

## The Gas-phase Chemical Evolution of Dark Clouds\*

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### *Abstract*

A rich chemistry exists within dark clouds. In the most chemically studied dark cloud, Taurus molecular cloud one (TMC-1), more than 40 molecules have been detected. In this paper I look at the current isochoric, i.e. constant density, isothermal time-dependent gas-phase chemical models of dark clouds such as TMC-1 and very briefly outline the present understanding of the chemistry of these objects. The above chemical models agree very well with the observed abundances of almost all chemical species at times earlier than steady state, i.e. earlier than thirty million years. However, the models are fraught with uncertainty and are not physically realistic representations of the full dynamical evolution of dark clouds from a more diffuse state. Nevertheless the agreement with observation is striking.

### 1. Introduction

The purpose of this paper is to give the reader a very brief introduction to current isochoric, isothermal time-dependent gas-phase chemical models of dark clouds. This work is not intended as a review of interstellar chemistry, for which one is referred to the excellent review of Herbst (1990). This paper simply outlines the chemical model and discusses how well such models fare when compared with observation. A brief account of the chemistry of dark clouds, and the role of the dust, is given as well as some of the uncertainties associated with these models; one in particular is examined. Finally the possible role of interstellar chemistry in star formation is discussed.

The quiescent dark cloud, TMC-1, is one of the most chemically studied. It is at a distance of  $\sim 115$  pc from our solar system in the constellation of Taurus. The composition of this cloud is mostly  $\text{H}_2$  and He with a total mass of one solar mass. Approximately 1% of this mass is dust which is critically important for the existence of molecules. The dust shields these molecules from the very destructive interstellar radiation field, commonly and crudely approximated to a  $10^4$  K black body with a dilution factor of  $10^{-14}$ . The cloud is opaque to visible and ultraviolet light because of the relatively high density of the dust. The kinetic temperature of the gas is  $\sim 10$  K and the density  $[\text{H}_2] \sim 10^4$  molecules per  $\text{cm}^3$  (Duley and Williams 1984). The observed spectral lines show little evidence for cloud rotation or collapse. Therefore it is an ideal source for interstellar chemical

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**Table 1. Observed chemical species and associated fractional abundances with respect to H<sub>2</sub> in TMC-1**

Species	Fractional abundance <sup>A</sup>	Species	Fractional abundance <sup>A</sup>
CO	$8 \times 10^{-5}$	C <sub>2</sub>	$5 \times 10^{-8}$
OH	$3 \times 10^{-7}$	CH	$2 \times 10^{-8}$
C <sub>2</sub> H	$8 \times 10^{-8}$	C <sub>3</sub> H	$5 \times 10^{-10}$
C <sub>4</sub> H	$2 \times 10^{-8}$	C <sub>5</sub> H <sup>B</sup>	$4 \times 10^{-10}$
C <sub>6</sub> H	$1 \times 10^{-9}$	C <sub>3</sub> H <sub>2</sub>	$2 \times 10^{-8}$
CH <sub>3</sub> C <sub>2</sub> H	$6 \times 10^{-9}$	CH <sub>3</sub> C <sub>4</sub> H	$2 \times 10^{-9}$
CN	$3 \times 10^{-8}$	HCN	$2 \times 10^{-8}$
HNC	$2 \times 10^{-8}$	CH <sub>2</sub> CN <sup>C</sup>	$5 \times 10^{-9}$
CH <sub>3</sub> CN	$1 \times 10^{-9}$	HC <sub>2</sub> CN	$6 \times 10^{-9}$
HC <sub>4</sub> CN	$3 \times 10^{-9}$	HC <sub>6</sub> CN	$1 \times 10^{-9}$
HC <sub>8</sub> CN	$3 \times 10^{-10}$	CH <sub>3</sub> C <sub>2</sub> CN	$5 \times 10^{-10}$
C <sub>2</sub> CN	$1 \times 10^{-9}$	C <sub>2</sub> H <sub>3</sub> CN	$2 \times 10^{-10}$
NH <sub>3</sub>	$2 \times 10^{-8}$	N <sub>2</sub> H <sup>+</sup>	$5 \times 10^{-10}$
HCO <sup>+</sup>	$8 \times 10^{-9}$	C <sub>2</sub> O <sup>D</sup>	$6 \times 10^{-11}$
C <sub>3</sub> O	$1 \times 10^{-10}$	HC <sub>2</sub> CHO <sup>E</sup>	$1 \times 10^{-10}$
H <sub>2</sub> CO	$2 \times 10^{-8}$	CH <sub>2</sub> CO	$1 \times 10^{-10}$
CH <sub>3</sub> OH	$4 \times 10^{-9}$	CH <sub>3</sub> CHO	$6 \times 10^{-10}$
CS	$1 \times 10^{-8}$	HCS <sup>+</sup>	$6 \times 10^{-10}$
OCS	$2 \times 10^{-9}$	SO	$5 \times 10^{-9}$

