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FORMATION AND DESTRUCTION OF NITROUS OXIDE
IN LEAN, PREMIXED COMBUSTION

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INTRODUCTION
Nitrous Oxide (N\textsubscript{2}O) is the principal source of stratospheric nitric oxide\textsuperscript{1,2}, which, in turn, is a major scavenger of stratospheric ozone. N\textsubscript{2}O affects the earth's radiation balance and is a greenhouse gas since it absorbs strongly in the infrared\textsuperscript{3}. Nitrous oxide concentration in the atmosphere is increasing at the rate of 0.2% per year\textsuperscript{4}, and combustion is a major contributor to the nitrous oxide budget\textsuperscript{5,7}, but the actual quantification of this is difficult to evaluate since there is an extremely small data base. Despite its importance, the factors which control N\textsubscript{2}O emissions are not well understood. In order to develop a more fundamental understanding of N\textsubscript{2}O combustion chemistry experiments were conducted on premixed flames, and compared to a chemical kinetic model.

APPARATUS
A McKenna Products flat-flame burner was used to stabilize a laminar, one-dimensional, atmospheric pressure flame. Radial and axial temperature and composition profiles were determined. Burner position was varied, relative to fixed probes by micrometer adjusting screws, and probe elevation was independently verified by a Gaertner cathetometer, to within 0.2 mm. Temperatures above the burner were measured with a platinum-platinum-13% rhodium thermocouple with a bead diameter of 0.75 mm and wire diameters of 0.10 mm. Measurements reported were not corrected for radiation or conduction losses. Combustion gases were extracted through a 3.0 mm O.D. quartz microprobe with an orifice of 0.37 mm, and configured into an L-shape. Two drying tubes filled with Aquasorb (P\textsubscript{2}O\textsubscript{5}) removed moisture from the sample prior to analysis. The sample line, up to and including the first dessicant tube, was heated to 75°C.

Nitric oxide and total nitrogen oxides (NO\textsubscript{x}) were detected by a Thermo-Electron model I4A chemiluminescence analyzer. Nitrous oxide and the major products of combustion were quantified by a Hewlett-Packard model 5880A gas chromatograph, using an electron capture detector (ECD) and a thermal conductivity detector (TCD). N\textsubscript{2}O and CO\textsubscript{2} were separated from air by a 3.7 m column packed with 80/100 mesh Porapak-R. Oxygen and nitrogen were separated by a 1.8 m column packed with 80/100 mesh molecular sieve MS-SA. Helium was used as the carrier gas and the oven temperature was maintained at 50 °C. Electron capture detector response was substantially non-linear, and sensitive to background contaminants in the carrier gas. A baseline adjusted, multiple point calibration technique was performed for accurate N\textsubscript{2}O quantification, and errors are estimated to be less than 7 percent.

RESULTS
Nitrous oxide production and destruction were investigated as a function of bulk flow rate, equivalence ratio, nitrogen compound type, nitrogen concentration, and fuel type. Normal operating conditions were: total flow rate, 28000 standard cubic centimeters per minute (sccm); equivalence ratio, 0.86; and doped N-atoms, 2450 ppm of the reactant mixture. Axial profiles were taken 3 mm away from the center of the 6 cm diameter burner.

Mole fractions for CO\textsubscript{2} and O\textsubscript{2} near the burner center, at elevations greater than 0.5 mm, varied less than 5 percent from the values predicted at the known fuel-lean equivalence ratio of 0.86. NO\textsubscript{2}, which was determined by subtracting NO from total oxides of nitrogen (NO\textsubscript{x}), was always less than its level of detectability (50 ppm) near the burner center.

The first set of experiments involved changing the bulk flow rate while keeping reactants in the same proportions. The primary effect of increasing the total flow rate was to increase the peak flame temperature. For three heat release rates ranging from 1.4 to 1.9 kW, peak temperatures varied from 1850 to 1950 K. Axially measured N\textsubscript{2}O concentrations for these three bulk flow rates are plotted in Fig. 1. Peak N\textsubscript{2}O concentration is seen to vary inversely with temperature. It was also found to vary inversely with equivalence ratio. The N\textsubscript{2}O profile shape is similar to that observed by MacLean and Wagner\textsuperscript{8}, who found that N\textsubscript{2}O was formed as an intermediate species early in the well-controlled environment of an ammonia/oxygen flame, and was destroyed after a few millimeters. In the post-flame region (z > 1 mm), NO accounted for 67 percent of the...
total doped nitrogen.

\[ \text{CH}_4/\text{Air}/\text{NH}_3 2450 \text{ppmN} \]

Figure 1. Axial profiles of nitrous oxide for three heat release rates. Peak temperatures varied from 1850 to 1950 K.

The initial concentration of NH\(_3\) was varied from 2450 to 3300 ppm, and this corresponds to a change in the dopant/fuel ratio from 3 to 4 mole percent. Early-N\(_2\)O increased by nearly a factor of two (17 ppm maximum), but N\(_2\)O survival into the post-flame region was unaffected (less than 1 ppm). Conversion of doped nitrogen to NO decreased slightly to 63 percent for the larger initial NH\(_3\) concentration.

