Synthesis of Molecules in Interstellar Clouds & Star Formation*

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Study of the formation and destruction processes of interstellar molecules may throw certain light on interstellar medium. Formation and destruction processes of some interstellar molecules are proposed on the basis of laboratory data. The abundances of these molecules are calculated under steady-state condition. The calculated values are then compared with the observed values, obtained by different investigators. It appears that gas phase ion-neutral reactions are capable of synthesizing most interstellar molecules. The role of ion-neutral reactions to star formation has also been discussed.

1. Introduction

There are two types of clouds, namely diffuse and dark, in interstellar space. In diffuse clouds, the average number density is $10^{-10}$ cm$^{-3}$, the gas kinetic temperature is $\sim 80$ K and radiations of shorter wavelengths (UV radiation) penetrate them. In dark clouds, the average number densities range from $10^3$ to $10^7$ cm$^{-3}$, gas kinetic temperatures from 10 to 200 K and ultraviolet radiation is not present in the interior of these clouds. A large number of molecules have been detected in interstellar space. For the formation and destruction processes of interstellar molecules, varieties of gas phase reactions may occur such as ion-neutral reactions, neutral-neutral reactions, photo-ionization and photodissociation, cosmic ray ionization and dissociation and ion-electron recombinations. Also catalytic formation on the surfaces of dust grains may be an important process. The relative importance of these processes depends on the total density and on the interstellar radiation field. In dark clouds cosmic ray ionization plays the dominant role. In calculating the abundances of interstellar molecules in dark clouds a model of the cloud is required. We have assumed the mass of the cloud to be of the order of $300 M_\odot$ ($M_\odot$ being the solar mass), optical attenuation coefficient to be 4 mag, ionization of elements to be mainly by cosmic rays, average gas temperature to be $\sim 50$ K and total number densities of molecules to be $10^5 - 10^6$ cm$^{-3}$. The abundances of molecules are then calculated under steady state condition and compared with the observed values. The importance of ion-neutral reactions for star formation has also been discussed.

2. Formation and Destruction Processes

2.1 Nitroxy (HNO)

The presence of interstellar nitroxy has been confirmed by Ulich et al. and its observed abundance in Sgr B2 is of the order of $10^{-9} n(H)$, where $n(H)$ is the total number density of the molecules. Nitroxy may be formed by the radiative association of NO$^+$ and H$_2$ (Ref. 2). The nitrosonium ion, NO$^+$, may be formed by the following reaction.

$$\text{NO}^+ + \text{C}^+ \rightarrow \text{NO}^+ + \text{C}$$  \hspace{1cm} (I)

It will be lost by recombination with electrons as follows.

$$\text{NO}^+ + e^- \rightarrow \text{N} + \text{O}$$  \hspace{1cm} (2)

Finally through dissociative electron recombination, HNO is obtained.

$$\text{H}_2\text{NO}^+ \rightarrow \text{HNO} + \text{H}$$  \hspace{1cm} (4)

The main loss processes of HNO are

$$\text{HNO} + \text{C}^+ \rightarrow \text{CH}^+ + \text{NO}$$  \hspace{1cm} (5)

$$\rightarrow \text{NO}^+ + \text{CH}$$  \hspace{1cm} (6)

$$\text{HNO} + h\nu \rightarrow \text{H} + \text{NO}$$  \hspace{1cm} (7)

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Huntress and Mitchell\(^2\) have suggested that the rate coefficient for radiative association reaction is \(5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}\). Rate coefficient for reactions (5) and (6) is assumed to be \(10^{-9} \text{ cm}^3 \text{ sec}^{-1}\) and the photodissociation cross-section to be \(10^{-16} \text{ cm}^2\) (Ref. 5). The attenuated photoflux \(F(\lambda)\) at 5891 Å in the interior of dark cloud is calculated and found to be \(\sim 4 \times 10^5 \text{ em}^{-2} \text{ sec}^{-1}\) using the relation

\[
A_\lambda = -2.5 \log \left( \frac{F(\lambda)}{F_0(\lambda)} \right)
\]

where

- \(A_\lambda\) Attenuation coefficient
- \(F_0(\lambda)\) Stellar flux at the earth in the absence of extinction

