CHEMICAL EVOLUTION OF INTERSTELLAR CLOUDS AND VARIATIONS OF MOLECULAR ABUNDANCES

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ABSTRACT

The abundances of simple molecules are examined in terms of the time-dependent cloud evolution. The formation and destruction mechanisms of H_2CO are reviewed. The average value of the fractional abundance of H_2CO is derived to be in the range of 10^{-10} to 5×10^{-9}. This is comparable to the observed values. The expected variations of the molecules formed from or destroyed by CO, CI, and C^+ whose abundances depend on the evolutionary state of the cloud are discussed.

I. INTRODUCTION

Over forty different molecules have been found in interstellar clouds. The formation and destruction mechanisms of simple molecules such as CO, OH, and H_2CO are fairly well understood, although those of complex molecules have not been completely known. Some of the molecules show abundance variations that the abundances of the interstellar molecules are not only dependent on those mechanisms but also are inexplicably linked with the evolution of interstellar clouds. The molecular chemistry and radiation properties will affect cloud evolution because they are responsible for, or contribute to, condensation and fragmenta-tion of clouds (Glassgold and Langer 1976). The evolution of interstellar clouds affects the abundances of the molecules found within them because different chemistries dominate molecule production under different conditions of density, n, temperature, T, and radiation field, $I(V)$, and the time scales of dynamical evolution are often less than or comparable to the time required to reach essentially steady state asymptotic (time independent) values (Langer and and Glassgold 1976).

Herbst and Klemperer (1973, hereafter HK) showed a number of homogeneous gas-phase chemical reactions which are likely to occur in dense interstellar clouds, and they calculated steady state abundances of about 35 species

for clouds of density $10^4 \lesssim n_H \lesssim 10^6$ cm^{-3}. This model assumption, however, makes physical sense only if the chemical steady-state time constants are shorter than the cloud lifetime. The times they calculated to reach steady state for H_2CO, H_2, H_3, HCO all fall within the free-fall gravitational collapse times for clouds of gas density $10^4 \sim 10^6$ cm^{-3} which range from 3×10^5 to 3×10^4 yr. Cloud lifetime may be considerably longer than this.

However, Oppenheimer and Dalgarno (1975) showed that the CO abundance is varying with a longer time scale. According to their calculations, the number density of CO increases at about 10^5 yr (of the lifetime of the could) and reaches maximum and decreases slowly to maintain a constant density at about 7×10^6 yr. They also showed cloud temperature decreases rapidly to a minimum value of about 14 K at the same time when CO reaches maximum. The time scale for essentially complete conversion of C^+ to CO in interstellar clouds which can be comparable to, or greater than dynamical time scales for evolution is calculated by Langer (1976b). He suggested that the steady state (time independent) abundances are inappropriate since the CO abundance is varying with time.

Turner and Thaddeus (1977) found abundance variations for the molecules they observed. They observed HCN, CN H_2H^+, and HCO^+, and made a detailed study of the spatial relationship to these four species in different clouds. They found that the abundance ratios are varying from cloud to cloud. From this investigation, they concluded that the relative abundance of CO may be considerably lower in some regions than previously believed. Wooten et al. (1978) also observed HCO^+, H_2CO, HCN, and ^{13}CO in various regions and compared their abundances. The abundances of some species vary up to three orders of magnitude from cloud to cloud. They divided the regions studied into two groups, A and B. The clouds in group A are cold ($T_K < 20$ K) and have moderate density (n $\sim 10^4$ cm^{-3}) and high abundances. The clouds in group B are warmer ($T_K > 20K$) and denser (n $\sim 10^5$ cm^{-6}) but have lower abundances. Since the time dependent models of chemical evolution by Langer (1976b) have found that many molecules,

including CO, do not reach their equilibrium abundance for long periods of time, they interpreted their results that group A clouds are more chemically evolved than group B clouds.