Four N-containing compounds (N\(_2\), NO, N\(_2\)O and NH\(_3\)) were added separately to the reactants to investigate effects of precursor chemistry and N\(_2\)O destruction efficiency, and the results are shown in Fig. 2. Regardless of the dopant chosen, N\(_2\)O is seen to be consumed rapidly in the post-flame mixture. The destruction is essentially complete at heights greater than 1.5 mm, however, the early-flame concentration of N\(_2\)O decreases by a factor of 2 when NO is the nitrogen-containing dopant, as compared with NH\(_3\). Doping with N\(_2\) produces the smallest amount of early-N\(_2\)O. With direct N\(_2\)O addition, destruction ensues immediately, and although N\(_2\)O present just after the flame (approx. 1 mm) is more abundant than with any other dopant, ultimately all but 1 ppm is destroyed. Measured NO profiles from the same doping experiment are presented as Fig. 3. The conversion of doped nitrogen to NO is quantified approximately as 1, 83, 13 and 67 percent respectively for the dopants N\(_2\), NO, N\(_2\)O and NH\(_3\).

Experiments with hydrogen as fuel were also conducted, and the results showed that the N\(_2\)O profiles in hydrogen flames are similar to those obtained from the methane-doped flames. The peak N\(_2\)O concentration was larger (20 ppm), and this is likely to be due to the lower flame temperature of 1050 K rather than the change of fuel type.

The H\(_2\)/air case was chosen to compare model predictions to the experiments. Modelling calculations were performed using a microcomputer version of CHEMKIN-910. A mechanism containing 60 reversible reactions and thermodynamic data11 for 19 species was input to the model. Forty-seven of the reactions were taken from the H/N/O mechanism of Roby and Bowman12, and 13 were added from a variety of sources. Table 1 presents the 13 reactions not used by Roby and Bowman. The comparison is presented as Fig. 4, where NO is seen to be predicted satisfactorily by the model. However, the predicted N\(_2\)O profile agrees poorly with the experimental one, and it appears than our description of the destruction chemistry is even less satisfactory than the formation chemistry.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>PRE-EXP</th>
<th>TEMP EXP</th>
<th>ACT ENG</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)O+M=N(_2)+O+M</td>
<td>6.9000+24</td>
<td>-2.5000</td>
<td>64960.</td>
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<tr>
<td>O+N(_2)=NO+NO</td>
<td>6.9000+14</td>
<td>0.0000</td>
<td>26610.</td>
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<tr>
<td>O+N(_2)=N+O</td>
<td>1.0000+15</td>
<td>0.0000</td>
<td>28800.</td>
</tr>
<tr>
<td>NH(_3)+M=NH(_2)+H+M</td>
<td>3.0000+17</td>
<td>0.0000</td>
<td>94400.</td>
</tr>
<tr>
<td>NH(_3)+M=NH(_2)+H(_2)+M</td>
<td>7.5000+15</td>
<td>0.0000</td>
<td>94400.</td>
</tr>
<tr>
<td>NH(_2)=NH(_2)+H</td>
<td>3.0000+17</td>
<td>-5.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>NH(_2)=NH(_2)+H</td>
<td>3.0000+17</td>
<td>-5.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>NH(_2)+H=NH(_2)+H</td>
<td>7.0000+12</td>
<td>5.0000</td>
<td>2000.0</td>
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<tr>
<td>NH(_2)+H(_2)=NH(_3)+H</td>
<td>8.0000+13</td>
<td>0.0000</td>
<td>10600.</td>
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<tr>
<td>NH(_3)+M=NH(_2)+H(_2)</td>
<td>7.0000+12</td>
<td>5.0000</td>
<td>2000.0</td>
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<tr>
<td>N(_2)+O=O+N(_2)+O</td>
<td>6.0000+12</td>
<td>0.0000</td>
<td>7500.0</td>
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<td>H(_2)O+M=H(_2)+O</td>
<td>5.0000+14</td>
<td>0.0000</td>
<td>1000.0</td>
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<tr>
<td>N(_2)+O+N(_2)+H(_2)</td>
<td>5.0100+14</td>
<td>0.0000</td>
<td>24620.</td>
</tr>
</tbody>
</table>

Table 1. Elementary reactions not included in reference 12.

Because N\(_2\)O levels throughout these laboratory experiments were never as high as those
CONCLUSIONS

Nitrous oxide is formed in lean CH<sub>4</sub>/air and H<sub>2</sub>/air flames doped with various nitrogen compounds, but it does not survive into the post flame region. Nitrous oxide concentration was found to depend inversely upon final flame temperature and equivalence ratio and directly upon nitrogen compound concentration. In decreasing order of observance of early-N<sub>2</sub>O, four nitrogen-containing dopants can be ranked: N<sub>2</sub>O, NH<sub>3</sub>, NO and N<sub>2</sub>. Nitrous oxide profiles were similar in CH<sub>4</sub>/air and H<sub>2</sub>/air flames. Radial profile measurements showed increased amounts of N<sub>2</sub>O existing near the burner edge. Comparison between calculated NO and N<sub>2</sub>O profiles and those measured in an H<sub>2</sub>/air flame showed that NO was satisfactorily predicted by the model, but that significant difficulties exist with the N<sub>2</sub>O kinetics.

ACKNOWLEDGMENTS

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3. Carbon Dioxide Assessment Committee, "Changing Climate" (1983), Board on Atmospheric Sciences and Climate, Commission on Physical Sciences, Mathematics and Resources, National Research Council.