I. INTRODUCTION

The reaction rate coefficient for reaction (2) when H$_3$C$^+$ is the third-body, M, was reported in 1979 (Ref. 1) to have a radiative association mechanism. In that original work, two pieces of information were used to make the deduction. It was observed that the number of CH$_3$H$_2$ ions detected decreased with time, and that the removal of CH$_3$H$_2$ ions from the ion trap caused a decrease in the reaction rate coefficient. A radiative association mechanism has been identified for the reaction. It is therefore deduced that the reaction rate coefficient for the third-body, M, can be written as

$$k_{\text{reaction}} = \frac{1}{[\text{H}_3\text{C}^+][\text{HCN}][\text{H}_2\text{C}]=1\times10^{-12} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}}$$

A similar decrease also occurred in the number of HCN molecules detected, and it was suggested that the HCN molecules were being formed by a radiative association mechanism. The reaction rate coefficient for reaction (2) was determined to be

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A very different result was presented by Kompa, Bass, and Bowles in 1983. They followed the three-body stabilized reaction of HCN and found that the reaction rate coefficient was

$$k_{\text{reaction}} = \frac{1}{[\text{H}_3\text{C}^+][\text{HCN}][\text{H}_2\text{C}]=1\times10^{-12} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}}$$

A year later, the reaction rate coefficient was determined to be

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coefficient must be less than $\sim 5 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$.\footnote{14}

All the three-body reaction studies at low pressures ($< 10^{-3}$ Torr) used both the parent ion abundance, CH$_3^+$, and the product ion abundance, C$_2$H$_4$N$^+$, to determine the reaction rate coefficient. This differs from the radiative association rate constant measurements measured in the trapped-mode ICR experiments, where only the CH$_3^+$ ion was followed. In point of fact at no time has the presence of a product ion for the "radiative association" reaction been accounted for in the ICR trapped mode experiments.

A MIKES-CID study\footnote{15} was able to show that at high pressure ($10^{-4}$ Torr) the low energy collisionally stabilized products had the structure of CH$_3$CNH$^+$. At lower pressures ($< 10^{-5}$ Torr) the adduct had a structure like that of CH$_3$NCH$^+$.

Gilbert and McEwan\footnote{16} and Smith \textit{et al.}\footnote{17} using RRKM methods, modeled the CH$_3^+$/HCN system. The model was found to be very sensitive to the structure of the collision complex and the transition state back to reactants. They concluded that the CH$_3$NCH$^+$ is the structure of the association product that best fits the kinetic data of both the ICR and SIFT, even though the CH$_3$CNH$^+$ structure has the lower heat of formation.

Results of four different experiments will be presented and discussed. One will be the results of the low-pressure trapped-mode ICR and FT-ICR experiments between 10$^{-7}$ and 10$^{-6}$ Torr. The other two results will be higher pressure results from drift-mode ICR and tandem ICR-dempster-ICR experiments between 10$^{-5}$ and 10$^{-3}$ Torr. An interpretation will be presented and applied to the observations from the four different experiments.

The new experiment is the FT-ICR. A reexamination of the tandem ICR-dempster-ICR experiment will also be presented.

II. EXPERIMENT

The trapped-mode ICR and drift-mode ICR experiments were not performed as part of this work. Descriptions of these experiments can be found in the references cited.

A. FT-ICR

The FT-ICR experiments were performed using an OMEGA 50 IonSpec (Ref. 11) Fourier transform mass spectrometer. Briefly, the instrument utilized computer controlled digital FT-ICR technology. Special features of this instrumentation included sequential multiple double resonance ejection, pulsed gas inlet system, and a 10 in. Walker Scientific electromagnet. The magnetic field was typically 1.1 T. The cell was a single 5.0 cm cube. Electron impact ionization was used to initiate ionization. The cell was pumped by a Balzer 330 s$^{-1}$ turbomolecular pump.

B. Tandem ICR-dempster-ICR

This instrument was built at UCSB and has been described previously.\footnote{18} It has been relocated to the JPL (see Acknowledgments).

The design is an adaptation of that used by Smith and Futrell.\footnote{19} Instead of the standard dempster source an ICR cell was used as the ion source. Ions generated in this cell are accelerated to typically 3000 V and bent through 180°. A second ICR cell is located 4.74 cm from the first, the 15 Dalton ions are guided into this second ICR by adjusting the magnetic field. The ions are decelerated and introduced into the second ICR through a 0.5 mm thick Wein filter which is 3.8 mm long. This design only allows ions with less than 0.3 eV of translational energy to enter the detection cell. A Wronka bridge detection circuit\footnote{20} was used to measure the ion abundances within the detection cell.

