_2CHNCH^+$  and  $t-(CH_3)_3CNCH^+$ . To test for the first possibility, we may calculate the heats of formation of  $s-(CH_3)_2CHCNH^+$  and  $t-(CH_3)_3CCNH^+$ . The proton affinity of *sec*-propyl cyanide is 192 kcal/mol; the proton affinity of *tert*-butyl cyanide may be obtained by extrapolation from the series of homologous cyanides as 193 kcal/mol.<sup>11</sup> Combined with the  $\Delta H^\circ_f$  values for the neutrals,<sup>12</sup> the heat of formation of  $s-(CH_3)_2CCNH^+$  is found to be 180 kcal/mol; the heat of formation of  $t-(CH_3)_3CCNH^+$  is found to be 174 kcal/mol. On the other hand, from  $\Delta H^\circ_f$  of  $s-C_3H_7^+$  and  $t-C_4H_9^+$ ,<sup>13</sup> and using the thermodynamic data for reactions 7 and 8 in Table I, we find  $\Delta H^\circ_f$  for  $s-C_3H_7^+ \cdot HCN$  produced in reaction 7 is 193 kcal/mol;  $\Delta H^\circ_f$  for  $t-C_4H_9^+ \cdot HCN$  formed

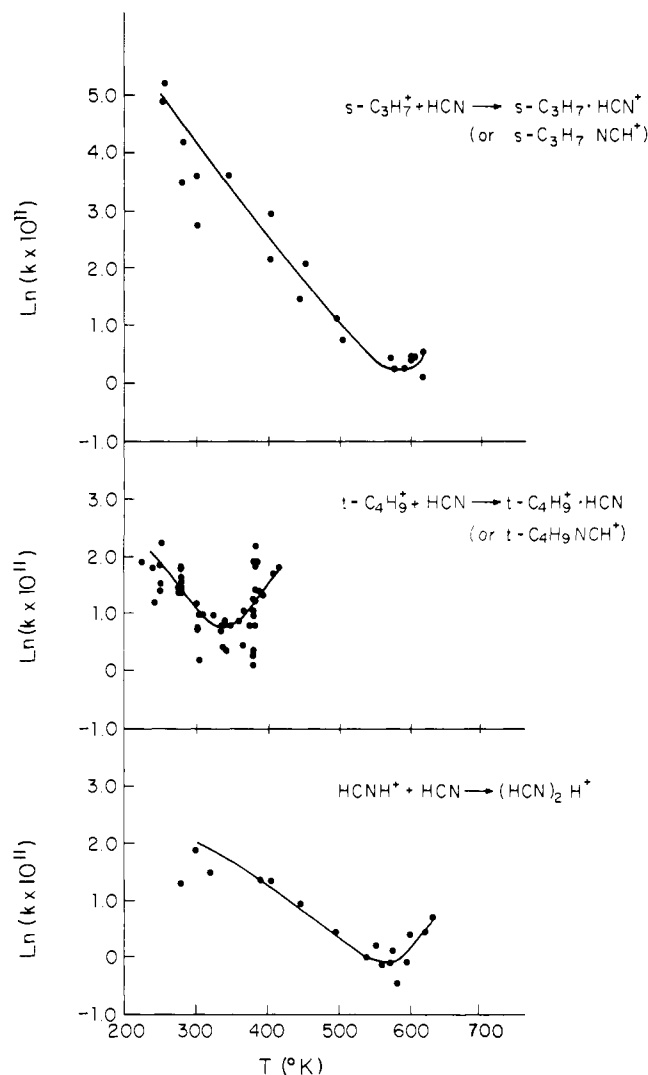
in reaction 8 is 186 kcal/mol. The heats of formation of the products of the association of *s*-C<sub>3</sub>H<sub>7</sub><sup>+</sup> and of *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> with HCN are higher by 13 and 12 kcal/mol respectively than the heats of formation of the corresponding protonated cyanides.

