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# Interstellar Deuterium Chemistry [and Discussion]

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# Interstellar deuterium chemistry

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An interstellar reaction scheme of the type described by E. Iglesias (*Astrophys. J.* **218**, 697 (1977)) has been extended to include deuterium chemistry and also isomeric forms of some molecules. The role of isomeric forms of the intermediates $CNH_2^+$ and $HCNH^+$ in the production of interstellar HCN and HNC is considered. The lowest triplet states of these ions probably play an important part in determining the proportions of HCN and HNC produced.

The results of numerical integration of the 108 coupled kinetic equations involved in the extended scheme are presented as time-dependent plots of concentrations of the different chemical species.

Calculated concentrations at a molecular cloud age of 10 Ma (1 Ma = $10^6$ years) are within the experimental uncertainties for 11 of the 14 species for which suitable observational data are available.

Predicted values of HX/DX ratios fall into three broad groups around $10^2$, $10^3$ and the accepted cosmic H/D ratio, $10^5$, and observations are broadly in agreement. Some reported enrichments that are higher than the predicted figures may arise from the use of data for optically thick molecular lines. Some previously unpublished observations of DNC and $HN^{13}C$ illustrate doubts associated with optically thick lines.

## Introduction

Since the discovery about a decade ago of the first of a growing list of polyatomic interstellar molecules in various dark nebulae, there have been a number of proposed reaction schemes for their formation and destruction (Solomon & Klemperer 1972; Herbst & Klemperer 1973; Aannestad 1973; Watson 1974; Allen & Robinson 1976; Black & Dalgarno 1977; Mitchell *et al.* 1978; Iglesias 1977; Gerola & Glassgold 1978; Prasad & Huntress 1980*a*, *b*). Most of these schemes have focused attention on gas-phase reactions of zero activation energy – particularly ion–molecule reactions – although Allen & Robinson make a persuasive argument for considering heterogeneous processes catalysed by the smallest dust grains in the nebula. There is general acceptance of the idea that dust grains are crucial for the production of molecular hydrogen from its atoms and that the gaseous molecules are steadily condensing on the cold grains.

While some of the observations on interstellar molecules can be accounted for satisfactorily on the basis of gas-phase chemical models there are some discrepancies, implying that these models could still be improved (see, for example, Prasad & Huntress 1980*b*). In particular, previous studies have not included deuterium in their reaction schemes. Although deuterium is only a minor constituent of interstellar clouds the observation of deuterium-containing molecules has attracted much attention, primarily because the establishment of the cosmic deuterium abundance is an important indicator of the nature of the Universe (Wagoner 1973).

In addition, one can point to some basic deficiencies in the models: they are based on the unrealistic model of a physically static and uniform molecular cloud and the chemical schemes have generally omitted isomeric forms of molecules. In the present investigations we have particularly scrutinized the problem of isomeric forms. Let us consider each of these aspects in turn.

### (*a*) *Deuterium chemistry*

Interest in deuterium-containing molecules increased when the first discovery, DCN (Jefferts *et al.* 1973), showed that there was nearly 1000-fold enrichment compared with the atomic D/H ratio of $2 \times 10^{-5}$ as measured by the Copernicus satellite (Rogerson & York 1973). Almost immediately it was suggested by Solomon & Woolf (1973) that the equilibration

$$\mathrm{HCN + HD \rightleftharpoons DCN + H_2} \quad (\Delta E/k = 456\ \mathrm{K})$$

or

$$\mathrm{HCN + D \rightleftharpoons DCN + H} \quad (\Delta E/k = 861\ \mathrm{K})$$

could produce the observed enhancement, appreciable values of $\Delta E$ arising from zero point vibrational energy differences.

These enrichment mechanisms were soon recognized as requiring too long a timescale and alternatives in which equilibration by means of ion–molecule processes such as

$$\mathrm{H_2CN^+ + HD \rightleftharpoons HDCN^+ + H_2}$$

and

$$\mathrm{D^+ + HCN \rightleftharpoons DCN + H^+}$$

were proposed (Watson 1974).

However, Brown (1977) pointed out that such equilibrations must be accompanied by the equally rapid and essentially complete conversion of HNC to HCN by the process

$$\mathrm{H^+ + CNH \rightleftharpoons HCN + H^+}.$$

The mere observation of HNC (or DNC) indicates that equilibria of these kinds cannot have been reached. We therefore have to look for kinetic effects that could produce the observed enrichments.