III. RESULTS AND DISCUSSION

A. Trapped-mode ICR

Typical results of experiments reported earlier from our laboratory\footnote{21} are shown in Fig. 1. The experiment consisted of recording CH$_3^+$ ion densities at different trapping times for known pressures of HCN in the ICR cell. The reaction rate coefficients for the reaction of CH$_3^+$ with HCN were found from the slope of the semilog plot of CH$_3^+$ abundance against the trapping time. Analysis of many such decays resulted in the reaction rate coefficient of $2 \times 10^{-10} \pm 10\% \text{ cm}^3 \text{s}^{-1}$. A typical mass spectrum of the ions in the ICR cell is shows ions present at masses 15, 16, 17, 26, 27, 28, 29, 38, 39, 40, 41, 42, and 43 Daltons. These correspond to the ions, CH$_3^+$, CH$_4^+$, CH$_2^+$, C$_2$H$_4^+$, CN$^+$, HCN$^+$, HCNH$^+$, C$_2$H$_5^+$, C$_2$H$_3^+$, C$_2$H$_2^+$, C$_2$H$_4^+$, CH$_2$CN$^+$, C$_3$H$_7^+$, C$_3$H$_5^+$, CH$_3$CNH$^+$, and C$_4$H$_7^+$. The pertinent reactions in the ICR cell are then

\begin{align}
\text{CH}_3^+ + \text{HCN} &\rightarrow \text{CH}_2\text{CN}^+ + \text{H} \\
\text{CH}_3^+ + \text{CH}_4 &\rightarrow \text{C}_2\text{H}_5^+ + 2\text{H}_2 \\
&\rightarrow \text{C}_2\text{H}_3^+ + \text{H}_2 + \text{H} \\
&\rightarrow \text{C}_2\text{H}_4^+ + \text{H}_2 \\
&\rightarrow \text{C}_2\text{H}_5^+ + \text{H} \\
\text{CH}_4^+ + \text{CH}_4 &\rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2 \\
\text{CH}_3^+ + \text{CH}_4 &\rightarrow \text{CH}_3^+ + \text{CH}_3
\end{align}
CH$_3^+$ + HCN → HCNH$^+$ + CH$_3$

→ CH$_3$CN$^+$ + H

(7)

CH$_3^+$ + HCN → HCNH$^+$ + CH$_4$

(8)

C$_2$H$_2^+$ + CH$_4$ → C$_3$H$_4^+$ + H$_2$

→ C$_3$H$_5^+$ + H

(9)

C$_2$H$_2^+$ + HCN → HCNH$^+$ + C$_2$H

→ CHCCN$^+$ + H

(10)

C$_2$H$_3^+$ + CH$_4$ → C$_3$H$_5^+$ + H$_2$

(11)

C$_2$H$_3^+$ + HCN → HCNH$^+$ + C$_2$H$_2$

(12)

C$_2$H$_4^+$ + CH$_4$ → C$_3$H$_5^+$ + H$_2$

(13)

C$_2$H$_4^+$ + HCN → HCNH$^+$ + C$_2$H$_4$

(14)

CN$^+$ + CH$_4$ → CH$_3^+$ + HCN

→ CH$_3^+$ + CN

→ HCN$^+$ + CH$_3$

→ HCNH$^+$ + CH$_3$

→ CH$_2$CN$^+$ + H$_2$

(15)

CN$^+$ + HCN → HCN$^+$ + CN

→ C$_2$N$_2^+$ + H

(16)

HCN$^+$ + CH$_4$ → HCNH$^+$ + CH$_3$

→ C$_2$H$_2^+$ + NH$_2$

(17)

HCN$^+$ + HCN → HCNH$^+$ + CN.

(18)

Of the ions produced in the ICR cell by electron impact and the reaction sequence (3)–(18), the protonated hydrogen cyanide ion, HCNH$^+$ is the most abundant. Using the double resonance technique all of reactions (3)–(18) could be verified, but the product ion of reaction (1) could not be confirmed. On several occasions double resonance experiments indicated a small fraction of the HCNH$^+$ ion was derived from CH$_3^+$, but this was not reproducible. A problem inherent in establishing a double resonance link between CH$_3^+$ and HCNH$^+$ is that the 28 Daltons signal is very large due to primary ionization of HCN and subsequent proton transfer to HCN.

