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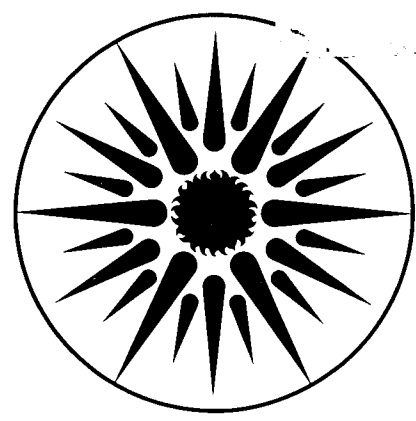
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R.J. Martin and N.J. Brown

August 1987

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FORMATION AND DESTRUCTION OF NITROUS OXIDE IN LEAN, PREMIXED COMBUSTION

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INTRODUCTION

Nitrous Oxide (N_2O) is the principal source of stratospheric nitric oxide^{1,2}, which, in turn, is a major scavenger of stratospheric ozone. N_2O affects the earth's radiation balance and is a greenhouse gas since it absorbs strongly in the infrared³. Nitrous oxide concentration in the atmosphere is increasing at the rate of 0.2% per year⁴, and combustion is a major contributor to the nitrous oxide budget⁵⁻⁷, 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_2O emissions are not well understood. In order to develop a more fundamental understanding of N_2O 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 0.37mm, and configured into an L-shape. Two drying tubes filled with Aquasorb (P_2O_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_x) were detected by a Thermo-Electron model 14A 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_2O and CO_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-5A. 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_2O 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 flowrate, 28000 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_2 and O_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 ratios. NO_2 , which was determined by subtracting NO from total oxides of nitrogen (NO_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_2O concentrations for these three bulk flow rates are plotted in Fig. 1. Peak N_2O concentration is seen to vary inversely with temperature. It was also found to vary inversely with equivalence ratio. The N_2O profile shape is similar to that observed by MacLean and Wagner⁸, who found that N_2O 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.

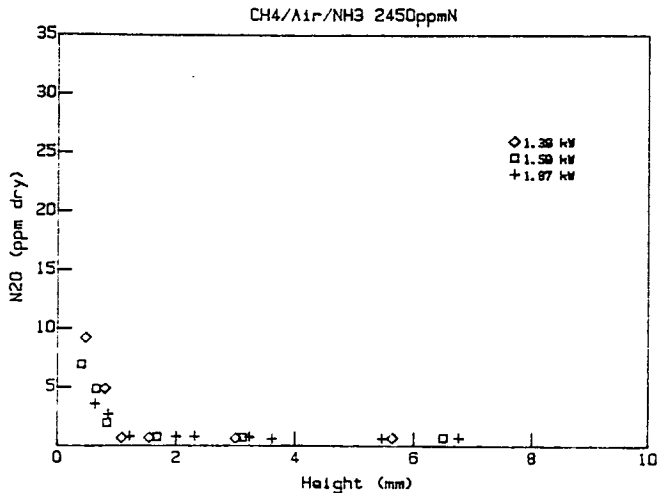


Figure 1. Axial profiles of nitrous oxide for three heat release rates. Peak temperatures varied from 1850 to 1950 K.

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_2O increased by nearly a factor of two (17 ppm maximum), but N_2O 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_2O and NH_3) were added separately to the reactants to investigate effects of precursor chemistry and N_2O destruction efficiency, and the results are shown in Fig. 2. Regardless of the dopant chosen, N_2O 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_2O 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_2O . With direct N_2O addition, destruction ensues immediately, and although N_2O present just after the flame (approx. 1 mm) is more abundant than

