

## INTERSTELLAR CLOUD EVOLUTION AND THE ABUNDANCE OF FORMALDEHYDE

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### ABSTRACT

The time scale for essentially complete conversion of  $C^+$  to CO in interstellar clouds can be comparable to, or greater than, dynamical time scales for evolution; therefore suggesting steady state time independent abundances to be inappropriate. The solutions for the time-dependent carbon chemistry in dense clouds,  $n \gtrsim 500 \text{ cm}^{-3}$ , indicate that significant amounts of neutral carbon will be present throughout a cloud's lifetime. These nonequilibrium values of C I can explain the relatively large abundances observed for formaldehyde, isotopes of carbon monoxide, and other trace molecules.

*Subject headings:* interstellar: molecules — molecular processes

### I. INTRODUCTION

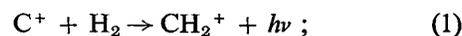
The molecules observed in interstellar clouds are inextricably linked with cloud evolution in two ways. First, their chemistry and radiation properties affect evolution because they are responsible for, or contribute to, condensation and fragmentation of clouds (Glassgold and Langer 1976a, c). Second, the evolution of interstellar clouds affects the abundances of the molecules found within them because (1) different chemistries dominate molecule production under different conditions of density,  $n$ , temperature,  $T$ , and radiation field,  $I(\nu)$ ; and (2) the time scales for dynamical evolution are often less than or comparable to the time required to reach essentially steady state asymptotic (time independent) values (Langer and Glassgold 1976).

It is for the few molecules which can have large abundances (e.g., CO,  $H_2O$ , and  $O_2$ ) that long times are required to reach equilibrium. The atomic and ionic forms of the carbon and oxygen chemistry (O I, C I, and  $C^+$ ) and the trace molecules which are formed from these constituents (e.g.,  $H_2CO$ , CH,  $CH_2$ ,  $^{13}CO$ ) 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. For example, formaldehyde observations in dark dense clouds suggest fractional abundances,  $x(H_2CO) \approx (4-8) \times 10^{-9}$  (Evans *et al.* 1975) where  $x(X) = n(X)/n$  and  $n = n(H) + 2n(H_2)$ . The steady state models of Herbst and Klemperer (1973) and Dalgarno, Oppenheimer, and Black (1973) fall short of explaining these abundances unless very large radiative association rates can be invoked. In this paper we show that formaldehyde and other trace molecules can be explained in terms of the large abundance of C I which is present during a cloud's lifetime in the time-dependent chemistry. Furthermore, we suggest that the incomplete conversion of C I to CO will be reflected in an enhanced  $^{13}CO/^{12}CO$  ratio as

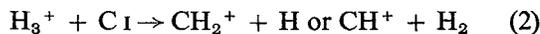
indicated by the measurements of Wannier *et al.* (1976).

### II. TIME DEPENDENCE OF CO AND C I

This section considers the time-dependent equations governing the abundance of carbon monoxide in dense regions of interstellar clouds,  $n \gtrsim 500 \text{ cm}^{-3}$  and  $T < 50 \text{ K}$ . Here the two gas phase reactions which initiate molecule production are: (1)  $C^+$  radiative association with  $H_2$  (Black and Dalgarno 1973):



and (2)  $H_3^+$  ion-molecule reactions with C I and O I (Herbst and Klemperer 1973; hereafter HK):



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 O I (for a listing see Glassgold and Langer 1976b; Langer 1976).

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

$$\frac{1}{n} \dot{x}_i = \sum_j a_j(i)x_j + \sum_{jk} b_{jk}(i)x_jx_k, \quad (4)$$

where the coefficients depend on  $n$ ,  $T$ ,  $I(\nu)$ , and  $\zeta_p$ , the cosmic-ray ionization rate. This system of equations can be reduced by using an adiabatic approximation for all species which have time scales much shorter than the molecules of primary interest (Langer and Glassgold 1976). These steady state solutions,  $x_i^{(0)}$ , of equation (4) are not time independent, however, since they may still be a function of the molecules of primary interest.

