PLASMA DIAGNOSTICS BY MATRIX ISOLATION SPECTROSCOPY

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ABSTRACT

Homogeneous plasma reactions have been analyzed by freezing plasma effluents onto a CsI window at 10°K and measuring FTIR spectra. Nitrogen plasmas with one percent of methane yield methyl radicals at low pressure and HCN and NH₃ at higher pressures (2 torr). A wide variety of oxidation products appear when oxygen was added in a stepwise fashion.

1. INTRODUCTION

Plasmas have received recent interest as a possible alternative method for detoxification²⁻⁴. The decomposition reactions of methane in nitrogen plasmas have been extensively studied and several reviews already exist⁴⁻⁸. This reaction is known to produce H₂, HCN and C₂H₂, with relative amounts depending on reaction conditions. The methane decomposition reaction is important to detoxification studies since the N₂-CH₄ plasma reaction produces a noxious product (HCN). It is important to determine how the product distribution changes when oxygen is added. Fraser et al. have recently completed a study of N₂-CH₄ plasmas⁹, where traces of oxygen were added in several of those experiments. In their work, gas chromatographic and mass spectrometric techniques were used to identify and quantitate reaction products. The present study was performed as a complement to the Fraser work since we are able to detect the presence of more reactive products such as radical intermediates and ozone.

2. EXPERIMENTAL

Matrix deposition techniques have been described elsewhere¹⁰. Briefly, diluted methane samples were passed through a 1/2" o.d. quartz tube which was open-ended for the low pressure discharge experiments (ca. 10mTorr total pressure in the
discharge region). Higher pressure (2 Torr) experiments were performed using a similar quartz tube which was pulled down to a 2mm orifice between the discharge zone and the collection window. Discharges were maintained using a 15 KV, 60 Hz alternating current power supply in several of the low pressure experiments, but the majority of the present work was performed using the pinhole tube and a 2450 MHZ microwave power supply which was held at 10-20W of forward power. The latter experiments resulted in a significantly higher methane decomposition ratio and a correspondingly higher product yield because of the increased power input and longer plasma residence time. Gas mixtures were prepared on an all-stainless steel and teflon vacuum line using research grade gases from Matheson, Inc. Methane was condensed at liquid nitrogen temperatures and degassed to remove any residual trace of volatiles. The remaining condensate was distilled into a storage can and diluted with nitrogen or nitrogen and oxygen. Gas samples were deposited at 5 mmole per hour for 4-5 hours, and the resulting solid was analyzed by FTIR spectroscopy in the 400-4000 cm⁻¹ spectral region using 1 cm⁻¹ resolution and 200-400 scans.

3. RESULTS

Several experiments were conducted at low pressure (ca. 10mTorr) using a low-power, 60 Hz high voltage alternating current discharge plasma so that the initial steps in the methane decomposition reaction could be determined. One experiment using a N₂/CH₄=200/1 ratio produced very strong absorptions of unreacted methane as well as a signal (optical density = 0.13) due to CH₃ radical at 611.0 cm⁻¹ and very weak absorptions due to ozone, carbon dioxide, carbon monoxide and nitrous oxide due to the presence of trace amounts of atmospheric impurities in the discharge. There was also indirect evidence for H₂ formation, presumably by H atom recombination, since the system background pressure rose to the 10⁻⁶ Torr range when the plasma was on during deposition, but fell back into the 10⁻⁷ Torr range when the plasma was extinguished. The assignment of the 611 cm⁻¹ feature to methyl radical was supported by warm-up studies which showed the absorption to diminish when the matrix was quickly cycled to ca. 30°C and returned to 10°C. A second series of experiments was performed under similar conditions except that oxygen was used as the carrier instead of nitrogen. The products of this reaction observed after plasma deposition were ozone, HO₂,¹² and CO₂ as well as unreacted methane. These results indicate that the initial step in the plasma decomposition of methane involves H₃C=H bond scission. Hydrogen atoms and methyl radicals formed by this reaction are then able to participate in subsequent reactions involving oxygen and nitrogen.