The most likely pathways would seem to be via $\mathrm{H_2D^+}$ or $\mathrm{CH_2D^+}$ produced by the preliminary processes

$$\mathrm{H_3^+ + HD \rightleftharpoons H_2D^+ + H_2} \quad (\Delta E/k \approx 178\ \mathrm{K})$$

and

$$\mathrm{CH_3^+ + HD \rightleftharpoons CH_2D^+ + H_2} \quad (\Delta E/k \approx 300\ \mathrm{K}).$$

In our calculations we have incorporated these reactions, and a number of others involving deuterium, in the overall reaction scheme similar to that listed by Iglesias (1977). Our modifications to his scheme involve adding some reactions that seem necessary in the light of more recent evidence (primarily alternative products for reactants already included) and deleting a few that now appear not to proceed at a significant rate. These are listed in table 1. We have adopted values of rate constants for all reactions, except where otherwise noted, as given by Prasad & Huntress (1980*a*). This gave a list of 168 reactions of the ion–molecule, charge-transfer and ion–electron recombination types, covering 64 species of H, C, N and O compounds, triggered predominantly by cosmic-ray ionization of $\mathrm{H_2}$ and He. When we include processes for the isomers and deuterated species, the scheme contains 529 reactions involving 108 species.

In the absence of specific experimental values we assumed that the rate constants for processes

TABLE 1

(*a*) *Reactions differing from those used by Iglesias*

1 $He^+ + NO \rightarrow O^+ + N + He$
2 $He^+ + CO_2 \rightarrow C^+ + O_2 + He$
3 $C^+ + O_2 \rightarrow CO + O^+$
4 $C^+ + CH \rightarrow CH^+ + C$
5 $C^+ + CH_2 \rightarrow CH_2^+ + C$
6 $C^+ + H_2CO \rightarrow CH_2^+ + CO$
7 $C^+ + H_2CO \rightarrow HCO^+ + CH$
8 $C^+ + H_2CO \rightarrow H_2CO^+ + C$
9† $CH_3^+ + N \rightarrow HCN^+ + H_2$
10† $CH_3^+ + N \rightarrow HCNH^+ + H$
11 $H^+ + H_2CO \rightarrow HCO^+ + H_2$
12 $CN^+ + H \rightarrow H^+ + CN$
13 $C^+ + NH_3 \rightarrow HCN^+ + H_2$
14 $O_2^+ + C \rightarrow CO^+ + O$
15 $C^+ + H \rightarrow CH^+ + h\nu$
16 $NH_3^+ + e^- \rightarrow NH_2 + H$
17 $CH_2^+ + e^- \rightarrow C + H_2$
18 $H_2CO^+ + e^- \rightarrow HCO + H$
19 $H_3CO^+ + e^- \rightarrow HCO + 2H$
20 $NH_3^+ + H_2O \rightarrow NH_4^+ + OH$
21 $NH_3^+ + H_2CO \rightarrow NH_4^+ + HCO$
22 $NH_2^+ + H_2O \rightarrow H_3O^+ + NH$
23 $NH_2^+ + H_2O \rightarrow NH_3^+ + OH$
24 $NH_2^+ + H_2O \rightarrow NH_4^+ + O$
25 $H_3O^+ + H_2CO \rightarrow H_3CO^+ + H_2O$
26 $He^+ + CN \rightarrow C + N^+ + He$
27 $He^+ + NCO \rightarrow O^+ + CN + He$
28 $He^+ + NCO \rightarrow CN^+ + O + He$
29 $C^+ + OH \rightarrow H + CO^+$
30 $C^+ + NH \rightarrow H + CN^+$
31 $HCO^+ + OH \rightarrow H_2O^+ + CO$
32 $CH_3^+ + O \rightarrow HCO^+ + H_2$
33 $H_2^+ + N \rightarrow NH^+ + H$
34 $HCO^+ + Na \rightarrow Na^+ + HCO$
35 $H_3CO^+ + e^- \rightarrow CO + H + H_2$
36 $O + NH \rightarrow OH + N$

(*b*) *Reactions included in Iglesias's scheme that are not included in this work*