The predominent process for the formation of small interstellar molecules is considered to be the ion-molecule reactions (HK, Watson 1973, 1974a) although such reactions seem unable to explain the presence of the large interstellar species, which may well be formed on grain surfaces. Current knowledge of formation processes on grain surfaces is too imprecise to permit a decisive comparison with observations. However, ion-molecule reactions are considerably better understood and, despite uncertainties in some individual reactions, seem able to predict rather definitely the relative equilibrium abundances of a few of the simpler interstellar molecules.

Precise comparisons of these theories with observations may not be easy because the observations rest on poorly determined abundances and on a small number of unrepresentative interstellar sources. A judicious selection of molecular species and a detailed observational survey of the spatial relaionship between those species would be required for a better comparison of theory and observations.

It is thought that the few molecules which can have large abundances (e.g., CO, H_2CO, and O_2) are required long times to reach equilibrium. The atomic and ionic forms of the carbon and oxygen chmistry (OI, CI, and C^+) and the trace molecules which are formed from these constituents (e.g., H_2CO, CH, CH_2, and ^{13}CO) will have a similar time dependence. These considerations may explain the observations of relatively large abundances of some trace molecules compared to theoretical estimates based on steady state calculations.

Formaldehyde observations by Evans (1975) and Minn and Greenberg (1979) estimate the fractional abundance $x(H_2CO) = (4 \sim 8) \times 10^{-9}$ where $x(X) = n(X)/n$ and $n = n(H) + 2n(H_2)$. The steady state models for the formation of the formaldehyde molecules by HK and Dalgarno et al. (1973) fall short of explaining these abundances unless very large radiative association rates can be invoked. In this paper we have examined the abundances of H_2CO, CH family molecules,

and molecules formed from reactions with CO in terms of the abundances of CI and CO which are present during the evolutionary lifetime of the cloud in the time-dependent chemistry.
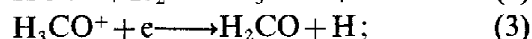
II. FORMATION AND DESTRUCTION MECHANISMS OF FORMALDE-HYDE

The general type processes that seem most likely to produce interstellar formaldehyde are: (i) association of atoms on grain surfaces (Watson and Salpeter 1972a, b) or possibly HCO^+ from the gas reacting with H_2 at a negative grain surface,

$$HCO^+ + H_2 + e \longrightarrow H_2CO + H; \quad (1)$$
$$\text{grain}$$
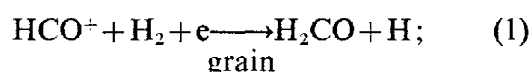
(ii) radiative association of HCO^+ (HK),

$$HCO^+ + H_2 \longrightarrow H_3CO^+ + h\nu \quad (2)$$
$$H_3CO^+ + e \longrightarrow H_2CO + H; \quad (3)$$

and (iiia) the reaction (Litvak 1972, Dalgarno et al. 1973)

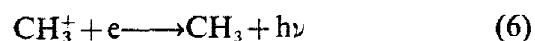$$CH_3 + O \longrightarrow H_2CO + H \quad (4)$$
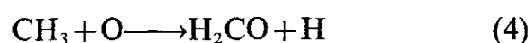
Confidence in process (i) suffers from lack of knowledge of the detailed mechanisms. The radiative association mechanism (ii) is studied by Fehsenfeld et al. (1974) in laboratroy and is shown to be unlikely to produce adequate quantities of formaldehyde because of its slow reaction rate.

In (iii) the chief difficulty is formation of CH_3 and the need for free, atomic oxygen in dense gas clouds. CH_3 (or CH_4, which could possibly be converted to CH_3 by gas reactions) might be ejected from grains by nonthermal processes on grain surfaces. Pure gas phase formation of CH_3 could occur through charge exchange with an atom of low ionization potential less than 9.84 eV,
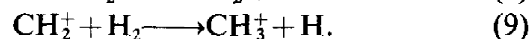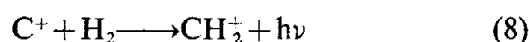
$$CH_3^+ + M \longrightarrow CH_3 + M^+ \quad (5)$$
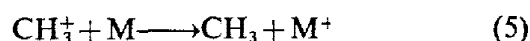
or the small fraction (probably $\lesssim 10^{-3}$) of electron recombinations that produce CH_3,