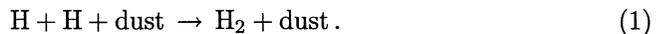
<sup>A</sup> Irvine *et al.* (1987a, 1987b) unless otherwise noted. <sup>B</sup> Cernicharo *et al.* (1987).

<sup>C</sup> Irvine *et al.* (1988a). <sup>D</sup> Ohishi *et al.* (1992). <sup>E</sup> Irvine *et al.* (1988b).

studies because there are no complicating effects to be taken into account. Table 1 lists some of the molecules observed in TMC-1 and their fractional abundances, i.e. their abundances relative to [H<sub>2</sub>].

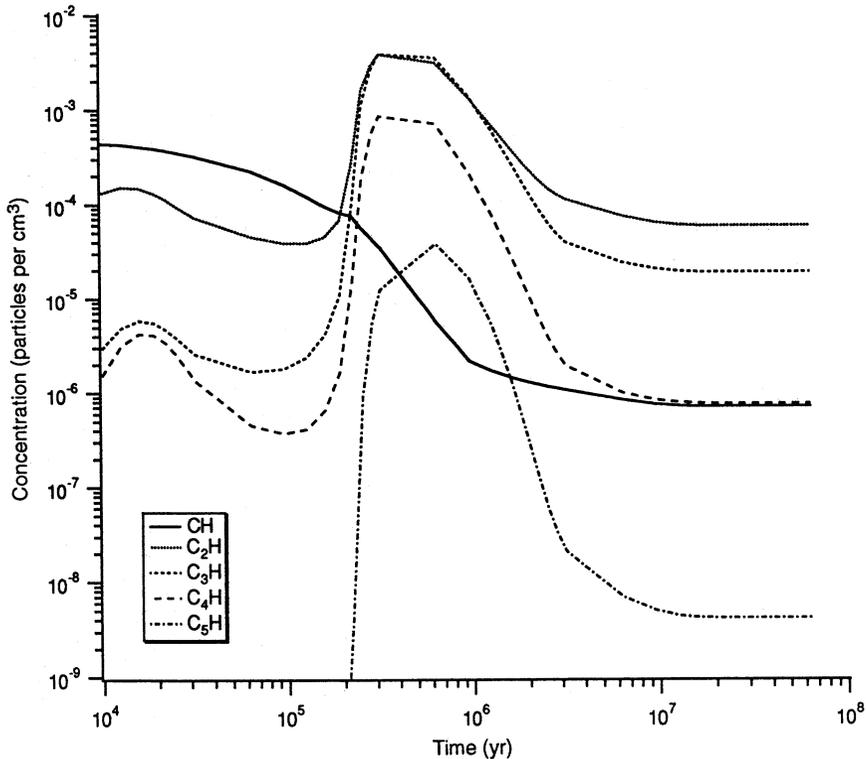
In order for a gas-phase model to predict/reproduce the abundances of the molecules found in Table 1 the reactions to be considered must proceed efficiently under the conditions pertaining to TMC-1. These reactions must have little or no energy barrier, and at most they can only involve two bodies because three body collisions are too improbable. The reactions that satisfy these two criteria are, in general, exothermic ion-molecule reactions. Thus the bulk of reactions in gas-phase chemical models of dark clouds are ion-molecule reactions.