1 $He^+ + O_2 \rightarrow O_2^+ + He$
2 $C^+ + CH_3 \rightarrow CH_3^+ + C$
3 $HN_2^+ + Na \rightarrow Na^+ + N_2 + H$
4 $CN^+ + Na \rightarrow Na^+ + C + N$
5 $H^+ + CN \rightarrow CN^+ + H$

† $k = 3.4 \times 10^{-11}\ cm^3\ s^{-1}$, from Fehsenfeld (1976), assuming an equal branching ratio for the two processes.

involving deuterium were equal to those for the corresponding reaction involving hydrogen. Where alternative isotopic products could be produced we assumed 50:50 branching ratios. Unhappily, we may be missing some important kinetic isotope effects in this assumption. We assumed an initial distribution of deuterium equally shared between D and HD.

### (*b*) *Isomers*

Some of the species included in the ion–molecule reaction schemes can exist in more than one isomeric form. A well studied example, the only one for which two isomers have been observed in dark nebulae, is HCN and its isomer HNC. We have attempted to include in our scheme an appropriate recognition of isomeric possibilities, at least in the HCN/HNC case, although again at certain points some rather arbitrary assumptions have to be made.

The most widely accepted mechanism for production of HCN is (Herbst & Klemperer 1973)

$$C^+ + NH_3 \rightarrow H_2CN^+ + H;$$

$$H_2CN^+ + e^- \rightarrow HCN + H.$$

However, unless there is a unimolecular isomerization during one or both of these processes the product will actualyl be HNC since the hydrogens are initially attached to nitrogen (Brown 1977). An elaborate molecular orbital study of the $H_2CN^+$ system (Conrad & Schaefer 1978) has shown that in the singlet electronic ground state of the species the most stable conformation is linear $HCNH^+$ with a second, less stable isomer $CNH_2^+$, with a shape analogous to formaldehyde, 1.99 eV higher in energy.

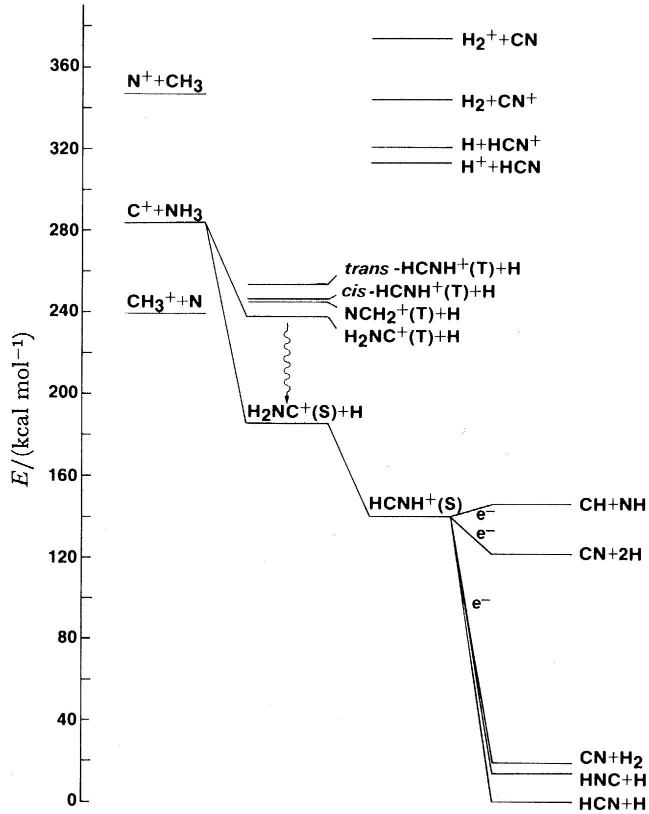


FIGURE 1. Relative energies of the $H_2CN^+$ isomers and related compounds, as calculated by Allen *et al.* (1980).

The above reaction of $C^+$ and $NH_3$ could also yield triplet state $H_2CN^+$ (the simple statistical result would be a 3 : 1 ratio of production of triplet to singlet). Allen *et al.* (1980) have shown that in the triplet state the lowest energy conformation is $CNH_2^+$, other isomers being about 0.2 eV or more higher in energy (figure 1).

