Thioformaldehyde (HICS), the sulphur analogue of formaldehyde (HICO), is widespread in the galaxy. It has been detected in interstellar clouds by using radio telescopes. Though it is chemically analogous to formaldehyde, its interstellar chemistry is different. Several neutral gas phase reaction processes are proposed for the formation of thioformaldehyde in dense clouds \( (n \sim 10^5 \text{ cm}^{-3}) \) where ultraviolet radiations are almost totally excluded and ionization arises from attenuated cosmic rays and from chemi-ionization. The predicted abundance of HICS is consistent with the observation.

### 1. Introduction

Thioformaldehyde (HICS), the sulphur analogue of formaldehyde (HICO), is widespread in the galaxy. It has been detected in interstellar clouds by using radio telescopes. Though it is chemically analogous to formaldehyde, its interstellar chemistry is different. Several neutral gas phase reaction processes are proposed for the formation of thioformaldehyde in dense clouds \( (n \sim 10^5 \text{ cm}^{-3}) \) where ultraviolet radiations are almost totally excluded and the molecules are ionized by cosmic rays and by chemi-ionization processes.

### 2. Formation Processes

#### 2.1 First Process (Radiative Association of \( \text{H}_2 \) and \( \text{CS} \))

The interstellar chemistry of hydrogen molecule has already been discussed in detail.\(^7\) In this case a typical molecular \( \text{H}_2 \) density of \( 10^6 \text{ cm}^{-3} \) and an ionizing rate of \( 10^{-16} \text{ sec}^{-1} \) appropriate to high energy cosmic rays have been taken for dense clouds.\(^5\) \( \text{H}_2\text{CS} \) may be formed by ion-molecule reaction. However, a loose cluster ion will be formed which will then be destroyed by dissociative recombination process. Oppenheimer and Dalgarno\(^8\) have suggested a radical reaction, viz.

\[
\text{CH}_3 + \text{S} \rightarrow \text{H}_2\text{CS} + \text{H}
\]

adopting a rate coefficient \( 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \) which is thought to be fast.\(^4\) They assumed that in the dense interstellar clouds \( \text{CH}_3 \) is formed by the following processes.\(^6\)

\[
\text{C}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + \nu \quad \ldots (1)
\]

\[
\text{CH}_2^+ + \text{H}_2 \rightarrow \text{CH}_3^+ + \text{H} \quad \ldots (2)
\]

\[
\text{CH}_3^+ + e \rightarrow \text{CH}_3 + \nu \quad \ldots (3)
\]

assuming that (i) the reaction (1) is very fast, (ii) reaction (2) is highly probable, and (iii) the rate coefficient of reaction (3) is not smaller than \( 10^{-3} \) times the dissociative recombination rate. In this paper several neutral gas phase reaction processes for forming thioformaldehyde in dense clouds \( (n \sim 10^5 \text{ cm}^{-3}) \) have been proposed where ultraviolet radiations are almost totally excluded and the molecules are ionized by cosmic rays and by chemi-ionization processes.

#### 2.2 Second Process (Dissociative Recombination of \( \text{H}_3 \) and \( \text{CS} \))

The formation and destruction mechanisms of CS have been discussed by Oppenheimer and Dalgarno.\(^3\) The observed abundance of CS is about \( 10^{-7} n(\text{H}_2) \text{ cm}^{-3} \) (Ref. 9). The principal chemical destruction mechanisms of H2CS include

\[
\text{H}_2\text{CS} + \text{C}^+ \rightarrow \text{H}_2\text{CS}^+ + \text{C}
\]

\[
\rightarrow \text{HCS}^+ + \text{CH}
\]

\[
\rightarrow \text{H}_2\text{CS}^+ + \text{H}
\]

\[
\rightarrow \text{CH}_3^+ + \text{CS} \quad \ldots (5)
\]

and

\[
\text{H}_2\text{CS} + \text{O} \rightarrow \text{OCS} + \text{H}_2 \quad \ldots (6)
\]
Recent laboratory experiments suggest that the rate coefficient of an ion-molecule reaction is

\[ K = 2\pi e \sqrt{\frac{\alpha}{\mu}} \approx 1 - 2 \times 10^{-9} \text{ cm}^3 \text{sec}^{-1} \tag{7} \]

where

- \( e \) Electronic charge
- \( \alpha \) Polarizability of the neutral reactant
- \( \mu \) Reduced mass of the ion

The rate coefficient of reaction (6) is assumed to be \( 10^{-13} \text{ cm}^3 \text{sec}^{-1} \). If \( K_1 \) (cm\(^3\) sec\(^{-1}\)) is the associative rate coefficient then the number density of thioformaldehyde molecules by this process becomes

\[ n_1 (\text{H}_2\text{CS}) \approx \frac{K_1 n(\text{H}_2) n(\text{CS})}{10^{-9} n(\text{C}^+) + 10^{-13} n(\text{O})} \text{ (cm}^{-3}\text{)} \tag{8} \]

2.2 Second Process (Radiative Association of CH\(_2\) and S)

The other route for H\(_2\)CS may be the radiative association of CH\(_2\) and S. This association appears to be exothermic. The loss processes of H\(_2\)CS are same as above. Hence

\[ n_2 (\text{H}_2\text{CS}) \approx \frac{K_2 n(\text{CH}_2) n(\text{S})}{10^{-9} n(\text{C}^+) + 10^{-13} n(\text{O})} \text{ (cm}^{-3}\text{)} \tag{9} \]

where \( K_2 \) (in cm\(^3\) sec\(^{-1}\)) is the associative rate coefficient.