It can be shown from arguments similar to those in Langer (1976) that the carbon monoxide abundance can be evaluated to a good approximation from the following reduced set of equations:

$$\frac{1}{n} \dot{x}(C^+) = g_C x(C\ I) + kx(He^+)x(CO) - [\alpha x_e + \frac{1}{2}k_{26} + kx(MO)]x(C^+); \quad (5)$$

$$\frac{1}{n} \dot{x}(CO) = [kx(H_3^+)x(CI) + \frac{1}{2}k_{26}x(C^+)]\Gamma + kx(C^+)x(MO) - [g_{CO} + kx(He^+)]x(CO); \quad (6)$$

$$\frac{1}{n} \dot{x}(MO) = kx(H_3^+)x(O) - [g_{MO} + kx(C^+) + k_{56}x(He^+)]x(MO); \quad (7)$$

where  $\Gamma = ax(O)/[g_{C_2} + ax(O)]$ ,  $g_x = G_x/n$ , and  $G_x$  = photodestruction rate in  $s^{-1}$ . Unless otherwise noted, the notation and rates are those listed in Langer (1976). For simplification many of the rates can be rounded off, and the following notation is adopted: (1) for ion molecule and charge exchange reactions,  $k = 2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ; (2) for neutral molecule reactions between radicals and atoms,  $a = 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ; (3) for radiative recombination,  $\alpha = 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ; and (4) dissociative recombination,  $\beta = 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ .

The first two terms in equation (6) are the rates at which neutral and ionized carbon are converted into CH, CH<sub>2</sub>, C<sub>2</sub>H, and C<sub>2</sub>. 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  $\Gamma$ . The third term represents production of CO initiated by reactions of C<sup>+</sup> with the oxygen-bearing molecules OH, H<sub>2</sub>O, and O<sub>2</sub>. The total abundance for these molecules is written,  $x(MO) = x(OH) + x(H_2O) + x(O_2)$ , and is given approximately by equation (7). The last terms represent the destruction of CO by photodissociation and He<sup>+</sup> dissociative charge exchange, respectively. These equations must be supplemented by the conservation conditions for the total available gaseous carbon,  $\xi_C$ , and oxygen,  $\xi_O$  [e.g.  $\xi_C \doteq x(CO) + x(C\ I) + x(C^+)$ ] and charge neutrality,  $x_e \approx x(C^+) + x_i$ , where  $x_i$  is the residual electron density from ions other than C<sup>+</sup> (e.g., S<sup>+</sup>, He<sup>+</sup>, H<sup>+</sup>, Mg<sup>+</sup>). Finally the steady state solutions for H<sub>3</sub><sup>+</sup> and He<sup>+</sup> can be used in equations (5)–(7); these are:  $x(H_3^+) \approx (\zeta_p/n)/(\alpha x_e + k\xi_O)$  and  $x(He^+) \approx (\xi_{He}\zeta_{He}/n)/[\alpha x_e + \frac{1}{2}k_9 + kx(CO)]$ , where  $k_9$  is the reaction rate for dissociative charge exchange  $He^+ + H_2 \rightarrow He + H + H^+$ . Johnson and Biondi (1974) have measured  $k_9$  to be  $10^{-13} \text{ cm}^3 \text{ s}^{-1}$  at 300 K; from these data Huntress and Anicich (1976) have estimated the temperature dependence to be  $1.6 \times 10^{-13} \exp(-160/T) \text{ cm}^3 \text{ s}^{-1}$ . The exact value will make a

difference for small abundances and/or early times because a large value of  $k_9$  suppresses  $x(He^+)$ . The most important, yet unknown, reaction rate in these equations is that for C<sup>+</sup> radiative association (eq. [1]). As in Langer (1976), this reaction rate is taken to be  $k_{26} = 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ ; although much larger values  $10^{-15}$  (Black and Dalgarno 1973) to  $10^{-14} \text{ cm}^3 \text{ s}^{-1}$  (Black, Dalgarno, and Oppenheimer 1975) have been suggested to explain molecular abundances in diffuse clouds.