The chemical model used in the calculations (model E from Bettens and Brown 1992) described in this paper produces the abundances of chemical species as a function of time. At  $t = 0$  the chemical species are assumed to be all in atomic form and all atoms with an ionisation potential less than hydrogen are ionised. The initial abundances of the atoms in the model are based on Morton's (1974) depleted solar abundances with the metals, Mg, Na, and Fe, depleted by a further two orders of magnitude. In the model the chemistry is allowed to evolve with time but the cloud temperature and density are assumed to remain constant. The model contains over 3000 gas-phase reactions with 215 different chemical species and one solid-phase reaction



The formation of H<sub>2</sub> upon the dust is necessary because it is not possible to produce enough H<sub>2</sub> via gas-phase chemistry. The abundances of the chemical species are allowed to evolve over a period of 100 million years. This is done

by producing a set of coupled, stiff (stiff because the rate constants of the reactions vary over many orders of magnitude), differential equations from the reaction set—the number of equations being the same as the number of chemical species—and solving them numerically using the Gear (1971) algorithm.



**Fig. 1.** The fractional abundances versus time of the molecules  $C_nH$ ,  $n = 1-5$ , relative to  $[H]+2[H_2]$  for a cloud at 10 K and a total hydrogen nuclei density of  $2 \times 10^4 \text{ cm}^{-3}$ .

## 2. Model Results

Two general points of interest come out of the results of the interstellar chemical model briefly described above. The first is that at times greater than about 30 million years the concentrations of all the chemical species remain effectively constant, i.e. an approximate steady state is reached. The second point is that the abundances of the more chemically complex species, i.e. chemical species that contain more than two elements heavier than hydrogen, pass through a maximum at around 300 thousand years. These two points are illustrated in Fig. 1 where the abundances of the molecules  $C_nH$ ,  $n = 1-5$ , are plotted versus time.

### (a) Comparison with Observation

Due to the many uncertainties associated with determining the fractional abundances of chemical species observed within dark clouds, an order of

magnitude error is usually associated with the observed fractional abundances. Bearing this in mind, models of the sort described above agree very well with the observation for virtually all smaller species, i.e. agreement is good for CO, OH, CN, HCN, H<sub>2</sub>CO, HCO<sup>+</sup> and C<sub>2</sub>H, at times after ~300 thousand years (Brown and Rice 1986).

What of the more complex species such as C<sub>n</sub>H,  $n = 2-6$  or HC<sub>2n</sub>CN,  $n = 1-4$ ? At steady state times, i.e. at ~30 million years, agreement is very poor, the calculated abundances being orders of magnitude below observation. At earlier times agreement is better with some modellers advocating times of ~300 thousand years (Herbst and Leung 1989, 1990) while others ~3 million years (Brown *et al.* 1990). Both groups of modellers have problems with a few molecules. For example, if 300 thousand years is chosen, then N<sub>2</sub>H<sup>+</sup> is not in good agreement with observation, and as well some species are over-produced. Yet if ~3 million years is chosen CH is in poor agreement with observation. However, overall agreement is quite good for the majority of chemical species for times earlier than the steady state.

