THE FORMATION OF INTERSTELLAR MOLECULES VIA RADIATIVE ASSOCIATION REACTIONS

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ABSTRACT

The radiative association rate coefficients and their temperature dependences have been estimated for several likely interstellar ion-molecule reactions from laboratory collisional association rate data. They include the $CH_3^+ + H_2$ and $CH_3^+ + H_2O$ reactions, which we suggest lead to CH_4 and CH_3OH respectively, and the critical association reaction $C^+ + H_2$.

RADIATIVE ASSOCIATION RATES FROM LABORATORY COLLISIONAL RATE DATA

Our initial studies of the ternary association reactions of CH_3^+ ions with the molecules X = H_2, N_2, O_2, CO and CO_2 showed that their rate coefficients, k_3, varied with temperature according to the relation $k_3 = AT^{-n}$, where $n \sim 4$ between 300 K and 225 K (Smith and Adams, 1978a). From this data we have deduced the lifetimes against unimolecular decomposition of the excited intermediate complexes $(CH_3X^+)^*$ and, on the assumption that $(CH_3X^+)^*$ can be stabilised via the emission of an infra-red photon (radiative lifetime $\sim 10^{-3}$s), we have shown that the corresponding binary radiative association reactions (rate coefficients k_r) will proceed at significant rates at the temperatures of interstellar clouds (Smith and Adams, 1977, 1978b). Especially interesting is the $CH_3^+(H_2, CH_5^+)h\nu$ reaction for which we deduce a value of k_r at 50K of $4.0 \times 10^{-13} cm^3 s^{-1}$ and which we suggest generates CH_4 in dense clouds in a relative abundance of $\sim 10^{-4}$.

Subsequent to these studies we have confirmed the T^{-n} variation of k_3 for the above reactions down to a temperature of $\sim$100 K (Adams et al., 1979), and now we have extended the temperature range upwards to $\sim$500K for the H_2 and CO reactions, firmly establishing the power law temperature dependence over the range $\sim$100K to $\sim$500 K for these reactions.

The collisional association reactions of CH_3^+ ions with the polar

B. H. Andrew (ed.), Interstellar Molecules, 323–324.

molecules H_2O, NH_3, CH_3OH and H_2CO are especially rapid, k_3 for these being appreciable fractions of their collisional rate coefficients even at 300 K, and consequently their k_r in interstellar clouds should be large. Thus we have suggested that these reactions will contribute significantly to the synthesis of the interstellar CH_3OH and H_2CO via the reaction sequence

$$CH_3{}^+ \xrightarrow{H_2O} CH_3H_2O^+ \xrightarrow{e} CH_3OH$$

$$CH_3{}^+ \xrightarrow{CH_3OH} H_3CO^+, CH_3CH_3OH^+ \xrightarrow{e} H_2CO, C_2H_5OH/(CH_3)_2O$$

This suggested scheme is not inconsistent with the astronomical observations of Gottlieb et al. (1979).

It seems likely that many other radiative association reactions contribute to molecular synthesis in interstellar clouds. Therefore we are continuing our laboratory studies over the wider temperature range now attainable in our experiment. Special attention is being given to the reactions of those interstellar ions which, like $CH_3{}^+$, do not undergo significant binary reaction with H (e.g. C^+, $C_2H_2{}^+$, $C_2H_3{}^+$, $NH_4{}^+$, HCO^+ and H_3CO^+), and are thus available to undergo the generally slower radiative association reactions. To date we have studied the reaction $C^+ + H_2 + He \rightarrow CH_2{}^+ + He$, for which $k_3 \approx 7.5 \times 10^{-27} T^{-1.2} cm^6 s^{-1}$ over the temperature range $\sim$100 K to $\sim$500 K. The importance of the corresponding radiative association reaction, $C^+(H_2, CH_2{}^+)h\nu$ is well known, and several theoretical estimates of k_r have been made. These have varied from 10^{-17} to $10^{-14} cm^3 s^{-1}$, depending on the radiation emission process envisaged. Using the analysis adopted for the $CH_3{}^+$ reactions we deduce a value for k_r which lies within the range 10^{-16} to $10^{-15} cm^3 s^{-1}$ at 50 K, assuming, as before, that the $(CH_2{}^+)^*$ excited complex decays via the emission of an infra-red photon. Other collisional association reactions which we have as yet only studied briefly include those between $C_2H_2{}^+$, $C_2H_3{}^+$, $C_2H_4{}^+$ and CO, which proceed at very appreciable rates ($k_3 \sim 10^{-29} cm^6 s^{-1}$ at 300 K).

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