If H<sub>3</sub><sup>+</sup> is neglected, the solution to the rate equations reproduces the time-dependent results of Oppenheimer and Dalgarno (1975) and the steady state results of Langer (1976). Briefly, these are: (1) essentially complete conversion of the available gaseous carbon into CO does not occur in the C<sup>+</sup> radiative association chemistry, and considerable C I can be present; (2) the value of  $x(CO, t = \infty)$  reaches a maximum at some characteristic optical depth into a cloud and decreases at larger depths; and (3) the conversion time  $\mu(CO)^{-1} \geq 10^6 \text{ yr}$  at large extinctions. (Here we use the approximate relation for the CO time scale parameter,  $\mu(CO) = n[g_{CO} + kx(H_3^+)\Gamma]$ .) To illustrate these points, when  $n = 10^3 \text{ cm}^{-3}$ , the maximum value of  $x(CO, \infty)/\xi_C$ ,  $\sim 0.25$ – $0.5$ , occurs at  $\tau_V (\equiv N/2 \times 10^{21} \text{ cm}^{-2})$ , the extinction into the cloud in the visible,  $\sim 2$ – $3$ . Furthermore, in this region  $\mu(CO)^{-1} \approx 1.3 \times 10^6 \text{ yr}$ , which is larger than the Jeans time for gravitational collapse,  $\tau_J (\approx 3.4 \times 10^7 n^{-1/2} \text{ yr}) = 1.1 \times 10^6 \text{ yr}$ . At large  $\tau_V$  such that  $g_C \ll kx(He^+)$ , the decrease in  $x(CO, \infty)/\xi_C$  occurs because CO is destroyed by He<sup>+</sup>, while C I is hardly destroyed. In the limit  $g_C \rightarrow 0$  all the carbon will eventually end up as C I. Once H<sub>3</sub><sup>+</sup> is included as a destruction mechanism for C I, this result is no longer true and significant  $x(CO)$  are possible (Langer 1976).

The  $x(H_3^+)$  can be large enough to produce a significant amount of CO if  $x_e \lesssim$  a few times  $10^{-6}$ . Thus full conversion of the gaseous carbon into CO (i.e.,  $x(CO) \geq 0.98 \xi_C$ ) is possible only at large optical depths and high densities where C<sup>+</sup> and heavier ions can recombine to the extent that  $x_e < 2 \times 10^{-6}$  (Langer 1976). Furthermore, significant values of  $x(H_3^+)$  occur only after most of this recombination has taken place. The role of H<sub>3</sub><sup>+</sup> will depend critically on  $x_e$ , which itself is a complicated function of the radiation field,  $\zeta_p$ ,  $\xi_C$ , and the metal abundance,  $\xi_M$ .

Consider, for example, the solution of the above equations for  $n > 500 \text{ cm}^{-3}$  [ $n(H_2) > 250 \text{ cm}^{-3}$ ] at large optical depths such that  $x(C^+, \infty) < 2 \times 10^{-6}$ . For purposes of discussion the carbon is taken to be completely ionized initially. This C<sup>+</sup> will recombine on a time scale  $\lesssim 10^5 \text{ yr}$ ; less than  $\sim 10$  percent of the carbon goes into CO and the remainder is primarily C I. Some of this neutral carbon is then converted via reaction (2) to CO on a time scale  $\mu(CO)^{-1} \sim 10^6 \text{ yr}$  that is much longer than the recombination time. Once the H<sub>3</sub><sup>+</sup> is a significant source of CO, it will also produce H<sub>2</sub>O, OH, and O<sub>2</sub>. A small fractional abundance of these molecules,  $\sim 10^{-7}$ , is important for destroying the remaining (residual) C<sup>+</sup> because  $kx(MO) = 2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1} > \alpha x_e + \frac{1}{2}k_{26}$ . Values of

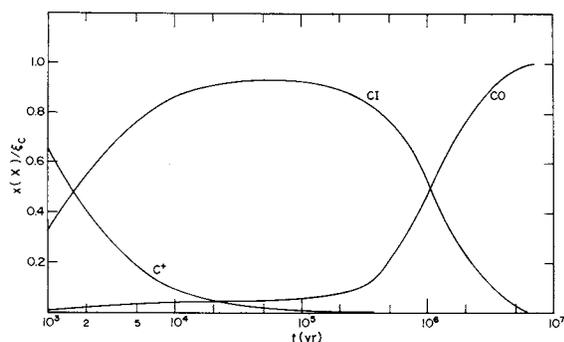


FIG. 1.—The abundances  $x(X)/\xi_C$  for  $C^+$ , CO, and C I in dense dark clouds are plotted as a function of time (see text for details).