### (b) *Dust in Dark Clouds*

As mentioned earlier the presence of dust in dark clouds is critical for (1) the existence of molecules and (2) the formation of H<sub>2</sub>. However, there is a problem with gas-phase chemical models that are allowed to evolve to steady state. The problem is that chemical species other than H<sub>2</sub> and He are thought to be quite likely to stick to the dust upon collision. It has been shown, if this effect is included in gas-phase models with no efficient desorption mechanism, that freeze-out of all molecules occurs in the time  $3 \times 10^9 \text{ yr} / \{[\text{H}] + 2[\text{H}_2]\}$  (Iglesias 1977). If this were the case then all observed dark clouds containing molecules would have to be younger than the freeze-out time. The problem remains (though many mechanisms have been proposed, cf. the introductory discussion of Brown and Charnley 1990) of finding an unambiguous efficient desorption mechanism for removal of chemical species from the dust in dark clouds.

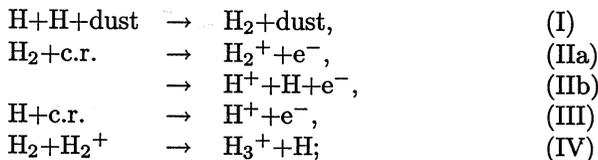
There is no question that at least some molecules stick to the dust as observations for clouds of  $A_V > \sim 20$  mag (though there are exceptions) show the existence of mantles of 'ice' upon the dust, evident by the characteristic 3.1  $\mu\text{m}$  amorphous OH ice stretch (Whittet *et al.* 1988; Harris *et al.* 1978). In regions where there is an infrared source embedded in a cloud it is possible to study the composition of this volatile mantle through the absorption features present. For instance Allamandola (1987) has suggested that the mantle is composed of mostly H<sub>2</sub>O and CH<sub>3</sub>OH with traces of other simple molecules, CO, NH<sub>3</sub>, ketones, aldehydes and carbonyls.

Thus at least some of the material in molecular clouds sticks to the dust, but unless all dark clouds are young, there must be an efficient desorption mechanism to remove material from the dust. Due to the success gas-phase models have had in predicting the abundances of almost all interstellar molecules in dark quiescent clouds, many time-dependent models have ignored the dust, except for the formation of H<sub>2</sub>, by assuming that the dust does not play a more important role in synthesising molecules. The reader should be aware, however, that many authors have examined grain-surface chemistry and a combination of grain-surface and gas-phase chemistry (see Brown and Charnley 1990 and references therein).

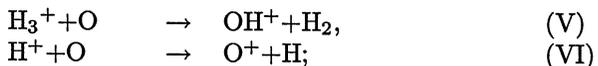
*(c) Initiation of the Chemistry*

As stated earlier, ion-molecule reactions generally proceed without activation energy. Thus the presence of ions within dark clouds is critically important for gas-phase molecular synthesis. The ions are generated in dark clouds via cosmic ray (hereafter, c.r.) ionisation. Below is a simplified summary of the initiation of the gas-phase chemistry of H, C, O and N:

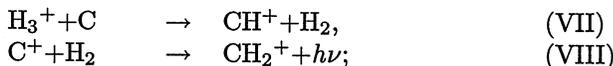
## Hydrogen chemistry initiation



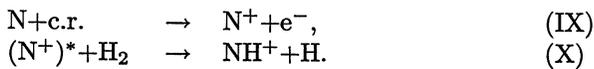
## Oxygen chemistry initiation



## Carbon chemistry initiation



## Nitrogen chemistry initiation



The hydrogen atom abstraction reaction (IV) generates the very important acid  $\text{H}_3^+$ . This species is seen to aid in the initiation of the chemistry of oxygen (V) and the chemistry of carbon (VII). The charge transfer reaction (VI) is slightly endothermic (by  $T = 232$  K) and thus proceeds slowly in cold ( $T = 10$  K) dark clouds; however, in warmer dark clouds, such as those found in Orion, the reaction is significant. The radiative association reaction (VIII) has not yet been directly measured in the laboratory, but its rate has been deduced from the three-body rate constant (Herbst 1982, 1985). The chemistry of nitrogen is interesting because reaction (X), where  $\text{N}^+$  is in the  $^3\text{P}$  state and  $\text{H}_2$  is para, is found to possess a barrier to reaction of 168.5 K (Marquette *et al.* 1988) and yet there is enough translationally hot  $\text{N}^+$  within a dark cloud to power this reaction (Brown *et al.* 1990).