The remaining experiments were conducted at higher pressure by constricting the quartz tube between the plasma zone and the low temperature deposition plate. Constricting the flow increases the residence time of the gas in the plasma zone and allows time after the plasma zone for recombination.
reactions to occur. For this work, a microwave power source was chosen in order to deposit more energy into the plasma. As a result, nearly all (>99%) of the methane was destroyed by the plasma, and the following section details the products formed at very low oxygen concentrations, and how the product distribution changes as the oxygen concentration increases.

Table I lists the principal products detected when N$_2$/CH$_4$ samples were discharged and condensed. Also, new products appearing as the oxygen concentration increases and those which decrease with added oxygen are listed.

The most intense product absorption (o.d. > 2.0) was found at 3287.3 cm$^{-1}$ compared to the 3287.6 cm$^{-1}$ literature value for HCN monomer isolated in solid nitrogen$^{13}$. Other HCN monomer absorptions were observed at 2097.4, 746.9, and 736.4 cm$^{-1}$ compared to literature values of 2097.3, 745.6 and 736.0 cm$^{-1}$, respectively$^{13}$. Eight other absorptions flanking the HCN monomer peaks are attributed to HCN aggregates after King and Nixon$^{13}$. In addition, very weak absorptions at 3316 and 3263 cm$^{-1}$ are assigned to perturbed HCN since they are in that spectral region. Most likely, these are HCN polymer absorptions not observed in the earlier work due to their low intensity. Another likely assignment for these absorptions is to HCN molecules weakly bonded to a proton acceptor (such as NH$_3$).

The next most intense absorption occurred at 3566.7 cm$^{-1}$ in the N$_2$/CH$_4$ discharge experiments. This frequency compares quite favorably to the value of 3567 cm$^{-1}$ reported by Milligan and Jacox for HNC isolated in solid nitrogen$^{14}$. Other HNC absorptions have been reported at 2035, 559 and 538 cm$^{-1}$. We have found new absorptions at 2034.1, 560.1, and 539.2 cm$^{-1}$ in agreement with the earlier work$^{14}$.

Absorptions due to traces of atmospheric impurities are the next most prominent class of characterized species in the spectrum. These are in the order of prominence, CO at 2140 (o.d. = 0.48) cm$^{-1}$ (from this point, numbers in parentheses in this position indicate the observed optical densities of the absorptions), CO$_2$ at 2348 (.27) and 662 (.05) cm$^{-1}$, H$_2$O at 3727 (.05) and 1598 (.05) cm$^{-1}$, N$_2$O at 2236 (.04) cm$^{-1}$ and NO at 1875 (.01) cm$^{-1}$. A weak absorption at 2153 (.035) cm$^{-1}$ is tentatively assigned to the HCN-CO aggregate species. A weak band at 2328 cm$^{-1}$ is attributed to absorption by solid N$_2$ activated by interactions with CO$_2$ and perhaps other species in the matrix$^{17-19}$.

A moderately intense band at 970 cm$^{-1}$ (0.25) and weaker bands at 3430 (.03), 3331 (0.02), and 1631 (0.08) cm$^{-1}$ are attributed to NH$_3$ in agreement with literature assignments$^{20-22}$. A weak band at 1306 (.09) cm$^{-1}$ due to the most intense undecomposed methane absorption was observed with variable intensity, but always much reduced (>99%) from that observed without plasma discharge. It is difficult to correlate its intensity to a breakdown efficiency since it depended heavily upon the time required to establish a discharge which varied

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considerably. Finally, a very weak absorption at 1286.1 cm\(^{-1}\) (0.02) is attributed to diimide, \(\text{N}_2\text{H}_2\).\(^{23}\)

The remaining absorptions were very weak and not initially recognizable. Isotopic experiments have been conducted in order to obtain more information as to their identity. Those results will be presented elsewhere. More importantly from a practical point of view, the yields of the various products with increasing oxygen concentration have been assessed in order to help determine the products which would be expected in air and how these products were derived.