B. FT-ICR

These results are new. We were able to observe the reaction of CH$_3^+$ with HCN using FT-ICR technology on an IonSpec FT-ICR mass spectrometer. The methyl ion was generated by electron impact on methane in a one cell instrument with HCN present during the whole experiment. A pulsed valve was used to introduce the methane into the spectrometer. The valve was open for 2 ms. After a delay of 80 ms, a 5 ms pulse of electrons was used to ionize the gases. In a resultant mass spectrum ions were identified at 15, 16, 17, 27, 28, 29, and 42 Daltons. Minor peaks at 18 and 19 Daltons were also present. The mass spectrum at this stage was identical to the trapped-mode ICR experimental results. All ions were then ejected from the cell by sequential double resonance ejection except the CH$_3^+$ ion at 15 Daltons. The ejection sequence started 15 ms after the electron pulse and lasted for about 16 ms. The reaction of CH$_3^+$ and HCN was then allowed to proceed and the ions in the cell were monitored for the next 210 ms as they reacted. Figure 2 shows the results of one of these experiments as data points. It is noted that the methyl ion concentration decreases exponentially with time, while the protonated HCN species increases. The protonated methyl isocyanide product, representing the collision complex and the radiative association product ion, stays at a steady state level of a few percent. We also found the HCNH$^+$ ion signal decreased when the CH$_3^+$ ion was ejected using a double resonance rf field as it also did when the 42 Dalton ion was irradiated. This second observation of a decrease in HCNH$^+$ upon double resonance ejection of (CH$_3$NCH$^+$)*, indicates some HCN$^+$ ions are derived from CH$_3$NCH$^+$, via reaction (19),

\[ \text{CH}_3\text{NCH}^+ + \text{HCN} \rightarrow \text{HCNH}^+ + \text{CH}_3\text{NC}. \]  (19)

Although reaction (19) is endothermic by 1.48 kJ/mol for reactants in their ground states, the formation process for CH$_3$NCH$^+$ in reaction (1) is so exothermic that the CH$_3$NCH$^+$ ion should have sufficient excess internal energy to drive the reaction. Several other reactions were considered linking the CH$_3^+$ ion to the HCNH$^+$ ion, but reaction (19) was the least endothermic option.

These observations allow us to present the following mechanism to represent the reaction sequence in the system:

CH$_3^+$ + HCN → (CH$_3$NCH$^+$)*

(20)

(CH$_3$NCH$^+$)* → (CH$_3$NCH$^+$) + hν

(21)

(CH$_3$NCH$^+$) + M → CH$_3$CNH$^+$ + M

(22)

(CH$_3$NCH$^+$) + HCN → HCNH$^+$ + CH$_3$NC

(23)

CH$_3$CNH$^+$ + HCN → no reaction.

(24)

A model based on reactions (20)–(24) is plotted in Fig. 2 as a set of solid lines. We note that in this model the collision
complex (CH$_3$NCH$^+$)* can be stabilized by either radiative association or collision stabilization. The collisionally stabilized CH$_3$CN is not reactive with HCN, while the radiatively stabilized (CH$_3$NCH$^+$)* is. The results of two further experiments were examined to test the proposed mechanism.

C. Drift-mode ICR

The drift-mode ICR results we have called on were extracted from literature sources. The experiments consist of observing the parent ions and product ions as a function of the cell pressure. The CH$_3$/HCN system has been examined in this way for the parent neutral, HCN, as well as other third bodies like He, Ne, and Ar. The analysis performed was to measure the peak heights of both the reactant and the products and using the power absorption equations to determine an effective second order reaction rate coefficient. The effective second order reaction rate coefficients were then plotted against the third body pressure. Figure 3 shows these results and reveals that the effective second order reaction rate coefficients increase linearly with pressure in this range and have an apparent zero intercept. This observation appears at first to indicate that the association reaction is third order and has no measurable second order reaction rate coefficient. This was in fact the conclusion of Kemper, Bass, and Bowers on viewing their results. The drift-mode operation of the ICR results in the reaction sequence (3)–(18) competing simultaneously with reactions (20)–(24). A mass spectrum taken in the drift-mode reveals the multiple ion problem observed in the trapped-mode.

To confirm their predictions, Kemper, Bass, and Bowers used the tandem ICR-dempster-ICR instrument which avoids complications of multiple many ions and neutrals that occur in the reaction region of a single cell instruments.

D. Tandem ICR-dempster-ICR

The results we present from this instrument are from one previous study plus some new results using the same instrument as in the earlier study. The literature results from the tandem instrument were entirely consistent with the drift-mode ICR results, in that collisional stabilization of the association complex is found to be very efficient. These earlier results which are characteristic of both the drift-mode ICR and tandem instruments, are shown in Fig. 3 and present the variation in effective second order reaction rate coefficient with the third body pressure. There is an important distinction between the drift-mode ICR and the tandem instruments. In the tandem, the ion source is completely separate from the reaction region. Methyl ions are generated in the source ICR cell from either methane or methyl bromide. The dempster section transfers the methyl ions from the source cell into the ICR reaction-detection cell. HCN at a known pressure is added into the reaction-detection ICR cell and the reactant and product ions are all monitored.