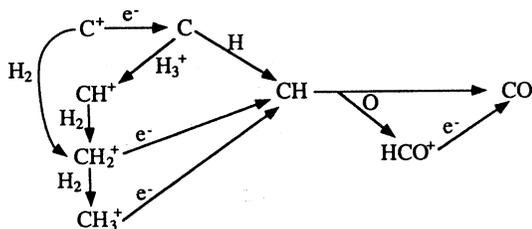


Fig. 2. A simplified schematic representation of the synthesis of CO in a dark cloud at 10 K and a total hydrogen nuclei density of  $2 \times 10^4 \text{ cm}^{-3}$ .

*(d) The Chemistry of CO*

For interest I include the early time synthesis of the most abundant molecule apart from  $\text{H}_2$ , i.e. the synthesis of CO. Fig. 2 is a simplified schematic

representation of the synthesis of CO in dark clouds at times earlier than steady state. The formation of CO from  $C^+$  is all but complete in  $\sim 10^6$  yr, and at steady state CO contains 99.8% of the initial carbon abundance.

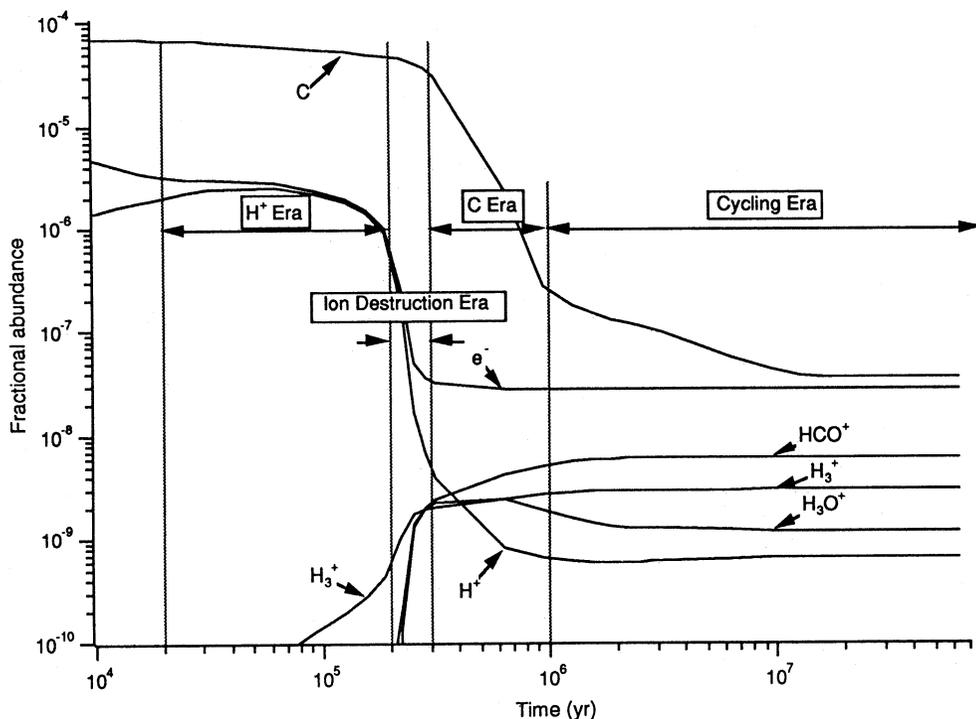


Fig. 3. The abundances versus time of the different chemical species that define the different chemical eras indicated, during the life of a dark cloud at 10 K and a total hydrogen nuclei density of  $2 \times 10^4 \text{ cm}^{-3}$ .

