

# THE FORMATION OF COMPLEX INTERSTELLAR MOLECULES BY RADIATIVE ASSOCIATION

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A new statistical theory of ion-molecule association reaction rate coefficients has been formulated and found to give good agreement with three-body association rate coefficients studied in the laboratory in the temperature range 100–300 K (Herbst 1979a). The theory indicates that certain radiative association reactions proceed rapidly at low interstellar temperatures to produce complex interstellar molecules, as suggested by Smith and Adams (1978).

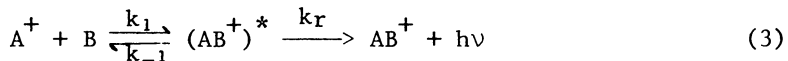
Radiative association is a process in which two gaseous molecules A and B react to form the species AB and a photon:



The process has not been generally studied in the laboratory because, at laboratory pressures, three-body association



normally dominates (Herbst 1979a,b). Some detailed theoretical work on the radiative association of small species such as  $\text{CH}^+$  and  $\text{CH}_2^+$  has been undertaken. Herbst (1976) has formulated a less detailed, statistical theory for the rate coefficients of radiative association reactions between molecular ions and neutrals. The motivation behind his work was the feeling that normal ion-molecule pathways could not produce complex interstellar molecules. In the theory, radiative association between the species  $A^+$  and B is modeled as the series of processes



where  $(AB^+)^*$  is a "complex" that is formed with a collision frequency  $k_1$  ( $\text{cm}^3\text{s}^{-1}$ ), decays randomly with rate coefficient  $k_{-1}$  ( $\text{s}^{-1}$ ), or can be stabilized via emission of an infra-red photon with rate coefficient  $k_r$  ( $\text{s}^{-1}$ ). The overall rate coefficient for radiative association

$k_{RA}$  ( $\text{cm}^3\text{s}^{-1}$ ) is given by the formula

$$k_{RA} = (k_1/k_{-1})k_r \quad (4)$$

if  $k_{-1} \gg k_r$ . Using this equation, Herbst (1976) calculated the rate coefficients of several radiative association processes. He concluded that radiative association is in general much slower than normal ion-molecule reactions and that only if the dominant species  $\text{H}_2$  were a reaction partner could radiative association even be competitive in dense interstellar clouds.

More recently, Smith and Adams (1978) investigated three-body association rate coefficients for  $\text{CH}_3^+$  and various neutrals using helium as the third body C. The overall rate coefficient  $k_{3B}$  ( $\text{cm}^6\text{s}^{-1}$ ) can be modeled by the relation

$$k_{3B} = (k_1/k_{-1})k_2 \quad (5)$$

at sufficiently low pressures (Herbst 1979a), where  $k_2$  is the collisional de-excitation frequency of the collision complex and  $k_1$  and  $k_{-1}$  are as defined above. Smith and Adams (1978) found  $k_{3B}$  to possess typically a strong inverse temperature dependence of the type  $T^{-n}$  where  $n > 3$  in the range 225–300 K. They then estimated  $k_{RA}$  for the analogous radiative association reactions involving  $\text{CH}_3^+$  and various neutrals by estimating  $k_2$  and  $k_r$  (Herbst 1976) and using relation (4). Boldly extrapolating to  $T \leq 50$  K, Smith and Adams (1978) deduced  $k_{RA}$  at these temperatures to be at or near the collision frequency for some, but not all of the reactions involving  $\text{CH}_3^+$  and neutrals. Although their procedure is open to criticism (Herbst 1979c), discrepancies between their work and theory (Herbst 1976) were sufficient to provoke a re-investigation of the statistical theory of radiative association. It was ascertained that the theory violated the principle of detailed balancing (Herbst 1979a) which relates  $k_1$  and  $k_{-1}$  via the equation

$$k_1 q_{A^+} q_B = k_{-1} q_{AB^+} \quad (6)$$

where  $q_{A^+}$ ,  $q_B$ , and  $q_{AB^+}$  are molecular partition functions per unit volume. Use of equation (6) in relations (4) and (5) results in statistical theories for  $k_{RA}$  and  $k_{3B}$  that do not violate detailed balancing. Herbst (1979a) utilized such a statistical theory to calculate values for  $k_{3B}$  that agree well in temperature dependence and magnitude with the work of Smith and Adams (1978) and more recent experimental work in the temperature range 100–300 K. Thus, a proper statistical theory can reproduce laboratory three-body results.

The corrected statistical theory has now been applied to radiative association at low interstellar temperatures (Herbst 1979c). In general, the low temperature extrapolations of Smith and Adams (1978) have been found to be somewhat optimistic, but in no case have there been discrepancies of more than two orders of magnitude with our calculated results. The statistical theory thus indicates that

in favorable cases (e.g., some  $\text{CH}_3^+$  reactions) radiative association rate coefficients can approach collision frequencies at temperatures under 50 K. Favorable cases are those in which no activation energy barriers exist to block facile formation of a tightly-held complex, no normal exothermic channels are readily available to the tightly-held complex, and the density of vib-rotational states of the complex is large. The last factor depends on both the dissociation energy  $D_0$  of the product molecule and its size. To illustrate these effects, Table I contains some calculated values of  $10^9 k_{\text{RA}}$  at 10 K and 50 K for reactions of possible interstellar importance. (Note that a typical ion-molecule collision frequency is  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$  so that  $10^9 k_{\text{RA}}$  can be considered a sticking probability.). As can be seen, radiative association reactions of  $\text{CH}_3^+$  with CO,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  are facile for  $T \leq 50 \text{ K}$