The phosphorescent lifetime from the triplet state will be considerably shorter than the collision lifetime, so that the ultimate fate of the triplet state $CNH_2^+$ should be first a

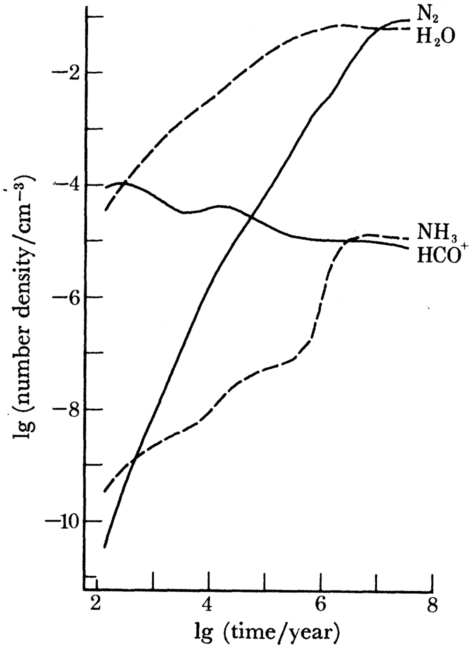
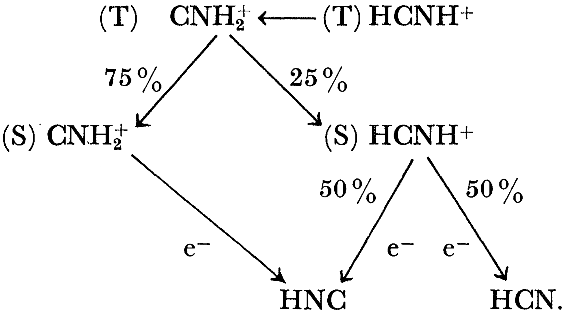


FIGURE 2. Absence of steady-state conditions for four major constituents of molecular clouds.

phosphorescent decay to singlet state $CNH_2^+$ or possibly to $HCNH^+$, then dissociative recombination with an electron to yield HNC or HCN. We have arbitrarily assumed that the phosphorescent decay of triplet $CNH_2^+$ yields 75% singlet $CNH_2^+$ and 25% singlet $HCNH^+$, that the former yields HNC by recombination with an electron while the latter yields HCN and HNC with equal probability, thus:



Alternative pathways to HCN or HNC start from N and $CH_3^+$ or $N^+$ and $CH_3$. The first of these seems to be more important but, because the ground state of N is $^4S$, it will lead to triplet state $H_2CN^+$, which will isomerize to $CNH_2^+$ and then, as just discussed, yield HNC by dissociative recombination.

## RESULTS

For our initial studies we chose a static, uniform cloud with $n(H_2) = 10^4\,cm^{-3}$ and kinetic temperature 30 K. We followed Iglesias in assuming an initial $H:H_2$ number ratio of 4 : 3 and used his case I elemental abundances (which are mostly the depleted solar abundances of Morton (1974)). We have not included any condensation on grains in the present calculations.

