

THE FORMATION OF THERMAL AND FUEL NO_x FOR RADIANTLY STABILIZED COMBUSTION

SHI-KIN TANG, STUART W. CHURCHILL

Department of Chemical Engineering

NOAM LIOR

Department of Mechanical Engineering and Applied Mechanics, The University of Pennsylvania, Philadelphia, Pennsylvania

Previous studies of combustion in a refractory tube with premixed propane and air or vaporized hexane droplets in air have demonstrated the existence of multiple stationary states; thin, stable and non-oscillatory flames; and a low production of thermal NO_x (5–40 ppm). These studies were all limited to an equivalence ratio of approximately 0.80. In the current work a complete range of equivalence ratios was investigated for hexane droplets, vaporized completely prior to combustion. The concentration of thermal NO_x was found to peak at about 100 ppm for the stoichiometric ratio, to fall off rapidly as the equivalence ratio increased above unity and to fall off even more rapidly to less than 5 ppm as the equivalence ratio decreased to 0.6. The decrease for $\phi < 1$ is attributable to the lower flame temperatures but that for $\phi > 1$ is presumably due to the absence of free oxygen as well.

Experiments were also carried out for hexane doped with 0.795% wt. nitrogen in the form of diethylamine, isobutylamine, pyridine and piperidine. The formation of NO_x from these materials was found to be independent of the residence time in the post-flame zone. This result implies complete conversion within the flame front in accordance with prior conjectures.

The conversion of fuel-nitrogen to NO_x was essentially 100% for $0.6 < \phi < 1$, fell off rapidly for $\phi > 1$ and precipitously for $\phi < 0.6$. Thermal NO_x was found to be additive to fuel NO_x. This behavior was quantitatively similar for all four nitrogen compounds and is in close agreement with prior results of other investigators for other nitrogen compounds and flat laminar flames. Increasing the concentration of nitrogen in the fuel resulted in a decreased conversion to NO_x, particularly for $\phi > 1$, again in agreement with the observations of prior investigators for flat laminar flames.

Introduction

Previous experimental work by Churchill and coworkers^{1,2,3,4} has shown that flames from premixed propane and air and from evaporated hexane droplets and air can be stabilized inside a refractory tube without a flameholder. Backmixing is negligible in this combustion process, and stabilization is wholly due to thermal feedback by wall-to-wall radiation inside the tube and longitudinal thermal conduction in the tube wall. Multiple stationary states within the combustion chamber have been predicted from a theoretical model^{5,6} and confirmed experimentally.^{2,4}

The wall temperature profile is very stable for

each of the stationary states owing to the large thermal inertia of the ceramic enclosure relative to that of the flowing gas and liquid. The flame front is very thin, free of oscillations and nearly invisible. The maximum temperature of the flame slightly exceeds the theoretical adiabatic value owing to the thermal feedback. The temperature of the burned gases decreases almost linearly to slightly below the theoretical adiabatic value at the exit from the combustion chamber, thereby providing a nearly isothermal post-flame zone. The rate of formation of NO_x is essentially uniform within this zone, and hence controllable by choosing the appropriate stationary state and thereby the extent of the zone. The total NO_x formation has been found to be

exceptionally low (5–40 ppm) for equivalence ratios of approximately 0.80.

The objective of the current investigation has been to study the formation of thermal NO_x over a wider range of equivalence ratios of hexane and air than previously investigated with the burner and to determine the effect of fuel-nitrogen of several types and concentrations.

Experimental Apparatus

The apparatus used in this work is essentially the same as that used by Goepf et al.,⁴ and hence will only be described functionally. As shown in Fig. 1 the evaporation tube and combustion chamber consisted of a round, straight channel 9.7 mm in diameter and 1221 mm long, of which the first 970 mm was a thermally insulated aluminum oxide tube and the final 251 mm the central hole in a cast alumina block. This central hole was surrounded by six outer holes in which a propane-air mixture was burned to prevent radial heat losses.

A single chain of uniformly sized and uniformly spaced droplets was generated by passing reagent-grade liquid hexane through a rotameter and then through a hypodermic tube vibrated at 5 kHz. Compressed air was filtered, metered, preheated and introduced into the ceramic tube above the hexane inlet as shown. The temperature profile along the

inner wall of the evaporation tube and combustion chamber was measured with a series of thermocouples near the surface.

A sample of the gas stream leaving the combustion chamber was pulled through a fused-quartz tube, cooled, subcooled for water removal, and analyzed for CO , CO_2 , O_2 , NO and NO_x .