In order to examine whether the association products are protonated *sec*-propyl and *tert*-butyl isocyanide, heats of formation and proton affinities of these molecules would be required. Unfortunately, the thermodynamic data are not available. We shall therefore try to estimate these quantities tentatively as follows. The heat of formation of HNC was calculated by Shaefer and Pearson to be 15 kcal/mol higher than that of HCN.<sup>14</sup> The heat of formation of CH<sub>3</sub>NC is also higher than that of CH<sub>3</sub>CN by a similar difference, i.e., 15–17 kcal/mol.<sup>14</sup> We shall assume that the heats of formation of (CH<sub>3</sub>)<sub>2</sub>CHNC and (CH<sub>3</sub>)<sub>2</sub>CHCN are also higher by about 15 kcal/mol than those of (CH<sub>3</sub>)<sub>2</sub>CHNC and (CH<sub>3</sub>)<sub>3</sub>CCN, respectively. Pearson and Shaefer<sup>15</sup> also found that the most stable configuration of protonated HCN is a linear HCNH<sup>+</sup> ion; this is the most stable form of the (CNH<sub>2</sub>)<sup>+</sup> species and will therefore be the most stable form of the ion formed by the protonation of HNC. Thus the difference between the proton affinities of HCN and HNC must be equal to the difference between the heats of formation of the neutral HCN and HNC molecules, i.e., 15 kcal/mol. In the absence of other information, we shall assume that this difference also applies to the proton affinities of RCN and RNC molecules. In other words, we assume that alkyl substitution has similar effects on the proton affinities of cyanides and isocyanides, a situation that would be comparable to the linear relationship between proton affinities of cyanides and amines observed by Beauchamp et al.<sup>11</sup> To the extent that these qualitative arguments are valid, the heats of formation of protonated alkyl isocyanides will be higher than those of protonated alkyl cyanides by about the same amount as is the difference between the heats of formation of the neutrals, i.e., by about 15 kcal/mol. Experimentally, we found that the heats of formation of the association products, *s*-C<sub>3</sub>H<sub>7</sub><sup>+</sup>·HCN and *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup>·HCN were higher by 12 and 13 kcal/mol respectively than the corresponding protonated cyanides. Taking into account the approximations of the preceding discussion and the limits of accuracy of experimental data, we conclude that the data are consistent with the identification of the products as protonated isocyanides (CH<sub>3</sub>)<sub>2</sub>-CHNCH<sup>+</sup> and (CH<sub>3</sub>)<sub>3</sub>CNCH<sup>+</sup>.

The formation of isocyanides is also reasonable from the mechanistic point of view, since it requires a nucleophilic attack by an N atom of HCN, bearing a large fractional negative charge, on the positive charge centers in the (CH<sub>3</sub>)<sub>2</sub>C<sup>+</sup>H and (CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup> ions.

**Kinetics of the Condensation Reactions.** Rate constants for the association reactions 1, 7, and 8 were obtained from the variation of ion intensities with reaction time by methods similar to that used in previous publications.<sup>1,6</sup> In comparison with previous kinetic studies, the precision of the present measurements was inferior, and replicate measurements of a given rate constant varied by as much as a factor of 2. A possible source of errors in the kinetic measurements is that kinetic data are taken from experiments in which different reaction mixtures were used. Because of difficulties in the preparation of HCN and because of possible variation in the extent to which this polar molecule adsorbed to the walls of the gas handling system in different experiments, the actual concentration of HCN in the mixture in the ion source may have been in error by up to a factor of 2. In data taken from single sets of experiments the precision is somewhat better. For example in pressure studies such as shown in Figures 8 and 9 the precision was usually within ±40%.

In investigating the temperature dependence of the kinetics of the association reactions we observed a complex and unusual



**Figure 7.** Second-order rate constants for the association reactions of HCNH<sup>+</sup>, *s*-C<sub>3</sub>H<sub>7</sub><sup>+</sup>, and *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> with HCN as a function of temperature. All the measurements for the reaction of HCNH<sup>+</sup> were performed at a third-body density within ±10% of  $N_{\text{CH}_4} = 5.0 \times 10^{16} \text{ cm}^{-3}$ , for the reaction of *s*-C<sub>3</sub>H<sub>7</sub><sup>+</sup> at  $N_{\text{CH}_4} = 4.8 \times 10^{16} \text{ cm}^{-3}$ , and the reactions of *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> at  $N_{\text{CH}_4} = 4.4 \times 10^{16} \text{ cm}^{-3}$ . Precision of the rate constants is estimated as ±20%.