### (e) The Chemistry of the More Complex Species

While the chemistry for each of the smaller species is unique, the chemistry of the more complex species is somewhat similar. There are, however, different dominating chemistries for the more complex species at different epochs during cloud evolution. Fig. 3 shows the different chemical eras and the chemical species defining them. Prior to the  $H^+$  era by far the most dominant ion is  $C^+$ . Although it is not shown, the end of the dominance of  $C^+$  occurs at 20 thousand years into the life of the cloud. During this initial period of the cloud's life there is some build up of complex species through reactions of the kind



In the  $H^+$  era, which lasts from 20 thousand years up until 200 thousand years, the most dominant ion is  $H^+$ . In this era there is a levelling off of, and in some cases even a drop in, the abundances of the complex species (see Fig. 1). This

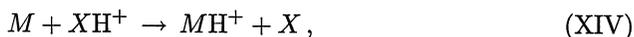
is due to charge transfer reactions of the following kind, which do not add to the complexity of the species  $M$ ,



At the end of the  $\text{H}^+$  era a large fraction of the initial amount of H has been converted into  $\text{H}_2$  via reaction (I). In the ion destruction era ( $t = 200$  to 300 thousand years) the ions that depend on the formation of  $\text{H}_2$  are rapidly produced. These ions are  $\text{HCO}^+$ ,  $\text{H}_3^+$  and  $\text{H}_3\text{O}^+$ , and they react efficiently with electrons leading to a rapid drop in the electron abundance. The ion  $\text{H}^+$  is very quickly destroyed by species that also depend on the abundance of  $\text{H}_2$ . In this era, however, the abundance of C remains high. Also with the drop in abundance of  $\text{H}^+$ , the abundance of  $\text{C}^+$  becomes comparable with that of  $\text{H}^+$ ; both  $\text{C}^+$  and  $\text{H}^+$  are the most abundant ions in this era. Therefore reactions of the kind (XI) and (XIII) below rapidly produce complex species. This is the reason for the maximum of many complex species occurring at the end of the ion destruction era.



The next era is the C era from 300 thousand years to one million years, the time when C is converted into the reservoir species, CO. The complex species drop in abundance during this time as both reactions (XI) and (XIII) become slower. Finally the cycling era is reached after a million years of cloud evolution when the most abundant reactive ions,  $\text{HCO}^+$ ,  $\text{H}_3^+$  and  $\text{H}_3\text{O}^+$ , simply cycle material in the manner shown in reactions (XIV) and (XV) below. During this era steady state is reached as the elements C, N and O find their way into their respective reservoir species.



where  $X$  is CO,  $\text{H}_2\text{O}$  and  $\text{H}_2$ .

#### (f) Concluding Remarks and Uncertainties

Current isochoric, isothermal, time-dependent gas-phase chemical models of dark clouds such as TMC-1 agree quite well with the observed abundances of almost all chemical species at times earlier than steady state, i.e. at times earlier than 30 million years. However, these models contain uncertainties, some of which are listed below.

The dark clouds modelled are almost certainly evolving dynamically with time, i.e. the pressure and temperature are changing. Does this have a significant effect on the predicted molecular abundances (for instance see the two dynamic chemical models by Tarafdar *et al.* 1985; Gerola and Glassgold 1978)? Rate constants and branching ratios for many ion-molecule reactions are unknown, and have to be deduced from theory or estimated by analogy with similar reactions. This, of course, can have a large impact on the abundances of molecular species

(Millar *et al.* 1987; Bates and Herbst 1988). In the next section I address one set of reactions which, if they proceed at a significant rate, have a very large impact on the abundances of observed chemical species. Another uncertainty is the depletion of the elements in dark clouds; it is normally assumed that the dark cloud depletions are the same as diffuse cloud depletions. The influence of the dust on the gas-phase chemistry is another uncertainty. Given that freeze-out does occur, is the effect on the gas-phase chemistry, just prior to freeze-out of the molecules onto the dust, really significant? If freeze-out does not occur, is there significant chemical processing on the dust before ejection of the mantle material? There are also uncertainties associated with c.r. ionisation of the gas, apart from the rate itself; the ionisation of the gas produces fast electrons which can electronically excite  $H_2$  which, when it radiatively decays, produces molecule-destructive ultraviolet radiation (Sternberg *et al.* 1987). Given all these uncertainties the agreement with observation is quite striking. It is presumed, therefore, that the essential chemistry is properly described.