The abundances\(^6\) of \(C^+\) are

\[
\log \left[ \frac{[C^+]}{[n(H)]} \right] \sim -9.67 \quad \text{for} \quad [n(H)] = 10^5 \text{ cm}^{-3}
\]

and

\[
\log \left[ \frac{[C^+]}{[n(H)]} \right] \sim -10.61 \quad \text{for} \quad [n(H)] = 10^6 \text{ cm}^{-3}
\]

Thus the calculated abundances of \(\text{HNO}\) is \(\text{HNO}/\text{n(H)} \sim 4 \times 10^{-9}\), which agrees well with the observed value\(^1\). Another route for the formation of \(\text{HNO}\) is

\[\text{NH}_3 + \text{O} \rightarrow \text{NH}_2\text{O}^+ + h\nu \quad \text{(8)}\]

followed by

\[\text{NH}_2\text{O}^+ + e^- \rightarrow \text{HNO} + \text{H}_2 \quad \text{(9)}\]

This process may also produce required amount of \(\text{HNO}\), if the rate coefficient\(^2\) for reaction (8) is \(10^{-13} \text{ cm}^3 \text{ sec}^{-1}\).

2.2 Methanimine (\(\text{CH}_2\text{NH}\))

Methanimine has been detected in interstellar clouds and its observed abundance in Sgr B2 is \(10^{-10} \text{n(H)}\). Smith and Adams\(^7\) have suggested that the radiative association reaction of \(\text{CH}_3^+\) and \(\text{NH}_3\) followed by the dissociative electron recombination process may lead to the formation of \(\text{CH}_2\text{NH}\). But the calculated abundance does not agree with their observed value\(^7\). It may be formed through the ion-neutral reactions as follows

\[\text{CH}_3^+ + \text{NH}_3 \rightarrow \text{CH}_2\text{NH}_2^+ + \text{H} \quad \text{(10)}\]

or

\[\text{CH}_3^+ + \text{NH}_3 \rightarrow \text{CH}_2\text{NH}_3^+ + \text{H}_2 \quad \text{(11)}\]

followed by

\[\text{CH}_2\text{NH}_2^+ + e^- \rightarrow \text{CH}_2\text{NH} + \text{H} \quad \text{(12)}\]

The laboratory rate coefficients for reactions (10) and (11) found in the laboratory are \(1.2 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}\) (Ref. 8) and \(1.5 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}\) (Ref. 9), respectively. The abundances\(^6\) of \(\text{CH}_2^+\) and \(\text{CH}_3^+\) are

\[
\log \left[ \frac{[\text{CH}_2^+]}{[\text{n(H)}]} \right] \sim -15.69 \quad \text{for} \quad [\text{n(H)}] = 10^6 \text{ cm}^{-3}
\]

and

\[
\log \left[ \frac{[\text{CH}_3^+]}{[\text{n(H)}]} \right] \sim -11.89 \quad \text{for} \quad [\text{n(H)}] = 10^6 \text{ cm}^{-3}
\]

The observed abundance\(^6\) of \(\text{NH}_3\) is \(10^{-8} \text{n(H)}\) \text{ cm}^{-3}\). The loss processes of \(\text{CH}_2\text{NH}\) may be as follows\(^1\).

\[\text{CH}_2\text{NH} + \text{C}^+ \rightarrow \text{CH}_2\text{NH}^+ + \text{C} \quad \text{(13)}\]

Calculated abundance of methanimine formed through reaction (11) agrees well with the observed value\(^2\). However, reaction (10) cannot produce the required amount of methanimine. Radiative association of \(\text{H}_2\text{CN}^+\) ions with \(\text{H}_2\) through the reaction

\[\text{H}_2\text{CN}^+ + \text{H}_2 \rightarrow \text{CH}_2\text{NH}_2^+ + h\nu \quad \text{(14)}\]

followed by electron recombination process yields methanimine.

The calculated rate coefficient\(^1\) for reaction (14) at 50 K is \(2.7 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}\) and the laboratory rate coefficient\(^1\) for that reaction is of the order of \(10^{-16} \text{ cm}^3 \text{ sec}^{-1}\). The reaction of \(\text{C}^+\) and \(\text{NH}_3\) may lead to the formation of \(\text{H}_2\text{CN}^+\) and get lost principally by recombination with electrons.