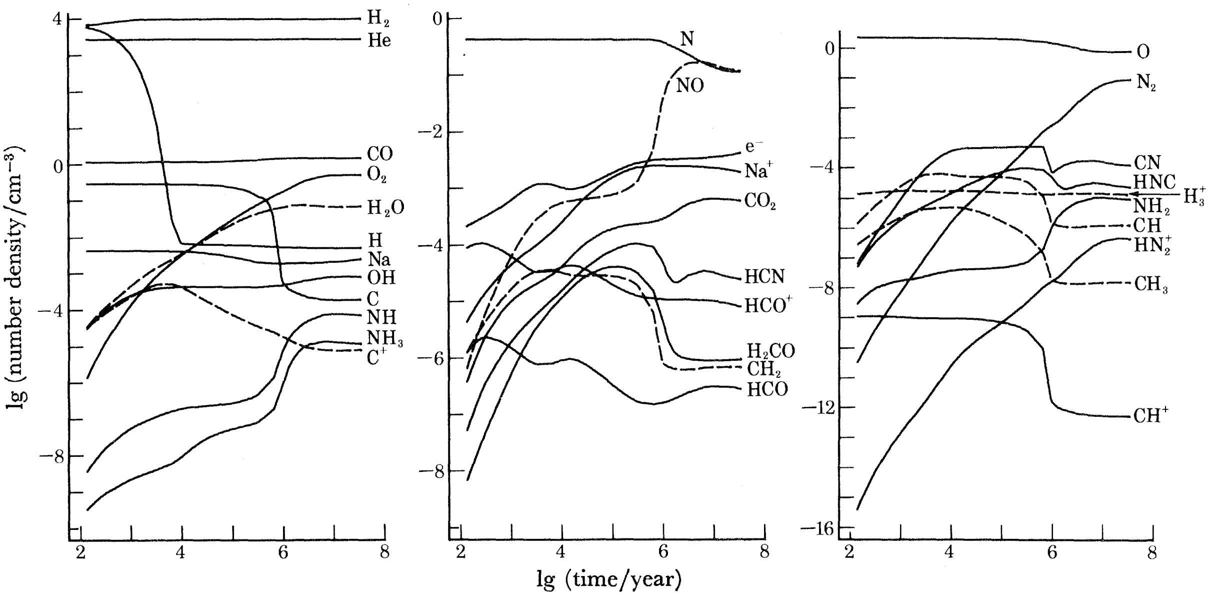


FIGURE 3. Time evolution of concentrations for molecular cloud with $n(H_2) = 10^4\ cm^{-3}$ and $T_{kin} = 30$ K.

TABLE 2. COMPARISON OF CALCULATED FRACTIONAL ABUNDANCES (RELATIVE TO $H_2$) AT CLOUD AGE 10 Ma WITH EXPERIMENTAL VALUES FOR THE ORION MOLECULAR CLOUD

| | lg *f* (calc.) | | | | | |
|---|---|---|---|---|---|---|
| molecule | $T = 10$ K $n(H_2) = 10^4\ cm^{-3}$ | $T = 30$ K $n(H_2) = 10^4\ cm^{-3}$ | $T = 90$ K $n(H_2) = 10^4\ cm^{-3}$ | $T = 90$ K $n(H_2) = 10^5\ cm^{-3}$ | lg *f* (obs.) | reference |
| $H_2CO$ | −10.0 | −10.0 | −10.3 | −9.8 | −8.7 to −8.4 | Evans *et al.* (1975) |
| CH | −9.9 | −9.9 | −9.8 | −10.9 | −9 | Rydbeck *et al.* (1976) |
| CO | −3.8 | −3.8 | −3.8 | −3.8 | −4.4 | Liszt *et al.* (1974) |
| CN | −7.6 | −7.8 | −8.7 | −10.5 | −9 | Turner & Gammon (1975) |
| HCN | −8.3 | −8.5 | −9.2 | −10.0 | −9.2 to −9.7 | Gottlieb *et al.* (1975) |
| HNC | −8.3 | −8.5 | −9.2 | −10.0 | −9.9 to −10.4 | Brown *et al.* (unpublished) |
| $HCO^+$ | −9.3 | −9.0 | −8.6 | −9.4 | *ca.* −10.3 | Snyder *et al.* (1976*a*) |
| HCO | −10.7 | −10.5 | −10.4 | −10.8 | *ca.* −11† | Snyder *et al.* (1976*b*) |
| $N_2H^+$ | −10.7 | −10.4 | −9.8 | −10.6 | *ca.* −10.5 | Turner (1974) |
| $H_2O$ | −5.1 | −5.2 | −5.3 | −5.3 | *ca.* −5 | Phillips *et al.* (1978) |
| $NH_3$ | −8.9 | −8.9 | −9.2 | −8.8 | −6.3 | Sweitzer (1978) |
| NO | −4.8 | −4.8 | −5.6 | −6.3 | *ca.* −8‡ | Liszt & Turner (1978) |
| HNO | −10.0 | −10.0 | −10.0 | −11.1 | *ca.* −11† | Ulich *et al.* (1977) |
| OH | −7.0 | −7.1 | −7.1 | −8.0 | −7.3 | Zuckerman & Turner (1975) |

† In NGC 2024. ‡ In Sgr. B2.

The results of numerically integrating the set of 108 coupled differential equations are illustrated in figures 2 and 3.