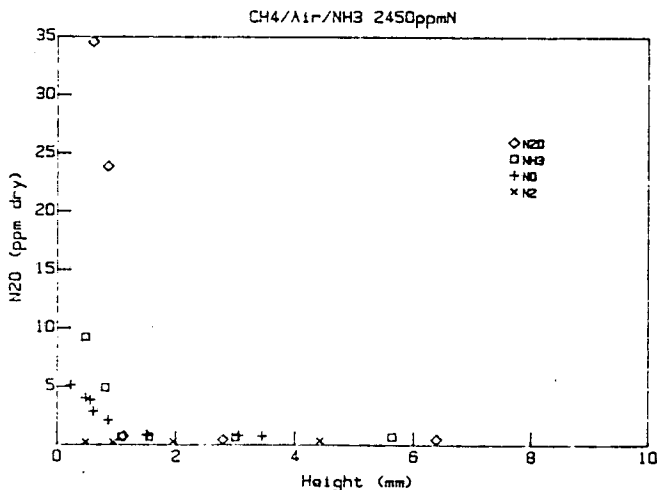


Figure 2. Axial nitrous oxide profiles for four nitrogen-containing dopants.

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_2O and NH_3 .

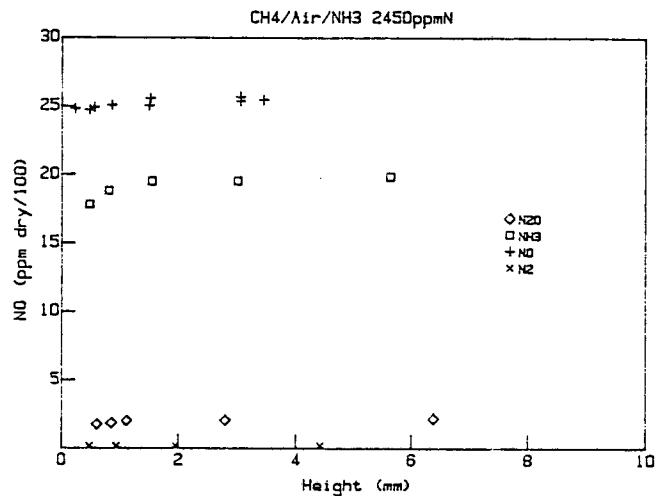


Figure 3. Axial nitric oxide profiles for four nitrogen-containing dopants.

Experiments with hydrogen as fuel were also conducted, and the results showed that the N_2O profiles in hydrogen flames are similar to those obtained from the methane-doped flames. The peak N_2O 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^{9,10}. 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 I presents the 13 reactions not used by Roby and Bowman¹². The comparison is presented as Fig. 4, where NO is seen to be predicted satisfactorily by the model. However, the predicted N_2O profile agrees poorly with the experimental one, and it appears that our description of the destruction chemistry is even less satisfactory than the formation chemistry.

	PRE-EXP	TEMP EXP	ACT ENG
$\text{N}_2\text{O}+\text{M}=\text{N}_2+\text{O}+\text{M}$.690D+24	-2.5000	64960.
$\text{O}+\text{N}_2\text{O}=\text{NO}+\text{NO}$.690D+14	.00000	26610.
$\text{O}+\text{N}_2\text{O}=\text{N}_2+\text{O}_2$.100D+15	.00000	28000.
$\text{NH}_3+\text{M}=\text{NH}_2+\text{H}+\text{M}$.300D+17	.00000	94400.
$\text{NH}_3+\text{M}=\text{NH}+\text{H}_2+\text{M}$.750D+15	.00000	94400.
$\text{NH}+\text{H}+\text{M}=\text{NH}_2+\text{M}$.300D+17	-.50000	.00000
$\text{N}+\text{H}+\text{M}=\text{NH}+\text{M}$.300D+17	-.50000	.00000
$\text{NH}_2+\text{N}=\text{NH}+\text{NH}$.700D+12	.50000	2000.0
$\text{NH}_2+\text{NH}_2=\text{NH}_3+\text{NH}$.800D+13	.00000	10060.
$\text{NH}_3+\text{N}=\text{NH}+\text{NH}_2$.700D+12	.50000	2000.0
$\text{N}_2\text{O}+\text{OH}=\text{N}_2+\text{HO}_2$.600D+12	.00000	7500.0
$\text{HNO}+\text{N}=\text{NH}+\text{NO}$.500D+14	.00000	1000.0
$\text{NH}_2+\text{NO}=\text{N}_2\text{O}+\text{H}_2$.501D+14	.00000	24620.

