THE DISTRIBUTION OF METHYLAMINE IN THE JOVIAN ATMOSPHERE

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Abstract. An estimate of the methylamine concentration on Jupiter has been made. The maximum production rate of $6 \times 10^{4} cm^{-3}$ (Jovian day)$^{-1}$ occurs in the vicinity of 60 km above the ammonia cloud layer. If the downward transport of methylamine equals the production rate, then the volumetric mixing ratio is 3×10^{-11}.

Introduction

Although hydrocarbon [Strobel, 1973a] and ammonia photochemistry [Strobel, 1973b; Atreya, Donahue and Kuhn, 1977] have been studied in the Jovian atmosphere, there has been only one investigation of possible coupling between the two systems to yield compounds containing both carbon and nitrogen. Cadle [1962] estimated that methylamine formation would yield a mixing ratio of about 1.9×10^{-7} at total number density of $1.5 \times 10^{15} cm^{-3}$. However, since that time, our knowledge of the reactions, reaction rates, and the structure of the Jovian atmosphere has greatly improved. Strobel [1973b] argued that the chemistry of hydrocarbons and ammonia can be considered separately since photolysis of the hydrocarbons occurs high in the atmosphere while photolysis of ammonia occurs much lower. However, it is possible that the methyl and amino radicals react to form measureable amounts of methylamine at elevations about 60 km above the ammonia cloud layer where concentrations of the radicals are comparable.

Thus, it is the purpose of this study to estimate the methylamine concentration in the Jovian atmosphere on the basis of the possible overlap between the regions of hydrocarbon and ammonia photochemistry. Such studies are important since they provide information for future Jovian atmospheric probes and may also give us insight to chemical processes which may have occurred in a very early reducing stage of the earth's atmosphere. The efficacy of methylamine formation via photochemically produced hot hydrogen atoms [Ferris and Chen, 1975] is not considered since the effect is probably secondary; CH_3NH_2 production occurs in the region of the atmosphere where the total number density is about $10^{18} cm^{-3}$. Thus the collision frequency is still quite large and thermalization of hot hydrogen atoms should be rapid.

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Methodology

The production of CH_3NH_2 will be determined by the relative rates of

$$CH_3 + NH_2 \rightarrow CH_3NH_2$$

$$CH_3 + CH_3 \rightarrow C_2H_6$$

$$CH_3 + H \rightarrow CH_4$$

$$NH_2 + NH_2 \rightarrow N_2H_4$$

$$NH_2 + H \rightarrow NH_3$$

In the region of the atmosphere corresponding to a total number density of $10^{18} cm^{-3}$, the concentrations of the CH_3 and NH_2 radicals are comparable, and the reaction forming CH_3NH_2 will be competitive with the others listed above. Higher in the atmosphere, the second and third reactions dominate, while lower in the atmosphere the last two are most important. Note, that if [H] is very much larger than [CH_3] or [NH_2], then formation of CH_3NH_2 would be inhibited; the minimum H concentration occurs in just the region where [CH_3] and [NH_2] are comparable.

The reactions assumed for this study are given in Table 1. The rates are as given in Strobel [1973a] and Atreya, Donahue and Kuhn [1977] with the exception of R6 and R9. The rate of R6 was estimated [Pryor, 1966] from the rates of R5 and R12 to be $1.1 \times 10^{-10} cm^{3} sec^{-1}$. The rate of R9 was determined from the work of Volpi and Zocchi [1966]. Photochemical equilibrium is assumed for the radicals. CH_4, NH_3, and C_2H_2 are not appreciably changed from the uncoupled schemes since their concentrations are much larger than [CH_3NH_2]. To estimate an upper limit to the CH_3NH_2 concentration, we allowed no chemical loss and required the downward flux to equal the total production rate.

Input parameters to the model calculations are given in Figure 1. The total number density and height (referenced to $3 \times 10^{19} cm^{-3}$) are the same as in Atreya, Donahue and Kuhn [1977]. Strobel's [1973a] height scale was adjusted to agree with our number densities, and [CH_4], J1 (the photodissociation rate for CH_4) and [C_2H_4] were extrapolated from his study. He does not show J1 for number densities greater than 10^{15} cm^{-3}; however, these can be determined from the photochemical equilibrium equation for CH_3 since