$$CH_3^+ + e \longrightarrow CH_3 + h\nu \quad (6)$$

instead of dissociation,

$$CH_3^+ + e \longrightarrow CH_2 + H \text{ (or } CH + H_2) \quad (7)$$
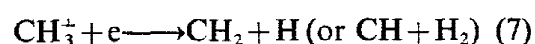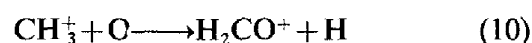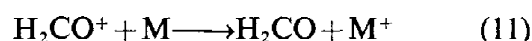
In clouds that are mainly H_2, CH_3^+ can be formed readily through (Watson 1973, 1974b; Black and Dalgarno 1973)

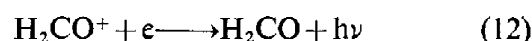$$C^+ + H_2 \longrightarrow CH_2^+ + h\nu \quad (8)$$
$$CH_2^+ + H_2 \longrightarrow CH_3^+ + H. \quad (9)$$

A variation of (iiia) is (Dalgarno et al. 1973) (iiib),

$$CH_3^+ + O \longrightarrow H_2CO^+ + H \quad (10)$$

followed by

$$H_2CO^+ + M \longrightarrow H_2CO + M^+ \quad (11)$$

or again the small fraction (probably $\lesssim 10^{-3}$) of recombinations,

$$H_2CO^+ + e \longrightarrow H_2CO + h\nu \quad (12)$$

that occur instead of dissociation

$$H_2CO^+ + e \longrightarrow H_2 + CO \text{ (or } H + HCO). \quad (13)$$
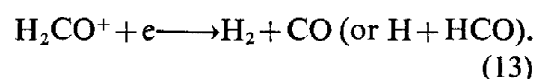
Though it has been ignored previously, the reaction $H_2CO^+ + H_2 \longrightarrow H_3CO^+ + H$ might be energetically allowed (Haney and Franklin 1969). For this to be important, an appreciable fraction of the electron recombinations must then produce formaldehyde ($H_2CO^+ + e \longrightarrow H_2CO + H$) instead of dissociation ($H_3CO^+ + e \longrightarrow HCO + H_2, CO + H_2 + H$). Data for H_2 and HCO^+ are not necessarily relevant for the H_3CO^+ formed by the above reaction. The reaction $CH_3^+ + O$ will not contribute to $x(H_2CO)$ because the reaction procuct is $HCO^+ + H_2$ with a rate $4.4 \times 10^{-10} cm^3 s^{-1}$ and not $H_2CO^+ + H$.

The formaldehyde molecule is primarily destroyed by the following processes: (1) photodissociation; (2) ion-molecule reactions and charge exchange with C^+ and other ions (e.g., H_3^+, H^+, He^+); and (3) the neutral-molecule reactions with oxygen, $H_2CO + O \longrightarrow HCO + OH$. This last reaction has a rate coefficient $a_{10} = 1.8 \times 10^{-13} cm^3 s^{-1}$ and will be important at high densities.
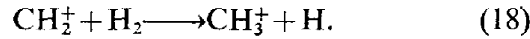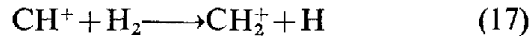
III. FRACTIONAL ABUNDANCE OF FORMALDEHYDE