$x(\text{MO}) \sim 10^{-5}$  can be achieved in a time  $\sim 2 \times 10^5$  yr, and can reduce  $x(C^+)$  rapidly to  $\sim 10^{-8}$ – $10^{-7}$ .

In Figure 1 are plotted the results of a sample calculation for the time dependence of  $C^+$ , CO, and C I given by equations (5)–(7) at large optical depths and high densities. The values chosen for the parameters used in this calculation are:  $n = 10^4 \text{ cm}^{-3}$ ,  $x_i = 5 \times 10^{-7}$  (primarily from metals, see Langer 1976),  $\zeta_p = 10^{-17} \text{ s}^{-1}$ ,  $T = 20 \text{ K}$ ,  $k_{26} = 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ ,  $\tau_V > 5$ , and  $x(C^+, 0) = \xi_C$ . The results for  $x(X)/\xi_C$  are plotted as a function of time in years. The  $C^+$  recombines very rapidly (in less than  $10^5$  yrs) and goes mostly to C I, but some proceeds via reaction (1) to CO. The C I, which reaches a peak at this time, is converted by  $\text{H}_3^+$  to CO on a comparatively long time scale. Significant C I exists,  $x(\text{C I})/\xi_C > 0.1$ , for times up to  $3 \times 10^6$  yr, while CO does not reach its asymptotic value until times greater than  $5 \times 10^6$  yr.

At large optical depths and high densities, where substantial conversion of  $C^+$  and C I to CO is possible ( $> 0.9 \xi_C$ ), it is important to compare the time for conversion with the dynamical times for cloud evolution in order to ascertain if complete conversion can be expected in dense clouds. Once the  $C^+$  has recombined, the CO time scale,  $\mu(\text{CO})^{-1}$ , is a function of  $\zeta_p$  and  $x_e$ . At large optical depths a quantitative theory of  $x_e$  is quite complicated because of the role of metals (Oppenheimer and Dalgarno 1974). Detailed calculations using  $\zeta_p = 10^{-17} \text{ s}^{-1}$  and  $\xi_M = 1.5 \times 10^{-6}$  (Langer 1976) show that  $x_e$  decreases slowly from  $5 \times 10^{-7}$  to  $7 \times 10^{-8}$  as  $n$  increases from  $10^4$  to  $10^6 \text{ cm}^{-3}$ . For this range of densities  $\mu(\text{CO})^{-1}$  decreases slightly from  $1.5 \times 10^6$  to  $8 \times 10^5$  yr, but is still much greater than the corresponding Jeans time,  $\tau_J = 3.4 \times 10^5$  to  $3.4 \times 10^4$  yr (though rotation and turbulence may increase this dynamical time somewhat).

At densities greater than  $10^4 \text{ cm}^{-3}$  the chemistry used here is an oversimplification of the ion molecule reactions which initiate CO production in dense dark clouds. For example,  $\text{H}_3\text{O}^+$  also destroys neutral carbon,  $\text{H}_3\text{O}^+ + \text{C} \rightarrow \text{HCO}^+ + \text{H}_2$  (HK), and  $\mu(\text{CO}) = nk[x(\text{H}_3^+) + x(\text{H}_3\text{O}^+)]$  is increased by only 1.5 at  $n = 10^4 \text{ cm}^{-3}$  but by as much as  $\sim 5$  if  $n = 10^6 \text{ cm}^{-3}$ .

This increase is not enough to make the abundances reach asymptotic values on a time scale less than dynamical times. Furthermore, thermal-chemical effects either reduce  $\tau_J$  or introduce instabilities with time scales less than  $\tau_J$  (Glassgold and Langer 1976a, c). From the above analyses it is concluded that the time scales for achieving complete conversion of the chemistry are comparable to, or longer than, dynamical times for evolution.