Table 1. Reactions Pertinent to Methylamine Formation on Jupiter

Reaction Number	Reaction	Rate Constant*	Reference
R1	$CH_2 + H_2 \rightarrow CH_3 + H$	7.0×10^{-12}	Braun et al. [1970]
R2	$CH_2 + CH_4 \rightarrow 2CH_3$	1.9×10^{-12}	Braun et al. [1970]
R3	$CH + H_2 + M \rightarrow CH_3 + M$	10^{-30} [M]	Braun et al. [1970]
R4	$CH_3 + H + M \rightarrow CH_4 + M$	8.5×10^{-29} [M]	Barker et al. [1970]
R5	$CH_3 + CH_3 + M \rightarrow C_2H_6 + M$	6×10^{-29} [M]	Kistiakowski and Roberts [1953]
R6	$CH_3 + NH_2 \rightarrow CH_3NH_2$	1.1×10^{-10}	see text
R7	$CH_4 + h\nu \rightarrow CH_2 + H_2$ $\rightarrow CH + H + H_2$	J1	see text
R8	$NH_3 + h\nu \rightarrow NH_2 + H$	J2	see text
R9	$C_2H_2 + H + M \rightarrow C_2H_3 + M$	4×10^{-14}[M]/(1.6 x 10^{16} + [M])	Volpi and Zocchi [1966]
R10	$NH_2 + H + M \rightarrow NH_3 + M$	6×10^{-30}[M]/(1+3 x 10^{-20} [M])	Gorden et al. [1971]
R11	$H + H + M \rightarrow H_2 + M$	8×10^{-33} $(300/T)^{0.6}$	Ham et al. [1970]
R12	$NH_2 + NH_2 \rightarrow N_2H_4$	1×10^{-10}	Gorden et al. [1971]

*The rate constants are in units of cm^3s^{-1} for two body reactions and cm^6s^{-1} for three body reactions.

he gives all other required variables to a number density of $10^{18}cm^{-3}$.

Temperature data required for evaluation of the rate of R11 is from Hunten [1976]. The eddy diffusion coefficient was varied as $M^{-1/2}$ [see, e.g., Lindzen, 1971] with a reference value of $2 \times 10^4 cm^2sec^{-1}$ for $M = 3 \times 10^{19}cm^{-3}$. This square root dependence gives a homopause value of $K = 3 \times 10^7 cm^2sec^{-1}$ which is within the acceptable range of 10^6-$10^9 cm^2sec^{-1}$ [Atreya and Donahue, 1976].

The photochemical equilibrium equations were reduced to a coupled set involving CH_3 and H, which were solved by Newton's iteration method with a convergence criterion of 10%. $[CH_3NH_2]$ was then determined from the combined continuity and eddy flux equation with a flux lower boundary condition at 20 km equal to the total CH_3NH_2 production rate. The upper boundary value at 75 km was varied from a volumetric mixing ratio of 2×10^{-11} down to 10^{-15}; the influence on the solution was less than a factor of two.

Results

The production rate of CH_3NH_2 is given in Figure 2. Only in a narrow height range (~10 km) is the production appreciable. The maximum is about $6 \times 10^4 cm^{-3}$ Jovian day^{-1} 58 km above the ammonia ice cloud. The total production rate is $8.5 \times 10^{11} cm^{-2}$ Jovian day^{-1}.

That CH_3NH_2 will be produced in only a narrow altitude range is clearly seen in Figure 3. In the vicinity of 60 km, $[NH_2]$ and $[CH_3]$ are comparable while above this elevation $[NH_2]$ decreases rapidly, and $[CH_3]$ exhibits a similar effect lower in the atmosphere. [H] also has a slight minimum near the level where $[NH_2]$ and $[CH_3]$ are comparable. These variations all tend to optimize methylamine production as described earlier. If the downward flux equals the total production rate, then the mixing ratio decreases slowly with depth below the level of maximum production; the average value is about 3×10^{-11}.

Various sensitivity studies have been made to determine the influence of the input parameters. Below 45 km, $[NH_2]$ and [H] (Figure 3) agree with the results of Atreya, Donahue and Kuhn [1977] as they should since CH_3NH_2 production is negligible. Similarly, above 75 km, the CH_3 and H results agree with Strobel [1973a]. Fortunately, the CH_3NH_2 mixing ratios are not strongly dependent on the CH_4 dissociation rates which have to be extrapolated from Strobel's [1973]a] study. Although CH_2 and CH are produced directly from CH_4 photodissociation and are the reactants