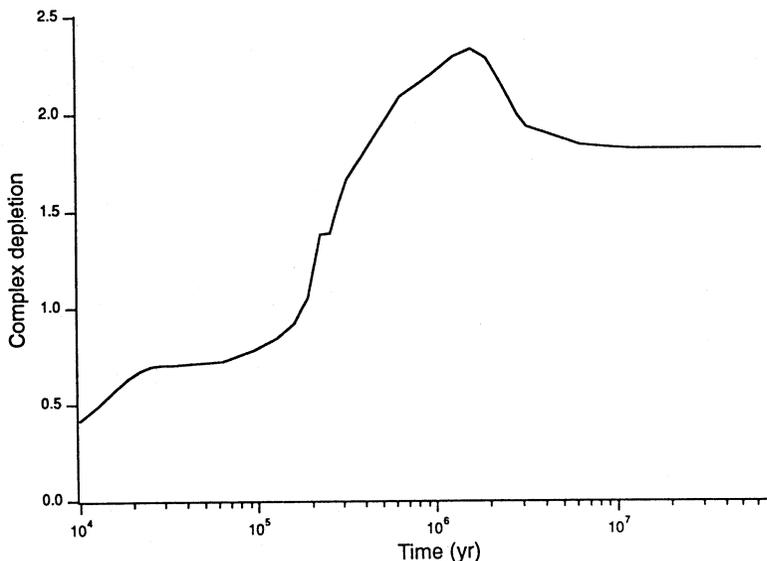


Fig. 4. The average logarithmic depletion of the series  $C_nH$ ,  $n = 1-5$ , versus time, relative to a model that does not include the neutral-neutral atomic oxygen reactions.

### 3. Neutral-Neutral Atomic Oxygen Reactions

Generally neutral-neutral reactions possess energy barriers which render them too inefficient under interstellar conditions. However, it has been proposed theoretically that atomic oxygen dipolar-radical reactions (a radical being defined here as a species that has a non-zero total electronic spin angular momentum) proceed without a barrier (Graff 1989). This is because atomic oxygen possesses an electronic quadrupole in its lowest fine structure level which can interact with the dipole of the other reactant. This means that reactions of the following type proceed efficiently:



When reactions of this kind are included in the gas-phase interstellar chemical model it is found that molecules containing more than three heavy atoms (non-hydrogen atoms) and two hydrogen atoms cannot be produced in great enough abundance to explain the observed abundances of these species (Bettens and Brown 1992). Fig. 4 illustrates this point, where the vertical axis is the average logged ratio of the  $[C_nH]$ ,  $n = 1-5$ , species in a model not containing reactions of the kind (XVI), compared with a model that does. This disagreement with observation is a very serious discrepancy; the best explanation being that all the reactions of type (XVI) do not, in fact, proceed.