The key to the production of H_2CO in this scheme is the production of CH_3, which

results from the reactions with CH_3^+. CH^+ is produced by gas phase reactions;

$$C^+ + H_2 \longrightarrow CH_2^+ + h\nu$$
(Black and Dalgarno 1973)   (14)

$$H_3^+ + CI \longrightarrow CH_2^+ + H \text{ or } CH^+ + H_2$$
(HK)   (15)

$$H_3^+ + OI \longrightarrow OH_2^+ + H \text{ or }$$
$$OH^+ + H_2$$ (16)

and rapidly followed by

$$CH^+ + H_2 \longrightarrow CH_2^+ + H$$ (17)
$$CH_2^+ + H_2 \longrightarrow CH_3^+ + H.$$ (18)
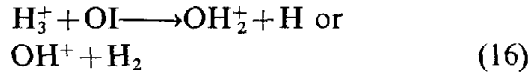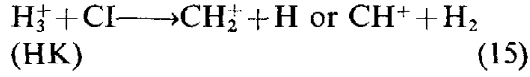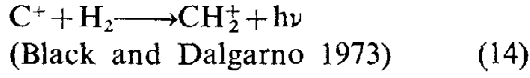
In the steady state calculations of HK, $x(CI)$ $\lesssim 5 \times 10^{-7}$ and hardly contributes to production of CH_3^+ while the C^+ radiative association considered by Dalgarno et al. (1973) and Watson et al. (1975) will be more important. The time-independent abundance of CI in dense clouds, however, is much larger than the value used by HK resulting in correspondingly larger values of $x(CH_3^+)$ and $x(H_2CO)$. The adiabatic approximation can be used for formaldehyde and its abundance is given approximately by,

$$x(H_2CO) = \frac{ax(O)\Gamma(CH_3)}{g_{CH_3} + k\Sigma x_i(X^+) + ax(O)}$$
$$\times \frac{(1/2k_{26}x(C^+) + kx(H_3^+)x(C)}{g_{H_2CO} + k\Sigma x_i(X^+) + a_{10}x(O),}$$ (19)

where the sum is over all the ions which destroy H_2CO, and where $\Gamma(CH_3) = \dfrac{[10^{-3}\beta x_e +}{[\beta x_e + kx(M) +}$

$\dfrac{kx(M)]}{0.4kx(O)]}$ is the branching ratio for forming CH_3 from CH_3^+, a is the effective rate for neutral-molecule reactions between radicals and atoms, k is the effective rate for ion-molecule and charge exchange reactions, β is the effective rate for dissociative recombination reactions, $g_x = G_x/n$ where G_x is the photodestruction rate per second, a_{10} is the effective rate for neutral-molecule reactions with oxygen, $H_2CO + O \longrightarrow HCO + OH$, $x(X)$ is the fractional abundance of X, x_e is the electron density, and $x_i(X^+)$ is the fractional abundance of the ions which destroy H_2CO. The value of $x(H_2CO)$ will be calculated using equation (19) after, we consider the time-dependent abundances if CO and CI on which $x(H_2CO)$ is heavily dependent.

IV. TIME DEPENDENT ABUNDANCES OF CO AND CI

The time-dependent variations of CO are calculated by Oppenheimer and Dalgarno (1975) and Langer (1976) and those of CI by Langer (1976). The time-dependent equations governing the abundance of carbon monoxide in dense regions of interstellar clouds, $n \geq 500$ cm^{-3} and $T < 50$ K are considered in this section. Two gas-phase reactions which initiate molecule production are: (1) C^+ radiative association with H_2 as given by equation (14) and (2) H_3^+ ion-molecule reactions with CI and OI as given by equations (15) and (16). These reactions eventually produce molecules such as OH, H_2O, CH, CH_2 and C_2H which are converted to CO either by ion-molecule reactions with C^+, or neutral-molecule reactions with OI.

The complete abundance problem requires solving a set of rate equations for the abundances x_i,

$$\frac{1}{n}\dot{x}_i = \sum_j a_j(i)x_i + \sum_{jk} b_{jk}(i)x_jx_k$$ (20)

where the rate coefficients depend on n, T, $I(\nu)$, and ζ_p, the cosmic-ray ionization rate.