Recently the formation and destruction mechanisms of CH\(_2\) have been discussed by Dalgarno and Black.\(^5\) Its abundance is still uncertain. The observed abundance of S is about \( 10^{-5} n(\text{H}_2) \text{ cm}^{-3} \) (Ref. 13).

2.3 Third Process (Neutral-Neutral Reaction)

The difficulties in forming CH\(_3\) encountered by Dalgarno et al.\(^5\) have been mentioned above. But it can be formed through the radiative association of CH and H\(_2\) and this is observed to occur at an appreciable rate in the flash photolysis of methane.\(^14\)

It is an exothermic reaction. The compound CH\(_3\) formed by this process may provide another route for H\(_2\)CS formation following the reaction

\[ \text{CH}_2 + \text{S} \longrightarrow \text{H}_2\text{CS} + \text{H} \tag{10} \]

If \( K_3 \) (in cm\(^{-2}\) sec\(^{-1}\)) is the rate coefficient of this reaction, then

\[ n_3 (\text{H}_2\text{CS}) \approx \frac{K_3 n(\text{CH}_3) n(\text{S})}{10^{-9} n(\text{C}^+) + 10^{-13} n(\text{O})} \text{ (cm}^{-3}\text{)} \tag{11} \]

And CH required for this process can be produced in a variety of ways.\(^15\)

3. Calculation of Associative Rate Coefficient

The radiative association process occurs in the following two steps

\[ X + Y \rightarrow (XY)^* \text{ Forward rate: } R_1 \text{ (in cm}^3\text{sec}^{-1}\text{)} \]

\[ (XY)^* \rightarrow XY + hv \text{ Rate } R_2 \text{ (in sec}^{-1}\text{)} \]

This type of association is known as “inverse vibrational predissociation”.\(^16\) At first it is assumed that \( R_1 \) is equal to the Langevin value and is of the order of \( 10^{-9} \text{ cm}^3 \text{sec}^{-1} \).

A complex of \( N \)-atoms is assumed to possess \( S (=3N-6) \) harmonic oscillators of identical frequency \( \nu \). If \( j \) is the excited quanta of the complex and if dissociation occurs when \( m \) (\( m \leq j \)) quanta are transferred to a single oscillator, the statistical rate of dissociation is given\(^3\) by

\[ R_1 = \frac{1}{(j^3 - 1)! j!} \frac{1}{(j^2 - 1)! (j-m)!} \text{ sec}^{-1} \]

The spontaneous emission rate constant \( (R_2) \) is approximately equal to \( 10^2 \) times the average number of excited infrared active oscillators in the complex. Hence the radiative association rate coefficient becomes

\[ R = \frac{R_1 R_2}{R_1 + R_2} \approx \frac{R_1 R_2}{R_1} \text{ cm}^3 \text{sec}^{-1} \]

In this case, the complex \((\text{H}_2\text{CS})^*\) has six normal modes and the value of \( R \) is approximately \( 2 \times 10^{-16} \text{ cm}^3 \text{sec}^{-1} \).

4. Conclusion

Doherty et al.\(^1\) have shown that for dense interstellar clouds the ratio \( n(\text{H}_2\text{CS})/n(\text{H}_2) \approx 10^{-8} \). Hence the proposed processes will be assessed against this value. From the first process it is found that

\[ \frac{n_1 (\text{H}_2\text{CS})}{n(\text{H}_2)} \approx 2 \times 10^{-9} \]

which agrees well with the observed value. The second process yields

\[ \frac{n_2 (\text{H}_2\text{CS})}{n(\text{H}_2)} \approx 3 \times 10^{-10} \]

which is approximately three times less than the observed value. The neutral-neutral rate coefficients surveyed by Nieles\(^7\) suggest that \( K_3 \approx 10^{-12} \text{ cm}^3 \text{sec}^{-1} \). Then,

\[ \frac{n_3 (\text{H}_2\text{CS})}{n(\text{H}_2)} < 10^{-10} \]
which does not agree with the observation. Hence it may be concluded that only the first two processes are able to supply required amount of $\text{H}_2\text{CS}$ in the dense interstellar clouds whereas the last process proves to be of no consequence.

References