As there is no direct evidence at present for C I in dark dense clouds, observation of the  $^3P_1 \rightarrow ^3P_0$  610  $\mu$  line is highly desirable. Indirect evidence for substantial  $x(\text{C I})$  and the corresponding incomplete conversion to CO may be found in the isotopic abundance measurements of  $^{13}\text{CO}$ . Observations by Wannier *et al.* (1976) of  $^{13}\text{CO}$  indicate that  $^{13}\text{CO}/^{12}\text{CO} \sim 2.5$  times the solar value of  $^{13}\text{C}/^{12}\text{C}$ . Wannier *et al.* (1976) have suggested that this larger value is indicative of the enrichment of  $^{13}\text{C}$  by ejection from stars since the solar system was formed. However,  $^{13}\text{CO}/^{12}\text{CO}$  can also be enhanced by the fractionation reaction,  $^{13}\text{C}^+ + ^{12}\text{CO} \rightleftharpoons ^{12}\text{C}^+ + ^{13}\text{CO} + \Delta E$ , where the forward reaction rate is  $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $\Delta E = 35 \text{ K}$  (Watson, Anicich, and Huntress 1976).

The isotope problem for CO can be analyzed by expanding the set of rate equations (5)–(7) to treat  $^{12}\text{C}$  and  $^{13}\text{C}$  separately, and to include the fractionation reaction. The results of these analyses are as follows: (1) when  $C^+$  radiative association dominates the production of CO,  $[x(^{13}\text{CO})/\xi_{^{13}\text{C}}]/[x(^{12}\text{CO})/\xi_{^{12}\text{C}}] \sim 3$  for  $T < 25 \text{ K}$  (for the previously cited example when  $n = 10^3 \text{ cm}^{-3}$  and  $\tau_V \sim 3$ ,  $x(\text{CO}, \infty)/\xi_{^{12}\text{C}} \approx 0.25$  and  $x(^{13}\text{CO})/\xi_{^{13}\text{C}} > 0.7$ ); (2) the response time for  $^{13}\text{CO}$  is rapid once  $x(^{12}\text{CO}) > 5 \times 10^{-6}$  and  $^{13}\text{CO}$  production is primarily from  $^{12}\text{CO}$ ; and (3) in the  $\text{H}_3^+$  chemistry fractionation is much less important, and in the steady state,  $[x(^{13}\text{CO})/\xi_{^{13}\text{C}}]/[x(^{12}\text{CO})/\xi_{^{12}\text{C}}] < 1.05$ . In conclusion, the  $x(^{13}\text{CO})/x(^{12}\text{CO})$  reflects the true isotopic abundance in dense dark clouds *only if* there is sufficient time for complete conversion of carbon to CO; otherwise, the  $^{13}\text{CO}$  will be enhanced. The measurements of Wannier *et al.* (1976) may suggest not just that  $^{13}\text{C}$  is enhanced outside the solar system, but that there is incomplete conversion of carbon to CO and, consequently, significant  $x(\text{C I})$  in dense clouds.

### III. FORMALDEHYDE IN DENSE CLOUDS

The results of § II suggest that the application of the  $\text{H}_3^+$  chemistry described by HK to molecular abundances in dense clouds must be modified to include time-dependent effects. Their use of steady state results and the choice  $x(\text{CO}) = \xi_C$  was based on the assumption that carbon monoxide was produced efficiently at some earlier stage of cloud evolution. But, as suggested above, this assumption is probably incorrect and  $x(\text{CO})$ ,  $x(\text{O})$ , and  $x(\text{C I})$  cannot be set equal to their steady state time-independent values. The abundances of the trace molecules will be modified considerably when the time dependence of C I is considered. It will first be shown that the formaldehyde abundance in dense clouds can best be understood in

terms of the time-dependent chemistry. Following this discussion on  $\text{H}_2\text{CO}$ , the abundances of several other trace molecules will be estimated.

The production of formaldehyde from the neutral molecule reaction  $\text{CH}_3 + \text{O} \rightarrow \text{H}_2\text{CO} + \text{H}$  has been discussed by Dalgarno, Oppenheimer, and Black (1973) and elaborated upon by Watson, Crutcher, and Dickel (1975). The major contribution of the present work is the increase at finite times in  $x(\text{CH}_3)$  due to large  $x(\text{C I}, t)$ . The  $\text{CH}_3$  is formed from  $\text{CH}_3^+$ , either by charge exchange with metals (M) with ionization potentials less than 9.84 eV, or by dielectronic recombination at a rate  $10^{-3}$  of the total recombination rate  $\beta(\text{CH}_3^+) = 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  (Dalgarno, Oppenheimer, and Black 1973). The reaction  $\text{CH}_3^+ + \text{O}$  will not contribute to  $x(\text{H}_2\text{CO})$  because the reaction product is  $\text{HCO}^+ + \text{H}_2$  (Fehsenfeld 1976) with a rate  $4.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and not  $\text{H}_2\text{CO}^+ + \text{H}$ .