A number of points can be made. First, from figure 2 it is clear that an overall steady-state concept is unsatisfactory. Even when we limit our attention to just the four species H, $NH_3$, $H_2O$ and $HCO^+$ we find no time at which all four concentrations are stationary. The relative concentrations of these species vary greatly throughout the history of the evolution of the molecular cloud. Since it is widely accepted that the typical age of a molecular cloud is 10 Ma we have in the main focused on that epoch for comparisons with observation.

For the non-deuterated species there are no notable deviations in our predicted molecular concentrations from those of Prasad & Huntress. Table 2 illustrates the kind of agreement between fractional concentrations of species ($[X]/[H_2]$) at cloud age 10 Ma compared with observational data for the Orion molecular cloud OMC1. Table 2 also lists the results of calculations based on both higher and lower kinetic temperatures and higher total concentrations than were used to obtain the curves in figures 2 and 3. The most appropriate column for comparison with OMC1 data is probably that for $T = 90$, $n(H_2) = 10^5\,cm^{-3}$.

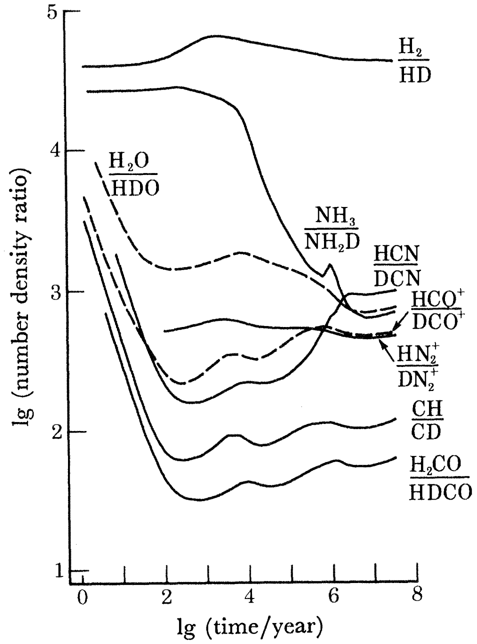


FIGURE 4. Time dependence of [HX]/[DX] for selected interstellar molecules.

The agreement between calculated and observed fractional abundances is about an order of magnitude in almost all cases. We regard this as satisfactory agreement when it is recognized that observed values are based on assumptions that are not always secure and relate to a cloud with $T_{kin}$ and $H_2$ concentration rather different from those of our model cloud. The greatest discrepancy is for ammonia where we predict concentrations about $10^3$ too small. Prasad & Huntress (1980*b*) predict similarly low values but compare their results with an earlier experimental value of $\lg f \approx -8$ (Morris *et al.* 1973). It seems likely that present ion–molecule reaction schemes do not yet correctly describe interstellar ammonia production or destruction, or both.

If we turn now to deuterated species, an interesting feature emerges. It is best illustrated by plotting $R = HX/DX$ ratios as a function of molecular cloud age (figure 4). One finds three broad categories of species: (*a*) $R \approx 10^5$; (*b*) $R \approx 10^3$; (*c*) $R \approx 10^2$. Species belonging to these different categories are shown in table 3.

It seems significant that the present model calculations predict very substantial enrichments for all of those molecular species for which deuterated versions have actually been detected and which are included in our model. (Our present model, however, does not yet extend to cyanoacetylene.) A summary of relevant observational data is presented in table 4. It includes, for

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DNC/HNC, some previously unpublished measurements made by our group at Kitt Peak 11 m telescope in November 1977. The results are shown in more detail in table 5. In contrast to other studies by Snell & Wootten (1979) and Turner & Zuckerman (1978), who used almost solely the $J = 1 \rightarrow 0$ transition of the main isotopic species of HNC for reference, we used the corresponding transition of $HN^{13}C$ because it appears to be optically thin in all sources listed, whereas the main species line is optically thick. Our values of the relative abundance should therefore be more reliable. We notice that all values based on comparison with $HN^{13}C$ lead to DNC/HNC ratios in the range 0.01–0.04 except for the sources L63 and L134N for which the $HN^{13}C$ line was measured on a different telescope of very different beamwidth. We are doubtful whether variations of the ratio DNC/HNC from source to source have yet been established with confidence, but there is a suggestion that the coldest clouds have greater enrichments.