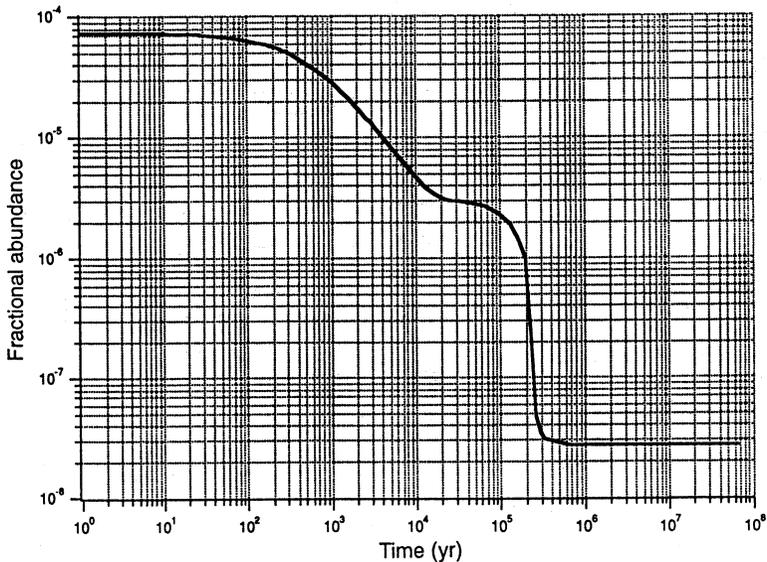


Fig. 5. The fractional ionisation, defined here as  $[e^-]/\{[H] + 2[H_2]\}$ , in the gas phase versus time for a cloud at 10 K and a total hydrogen nuclei density of  $2 \times 10^4 \text{ cm}^{-3}$ .

#### 4. Interstellar Chemistry and Star Formation

It is certainly possible that chemistry can influence star formation, the amount of ionisation within a cloud being one possible mechanism. The fractional ionisation in the gas phase is set by the chemistry and is shown in Fig. 5 as a function of time. If magnetic fields are responsible for clouds being held up against collapse then one would expect that the amount of ionisation would have a direct impact on star formation. Spitzer (1978) has shown that the time required for the magnetic flux to diffuse out of the interstellar cloud is of the order of  $t_D \sim 5 \times 10^{13} f(e^-) \text{ yr}$ , where  $f(e^-)$  is the fractional ionisation\*. Thus we see that, at times before the ion destruction era, the diffusion time is far too long to be of interest, but after this time  $f(e^-) \sim 3 \times 10^{-8}$  and  $t_D \sim 2 \times 10^6 \text{ yr}$ . This

\* Note that Spitzer's calculation assumed that the gas was atomic and not molecular hydrogen, and that the quantity  $\langle u\sigma_s \rangle$  is for  $C^+-H$  collisions. The major ions after the ion destruction era are  $Mg^+$ ,  $Na^+$ ,  $Fe^+$ ,  $HCO^+$ ,  $H_3^+$  and  $H_3O^+$ . However, the calculated diffusion time is still good for an order of magnitude estimate.

indicates that, after the ion destruction era, in a few million years cloud collapse will presumably resume, previously being held up by the magnetic field. The effect of c.r. ionisation upon the fractional ionisation has some very interesting implications for the very strong far-infrared/radio correlation observed in recent years (Dickey and Salpeter 1984; Wunderlich *et al.* 1987; Roy *et al.* 1991). However, it is not appropriate here to elaborate further on this point; the reader is referred elsewhere for a discussion (Bettens *et al.* 1992).

Tarafdar *et al.* (1985) stated that: 'The temperature structure of a cloud is of paramount importance in its collapse.' The dominant species for the cooling of the gas in our dark cloud ( $T \sim 10$  K) are  $C^+$ , C and CO. Thus the chemical evolution from  $C^+ \rightarrow C \rightarrow CO$  must be considered because this process changes the cooling characteristics of the gas. The conversion of the gas from atomic to molecular, via reaction (I), will also influence the internal pressure of the gas. The heat released in the chemical reactions taking place within the cloud must also be considered as a heat source in dark clouds because it is of the same order as c.r. heating. All of the above chemical effects will influence star formation to a lesser or greater extent and should be taken into consideration in any model of star formation.

## 5. Conclusions

It has been shown that the current isochoric, isothermal time-dependent gas-phase chemical models of dark clouds are quite successful at reproducing/predicting the abundances of most of the observed chemical species seen in TMC-1. It is also likely that these interstellar chemical models will have wider applications, for instance in star formation where, in fact, the chemistry may have some influence.

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