

Short Communication

Methylamine formation in the vacuum ultraviolet photolysis of methane and ammonia mixtures

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The early work of Miller [1, 2] and of Sagan and Miller [3] has demonstrated that the synthesis of organic compounds of biological importance can be achieved by passing electrical discharges through mixtures of methane, ammonia and water. This work has been greatly amplified, beginning in the early 1960s, by Ponnampereuma and coworkers [4 - 6] whose investigations underscore the great implications with respect to chemical evolution of the synthesis of such compounds as HCN, CH₃CN, α -aminonitriles and colored polymers which yield amino acids upon acid hydrolysis. The experiments of Sagan and Khare [7] have demonstrated that a corresponding organic synthesis can be attained when methane and ammonia mixtures containing hydrogen sulfide are exposed to UV light. More recently, Toupance *et al.* [8] have extended this work to include vacuum UV photochemical initiation at wavelengths significantly shorter than 180 nm. In particular, Raulin *et al.* [9] have emphasized the importance of quantitative laboratory simulation experiments in the far-UV, involving gas mixtures such as methane and ammonia in excess hydrogen, as a means of predicting possible reaction products in planetary atmospheres.

The dominance of Lyman α (121.6 nm) in the solar vacuum UV suggests a possible photochemical initiation in real planetary atmospheres. The present work is part of a continuing study [10] which attempts to identify the fundamental photochemical events that may occur in the atmospheres of the outer planets or their satellites and that can trigger the formation of complex organic molecules [11].

The interpretation of the results reported here does not specify that any particular planetary atmosphere is "simulated". Rather, the point is made that the photochemical formation of methylamine is demonstrated when mixtures of methane and ammonia are subjected to vacuum UV radiation near Lyman α , where both molecules undergo photolysis. The case is made that CH₃ and NH₂ are produced and lead inevitably to C₂H₆ and CH₃NH₂ (and presumably N₂H₄). It has been pointed out by Strobel [12, 13] that the NH₃ mixing ratio in the atmosphere of Jupiter is so small in

the region where methane absorbs that photochemical interactions between methane and ammonia can be ignored. Further, in the deeper atmosphere where the NH_3 mixing ratio is much larger, only NH_2 and thermal hydrogen atoms are produced and the conditions are not favorable for the coexistence of CH_3 and NH_2 in any region of the Jovian atmosphere. Thus, McNesby's suggestion [14] that a zone exists in the Jovian atmosphere where both molecules are photodissociated has been dismissed. However, the recent discovery [15] that the absorption coefficients of methane have been seriously overestimated between 145 and 165 nm suggests that there may well be a region of the Jovian atmosphere in which both methane and ammonia are photodissociated and where methylamine is produced. Thus the question of why methylamine formation has never been reported in simulation experiments assumes renewed importance.

We conducted experiments which show beyond any doubt that the photolysis of mixtures of methane and ammonia at 123.6 nm, the wavelength of the krypton resonance line [14], results in copious formation of methylamine early in the reaction.

The experiments were performed with mixtures of 20 Torr CH_4 and 20 Torr NH_3 . The intensity of the krypton resonance lamp at 123.6 nm was approximately 10^{16} quanta s^{-1} *. A vacuum monochromator scan (McPherson 0.3 m scanning monochromator) revealed no other appreciable radiation below 320 nm except the other krypton resonance line at 116.5 nm, the intensity of which is approximately 10% of that of the 123.6 nm line. Immediately following photolysis the reaction mixture was cooled to 77 K and the volatile products plus reactant methane were removed by pumping the system to a vacuum of 10^{-3} Torr. After warming to room temperature about 5% of the remaining reaction mixture was transferred to the gas chromatograph which incorporated a flame ionization detector. Figure 1 shows the gas chromatogram of the reaction products. Methylamine was clearly resolved from the other products (which included propane, ethane, possibly ethylene and acetylene) by the chromatographic column Carbo-pack B modified with 0.8% KOH and 4% Carbowax 20M [16]. Although some of the peaks have not yet been identified, the presence of methylamine was well established by (1) exhaustive retention time measurements and (2) co-injections of methylamine and propane. The latter eliminated any possible ambiguity resulting from the close proximity of propane to methylamine in the chromatogram. The unreacted mixture of methane and ammonia gave only a methane signal and no detectable signal at the methylamine retention time.

Additional evidence for the identification of methylamine was provided when the photolysis of methane and ammonia was performed at low temperature, 77 K. In this experiment the cold surface was situated 1 mm from the lamp window. About 25 - 50% of the radiation was transmitted through the

*The wavelength of the krypton resonance line is very close to that of Lyman α and is simpler to generate.

pure gaseous methane [17] to the cold solid solution of methane-ammonia so that photolysis of gaseous methane *and* photolysis of a solid methane-ammonia solution were occurring simultaneously. The methylamine produced during photolysis was trapped at the cold surface and remained there until analysis was initiated, thus minimizing migration of methylamine to the cell walls during photolysis. After photolysis the reaction mixture was pumped to a high vacuum as before to remove the volatile products and methane reactant. The remaining reaction mixture was then warmed to room temperature and samples were injected at various time intervals into the gas chromatograph. The results (Fig. 2) show that, although the observed quantity of methylamine was greatly increased by photolysis in the configuration described, it disappeared rapidly on standing when the system was