Table 3. Classification of molecular enrichments

| lg (HX/DX)... | 5 | 3 | $\leqslant 2$ |
|---|---|---|---|
| | $H_2$ | $OH^+$ | $CH_3^+$ |
| | $H^+$ | $CH^+$ | $H_3^+$ |
| | $H_2^+$ | $HN_2^+$ | CH |
| | $NH^+$ | $H_3O^+$ | $CH_2$ |
| | $NH_3^+$ | OH | $CH_3$ |
| | | HCN | $H_2CO$ |
| | | $H_2O$ | $H_3CO^+$ |
| | | $H_2O^+$ | $H_2CO^+$ |
| | | $HCO^+$ | $C_2H^+$ |

Table 4. DX/HX in various molecular clouds

| | distance from galactic centre / kpc | $T_{\mathrm{kin}}$ / K | $\mathrm{DCN}^{(1)}/\mathrm{HCN}$ | $\mathrm{DCO}^{+(2)}/\mathrm{HCO}^+$ | $\mathrm{NH_2D}^{(3)}/\mathrm{NH_3}$ | $\mathrm{N_2D}^{+(4)}/\mathrm{N_2H}^+$ | $\mathrm{DNC}^{(5)}/\mathrm{HNC}$ | $\mathrm{HDO}^{(6)}/\mathrm{H_2O}$ | $\mathrm{HDCO}^{(7)}/\mathrm{H_2CO}$ |
|---|---|---|---|---|---|---|---|---|---|
| SGR B2 | 0.1 | 25 | 0.018 | — | 0.02 | — | — | — | — |
| W51 | 7.6 | 45 | 0.126 | — | — | — | — | — | — |
| M17 | 8.0 | 55 | 0.126 | — | — | — | — | — | — |
| DR21 | 9.9 | 30 | 0.084 | — | — | — | 0.01 | — | — |
| DR21 (OH) | 9.9 | 30 | 0.21 | 0.06 | — | — | 0.01 | — | — |
| ORI A (OH) | 10.9 | 70 | 0.18 | — | 0.05 | — | 0.01 | $10^0$–$10^{-3}$ | — |
| NGC 2264 | 11.1 | 25 | — | 0.09 | — | — | 0.04 | — | — |
| Heiles 2 | 10.0 | 10 | — | — | — | — | 0.03 | — | $10^{-1}$–$10^{-2}$ |
| L134 | 9.8 | 10 | — | 0.03 | — | — | 0.07 | — | — |
| L134N | 10.2 | 10 | — | 0.8 | — | 2.22 | 0.17 | — | $10^{-1}$–$10^{-2}$ |
| L63 | *ca.* 10 | 17 | — | 0.8 | — | — | 0.15 | — | — |

*References*: (1) Penzias *et al.* (1977); (2) Guelin *et al.* (1977); (3) Turner *et al.* (1978); (4) Snyder *et al.* (1977); (5) Brown, Godfrey, Storey & Ninkov (unpublished); (6) Turner *et al.* (1975) and Phillips *et al.* (1978); (7) Langer *et al.* (1979).

The theoretical DX/HX ratios are mostly about an order of magnitude smaller than values derived from observations. Just how serious is this discrepancy is difficult to judge because, as shown in table 5, the method used to extract abundance ratios from observations can produce discrepancies of an order of magnitude. Two interesting predictions emerge from the theoretical data. First, formaldehyde is predicted to show a considerably greater deuterium enhancement than the other molecules. Langer *et al.* (1979), who detected HDCO in L134N and Heiles 2, pointed out the difficulties of deriving a reliable estimate of the $HDCO/H_2CO$ ratio in these clouds but suggest figures in the range $10^{-1}$ to $10^{-2}$. These clouds have lower kinetic temperatures than our chemical model cloud. However, although a temperature dependence has been proposed to account for variations in the HX/DX ratio (Snell & Wootten 1977), our model predicts (see table 6) only slight variation of the ratio with $T_{\mathrm{kin}}$. Secondly, ammonia is predicted to have a low level of enrichment in the early stages of cloud evolution, becoming comparable with that of other molecules only for cloud ages of about 10 Ma or greater.