Experimental Procedure

Owing to the great thermal inertia of the ceramic combustion chamber relative to that of the gas stream, many hours were required to establish a true equilibrium state. However this thermal inertia made it possible to establish quasi-stationary flames at the same fixed location for different flow rates of fuel and air, whereas a separate location for each would be attained at equilibrium.

In order to vary the equivalence ratio on the fuel-rich side ($\phi > 1$), the rate of flow of the fuel was varied for a fixed rate of flow of air. For the fuel-lean side ($\phi < 1$), the rate of flow of air was varied for a nearly fixed rate of flow of fuel. For runs of fixed equivalence ratio but varying flame-front location, the stationary state nearest to the exit of the tube was first established. Then the flow rates of air and fuel were decreased proportionately in steps, establishing quasi-stationary flames at a series of increasing distances from the exit. Finally

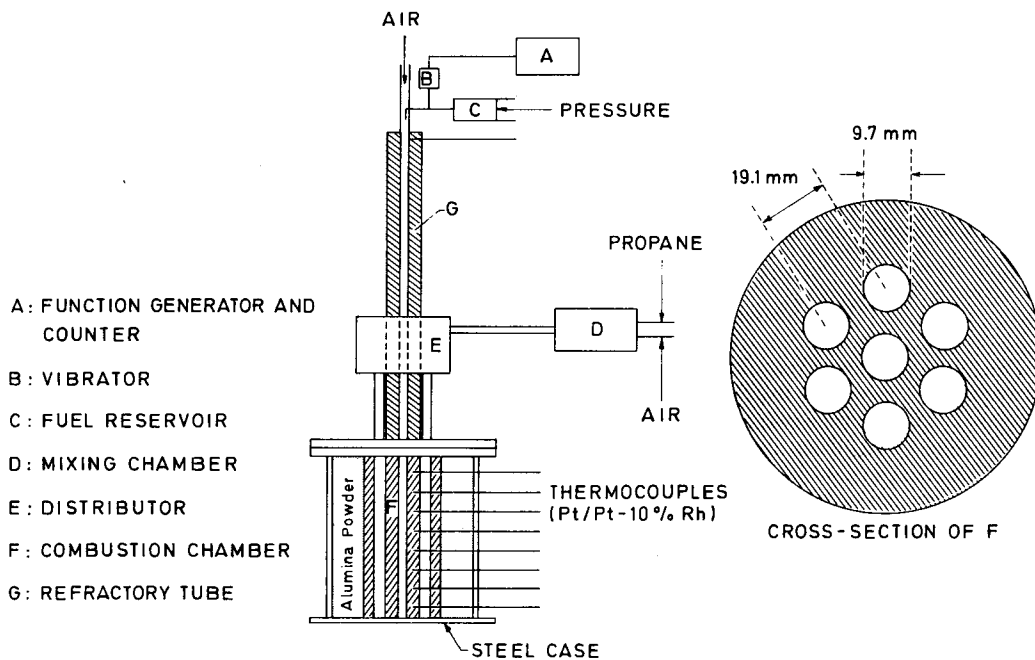


FIG. 1. Schematic diagram of experimental apparatus.

the initial flow rates were re-established with the flame at the location of the upstream-most stationary state.

When the rate of flow of fuel was varied, the initial spacing of the droplets (prior to acceleration by the stream of air) and their diameter varied. The diameter was calculated based on the observation of one droplet per vibration. Values varied from 215–291 μm . The initial spacing was determined from the flow rate and frequency of vibration using an experimental correlation. Values varied from 542–1261 μm . Based on theoretical calculations,⁶ the droplets were expected to evaporate completely ahead of the flame front for all of the conditions utilized in this work and this expectation was confirmed by visual observations. Hence the results herein are postulated to be independent of the diameter and spacing.

The flame-front location was arbitrarily defined as the point of inflection in a plot of the wall temperature versus distance along the combustion chamber. The gas temperature profile down the combustion chamber was not measured but was estimated from the measured wall temperature distribution using a theoretical model.⁶ The residence time in the post-flame zone of the combustion temperature was computed from the measured flow rates, the estimated gas temperature distribution and the nominal flame-front location.

In view of the findings of Johnson et al.,⁷ and others, the measured NO₂₊ was presumed to be formed all or in part in the sampling tube. Hence only values of NO_x are reported.