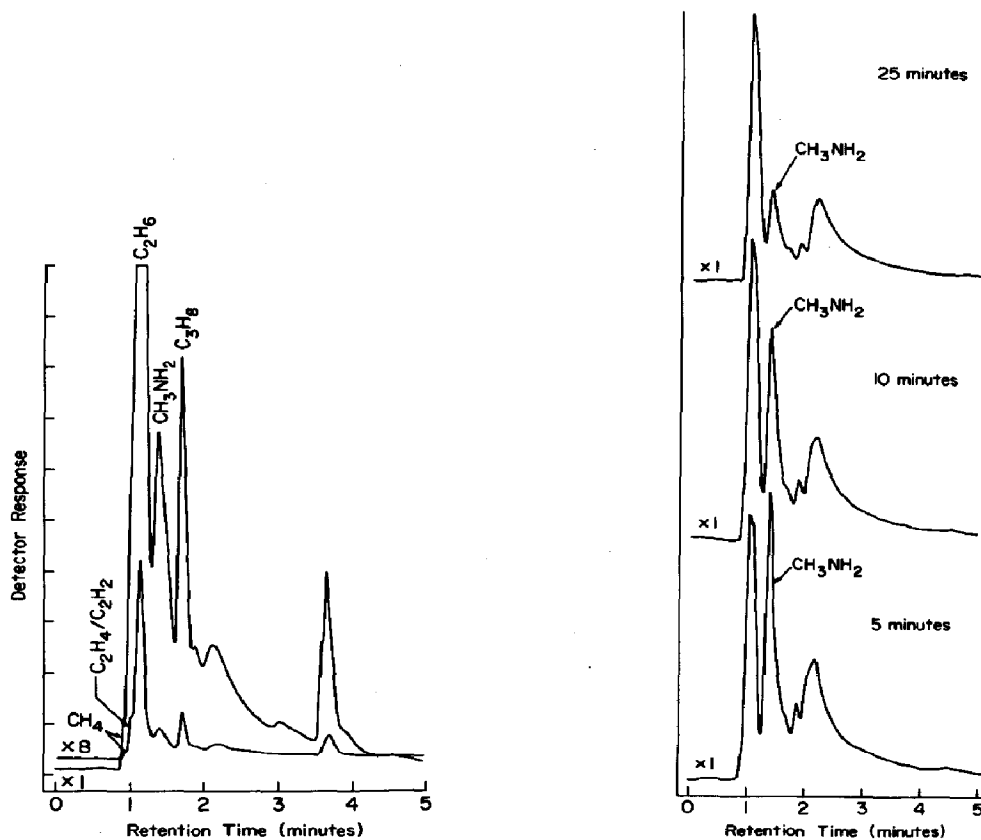


Fig. 1. A gas chromatogram of the products of the 123.6 nm photolysis of a mixture of 20 Torr CH_4 and 20 Torr NH_3 . The photolysis was conducted at room temperature. Column: Carbowax B, 0.8% KOH and 4% Carbowax 20M; 100 °C isothermal; 20 $\text{cm}^3 \text{min}^{-1}$ helium; 2.6 m \times 3.2 mm inner diameter; glass coil; flame ionization detection.

Fig. 2. Gas chromatograms of the low temperature (77 K) photolysis at 123.6 nm of a mixture of 20 Torr CH_4 and 20 Torr NH_3 showing the loss of methylamine with increasing time after termination of the reaction. The observed production of methylamine is greatly increased in this experiment. The chromatographic conditions are the same as those given in the caption to Fig. 1.

warm (probably by adsorption onto the walls of the vacuum system) as had been established in separate control experiments with methylamine standards. This observation may partly account for methylamine not having been previously reported as a reaction product. In real planetary or satellite atmospheres, or in laboratory simulations with continuum light sources, the extremely high light intensity to the red side of Lyman α probably results in rapid photolytic destruction of methylamine.

The presence of methylamine as a major product in these experiments suggests that it may be produced in the reducing environments of the outer planets and their satellites. Accordingly, its photolysis may provide the key to the formation of HCN and subsequently of more complex nitrogen-containing organic compounds and polymers. The enthalpies of formation of CH_3NH_2 and HCN are $-6.7 \text{ kcal mol}^{-1}$ and $+31.2 \text{ kcal mol}^{-1}$ respectively [18]. The enthalpy ΔH of reaction (1)



is therefore $37.9 \text{ kcal mol}^{-1}$, *i.e.* the reaction is endothermic by $37.9 \text{ kcal mol}^{-1}$. Lyman α and the krypton resonance line, corresponding to approximately $230 \text{ kcal mol}^{-1}$, each has more than enough energy to produce HCN (and rupture its C—H bond) by the photolysis of methylamine. A quantitative investigation of the initial products of the photolysis of methane and ammonia mixtures at various temperatures and pressures is in progress. The photolysis of methylamine in the vacuum UV is also being studied.

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Note added in proof

It has been brought to our attention that computations have been made [19] that dispute Strobel's [12, 13] conclusions and suggest that methylamine is formed in the Jovian atmosphere.