2.3 Methanol (\(\text{CH}_3\text{OH}\))

Gottlieb et al.\(^15\) had detected methanol in the dark clouds of interstellar medium. Its average abundance is of the order of \(10^{-7} \text{n(H)}\). It may be formed from the association of \(\text{CH}_3^+\) with \(\text{H}_2\text{O}\)

\[\text{CH}_3^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH}_2^+ + h\nu \quad \text{(15)}\]

followed by

\[\text{CH}_3\text{OH}_2^+ + e^- \rightarrow \text{CH}_3\text{OH} + \text{H} \quad \text{(16)}\]

The rate coefficients for reaction (15) at 100, 50 and 20 K are \(8 \times 10^{-11}, 2 \times 10^{-9}\) and \(2.5 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}\), respectively\(^7\). The observed abundance of \(\text{H}_2\text{O}\) in Orion A is found to be \(\text{H}_2\text{O}/\text{n} \geq 10^{-5.8}\) (Ref. 16). The loss processes of methanol are\(^1\)

\[\text{C}^+ + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH}^+ + \text{C} \rightarrow \text{CH}_3\text{O}^+ + \text{CH} \rightarrow \text{HCO}^+ + \text{CH}_3 \rightarrow \text{CH}_3^+ + \text{HCO} \quad \text{(17)}\]
\[ \text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_3 + \text{OH} \quad \text{... (18)} \]

The attenuated photon flux at 3200Å in the denser regions of dark clouds is approximately \(10^4 \text{ cm}^{-2} \text{ sec}^{-1}\). The calculated abundance ratio of methanol at 100, 50 and 20 K are \(8 \times 10^{-8}\), \(1.5 \times 10^{-7}\) and \(2 \times 10^{-7} \text{ cm}^{-3}\), respectively. These values agree well with the observed values.\(^7\)

An alternate path to methanol is \(\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH}^+ + H\quad \text{... (19)}\)

followed by

\[ \text{CH}_3\text{OH}^+ + \text{H} \rightarrow \text{CH}_3\text{OH}^+ + \text{H} \quad \text{... (20)} \]

\[ \text{CH}_3\text{OH}^+ + \text{H} \rightarrow \text{CH}_3\text{OH}^+ + \text{H} \quad \text{... (21)} \]

and reaction (16)

The laboratory rate coefficients for reactions (19) and (21) are, respectively, \(5.2 \times 10^{-10}\) and \(5 \times 10^{-13} \text{ cm}^3 \text{ see}^{-1}\) at 300 K. Methanol produced through reaction (19) is \(10^{-1}\) times the observed value.

2.4 Formic Acid (HCOOH)

Formic acid was detected in the denser regions or dark clouds of interstellar medium and its observed abundance is obtained as \(10^{-10} - 10^{-11} n(\text{H})\). It may be formed through the radiative association reaction for \(\text{CH}_3^+\) ions with \(\text{O}_2\) molecules

\[ \text{CH}_3^+ + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2^+ + h\nu \quad \text{... (22)} \]

followed by

\[ \text{CH}_3\text{O}_2^+ + e \rightarrow \text{HCOOH} + \text{H} \quad \text{... (23)} \]

The abundance of \(\text{O}_2\) is \((10^{-3}-10^{-5}) n(\text{H})\). The rate coefficients\(^7\) for reactions (22) at 100, 50 and 20 K are \(3 \times 10^{-15}, 4.8 \times 10^{-14}\) and \(1.9 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}\), respectively. Smith and Adams\(^7\) have suggested that reaction (22) may be only a minor channel for formic acid. Its loss processes may be as follows\(^11\):

\[ \text{C}^+ + \text{HCOOH} \rightarrow \text{HCO} + \text{CO}^+ \]

\[ \rightarrow \text{HCOOH}^+ + \text{C} \quad \text{... (24)} \]

and

\[ \text{HCOOH} + h\nu \rightarrow \text{HCO} + \text{OH} \quad \text{... (25)} \]

The calculated abundances of formic acid at 100, 50 and 20 K agree well with the observed value.