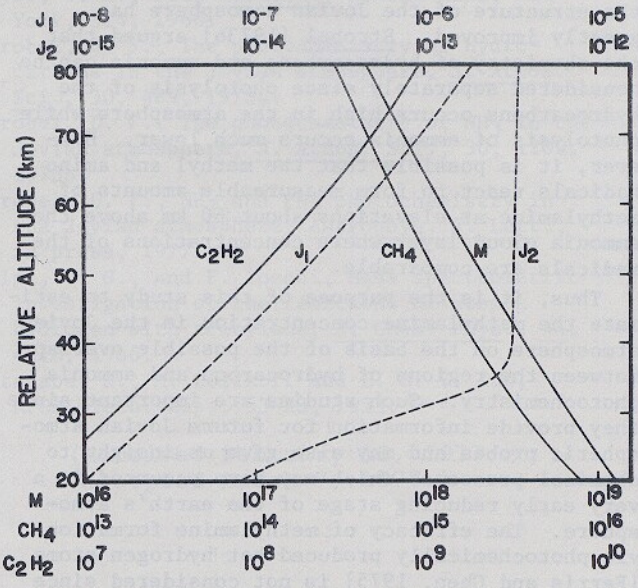

Figure 1. Input parameters to the model calculations. J_1 and J_2 are dissociation rates (sec^{-1}) for CH_4 and NH_3 respectively. Number densities for CH_4, C_2H_2, and the dissociation rate J_1 are from Strobel [1973a] adjusted to the number density of Atreya, Donahue and Kuhn [1977]. J_2 and the atmospheric number density M are from Atreya, Donahue and Kuhn [1977].

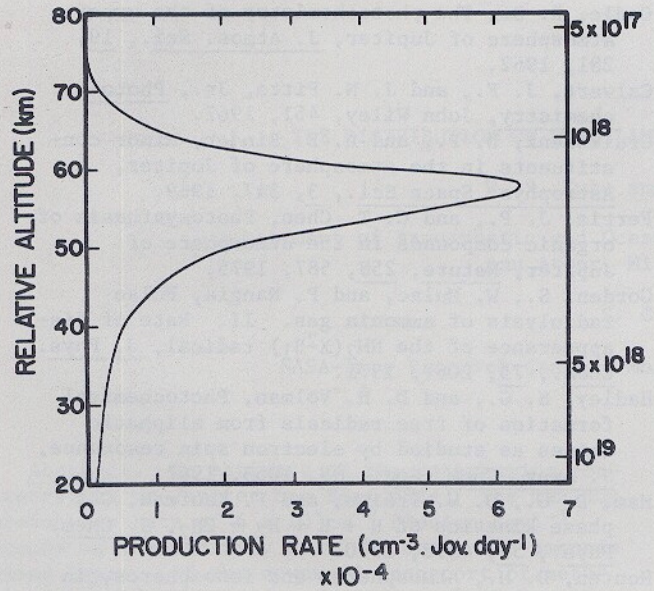

Figure 2. Production rate of methylamine versus height in the Jovian atmosphere.

producing CH_3, a smaller CH_3 concentration reduces the importance of R5 relative to R6 so that the change in $[CH_3NH_2]$ is much less than that in $[CH_3]$. For example, if J1 is reduced to one-tenth its value, then the CH_3 mixing ratio decreases by about a factor of ten but the reduction in CH_3NH_2 is only 30%. However, $[CH_3NH_2]$ does depend strongly on [H] through reactions R4 and R10. If, for example, [H] were ten times larger than calculated in our photochemical scheme, then the CH_3NH_2 mixing ratio would be only one-tenth as large as shown in Figure 3.

As discussed previously, the rate constant for CH_3NH_2 production has not been measured and was estimated from rates of similar reactions as $1.1 \times 10^{-10} cm^3 sec^{-1}$. If the rate were only one-tenth as large, then the mixing ratio for CH_3NH_2 would be about 1.5×10^{-11}, while a rate constant ten times larger would give a mixing ratio of 10^{-10}.

Conclusions

Based on this study, an *in situ* detection of methylamine in the Jovian atmosphere is likely not possible with present mass spectrometer techniques. Even utilizing enrichment procedures the minimum detection limit is about 10^{-9} [B. C. Kennedy, private communication, 1976], approximately one to two orders of magnitude larger than our estimate for the mixing ratio which corresponds to a column abundance of about 8×10^{-6} atm-cm down to the ammonia ice cloud. This is much smaller than the upper limit given by Cruikshank and Binder [1969] of 2 atm-cm which was based on laboratory infrared spectra of CH_3NH_2 and observational limitations of ground-based spectrometers.