The radiative association mechanism proposed by Herbst and Klemperer (1973) to explain the formaldehyde abundance ( $\text{HCO}^+ + \text{H}_2 \rightarrow \text{H}_3\text{CO}^+ + h\nu$ , followed by  $\text{H}_3\text{CO}^+ + e \rightarrow \text{H}_2\text{CO} + \text{H}$ ) is negligible here because of its slow reaction rate (Fehsenfeld, Dunkin, and Ferguson 1974; Herbst 1976). The  $\text{H}_2\text{CO}$  is primarily destroyed by the following processes: (1) photodissociation; (2) ion-molecule reactions and charge exchange with  $\text{C}^+$  and other ions (e.g.,  $\text{H}_3^+$ ,  $\text{H}^+$ ,  $\text{He}^+$ ); and (3) the neutral-molecule reaction with oxygen,  $\text{H}_2\text{CO} + \text{O} \rightarrow \text{HCO} + \text{OH}$ . This last reaction has a rate coefficient  $a_{10} = 1.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  at  $T = 300 \text{ K}$  (Niki, Daby, and Weinstock 1971) and will be important at high densities.

The key to the production of  $\text{H}_2\text{CO}$  in this scheme is the production of  $\text{CH}_3^+$  which results from the sequence of reactions initiated by (1) and (2) (and followed rapidly by:  $\text{CH}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + \text{H}$  and  $\text{CH}_2^+ + \text{H}_2 \rightarrow \text{CH}_3^+ + \text{H}$ ). In the steady state calculations of HK,  $x(\text{C I}) \leq 5 \times 10^{-7}$  and hardly contributes to production of  $\text{CH}_3^+$ , while the  $\text{C}^+$  radiative association considered by Dalgarno *et al.* (1973) and Watson *et al.* (1975) will be more important. Nonetheless, neither of these produce enough  $\text{CH}_3^+$  to explain  $x(\text{H}_2\text{CO})$ . The time-dependent abundance of C I in dense clouds, however, is much larger than the value used by HK resulting in correspondingly larger values of  $x(\text{CH}_3^+)$  and  $x(\text{H}_2\text{CO})$ . The adiabatic approximation can be used for formaldehyde, and its abundance is given approximately by:

$$x(\text{H}_2\text{CO}) \approx \frac{ax(\text{O})\Gamma(\text{CH}_3)}{g_{\text{CH}_3} + k \sum x_i(\text{X}^+) + ax(\text{O})} \times \frac{(\frac{1}{2}k_{26}x(\text{C}^+) + kx(\text{H}_3^+)x(\text{C}))}{g_{\text{H}_2\text{CO}} + k \sum x_i(\text{X}^+) + a_{10}x(\text{O})}, \quad (8)$$

where the sum is over all the ions which destroy  $\text{H}_2\text{CO}$ , and  $\Gamma(\text{CH}_3) = [10^{-3}\beta x_e + kx(\text{M})]/[\beta x_e + kx(\text{M}) + 0.4kx(\text{O})]$  is the branching ratio for forming  $\text{CH}_3$  from  $\text{CH}_3^+$ .

The values of  $x(\text{H}_2\text{CO})$  will depend on the evolutionary stage of each cloud and the details of the  $t$ -dependence of  $x(\text{C I}, t)$ . Rather than construct particular

