

THE NITROGEN CHEMISTRY IN INTERSTELLAR CLOUDS

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ABSTRACT. Our time dependent model of chemistry of dense interstellar clouds has been extended to study the formation of nitrogen bearing molecules. Here we present results for the calculations, under a variety of density, temperature, and elemental conditions, of the abundances of the following observationally important species: CN, HCN, HNC, NH₃, NO, and N₂H⁺.

1. NITROGEN CHEMISTRY

There is now general agreement that ion molecule reactions are responsible for the production of a wide variety of interstellar molecules. However, for a large number of observationally important molecules the chemistry and model calculations suffer from inconsistencies. The problems are due to a lack of relevant laboratory data on key reactions, inaccurate theories with which to extrapolate reaction rate coefficients to low temperatures, or uncertainties concerning the elemental abundances, physical conditions, and dynamical evolution relevant to interstellar clouds. In particular, the chemistries of many nitrogen bearing molecules are poorly known. For several years we have been developing a model of interstellar cloud chemistry with particular emphasis on understanding the time dependent evolution of chemical abundances including fractionation reactions (Graedel, Langer, and Frerking 1982; Langer et al. 1984, hereafter GLF and LGFA, respectively). Here we report preliminary results of the third part of our program which is to study the time dependence of the simpler nitrogen bearing molecules.

Early model calculations (Herbst and Klemperer 1973; Mitchell, Ginsburg, and Kuntz 1978) of the nitrogen chemistry relied on the reaction, H₃⁺ + N → NH₂⁺ + H, to initiate the nitrogen chemistry, since proton transfer, which is allowed for carbon and oxygen, is endothermic for nitrogen. Huntress (1977) pointed out that there was no evidence for reactions where an H₂⁺ is transferred, yet models of the chemistry (c.f. Prasad and Huntress, 1980) continued to employ this reaction because otherwise the observed abundances of N₂H⁺ and NH₃ could not be explained. We chose, instead, to ignore this reaction and suggested

that nitrogen might be able to enter into the gas phase chemistry efficiently by reacting with other molecular ions (e.g. $\text{CH}_3^+ + \text{N} \rightarrow \text{HCN}^+ + \text{H}_2$) and with radicals (e.g. $\text{CH} + \text{N} \rightarrow \text{CN} + \text{H}$). However, the production of N_2 , N_2H^+ , and NH_3 begins with $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$, and thus requires a source of N^+ . We suggest that He^+ dissociatively ionizing molecules with C-N and N-O bonds may provide sufficient N^+ to explain the observed N_2H^+ and NH_3 .

Since our last publication significant revisions in several reaction rate coefficients used in the model have had to be made as a result of laboratory measurements at low temperatures. The important changes are: an increase at low temperatures for $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$ by an order of magnitude (Luine and Dunn 1984); evidence for a small activation barrier ($E=85\text{K}$) for $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ (Luine and Dunn 1984); increased radiative association rates for C^+ and CH_3^+ with H_2 (Herbst (1985)); and neglect of the dissociative recombination reaction, $e + \text{H}_3^+$ (Smith and Adams 1984) which is now known not to occur for ground state H_3^+ . Unfortunately several important classes of reactions are not well studied at low temperatures and yet they can affect abundances dramatically. For example, the branching to various channels in dissociative recombination, as in $e + \text{H}_2\text{CN}^+$, which can form HCN, HNC, and CN, determines the relative abundances of the neutral products. Another example is the reaction rate coefficients and their activation barriers for neutral-neutral reactions, which are poorly known at low temperature (c.f. the discussion for $\text{CN} + \text{N}$ by Prasad and Huntress, 1980). Finally, Adams, Smith, and Clary (1985) have recently called into question the use of the canonical value of $10^{-9}/\text{cm}^3/\text{s}$ for the reaction rate coefficient for ion-molecule reactions at very low temperatures when the neutral molecule has a large permanent dipole moment (e.g. HCN, H_2CO , H_2O , and NH_3). Instead they recommend that values of 10^{-8} to $10^{-7}/\text{cm}^3/\text{s}$ are more appropriate. The results presented here were modeled before their paper was published but these larger values will not dramatically change model results (Herbst 1987).

2. RESULTS AND DISCUSSION

We have calculated abundances using the chemical model described in GLF and LGFA, but updated to include the revisions in reaction rate coefficients discussed above and other recent changes, these are described in more detail in Langer and Graedel (1986); the initial conditions are those of GLF and LGFA. We varied $n(\text{H}_2)$ from 10^3 to $10^4/\text{cm}^3$, temperature from 10 to 40K, and the elemental carbon to oxygen ratio from 0.7 to 1.3. In Table 1 we give the fractional abundances, $x(X)=n(X)/n(\text{H}_2)$, in steady state ($t > 5 \times 10^6$ years) of some important species with emphasis on nitrogen bearing molecules (only the dominant isotopic species are presented here).