An alternative mechanism, viz.

\[ \text{HCO}^+ + \text{H}_2\text{O} \rightarrow \text{HCOOH}^+ + h\nu \quad \text{... (26a)} \]

\[ \rightarrow \text{H}_2\text{O}^+ + \text{CO} \quad \text{... (26b)} \]

followed by

\[ \text{HCOOH}^+ + e \rightarrow \text{HCOOH} + \text{H} \quad \text{... (27)} \]

may give HCOOH (Ref. 2). If the rate coefficient for reaction (26a) is \(10^{-13} \text{ cm}^3 \text{ sec}^{-1}\) at 50 K, the calculated abundance agrees well with the observed values.\(^7\)

2.5 Methylamine (\(\text{CH}_3\text{NH}_2\))

From the transitions \(5_{15}-5_{05}(73.0 \text{ GHz}), 4_{14}-4_{04}(86.1 \text{ GHz})\) and \(2_{01}-1_{01}(8.8 \text{ GHz})\), the presence of interstellar methylamine was confirmed\(^18,19\). Its observed abundance is obtained as \(10^{-10} n(\text{H})\). Smith and Adams\(^7\) have suggested that the radiative association reaction

\[ \text{CH}_3^+ + \text{NH}_3 \rightarrow \text{CH}_3\text{NH}_2^+ + h\nu \quad \text{... (28)} \]

followed by

\[ \text{CH}_3\text{NH}_2^+ + e \rightarrow \text{CH}_3\text{NH}_2 + \text{H} \quad \text{... (29)} \]

may be a possible source of methylamine. The rate coefficients for reaction (28) at 100, 50 and 20 K are greater than \(4 \times 10^{-11}, 4 \times 10^{-10}\) and \(5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}\), respectively.\(^7\) The loss processes of methylamine are\(^11\):

\[ \text{C}^+ + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_2^+ + \text{C} \rightarrow \text{CH}_3\text{NH}_2 + \text{H} \]

\[ \rightarrow \text{H}_2\text{CN}^+ + \text{CH}_3 \rightarrow \text{CH}_3^+ + (\text{HCN} + \text{H}) \quad \text{... (30)} \]

\[ \text{CH}_3\text{NH}_2 + h\nu \rightarrow \text{CH}_3 + \text{NH}_2 \quad \text{... (31)} \]

The calculated abundance at 50 K does not agree with the observed value.\(^18,19\)

The heat of formation for \(\text{CH}_3\) is 33 K cal/mole (\(\sim 1.44 \text{ eV}\)) which can easily dissociate into \(\text{NH}_2^+ (\text{NH}_2^+ - \text{H})\) and may form \(\text{CH}_3\text{NH}_2^+\), whose ground state binding energy is 4.6 eV. The reaction of \(\text{CH}_3\) and \(\text{NH}_2^+\) is

\[ \text{CH}_3 + \text{NH}_2^+ \rightarrow \text{CH}_3\text{NH}_2^+ + \text{H} \quad \text{... (32)} \]

The complex, \(\text{CH}_3\text{NH}_2^+\), can produce methylamine by electron recombination process. The calculated rate coefficient for reaction (32) at 50 K is \(7 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}\). But this process cannot supply the required amount of methylamine.

Huntress and Mitchell\(^2\) have proposed that the radiative association reaction

\[ \text{CH}_3^+ + \text{NH}_3 \rightarrow \text{CH}_3\text{NH}_2^+ + \text{H}_2 \quad \text{... (33)} \]

followed by electron recombination, would yield an abundance of methylamine in fairly good agreement with observation for \([\text{CH}_3^+]/[\text{CH}_3]\), the value of which is \(\sim 10\), and rate coefficient for reaction (33), which is \(10^{-9} \text{ cm}^3 \text{ sec}^{-1}\).
3. Discussion

The reactions presented in Sec. 2 are able to produce a large variety of complex molecules observed in molecular clouds. In most of the cases laboratory rate coefficients have been used to calculate the abundances of the molecules. Still sufficient laboratory data for rate coefficients of radiative association and bimolecular reaction are needed at low temperatures to explain the observed abundances. Thus from the above study it is concluded that ion-neutral collisions play a dominant role for the formation and destruction of interstellar molecules. Hence, long-range polarization force will be an important one in molecular clouds. This force may help for ambipolar diffusion in self-gravitating clouds, where initial magnetic field is of the order of $10^{-6}$ gauss. Further, contraction of the cloud is not possible when both the gravitational and magnetic forces balance each other. In that case, ambipolar diffusion is the only proposed mechanism that can achieve the required reduction of magnetic flux in a self-gravitating cloud. Ambipolar diffusion does not alter the total magnetic flux threading a cloud, but simply redistributes the flux within the cloud. If field lines are straightened out, the redistribution of flux will reduce the magnetic energy of the cloud. Then, the ions will simply be 'held in place', and the neutrals driven by self-gravity continue to contract. Ultimately star formation takes place through gravitational collapse. Detailed dynamics of these processes are still under study.

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References