TABLE I Some Calculated Reaction Rates

Reaction	$D_0$ (eV)	$10^9 k_{\text{RA}}$ (10 K, 50 K)
$\text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_5^+$	1.7	$2 \times 10^{-3}$ , $2 \times 10^{-4}$
$\text{CH}_3^+ + \text{CO} \rightarrow \text{C}_2\text{H}_3\text{O}^+$	3.6	$6 \times 10^{-1}$ , $2 \times 10^{-2}$
$\text{CH}_3^+ + \text{H}_2\text{O} \rightarrow \text{CH}_5\text{O}^+$	2.8	$6 \times 10^{-1}$ , $9 \times 10^{-3}$
$\text{CH}_3^+ + \text{NH}_3 \rightarrow \text{CH}_6\text{N}^+$	4.5	$\sim 1$ , $\sim 1$
$\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_5^+$	0.4	$8 \times 10^{-8}$ , $1 \times 10^{-8}$
$\text{NH}_3^+ + \text{CO} \rightarrow \text{NH}_3\text{CO}^+$	0.3	$1 \times 10^{-8}$ , $4 \times 10^{-10}$
$\text{H}_2\text{CN}^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_4\text{N}^+$	1.5 (?)	$3 \times 10^{-2}$ , $5 \times 10^{-4}$

whereas reactions with small  $D_0$  ( $< 1 \text{ eV}$ ) are very slow even if eight-atom molecules are produced.

Huntress and Mitchell (1979) and Mitchell, Huntress, and Prasad (1979) have estimated that radiative association reactions, if rapid, can make most complex interstellar molecules. In Table II are compared a small selection of their required  $k_{\text{RA}}$  values with our calculated ones at 50 K. The neutral molecules resulting from subsequent ion-electron reactions are also listed.

TABLE II Comparison of Results With Model

Reaction	Eventual Product	Req. $k_{\text{RA}}$ /Cal. $k_{\text{RA}}$ (50 K)
$\text{C}^+ + \text{H}_2$	CH	1
$\text{CH}_3^+ + \text{H}_2$	$\text{CH}_4$	1
$\text{CH}_3^+ + \text{CO}$	$\text{CH}_2\text{CO}$	$> 10^{-1}$
$\text{CH}_3^+ + \text{H}_2\text{O}$	$\text{CH}_3\text{OH}$	$10^2$
$\text{NH}_3^+ + \text{H}_2$	$\text{NH}_3$	$1-10^2$
$\text{NH}_3^+ + \text{CO}$	HNCO	$10^7$
$\text{H}_2\text{CN}^+ + \text{C}_2\text{H}_2$	$\text{HC}_3\text{N}$	$> 10^3$

It can be seen that their proposed syntheses for methane, ketene, and possibly methanol and ammonia are not contradicted by our results, whereas their syntheses of HNC and maybe  $\text{HC}_3\text{N}$  are too rapid if our work is valid. Generalizing from these results, we emphasize that radiative association reactions likely are important in interstellar chemistry but that each reaction must be examined individually. The safest method for determining whether a given ion-molecule reaction will undergo facile low temperature radiative association is to determine whether or not a rapid three-body channel leading to a stable species occurs in the laboratory. If so, then a long-lived, tightly-held complex is indicated and our statistical theory can be utilized at low temperatures with some degree of confidence.

#### ACKNOWLEDGEMENTS

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#### DISCUSSION FOLLOWING HERBST

*Hagen:* Your calculations indicate that HNC cannot be formed by the radiative association of  $\text{NH}_3^+$  and CO; it is your "most negative" result. Our experiments show that this molecule is formed in large quantities by ultraviolet irradiation of low temperature (10 K) grain mantle analogs composed of solid CO and  $\text{NH}_3$ .

*Herbst:* The fact that the radiative association of  $\text{NH}_3^+$ +CO is too slow to produce the observed HNC abundance does not mean that there do not exist other, more efficient, such gas-phase syntheses.

*D. Smith:* The collisional association reaction  $\text{NH}_3^+$ +CO+He $\rightarrow$  $\text{NH}_3^+$ .CO+He does not proceed at a measurable rate at 300 K, whereas the  $\text{NH}_2^+$ +CO+He association reaction proceeds at a significant rate at 300 K.

*Allamandola:* You list rate constants as applicable at 10 K and 50 K. Do you take different activation energy effects into account at these

two different temperatures? If so, how do you do this? If not, while your rate constants at 50 K are probably very reliable I think that they may be significantly lower in the 10 K limit, because at this low temperature the thermal energies are now comparable to activation energies for many low activation energy reactions.

*Herbst:* The question of whether or not small activation energies exist in ion-molecule systems has not yet been addressed by low temperature experiments.

*Prasad:* A rate coefficient  $k=3 \times 10^{-10} \text{cm}^3 \text{s}^{-1}$  for the reaction  $\text{H}_2\text{CN}^+ + \text{C}_2\text{H}_2 \rightarrow \text{H}_4\text{C}_3\text{N}^+ + h\nu$  was required by Mitchell, Huntress and Prasad on the assumption that  $\text{HC}_3\text{N}$  was totally destroyed by reactions with  $-\text{C}^+$ . It is possible that reactions of  $\text{HC}_3\text{N}$  with  $-\text{C}^+$  merely recycle the former species. In this case  $\text{HC}_3\text{N}$  may have a long lifetime ( $\geq 10^{15} \text{s}$ ). The postulated radiative association mechanism would then become relevant to  $\text{HC}_3\text{N}$  synthesis even with the smaller  $k$  you predict.