behavior. One aspect of this phenomenon is that, as we shall discuss further presently, the kinetic order of the reactions varies in a complex manner with temperature. Second- or third-order kinetics are not always applicable. In order to illustrate the variation of kinetics with temperature, we plot the variation of the apparent second-order rate constant of the association reactions, as obtained from the rate of disappearance of reactants and appearance of products at a constant third-body number density at different temperatures (Figure 7). We observe that the rate constants do not show a monotonic inverse temperature dependence, as would be usual for ion-molecule association reactions, but a more complex behavior. However, it must be emphasized that these second-order rate constants are not always meaningful since under some conditions third-order kinetics, or kinetics intermediate between third and second order, apply. A complex change in the order of the reaction is shown in Figures 8 and 9 by the pressure studies for reactions 7 and 8.

In Figure 8, we observe that the second-order rate constant does not change with pressure at 250 K, i.e., the kinetics are second-order or pseudo-second-order. At 280 K,  $k$  increases with  $N_{\text{CH}_4}$  up to  $N_{\text{CH}_4} = 3 \times 10^{16} \text{ mol cm}^{-3}$ ; the reaction exhibits pseudo-second-order behavior at higher densities. At 395

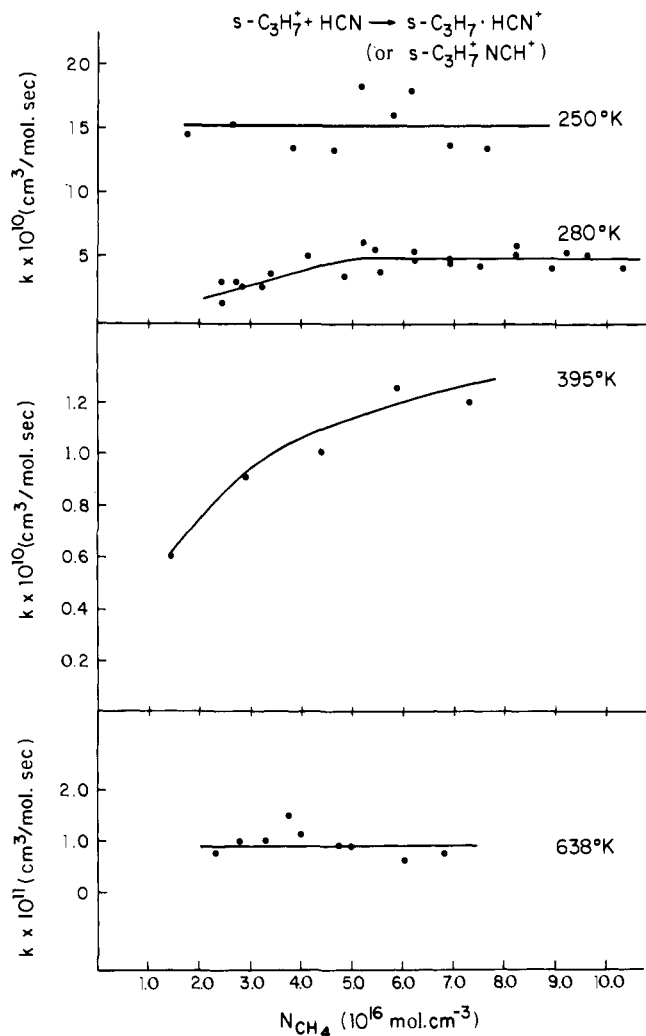


Figure 8. The dependence of the apparent second-order rate constant for the association of  $s-C_3H_7^+$  with HCN on the number density of the third body,  $CH_4$ , at four temperatures between 250 and 640 K.

K,  $k$  increases at least up to  $N_{CH_4} = 6 \times 10^{16} \text{ mol cm}^{-3}$  and possibly levels off above this density, although the data do not permit a reliable conclusion for the behavior above  $6 \times 10^{16} \text{ mol cm}^{-3}$ . An unusual observation is that at a yet higher temperature, 638 K, second-order behavior is again observed over the whole range of accessible densities. In a similarly unusual manner, the association of  $t-C_4H_9^+$  with HCN exhibits third-order kinetics at a low temperature (277 K) but second-order kinetics at a higher temperature (400 K) (Figure 9). As for the association of  $HCNH^+$  with HCN, pressure studies showed third-order kinetics from 200 to 540 K. At higher temperatures ( $T > 570 \text{ K}$ ), where reversible kinetics and a positive temperature dependence (Figure 7) seems to commence, the scattering of data in pressure studies did not allow a conclusive definition of the reaction order, although second-order kinetics was indicated.

