

AN ICR STUDY OF AN ASSOCIATION REACTION AT LOW PRESSURE

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ABSTRACT. An ICR investigation of the association reaction  
 $\text{CH}_3^+ + \text{HCN} \rightarrow \text{CH}_3\cdot\text{HCN}^+$   
 has shown the reaction follows second order kinetics over the pressure  
 range  $1 \times 10^{-6}$  to  $3 \times 10^{-4}$  Torr with a rate coefficient of  $2 \times 10^{-10}$   
 $\text{cm}^3\text{s}^{-1}$ . These results can be interpreted in terms of a saturated 3-body  
 or radiative association mechanism.

Investigations of the reactions of the gaseous ion  $\text{CH}_3^+$  with a number  
 of different molecules have shown the interesting feature that in several  
 reactions the formation of the association product follows second-order  
 kinetics<sup>1,2</sup>. The two main classes of association reactions that exhibit  
 second order kinetics are (a) saturated 3-body reactions and (b) radiative  
 association reactions. The application of radiative association reactions  
 to interstellar processes provides a convenient means of forming large  
 polyatomic molecules. However, even though radiative association has been  
 invoked in models of interstellar chemistry<sup>3,4</sup>, there is still little  
 direct experimental evidence for its participation as an important process.  
 The 3-body association process represented by reaction (1) and radiative  
 association by reaction (2)



can be understood in terms of two distinct steps. The first of these  
 steps (reaction (3)) is common to both 3-body and radiative association.



By using the steady state approximation applied to complex  $(\text{AB}^+)^*$  and  
 assuming that dissociation of  $(\text{AB}^+)^*$  is rapid compared with stabilization,  
 it is readily shown that the rate of production of the associated product

$AB^+$  is given by

$$d[AB^+]/dt = (k_3/k_{-3}) ([A^+][B])(k_4[M] + k_5). \quad (6)$$

The overall rate coefficients for 3-body and radiative association are therefore

$$k_1 = k_3k_4/k_{-3} \quad (7)$$

and

$$k_2 = k_3k_5/k_{-3} \quad (8)$$

As typical values for the rate coefficients  $k_4$  and  $k_5$  are  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and  $10^2\text{--}10^3 \text{ s}^{-1}$  respectively<sup>1,5</sup>, and  $[M] \sim 10^{15} \text{ molecules cm}^{-3}$  in most flow tube experiments<sup>1,2</sup>, then 3-body association should dominate radiative association.

We have applied the ion cyclotron resonance (ICR) technique to investigate the association process



and have found reaction (9) to follow second order kinetics throughout the entire pressure-range of the experiment, viz.  $1 \times 10^{-6} - 2 \times 10^{-4}$  Torr. Good agreement was found between rate coefficients determined in the trapping mode at the low end of the pressure range and the drift mode at the high end of the pressure range. The observed rate coefficient at room temperature (300 K) was  $k_9 = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and was independent of pressure. A most interesting feature of this work is that the observed rate coefficient for  $k_9$  is less than the value of  $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  reported by Schiff and Bohme<sup>2</sup> in their study of the much higher pressure range  $\sim 0.3$  Torr. There are two likely explanations for the difference. In this work the product  $k_4[M]$  is a factor  $\sim 10^4$  less than in the flow tube of Schiff and Bohme. Consequently we may be in a pressure regime where radiative association is the dominant mechanism for association whereas 3-body association is the major process at  $\sim 0.3$  Torr. Alternatively, as the  $\text{CH}_3^+$  ions in our work were formed by the impact of low energy electrons on  $\text{CH}_4$ , they may possess some vibrational excitation. A larger fraction of collisions between  $\text{CH}_3^+$  and HCN may then revert back to primary reactants (process  $k_{-3}$ ) than was the case for thermal ions in the study by Schiff and Bohme.

If the second explanation is true, then the fact that we have observed second-order kinetics implies a value for  $\tau_D$ , the lifetime of the complex  $(\text{CH}_3.\text{HCN}^+)^*$  to unimolecular decomposition at room temperature, of  $\geq 3 \times 10^{-3} \text{ s}$ .

#### REFERENCES

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