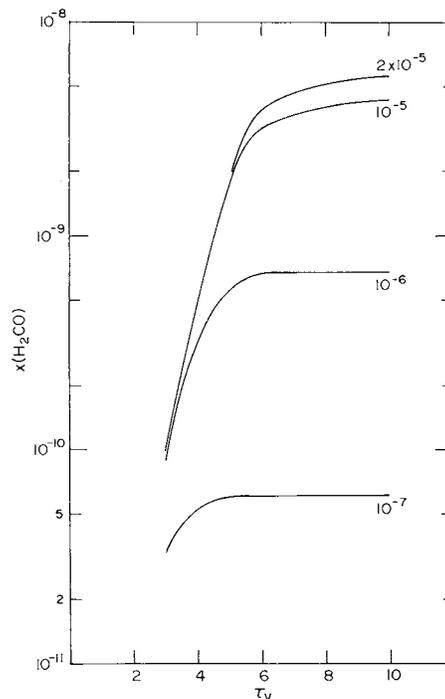
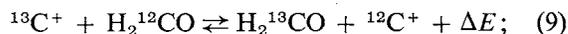


FIG. 2.—The formaldehyde abundance at  $n = 10^4 \text{ cm}^{-3}$  is plotted as a function of extinction into the cloud. Each curve is labeled with the value of  $x(\text{MO})$  used; the other parameters are discussed in the text.

cloud models, we have estimated a range of values for  $x(\text{H}_2\text{CO})$  appropriate to the conditions in interstellar clouds. Figure 2 shows the results of this sample calculation using the following set of parameters characteristic of dense clouds:  $n = 10^4 \text{ cm}^{-3}$ ,  $x_i = 10^{-6}$ ,  $\xi_{\text{C}} = 10^{-4}$ ,  $\xi_{\text{O}} = 2 \times 10^{-4}$ ,  $x(\text{O}) = 10^{-4}$ ,  $x(\text{M}) = 10^{-6}$ ,  $x(\text{H}_3^+) = 10^{-9}$ , and  $G_{\text{CH}_3} = G_{\text{H}_2\text{CO}} = 10^{-9} \exp(-1.5 \tau_v) \text{ s}^{-1}$ . Based on the results of § II we have adopted typical average values of  $x(\text{C I}) = 2 \times 10^{-5}$  and  $x(\text{CO}) = 8 \times 10^{-5}$ . The results are presented as a function of both  $\tau_v$  and  $x(\text{MO})$ . The contribution of C I to  $\text{CH}_3^+$  and  $\text{H}_2\text{CO}$  can be as large as two orders of magnitude more than that of  $\text{C}^+$  when  $x(\text{MO}) = 10^{-5}$ . The range of  $x(\text{H}_2\text{CO})$ ,  $\sim 10^{-10}$  to  $5 \times 10^{-9}$ , in this figure is in good agreement with the abundances and profiles found in dense clouds (Myers and Ho 1975). Factors of 3 or 4 may exist because of the uncertainties in  $x(\text{C I})$  and  $x(\text{H}_3^+)$ ; nonetheless, the relatively large  $x(\text{H}_2\text{CO})$  (Evans *et al.* 1975) is readily explained.

The relative abundance of the carbon isotopes of formaldehyde,  $x(\text{H}_2^{13}\text{CO})/x(\text{H}_2^{12}\text{CO})$ , will depend on the following factors: (1) the reaction rate for the isotopic exchange reaction,



(2) the abundances of  $^{12}\text{C}^+$  and  $^{13}\text{C}^+$ , which depend in turn on  $^{12}\text{CO}$  and  $^{13}\text{CO}$ , respectively; and, (3) the relative abundance of the neutral carbon from which formaldehyde is produced. The reaction rate for the

isotopic exchange reaction (9) has not been measured;  $\Delta E/k$  is estimated to be 50 K (Bertojo, Chui, and Townes 1974). Unlike the isotopic exchange reaction for CO, reaction (9) must compete with the ion-molecule reactions of  $C^+$  with  $H_2CO$ , which have a total reaction rate of  $4.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (Anicich, Huntress, and Futrell 1976); until it is measured its relative importance cannot be known. If isotopic exchange can be neglected  $x(H_2^{13}CO)/x(H_2^{12}CO) \approx x(^{13}C \text{ I})/x(^{12}C \text{ I})$ , which implies that if  $^{13}CO/^{12}CO$  is enhanced then  $H_2^{13}CO/H_2^{12}CO$  is diminished. Unfortunately, the neutral carbon ratio is unknown and the isotopic ratios of formaldehyde cannot be determined. Instead we have considered a range of possibilities consistent with the time-dependent model presented in this paper, and estimate that  $[x(H_2^{13}CO)/\xi_{^{13}C}]/[x(H_2^{12}CO)/\xi_{^{12}C}] \approx 0.25-1.0$ . If the reaction rate for (9) were  $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , this ratio could be increased by  $\sim 0.5$ .