The behavior observed in Figure 7 in the pressure studies at 250–395 K may be explained on the basis of the energy transfer mechanism:



The overall forward rate constant is given by

$$k_f = \frac{k_a k_s(M)}{k_b + k_s(M)} \quad (2)$$

In the high-pressure limit,  $k_s(M) \gg k_b$  and  $k_f = k_a$ ; the re-

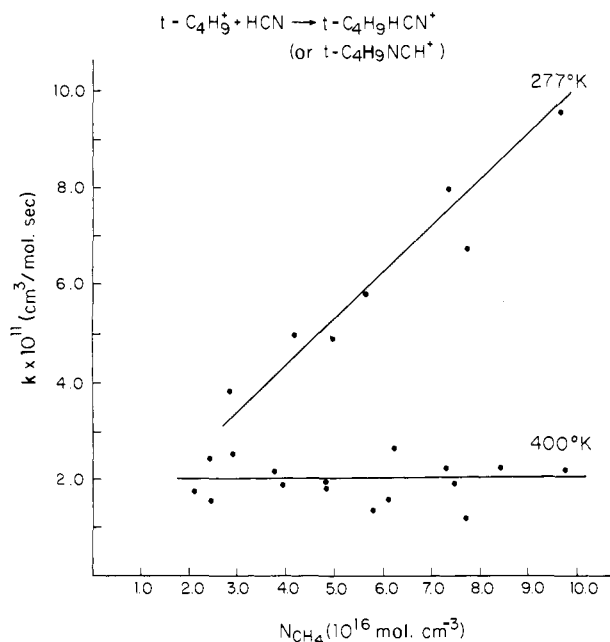


Figure 9. The dependence of the apparent second-order rate constant for the association of  $t-C_4H_9^+$  with HCN on the third-body density at 270 and 410 K.

action is second order (Figure 8, 250 K). In the low-pressure limit  $k_b \gg k_s(M)$  and  $k_f = (k_a k_s/k_b)(M)$ ; the reaction is third order. In intermediate cases the more complex rate constant given in eq 2 applies, and asymptotic approach to second-order kinetics with increasing ( $M$ ) is observed (Figure 8, 395 K). Since at the high-pressure limit  $k_f = k_a$ , we observe that for reaction 7,  $k_a^{250} = 15 \times 10^{-10}$  and  $k_a^{280} = 4.3 \times 10^{-10} \text{ cm}^3/(\text{mol} \cdot \text{s})$ . On inverting eq 2 we obtain:

$$\frac{1}{k_f} = \frac{k_b}{k_a k_s(M)} + \frac{1}{k_a} \quad (3)$$

Using eq 3,  $1/k_a$  may be obtained from the intercept of a plot of  $1/k_f$  vs.  $1/(M)$ . Using this method, we obtain  $k_a^{395} = 1.8 \times 10^{-10} \text{ cm}^3/(\text{mol} \cdot \text{s})$ . We note that  $k_a$  is not equal to the collision rate between  $C_3H_7^+$  and HCN, which may be calculated from ADO theory<sup>16</sup> at 250, 280, and 395 K at 2.3, 2.2, and  $1.9 \times 10^{10} \text{ cm}^3/(\text{mol} \cdot \text{s})$ , respectively. Rather  $(k_a/k_{ADO}) < 1$  and  $(k_a/k_{ADO})$  decreases with temperature. In a previous study we observed one case where an association reaction, that of  $C_2H_5(CH_3)_2NH^+$  with  $C_2H_5(CH_3)_2N$ , leveled off to a second-order rate-constant substantially below the collision rate.<sup>17</sup> Also, recently Bowers and co-workers indicated that  $k_a$  may be smaller than  $k_{\text{collision}}$ , and inversely related to temperature, even in the case of clustering reactions of smaller protonated amines.<sup>18</sup> Thus it may be a general phenomenon that not all collisions between reactants of ion-molecule association processes lead to complexes which may be stabilized by collision with a third body to form an observable association product.