TABLE 1
 FRACTIONAL ABUNDANCES IN STEADY STATE WITH $n(\text{H}_2) = 5 \times 10^3 / \text{cm}^3$ and $T=20\text{K}$

Species	$n(x)/n(\text{H}_2)^a$				
	C/O=0.7	0.9	1.1	1.3	TMC1
e	2(-7)	3(-7)	3(-7)	2(-7)	<5(-7)
H_3^+	3(-8)	3(-8)	3(-8)	3(-8)	
C^3	3(-7)	2(-6)	6(-6)	1(-5)	
CO	7(-5)	8(-5)	9(-5)	9(-5)	8(-5)
N	2(-5)	1(-5)	9(-6)	5(-6)	
N_2	9(-6)	1(-5)	9(-6)	7(-6)	
N_2H^+	7(-10)	5(-10)	4(-10)	4(-10)	1(-9)
NH_3	5(-8)	5(-8)	7(-8)	1(-7)	(2-20)(-8)
CN^3	1(-6)	6(-6)	1(-5)	2(-5)	>1(-8)
HCN	2(-8)	7(-8)	1(-7)	2(-7)	2(-8)
HNC	1(-8)	4(-8)	9(-8)	2(-7)	3(-8)
NO	6(-7)	4(-7)	2(-7)	1(-7)	

a. Abundances rounded off to one significant digit and $a(-b) = ax10^{-b}$

For comparison Table 1 lists abundances for the dark cloud, TMC1, (Irvine et al. 1985) which is typical of dense, low temperature regions. In general the model calculations agree within a factor of ten with the observed values, with the glaring exception of CN which is two to three orders of magnitude too large. If the model calculations can be trusted then there is some preference for the models with $C/O < 1$, however the chemically significant carbon abundance has not been determined in most dark clouds and this species could discriminate between models with different C/O ratios. We find that there is a negligible change in $x(X)$ with density and temperature except for NH_3 which decreases from 4(-7) to 5(-8) as T increases from 10 to 40K. The HNC/HCN ratio is sensitive function of the carbon abundance, increasing from 0.3 to 0.9, and if its chemistry were well established perhaps could be used to choose between different physical and elemental parameters. In none of these model calculations does this ratio exceed one, whereas values greater than one are observed in a few sources. In contrast to previous models of the chemistry (c.f. GLF) the abundances are no longer sensitive to the electron abundance because H_3^+ is not destroyed by electrons. We find that the two main sources of CN are dissociative recombination of HCNH^+ and $\text{C}_2 + \text{N}$, where C_2 is formed by dissociative recombination of C_2^+ . Therefore the CN abundance depends on the branching ratios and perhaps our results suggest that these channels have a small rate coefficient. We have also considered the suggestion that the reaction $\text{C}^+ + \text{NH}_3 \rightarrow \text{NCH}_2^+$ (an isomer) + H, will produce sufficient HNC by electron recombination to explain $\text{HNC/HCN} > 1$ (see discussion by GLF), but we find that it makes no difference to this ratio.

In Table 2 we show the change in fractional abundance with time for a few select species. At $t=0$ they are all zero and beyond 6×10^6 years they hardly differ from steady state.

TABLE 2
 FRACTIONAL ABUNDANCES VERSUS TIME FOR $n(\text{H}_2)=5 \times 10^3/\text{cm}^3$, $T=20\text{K}$, $\text{C/O}=0.7$

Time (10^6 years)	Species					
	CO	CN	N ₂ H	NH ₃	HCN	HNC/HCN
0.1	3.7(-5)	9(-6)	3(-11)	6(-8)	4(-7)	.31
0.2	5.0(-5)	9(-6)	1(-10)	1(-7)	2(-7)	.42
0.4	6.1(-5)	6(-6)	4(-10)	2(-7)	1(-7)	.57
0.6	6.5(-5)	3(-6)	5(-10)	9(-8)	6(-8)	.60
0.8	6.6(-5)	2(-6)	6(-10)	7(-8)	4(-8)	.60
1.0	6.7(-5)	2(-6)	6(-10)	6(-8)	3(-8)	.52
6.0	6.7(-5)	1(-6)	7(-10)	5(-8)	2(-8)	.46