Experimental Results

Nitrogen-Free Fuel

The previously reported results for propane-air and hexane-air flames in refractory tubes were limited to an equivalence ratio of approximately 0.8. Hence NO_x production was first measured for undoped hexane with a fixed flame-front location and a series of equivalence ratios. The experimental conditions and measured exit concentrations of NO_x are given in Table I. Exit concentrations of CO are given for the fuel-lean mixtures but not for the fuel-rich mixtures owing to unreliability of the measurements for such high values. The measured values of NO_x are plotted versus the equivalence ratio in Fig. 2. A peak value of 104 ppm occurs for the stoichiometric mixture, with a sharp decrease for fuel-rich mixtures (increasing ϕ) and an even more precipitous decrease for fuel-lean mixtures (decreasing ϕ). The corresponding mean rates of formation of NO_x in the post-flame zone are included in Table I.

Nitrogen-Doped Fuel

The NO_x concentration in the exit gas for hexane containing 4.18% wt. diethylamine is plotted in Fig. 3 versus the residence time in the post-flame zone. This series of tests was carried out by varying the total flow rate and hence the flame-front location for a fixed equivalence ratio of 0.61, as described under *Experimental Procedure*. The horizontal

TABLE I
Experimental Conditions and Results for Hexane-Air Flames 241.3 mm from Exit of Tube

w_a (kg/s)10 ⁴	w_f (kg/s)10 ⁵	ϕ	T_w K	T_{ad} K	CO % (dry basis)	NO _x ppm	τ_{NO_x} (mol/s.m ³)10 ²
5.215	1.733	0.51	458	1450	0.129	2.4	0.242
5.215	1.883	0.55	458	1520	0.149	2.4	0.242
5.215	2.017	0.59	458	1590	0.192	2.1	0.211
4.662	1.950	0.64	458	1675	0.0085	9.5	0.849
3.702	1.733	0.71	458	1790	0.007	14.5	1.023
3.542	1.883	0.81	450	1938	0.037	27	1.808
3.542	2.017	0.87	450	2028	0.076	57.5	3.831
3.542	2.300	0.99	450	2202	0.49	104	6.860
3.542	2.500	1.08	435	2124	—	94	5.685
3.542	2.783	1.20	435	1918	—	86	5.810
3.542	3.000	1.29	435	1849	—	79	5.419
3.542	3.200	1.38	435	1780	—	66	4.569
3.542	3.617	1.56	435	—	—	22	—
3.542	3.900	1.68	435	—	—	13	—
3.542	4.317	1.86	435	—	—	8.7	—

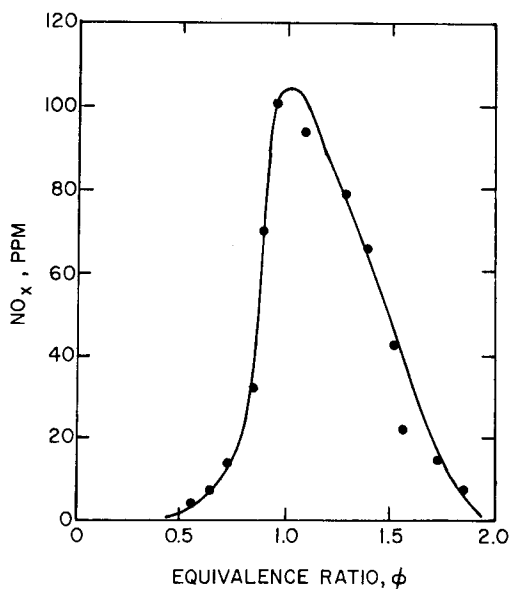


FIG. 2. Thermal NO_x concentrations from hexane-air mixtures (conditions in Table I).

dashed line represents complete conversion of the nitrogen in the fuel to NO_x . The thermal NO_x for these runs is estimated to be in the range from 2–8 ppm, and hence negligible with respect to that from the fuel-nitrogen. The observed independence from the post-flame residence time indicates that the conversion of the nitrogen in the fuel to NO_x occurred in the flame front itself as conjectured by Flagan, et al.,⁸ and others. The detailed conditions for these runs were given in Table II.