The effect of adding small amounts of oxygen to the \(\text{N}_2/\text{CH}_4\) plasmas was dramatic. The yield of all known products not containing oxygen (i.e., HCN, HNC and NH\(_3\)) decreased markedly, nearly a hundredfold for the 3287 cm\(^{-1}\) HCN absorption, for a sample containing 0.8\% CH\(_4\) and 0.4\% O\(_2\) as compared to one containing 0.8\% CH\(_4\) and no added O\(_2\). Most of the HCN and HNC absorptions were not detectable with 0.4\% added O\(_2\), but had ca. one-third of their original intensity in an experiment using 0.2\% added O\(_2\). NH\(_3\) absorptions also were obliterated by the addition of 0.4\% O\(_2\), but had 70\% of their original intensity in the 0.2\% O\(_2\) run. Absorptions due to CO\(_2\) and water were found to increase markedly as O\(_2\) was added. Also, absorptions due to NO, NO\(_2\), N\(_2\)O\(_3\) and N\(_2\)O\(_4\) were found to increase as O\(_2\) was added to the samples\(^{24}\). Nitrous oxide, N\(_2\)O, whose very intense 2236-cm\(^{-1}\) absorption was already detectable without added O\(_2\), grew enormously in intensity as O\(_2\) was added. It was also surprising to observe the manner in which N\(_2\)O grew. Its intensity was enhanced by a factor of 5 in the 0.2\% added oxygen experiment as compared to the "no-oxygen" run. However, in the 0.4\% oxygen run, the N\(_2\)O signal increased by another factor of 10-20. Ozone and NO\(_2\) increases in the latter experiment were even more dramatic. These two molecules were not observed in either the 0\% or 0.2\% added oxygen runs even though both have very intense absorptions in the infrared. Both appeared with very high intensity in the 0.4\% added O\(_2\) run. This phenomenon is reminiscent of a titration reaction. Additional absorptions due to C-13 and O-18 (for CO\(_2\)) and N-15 (for N\(_2\)O) labeled products from their naturally occurring abundance help explain several of the weak absorptions in the 0.4\% added O\(_2\) experiment.

There is clear evidence for the formation of nitrous acid. Absorptions at 3551.1, 1681.0, 865.2, 814.9, and 625.9 cm\(^{-1}\) compare to literature values of 3552, 1684, 865, 815 and 625 cm\(^{-1}\) for cis- and trans-HONO in solid nitrogen\(^{25,26}\). Identification of nitric acid, HNO\(_3\), is also indicated in the experiments employing 0.5 to 1\% added oxygen by weak absorptions at 3487 (0.04), 1698 (0.10), and 903 (0.02) cm\(^{-1}\) compared to literature values of 3490, 1697 and 902 cm\(^{-1}\)\(^{27}\).

Finally, one experiment was performed using a N\(_2)/O_2/\text{CH}_4 = 100/10/1\) ratio to more closely simulate a polluted air sample. This experiment resulted in the simplest spectrum of all yielding intense absorptions of CO\(_2\), N\(_2\)O, O\(_3\), and CO.
The unidentified 871 cm\(^{-1}\) feature persisted in this experiment (o.d. = 0.05) as did a weak band of HONO at 821 cm\(^{-1}\) (0.04). NO\(_2\) and NO absorptions were quite weak, apparently due to reaction with H\(_2\)O to form HONO and HNO\(_3\).

**TABLE I.**

Plasma Reaction Products Identified by FTIR Analysis of Effluent Condensate at 10°K (a) N\(_2\)/CH\(_4\) = 100/1 and (b) N\(_2\)/CH\(_4\)/O\(_2\) = 100/1/1 in Approximate Order of Infrared Intensity.

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**REFERENCES**


(9) M.E. Fraser, D.A. Fee, and R.S. Sheinson, submitted to Plasma Chemistry and Plasma Processing.