One would not expect carbon-nitrogen compounds other than methylamine to be presently amenable to observation since the methyl and amino radicals which produce methylamine should be the most abundant precursor radicals in the region where the hydrocarbon and ammonia chemistry overlap. Activation energies of small radical recombination reactions are equal to or near zero and one would not expect the rate constants for more complex radical-molecule reactions leading to other products to be larger than that for CH_3 and NH_2 recombination.

The actual methylamine concentration is most likely less than the value given here. Some photodissociation will occur near 1750Å [Calvert and Pitts, 1967] with cleavage of the N-H bond. Hadley and Volman [1967] have determined the primary photodissociation processes for CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$. One would expect combination of the primary photochemical products resulting from CH_3NH_2 dissociation with CH_3 and NH_2 to produce some dimethylamine and methyl hydrazine. Subsequent photodissociation of dimethylamine could yield trimethylamine and dimethylhydrazine. Rate constants for the possible reactions listed below, to our knowledge, have not been measured.

$$CH_3NH_2 + h\nu \rightarrow CH_3NH + H$$

$$CH_3 + CH_3NH \rightarrow (CH_3)_2NH$$

$$CH_3NH + NH_2 \rightarrow NH_2NHCH_3$$

$$(CH_3)_2NH + h\nu \rightarrow (CH_3)_2N + H$$

$$(CH_3)_2N + CH_3 \rightarrow (CH_3)_3N$$

$$(CH_3)_2N + NH_2 \rightarrow NH_2N)CH_3)_2$$

$$(CH_3)_3N + h\nu \rightarrow CH_3 + (CH_3)_2N$$

The absorption spectra for both di- and trimethylamine overlap the ammonia absorption and the cross sections for photodissociation are comparable. However, it is important to note that the optical depth at the $[M] = 10^{19} cm^{-3}$

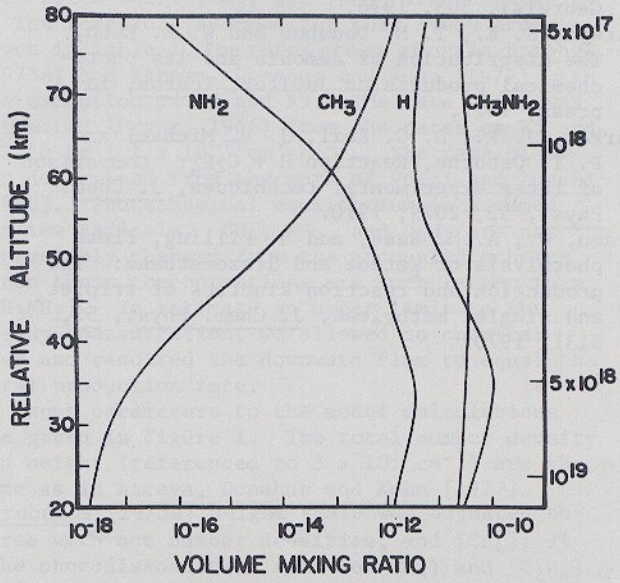

Figure 3. Volumetric mixing ratios for CH_3NH_2 and related radicals. Total atmospheric number densities are shown on the right ordinate.

level is less than 0.002 so that the ammonia photochemistry as formulated will not be altered by inclusion of methylamine formation.

Other factors which may influence the methylamine distribution are the recent studies of phosphine photochemistry and new measurements of methane photoabsorption cross sections.

Since the NH_3 and PH_3 absorption cross sections are similar, the photodissociation of NH_3 will compete with that of PH_3 resulting in a possibly larger NH_3 concentration [Prinn and Lewis, 1975] with a subsequently greater CH_3NH_2 concentration. However, the possible coupling between NH_3 and PH_3 photochemistry indicates that PH_3 can efficiently scavenge both H and NH_2 [Strobel, 1977]. The effect on $[CH_3NH_2]$ would however be minimal since a decrease in [H] would result in an increased amount of CH_3NH_2 and a decrease in $[NH_2]$ would decrease $[CH_3NH_2]$. Lack of information on pertinent rate constants under Jovian temperature and pressure conditions does not allow a quantitative estimate of such influence on $[CH_3NH_2]$.

New measurements by Mount et al. [1977] give CH_4 absorption cross sections at wavelengths greater than 1475Å approximately 200 times smaller than those currently accepted [Watanabe, 1953]. As stated previously, a 30% decrease in $[CH_3NH_2]$ requires a factor of ten decrease in $[CH_3]$ which is much larger than calculated with the new CH_4 cross sections. Thus, the revised CH_4 cross sections do not appreciably influence the calculated $[CH_3NH_2]$.

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