The carbon monoxide, CI, and C^+ abundances can be evaluated to a good approximation from the following reduced set of equations,

$$\frac{1}{n}\dot{x}(C^+) = g_c x(CI) + kx(He^+)x(CO)$$
$$- [ax_e + 1/2k_{26} + kx(MO)]$$
$$x(C^+)$$ (21)

$$\frac{1}{n}\dot{x}(CO) = [kx(H_3^+)x(CI) + 1/2k_{26}x(C^+)]$$
$$\Gamma + kx(C^+)x(MO)$$
$$- [g_{CO} + kx(He^+)]x(CO)$$ (22)

$$\frac{1}{n}\dot{x}(MO) = kx(H_3^+)x(O)$$
$$- [g_{MO} + kx(C^+) + k_{56}x(He^+)]$$
$$x(MO)$$ (23)

where $\Gamma = ax(O)/[g_{c_2} + ax(O)]$, $x(MO) = x$ (OH) + $x(H_2CO)$ + $x(O_2)$, a is the radiative recombination rate, k_9 is the reaction rate for the dissociative charge exchange $He^+ + H_2 \longrightarrow$ He + H + H$^+$, and K_{56} is the rate for $He^+ +$ (OH, $H_2O) \longrightarrow He +$ (O + H$^+$, etc).

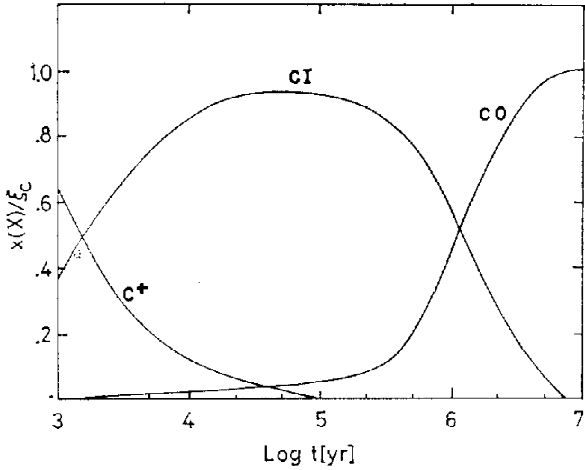In equation (21), the first term is the pho-

FIG. 1. The abundances $x(X)/\xi_c$ for C^+, CO and CI in dense dark clouds plotted as a function of time (adopted from Langer (1976)).

todestruction rate and the second, the rate at which He^+ and CO combine to produce C^+, O and He. In equation (22), the first two terms are the rates at which neutral and ionized carbon are converted into CH, CH_2, C_2H, and C_2. Neutral-molecule reactions of these species with oxygen eventually produce CO. The branching ratio for production of CO from these molecules to their total destruction is given by Γ. The thrid term represents production of CO initiated by reactions of C^+ with the oxygen-bearing molecules OH, H_2O, and O_2. The total abundance of these molecules is given by the last equation. The last terms of all the three equations with negative signs represent destructions of C^+, CO and MO respectively.

The results of calculations for time dependence of CO^+, C, and CI made by Langer (1976) are introduced in Figure 1. It shows that C^+ recombines very rapidly (in less than 10^5 yr) and goes mostly to CI, but some proceeds to CO. The CI, which reaches a peak at this time is converted by H_3^+ to CO on a comparably long time scale. Singnificant CI exists, $x(CI)$ $/\xi_c > 0.1$ where ξ_c is the carbon abundance, for time up to 3×10^6 yr, while CO does not reach its asymptotic value until times greater than 5×10^6 yr. This is much greater than the corresponding Jeans time $\tau_J = 3.4^1 \times 10^5$ to 3.4×10^4 yr. The time scales for achieving complete conversion of the chemistry are comparable to, or longer than, dynamical times for evolution.