With this configuration it becomes possible to detect very low densities of the product ions that have more than one source of production. The model that we proposed in reactions (20)–(24) for the association of CH$_3$ and HCN, as well as the results of the experiments with the FT-ICR instrument, suggest that HCNH$^+$ is the product of the proton transfer reaction between the radiatively stabilized collision complex (CH$_3$NCH$^+$)* and HCN. As we have noted earlier, other sources of HCNH$^+$ in single cell instruments obscure this reaction product. Our new experiments with the tandem did show low concentrations of HCNH$^+$ as predicted by the model. A mass spectrum of the ions seen in the tandem experiment is shown in Fig. 4. The abundances of ions at 15, 28, and 42 Daltons were recorded at different HCN pressures and their measured abundances are compared with calculations based on the model presented in reactions (20)–(24) in Fig. 5. The instrumental signal at 42 Daltons includes both the collision stabilized adduct and the radiative stabilized adduct. The points are experimental and the lines are the model calculations. Finally we have shown in Fig. 6, the relative amounts of CH$_3$NCH$^+$ predicted by the model arising from association from complexes stabilized by radiation.
compared to those stabilized by collision with a third body.

We have noted that the new tandem experiments confirm the predictions of the model, in that a small steady state concentration of HCNH$^+$ was observed in the 10$^{-4}$ Torr range of HCN. The earlier work on the tandem instrument on this system makes no mention of a product at 28 Daltons. Private communication with the authors on this work revealed no evidence that this peak was observed or even looked for. The very low concentrations of the HCNH$^+$ ion would however have made it very easy to have been overlooked. The observation of a very small but nevertheless significant density of HCNH$^+$ is vital for a complete understanding of the stabilization mechanism of the association complex in the CH$_7^+/HCN$ system.

IV. CONCLUSION

We have amalgamated measurements from four different techniques in order to understand the association mechanism between CH$_7^+$ and HCN. When used in isolation, the conclusions based on evidence from a single technique can be interpreted quite differently than conclusions based on the results of the four techniques taken together. It is the inclusion and extrapolation of results from isolated experimental methods that have led to conflicting statements about the association mechanism in the CH$_7^+/HCN$ system. The situation is very similar to the Indian fable in which an elephant is examined by six blind men. Each individual touches a different part of an elephant and each reaches a different conclusion as to the nature of the beast.

The amalgamation in this work of the results from all four techniques shows that the simplest mechanism that can explain all the observations is the one given in reactions (20)-(24). In brief, CH$_7^+$ does react with HCN by a radiative association channel, with a reaction rate coefficient of $k = 2 \times 10^{-10}$ cm$^3$ s$^{-1}$. The association complex also undergoes very efficient collisional stabilization. At the lower pressure IRC experiments (e.g., Trapping-mode), reaction times are 100 times longer than the higher pressure IRC experiments (e.g., drift-mode). Quite different outcomes of the collision complex can eventuate in the different pressure regimes making it difficult to extrapolate the results from one pressure regime to the other. The drift-mode and the tandem results which gave effective zero intercepts on their $k_s$ vs pressure plots (Fig. 3) cannot be interpreted as evidence that radiative association is unimportant in the CH$_7^+/HCN$ system. Rather, it simply reflects the fact that the time between collisions is shorter than the collision complex lifetimes to radiative stabilization. At all pressures higher than 8 x 10$^{-3}$ Torr (M=HCN), the collision stabilization process will be the major complex stabilization mechanism. This results from the fact that the radiative relaxation step is too slow to be competitive with the more probable stabilizing collision.

Finally, we note that the differences in reactivity between radiative stabilization complex (CH$_3$NH$^+$)* and the collisionally stabilized complex (CH$_3$CN$^+$) are consistent with earlier structural analysis of the products. As noted in the Introduction the high pressure MIKE-CID results indicate the collision stabilized product has the CH$_3$CN$^+$ structure. On the other hand Smith et al. found the CH$_3$CN$^+$ structure to be inconsistent with the transition state requirements. It seems reasonable to assume therefore, that the initial stabilized structure is the CH$_3$NH$^+$ ion by both stabilization channels which is reactive in the initial energy state towards HCN. Collisions with a third body rapidly isomerizes this to the more stable CH$_3$CN$^+$ ion which is unreactive towards HCN.

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4H. I. Schiff, G. I. MacKay, G. D. Vlamis, and D. K. Bohme, in Proceed-


9 IonSpec Corporation, 17951 Skypark Circle, Suite K, Irvine, California 92714.


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