The time dependence of a few nitrogen bearing species is very different from that of the other molecules. Most carbon and oxygen bearing species behave similarly to CO and reach steady state values within a few $\times 10^7$ years, while those containing nitrogen take nearly 6×10^6 years to do so. The carbon and oxygen chemistry is driven by H_3^+ and the time constant given by $t=(k_p(\text{H}_3^+))^{-1} = 1. \times 10^7$ years whereas the nitrogen chemistry depends on N^+ which is produced by $\text{He}^+ + \text{XN} \rightarrow \text{He} + \text{X} + \text{N}^+$ which has a typical reaction rate coefficient of several $\times 10^{-10}/\text{cm}^3/\text{s}$. Using the He^+ abundances in our calculations we find a time scale of 3×10^6 years for nitrogen chemistry. This time dependence for the N-bearing molecules is significant because it may allow ages to be determined for cloud material. It also suggests that steady state abundances may not be achieved for regions where dynamical activity (such as that produced by embedded stars and protostars) is recycling gas between dense clumps and the interclump medium (Goldsmith, Langer, and Wilson 1986). Perhaps differences among abundances in dense cold clouds are due to time dependent effects.

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DISCUSSION

GREENBERG: I have a question regarding C/O ratio which you have assumed. If you are using all the C relative to all the O available in any form in gas phase, then I can say that in whatever dust model you believe in, the amount of carbon that is used, is much more than you expect to find in this type of argument. The result is that if you start with 2:1 ratio of O/C you end up in a diffuse cloud with a ratio of 5:1. Therefore, I don't understand, assuming you have dust using up C, N, O, etc., how one can get O/C ratio as 1.

LANGER: Well, what I have always wondered about whether in the formation of something like H₂O very early in the cloud evolution and its freezing out on the grain surface, one can get sufficient amount of H₂O on the grain to create this kind of difference. There is growing evidence that there is very little water in the gas phase, except in Orion region, which is shocked and has blown the grains. It may be that the whole picture of more C than O in gas phase is wrong and then you can take those models to reflect production of C from the UV radiation which is not in these calculations.

GREENBERG: The amount of water on grains, say in TMC, does not use up that much oxygen. Perhaps we may be using up about 30% of the oxygen. All the available oxygen in the grain is in the organic refractory matter in the cores, and in the ice mantle. This still leaves a lot of oxygen available in the gas phase. Carbon, on the other hand, is used up in any model from 50 to 70% relative to cosmic abundance. Again you wind up with a high ratio of O/C. So, in order to provide extinction and the ice band, you still need to leave a lot of oxygen relative to carbon.

TURNER: It is interesting that $\frac{H}{H} > N = C^+$ is concluded not to form HNC. This suggests that the linear HCNH⁺ must be what forms HNC. Our recent observations find that (1) HCNH⁺/H₂ \approx few $\times 10^{-10}$, several orders of magnitudes higher than previous predictions; (2) HCNH⁺ seems to correlate with HNC but not so well with HCN. Do your calculations predict these aspects?

LANGER: I have not brought all my output but what I do remember is that at different times you get significant contributions from some of the neutral reactions like CH₂+N, such that abundance varies at different times because you are getting other channels which have nothing to do with HCNH⁺. They effect HCN but not HNC.

IRVINE: What is the status of the detection of interstellar HNO?

TURNER: Hollis (A & A of a couple of years ago) noted that the J = 2-2 transition of HNO was not seen. His earlier claim of the J = 1-0 transition was never really confirmed at 3 mm at Bell Laboratories (Linde et al.). I think it is reasonable to conclude that HNO has not been observed in the ISM.

LANGER: With respect to this C to N problem, I did not really point

out as there was no information from TMC-1 on NO. But most models predict an awful lot of NO if you have more O than C. Therefore, there are problems on both sides, which have not been resolved.

WILLIAMS: Can you comment on the mechanism talked about by Smith, Adams and Millar, which involves kinetically excited N^+ ions, which arise from Cosmic Ray ionization of molecules like N_2 , that is from N_2^+ . The N^+ being kinetically excited can react directly with H_2 which is likely first collision partner and therefore the reaction which is endothermic can take place.

HERBST: In the paper by Smith, Adams and Millar, the idea is that any reaction with He^+ is very exothermic and does give excited N^+ . That will then collide with H_2 . If the reaction dominates rather than elastic scattering, then the rate will be large enough.

D. SMITH: To clarify, the mechanism suggests that Cosmic Ray ionized He (He^+) + N_2 gives kinetically excited N^+ , and this answers the first part of the question regarding H_2 . The computed rate constant, which is almost gas kinetic for that reaction, in spite of the fact that it is in thermal condition, is endothermic.

LANGER: In that case, the time scale of these results will definitely change.

D. SMITH: The reaction H_3^+ or H_2D^+ + N presumably fractionate in that way deuterium into ammonia, whereas the other reaction N^+ + H_2 certainly would not. If you look into the ratio NH_2D/NH_3 , you may have some clue by which reaction the ammonia forms.

LANGER: That is a useful point. However not much observations about NH_2D are available.