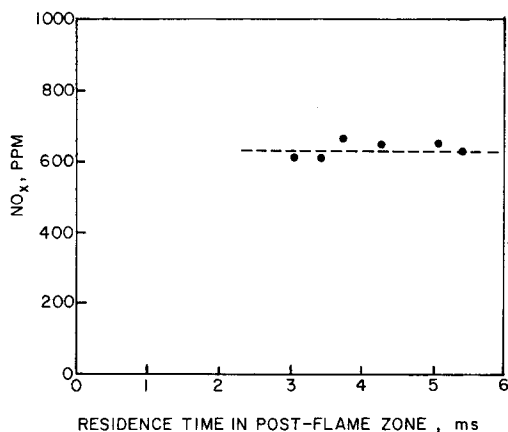


FIG. 3. Total NO_x concentrations from hexane with 4.15% wt. diethylamine and $\phi = 0.61$ (other conditions are given in Table II).
---- complete conversion of fuel nitrogen.

TABLE II
Experimental Conditions and Results for 4.15% wt. Diethylamine in Hexane at $\phi \sim 0.63$

w_a (kg/s) 10^4	w_f (kg/s) 10^5	T_o K	T_{ad} K	L_f mm	NO_x ppm
3.542	1.458	457	1657	94.8	620
4.182	1.737	457	1657	115.6	620
4.662	2.016	457	1718	123.2	680
4.502	1.876	457	1657	116.9	670
4.022	1.667	446	1647	116.9	700
4.022	1.667	450	1652	144.8	650
4.182	1.737	450	1652	147.4	700
4.662 ^a	2.016 ^a	450	1708	151.2	730
4.502	1.876	450	1652	160.1	700

a: $\phi = 0.66$.

The fractional conversion of fuel-nitrogen from diethylamine, isobutylamine, pyridine and piperidine is plotted versus the equivalence ratio in Figs. 4–7. The concentrations of these compounds were chosen to yield a fixed value of 0.795% wt. nitrogen in the fuel. The flame-front location was fixed at the same value as for the tests with pure hexane in Fig. 2. The operating conditions correspond very closely to those of Table I and hence are not reproduced herein. The thermal NO_x indicated in Fig. 2 for the same equivalence ratio was subtracted from the measured value of NO_x to obtain the conversions in Figs. 4–7. In all four cases the conversion of fuel-nitrogen to NO_x is essentially

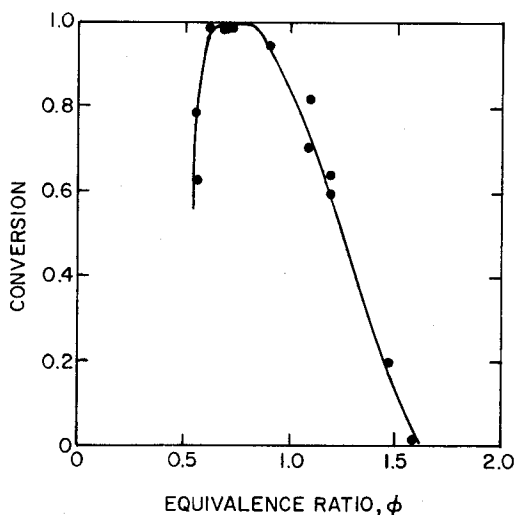


FIG. 4. Conversion of fuel-nitrogen to NO_x for hexane with 4.15% wt. diethylamine (same conditions as in Table I).

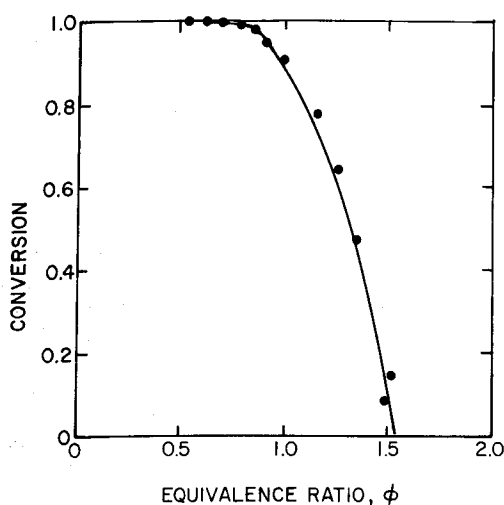


FIG. 5. Conversion of fuel-nitrogen to NO_x for hexane with 4.15% wt. isobutylamine (same conditions as in Table I).