Table I. Elementary reactions not included in reference 12.

Because N_2O levels throughout these laboratory experiments were never as high as those

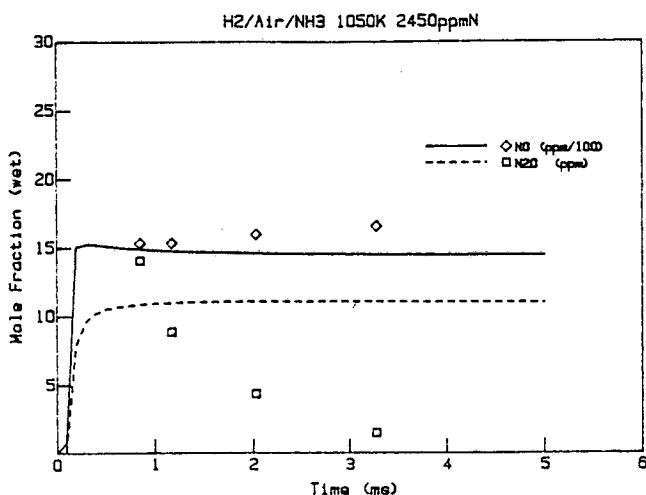


Figure 4. Calculated (line) and measured (point) profiles of NO and N₂O versus time.

measured in boilers 5-7, an experiment was performed to provide a qualitative picture of how mixing and heat transfer may play a role in the survival of N₂O into the exhaust of a full-scale combustor. A radial profile of N₂O, O₂, NO, and temperature at an elevation of 1.6 mm is presented in Fig 5. Near the burner center, and out to approximately 26 mm, these profiles are flat, confirming the one-dimensional behavior of the burner in this region. Beyond 26 mm, temperature and NO decrease steadily, and O₂ rises to approximately 20 percent. These measurements provide an indication of the degree of dilution of the combustion gases by surrounding room air near the burner edge. The N₂O levels do not follow the NO and temperature trend of a steady decrease with increasing radius. In fact, the steep rise in N₂O

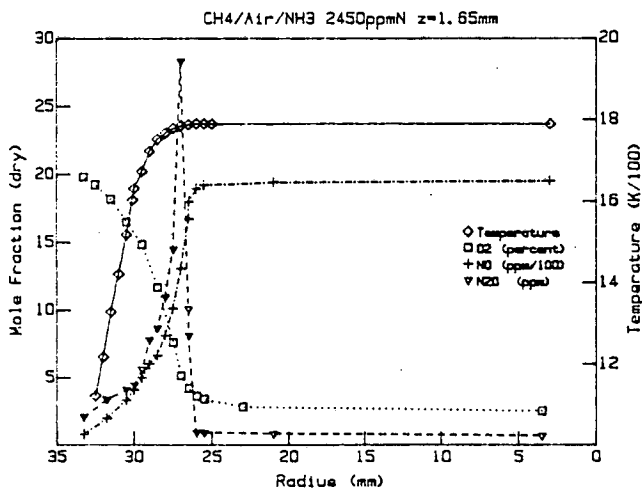


Figure 5. Radial temperature and concentration profiles at a height of 1.65 mm above the 6 cm diameter burner.

at the burner edge (27 mm radius) to nearly 28 ppm is higher than any center-burner measurement from a corresponding ammonia-doped flame. Lower temperatures and higher oxygen concentrations are potentially important factors in the increased survival of N₂O at the burner edge.

CONCLUSIONS

Nitrous oxide is formed in lean CH₄/air and H₂/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-N₂O, four nitrogen-containing dopants can be ranked: N₂O, NH₃, NO and N₂. Nitrous oxide profiles were similar in CH₄/air and H₂/air flames. Radial profile measurements showed increased amounts of N₂O existing near the burner edge. Comparison between calculated NO and N₂O profiles and those measured in an H₂/air flame showed that NO was satisfactorily predicted by the model, but that significant difficulties exist with the N₂O kinetics.

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