V. ABUNDANCES OF SIMPLE MOLECULES IN THE TIME-DEPENDENT CLOUD EVOLUTIONARY MODEL

In the previous section we have examined the time variations of CO and CI. Here we will first estimate the values of $x(H_2CO)$ which will depend on the evolutionary stage of each cloud, i.e., the details of the time dependence of x (CI, t), and then the other simple molecules whose abundance is dependent on the CO and C^+ abundances. For the calculation of $x(H_2CO)$, we used the following set of parameters which are charcteristic of the conditions of dense interstellar clouds (Langer 1976ab, HK, Oppen heimer and Dalgarno 1975): $a = 4 \times 10^{11} cm^{-3}$ s^{-1}, $k = 2 \times 10^{-9} cm^{-3} s^{-1}$, $k_{26} = 10^{-16} cm^{-3}$ s^{-1}, $n = 10^4 cm^{-3}$, $x_i = 10^{-6}$, $x(O) = 10^{-4}$, $x(H_3^+) = 10^{-9}$, $x(C) = 2 \times 10^{-5}$, $x_e = 2 \times$ 10^{-6}, $\beta = 10^{-6} cm^{-3} s^{-1}$, $x(M) = 10^{-6}$, $a_{10} = 1.8$ $\times 10^{-13} cm^{-3} s^{-1}$, and g_{H_2CO} and $g_{CH_3} = 10^{-9} exp$ $(-1.5 \tau_v) s^{-1} n^{-1}$ where τ_v is the optical depth. From the results of secion IV, we have adopted $x(CI) = 2 \times 10^{-5}$ and $x(CO) = 8 \times 10^{-5}$ as typical average values. By substituting into the equatons given in section IV the values of $10^{-6} \leq x(MO) \leq 10^{-5}$ which are an appropriate range for interstellar clouds (Langer 1976), we calculated $x(C^+)$ and derived the values of $x(H_2CO)$ for $2 < \tau_v < 10$. The range of $x(H_2CO)$ is $\sim 10^{-10}$ to 5×10^{-9}. This is in good agreement with the abundances found in dense dark clouds by Minn and Greenberg (1979), Myers and Ho (1975), and Evans et al. (1975). This enhanced abundance of H_2CO found in observations has not been able to explain by the steady state model of interstellar chemistry. Details of the abundance variation of H_2CO as a function of the cloud evolutionary time are being calculated and will be published elsewhere.

The abundances of all molecules which are derived from CH_3^+ such as CH and C_2H falmily molecules must also be reexamined in terms of the contributions of CI expected in a time-dependent model of abundances and cloud evolution. The variations of the abundance of the fundamental elements such as CO, CI, and C^+ in the cloud lifetime will affect the abundances of the molecules which are either formed from or destroyed by these elements. For ex-

ample, N_2H^+ is destroyed soley by the reactions with CO and CO_2, HCO^+ is formed predominantly by the reaction $H_3^+ + CO \longrightarrow HCO^+ + H_2$, and HCN is formed primarily by the reaction $C^+ + NH_3 \longrightarrow H_2CN^+ + H$ followed by $H_2CN^+ + e \longrightarrow HCN + H$. C^+ will also interact with the molecules, OH, NH, CH, H_2O, NH_2, CH_2, HCN, NH_3, and H_2CO producing HCO^+, N_2, CO, H^+, CN, C_2^+, HCN, C_2H^+, CCN^+, H_2CN^+, HC, and H(HK). Abundances of these molecules will be increased or decreased as the abundance of C^+ changes in the course of the cloud evolution. The increase of available C^+ would enhance the build up of larger carbon chain molecules such as CH_3CN and HC_2CN. Details and the extent to which these molecules increase remain to be examined.

VI. CONCLUSIONS

We have examined the abundances of simple molecules in terms of the time-dependent cloud evolution. Based on the time variations of the abundances of CO, CI, and C^+ in the cloud evolution, we can explain the enhanced abundance of $x(H_2CO)$. All the molecules which are derived from CH_3^+ such as CH and C_2H family molecules will have different abundances in a time-dependent model from those in the steady state model. The abundances of the molecules which are either formed from or destroyed by CO, CI, and C^+ will be increased or decreased from those of the steady state model as the abundances of these elements change in the course of the cloud evolution.

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