On the basis of eq 1 it is understandable that at low temperatures the second-order limit is reached at low third-body densities, as we observe in reaction 7 at 250 and 280 K. This is a result of the low value of  $k_b$  when the internal energy in the excited reaction complex is small. However, it is very unusual that an association reaction should change from third-order kinetics or kinetics intermediate between third- and second-order to second-order kinetics as the temperature is increased, as we observe in Figure 8. This unusual change is reminiscent of observations of Hiraoka and Kebarle,<sup>19</sup> who showed that  $C_2H_5^+$  associated with  $H_2$  to form a cluster ion in a third-order process at low temperatures ( $-160 < T < -100 \text{ }^\circ\text{C}$ ), that no association was observed between  $-130$  and  $-100 \text{ }^\circ\text{C}$ , but at

higher temperatures ( $-100 < T < 40$  °C) a condensation reaction yielding C<sub>2</sub>H<sub>7</sub><sup>+</sup> commences. This high-temperature condensation reaction exhibits a positive temperature coefficient and an activation energy of 1.2 kcal/mol. In a similar manner, we do observe a transition to positive temperature dependence for the association of both HCNH<sup>+</sup> and *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> with HCN at the highest temperatures where these processes could be observed (Figure 7). The scattering of data introduces uncertainty in the observation of the positive temperature dependences at high temperatures, since the variation of the rate constant is the same order of magnitude as the experimental scatter. However, the effect was reproducible in two sets of temperature studies in each reaction, and thus it is judged to be a real effect. In the reaction of C<sub>3</sub>H<sub>7</sub><sup>+</sup> with HCN a positive temperature dependence at high temperatures is indicated by the last few points on Figure 7, but the data are not conclusive.

The equilibrium measurements which indicated the formation of isocyanides in the reactions of *s*-C<sub>3</sub>H<sub>7</sub><sup>+</sup> and *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> with HCN were performed at the high-temperature range, where second-order kinetics and nonnegative temperature coefficients apply. The change in the nature of the reaction kinetics at low temperatures may indicate that the products are different at lower temperatures, maybe cluster ions rather than protonated molecules. Given the ease by which the carbonium ions and HCN should yield a protonated isocyanide, the formation of such an electrostatically bound complex and the presence of an activation barrier to condensation would be puzzling. Unfortunately, equilibrium could not be observed in these reactions at low temperatures and the heats of formation of the products at low temperatures cannot be ascertained.

As we noted earlier, ion-molecule condensation reactions may be of some interest in prebiotic chemistry.<sup>3</sup> HCN is believed to play a significant role in prebiotic organic synthesis;<sup>20</sup> this notion motivated Huntress and co-workers to examine the ionic chemistry of HCN by ICR techniques.<sup>21</sup> Under low-pressure conditions ( $P = 10^{-4}$  Torr) these workers found no significant ionic polymerization in gaseous HCN, although (HCN)<sub>2</sub><sup>+</sup> was observed. The present studies show that polymerization of protonated HCN does occur at pressures above 1 Torr. The evidence quoted above indicates that the gas phase polymers are hydrogen-bound clusters, which would probably decompose to monomeric HCN upon neutralization. However, structures other than the linear hydrogen-bound form of (HCN)<sub>*n*</sub>H<sup>+</sup> cannot be ruled out entirely on the basis of the present data. For example, the positive temperature coefficient, indicating an activation energy, in the formation of

(HCN)<sub>2</sub>H<sup>+</sup> at high temperatures (Figure 7) could be due to the formation of a chemically bound structure, such as (H<sub>2</sub>NCCN)<sup>+</sup>; cyanomethylimine is a known intermediate in the formation of an HCN oligomer in solution.<sup>22</sup>

The condensation of carbonium ions with HCN is probably more relevant than the reactions of HCNH<sup>+</sup> to organic synthesis in ionized reducing atmospheres. Hiraoka and Kebarle observed the formation of *s*-C<sub>3</sub>H<sub>7</sub><sup>+</sup> and *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> in ionized methane.<sup>23,24</sup> The present thermodynamic results show that these ions will condense with HCN to form protonated isocyanides. The RC-NC or bond in the product ions is likely to be preserved, or may rearrange to the more stable cyanide configuration, upon low-energy neutralization. Sequences of gaseous ionic processes may thus produce alkyl isocyanides or cyanides in ionized methane atmospheres containing HCN.

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