Table 5. Observations on HNC isotopic species on N.R.A.O. 11 m radiotelescope, Kitt Peak, November 1977

(Brown, Godfrey, Storey & Ninkov (unpublished).)

| source | $\Delta T_a^*$ (DNC) | $\Delta T_a^*$ ($HN^{13}C$) | $\Delta T_a^*$ (HNC) | | [DNC]/[HNC] | |
|---|---|---|---|---|---|---|
| | | | | (*a*) | (*b*) | (*c*) |
| Ori A (OH) | 0.13 | 0.40 | — | 0.01 | 0.05 | 0.06? |
| NGC 2264 | 0.32 | 0.28 | — | 0.04 | 0.2 | 0.04 |
| DR 21 (OH) | 0.18 | 0.50 | — | 0.01 | < 0.05 | 0.14 |
| DR 21 | 0.12 | 0.39(1) | — | 0.01 | — | — |
| L 63 | 0.37 | 0.24(2) | — | 0.15 | 2.0 | 1.3 |
| Heiles 2 | 0.19 | 0.47(3) | — | 0.03 | — | — |
| L 134N | 0.63 | 0.42(3) | — | 0.17 | 2.5 | 1.0 |
| N 134 | 0.49 | — | 0.92(2) | 0.7 | 1.7 | — |

(*a*) Present results based on $[\mathrm{DNC}]/[\mathrm{HNC}] = \frac{1}{40}\{\Delta T_a^* \Delta v)_{\mathrm{D}}/(\Delta T_a \Delta v)_{^{13}\mathrm{C}}\}\,(B_{^{13}\mathrm{C}}/B_{\mathrm{D}})^2$ for $J = 1 \rightarrow 0$ transitions.

(*b*) From Snell & Wootten (1979), based on comparison of $\Delta T_a^*$ for $J = 2 \rightarrow 1$ of DNC with $\Delta T_a^*$ for $J = 1 \rightarrow 0$ of HNC.

(*c*) From Turner & Zuckerman (1978), based on $J = 1 \rightarrow 0$ transitions of DNC and HNC.

*References*: (1) Brown *et al.* (1976); (2) Snell & Wootten (1977); (3) Frerking *et al.* (1979).

Table 6. Predicted lg ([HX]/[DX]) at 10 Ma, $n(H_2) = 10^4\ \mathrm{cm}^{-3}$

| HX | $T = 10$ K | $T = 30$ K |
|---|---|---|
| $H_2CO$ | 2.2 | 1.8 |
| $H_2O$ | 3.1 | 2.8 |
| $NH_3$ | 3.1 | 2.8 |
| HCN | 3.2 | 3.0 |
| $N_2H^+$ | 2.9 | 2.7 |
| $HCO^+$ | 2.9 | 2.7 |
| CH | 2.5 | 2.0 |
| $H_2$ | 5.0 | 5.0 |

The data in table 2 show that the [HCN]/[HNC] ratio is predicted to be unity and the observational data for Ori A (OH) correspond to a ratio of 5.† Thus our treatment of these isomers appears to be satisfactory. We plan to extend the present reaction scheme to include other isomer systems but face further problems with respect to branching ratios for the additional reaction channels involved.

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† We have been informed (Irvine *et al.*, personal communication) of a careful study of HCN/HNC ratios that include values as large as 60 for Ori A (OH). This points to some inadequacy in our treatment of this isomer problem. We have not found it possible to obtain significantly larger values of the ratio by including processes such as $CH_2 + N \rightarrow HCN + H$. (The corresponding reaction for HNC, namely $NH_2 + C \rightarrow HNC + H$, is negligible in our model.)

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## *Discussion*

J. Brooks (*British National Oil Corporation, Glasgow, U.K.*). Professor Brown discussed the absence of evidence for organic ring compounds in interstellar spectra. Our recent computerized g.c.–m.s. studies on the insoluble high molecular mass organic polymeric matter in the Allende and Murray carbonaceous chondrites show that carbon and carbon–sulphur ring structures are present. 1,2-Benzene dicarboxylic acid and benzene-sulphonamide derivatives were identified together with an interesting series of monocarboxylic aliphatic compounds. The ring compounds are considered to have formed by condensation on the mineral grains of the chondrite.

**R. D. Brown.** It was pointed out some years ago (Brown 1973, 1977) that the absence of cyclic interstellar molecules implies that heterogeneous catalytic reactions in general are not important in molecular clouds. The evidence cited by Dr Brooks supports the idea that, in the later stages of condensation of interstellar matter to form carbonaceous chondrites, heterogeneous reactions show their presence through the cyclic molecules that are produced.

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