The above discussion suggests that  $H_2^{12}CO$ , unlike  $^{12}CO$ , could be enhanced with respect to  $H_2^{13}CO$  when compared to terrestrial abundances. According to the model presented here, formaldehyde should reflect smaller isotopic ratio than CO for carbon thirteen. Observations in several dark dense clouds find  $x(H_2^{12}CO)/x(H_2^{13}CO) \geq 70-90$  (Evans and Kutner 1976; Matsakis *et al.* 1976) in qualitative agreement with the preceding discussion.

Other CH family molecules may have similarly larger abundances in the time-dependent model. For example,  $x(\text{CH}) + x(\text{CH}_2) \approx 10^{-8}$ , when the same parameters adopted for the previous calculation are used [this result is somewhat independent of  $x(C^+)$  in dark regions, Langer 1976]. The ratio of CH to  $\text{CH}_2$  will depend on the branching ratio for  $\beta(\text{CH}_3^+)$ . Only CH has so far been observed in dense clouds, and the first radio observations by Turner and Zuckerman (1974) toward Cas A give  $N(\text{CH})/N(H_2CO) \approx 1$ , in agreement with the above discussion. More recently Hjalmarsen *et al.* (1975) have published the results of over 100 observations of CH in dark clouds. For roughly 25 of these observations, formaldehyde measurements are also available and most of the values of  $N(\text{CH})/N(H_2CO)$  are consistent with the model presented in this paper. Rydbeck *et al.* (1976) compare

observations of CH and OH in a number of dark dense clouds and find  $N(\text{CH})/N(\text{OH})$  is either  $\approx 0.1-0.5$  if the excitation temperature equals the kinetic temperature, or  $\approx 0.04-0.14$  if CH is a weak maser. To a good approximation,  $x(\text{CH})/x(\text{OH}) \approx \gamma(\text{CH}_3^+ \rightarrow \text{CH})/\gamma(\text{OH}_3^+ \rightarrow \text{OH})x(\text{C I})/x(\text{O I})$ , where the  $\gamma$ 's are branching ratios for dissociative recombination to CH and OH. For the parameters adopted above, and assuming comparable branching ratios,  $x(\text{CH})/x(\text{OH}) \approx 0.2$  in qualitative agreement with the above observations. The range of observational ratios may be explainable in terms of density variations and the change of  $x(\text{C I})$  and  $x(\text{O I})$  with time. Detailed comparisons are not possible without further measurements of other molecular abundances and/or  $\tau_V$ .

The ethynyl radical,  $C_2H$ , has been detected in a number of sources with  $N(C_2H) \sim 10^{15} \text{ cm}^{-2}$  (Tucker, Kutner, and Thaddeus 1974), indicating that  $x(C_2H) > 5 \times 10^{-9}$  in dense regions. Based on the assumptions in this work,  $x(C_2H) = 3 \times 10^{-11}$  to  $3 \times 10^{-10}$  as  $x(\text{MO})$  varies from  $10^{-6}$  to  $10^{-5}$  at large  $\tau_V$ . The  $x(C_2H)$  depends directly on  $x(C^+)$  because it is produced from reactions of  $C^+$  with CH and  $\text{CH}_2$ . These estimates are too small to explain  $N(C_2H)$ ; a direct comparison is difficult because large  $x(C_2H)$  can be produced in the  $C^+-CO$  transition region where there is sufficient ultraviolet radiation to keep carbon slightly ionized (Langer 1976). Model calculations yield  $N(C_2H) \sim 10^{15} \text{ cm}^{-2}$  from this region alone, somewhat independent of density.

In conclusion, the abundances of all molecules which eventually derive from  $\text{CH}_3^+$  must be reexamined in terms of the contribution of C I expected in a time-dependent model of abundances and cloud evolution. Based on this model, we have shown how relatively large abundances of  $H_2CO$  and CH can be explained. Virtually all of the chemistry in dense clouds, including that for isotopic abundances, may have to be treated in a time-dependent analysis, possibly in conjunction with evolutionary models for the clouds.

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