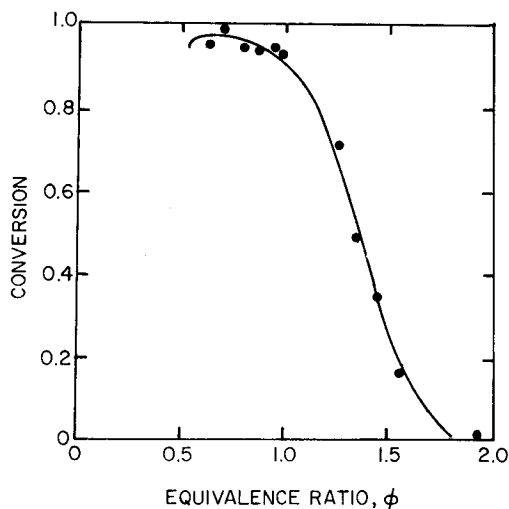


FIG. 7. Conversion of fuel-nitrogen to NO_x for hexane with 4.84% wt. piperidine (same conditions as in Table I).

complete for $0.6 < \phi < 1.0$. For $\phi > 1.0$ the conversion falls rapidly and for $\phi < 0.6$ precipitously. Curves representing the conversions for the four different nitrogen compounds are compared directly in Fig. 8. The similarity of the curves suggests that the conversion depends only slightly, if at all, on the chemical structure of the fuel-nitrogen.

The band of curves in Fig. 8 is superimposed in Fig. 9 on the experimental results of de Soete⁹ for ammonia and several different amines in a flat

laminar flame. In these tests either helium or argon was substituted for the nitrogen in the air. Reasonable agreement is to be noted, despite the greater concentrations of fuel-nitrogen in the experiments of de Soete and the radical difference in the type of flame.

The effect of the concentration of fuel-nitrogen

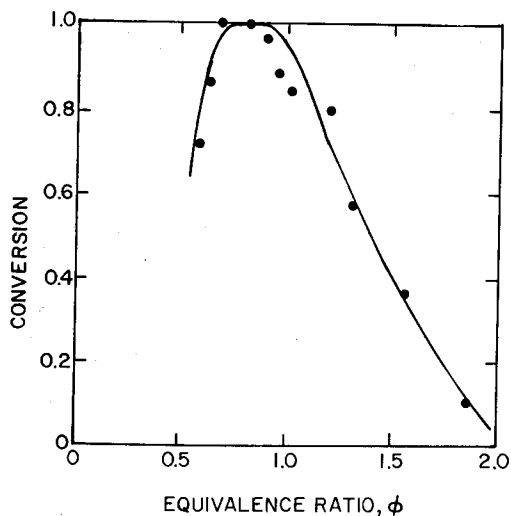


FIG. 6. Conversion of fuel-nitrogen to NO_x for hexane with 4.49% pyridine (same conditions as in Table I).

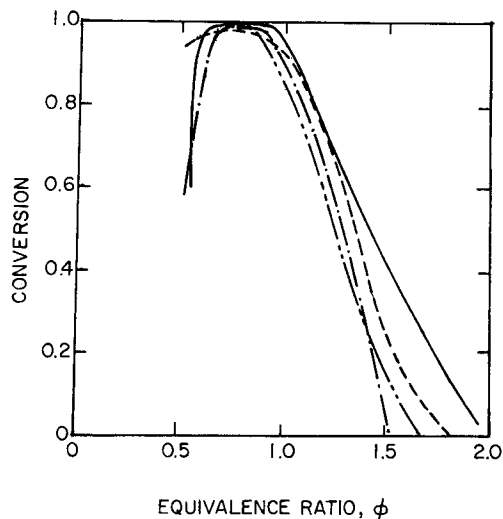


FIG. 8. Conversion of fuel-nitrogen to NO_x—comparison of results for four nitrogen compounds.

— pyridine
 - - - piperidine
 . . . diethylamine
 - · - isobutylamine

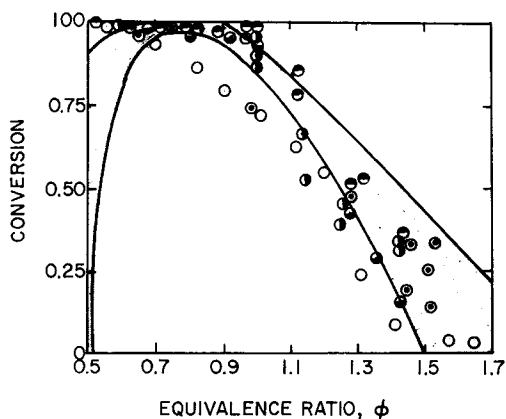


FIG. 9. Comparison of range of NO_x conversions (shaded region) with data of de Soete⁹ for C_2H_4 , O_2 and A or He with additions:

- 700-1300 NH_3
- 315-600 $\text{C}_2\text{H}_4(\text{NH}_2)_2$
- 1600 $\text{C}_2\text{H}_4(\text{NH}_2)_2$
- 175 $(\text{C}_4\text{H}_9)_2\text{NH}$
- 3400 $(\text{C}_2\text{H}_5)_3\text{N}$

is indicated by the data in Fig. 10 for pyridine in hexane. Complete conversion occurs near an equivalence ratio of unity for all three concentrations but the conversion begins to decrease at a lower equivalence ratio as the concentration increases. This result is consistent with the experiments of Fenimore.¹⁰

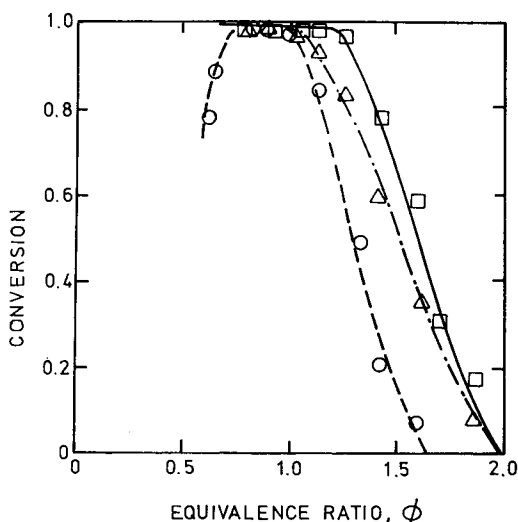


FIG. 10. Effect of Concentration of Pyridine on Conversion of Fuel-Nitrogen to NO_x .

- 0.16% wt.
- - - 0.53% wt.
- · · 2.10% wt.

Thermal and kinetic calculations utilizing the model of Choi and Churchill⁶ together with free-radical mechanisms are in progress for the conditions of this paper. Preliminary results are in quantitative accord with the experimental results.

Conclusions

The formation of thermal NO_x can be reduced as low as desired in combustion in a refractory tube either by decreasing or increasing the fuel-to-air ratio relative to the stoichiometric mixture. The reduction with decreasing fuel-to-air ratio is presumably related to the decreased temperature in the post-flame zone, while the reduction with increasing fuel-to-air ratio is due to the absence of excess oxygen as well.

Prior work suggests that quantitatively similar behavior would be expected for other hydrocarbon fuels. Also the total thermal NO_x formation was previously found to be proportional to the residence time in the post-flame zone, and hence controllable through choice of the appropriate stationary state.

Fuel-nitrogen is apparently converted almost wholly to NO_x in lean fuel-to-air mixtures with equivalence ratios from 0.6 to 1.0. As the equivalence ratio increases beyond unity the conversion to NO_x gradually decreases. The conversion to NO_x is independent of the residence time in the post-flame zone and therefore apparently occurs in the flame front itself.

The conversion of fuel-nitrogen to NO_x as a function of equivalence ratio appears to be relatively independent of the structure of the nitrogen-containing component. The quantitative agreement of the results herein with those of de Soete indicate that the variation of the conversion with equivalence ratio is also independent of the type of flame. The conversion to NO_x decreases somewhat with increasing concentration of fuel-nitrogen, particularly for equivalence ratios greater than unity.

The formation of NO_x from fuel-nitrogen is apparently independent of and additive to thermal NO_x .

In radiantly stabilized combustion in a refractory tube diffusion and mixing are minimal. Hence the similarity of the results for fuel-nitrogen with those for other devices and processes involving appreciable diffusion and mixing is a strong confirmation that the conversion to NO_x is kinetically controlled and confined to the flame front.

Nomenclature

- L_f distance from flame front to exit of combustion chamber, m
- r mean rate of formation of NO_x in post-flame zone, $\text{mol}/\text{s}\cdot\text{m}^3$

T_o inlet temperature of fuel-air mixture, K
 T_{ad} theoretical adiabatic flame temperature, K
 w_a rate of flow of air, kg/s
 w_f rate of flow of fuel, kg/s
 ϕ equivalence ratio (fuel-air ratio/stoichiometric fuel-air ratio)

Acknowledgement

The assistance of Lisa Pfefferle and Swan Cheng in the experimental work is gratefully acknowledged. The authors appreciate the partial financial support provided by NSF Grant ENG-75-20225.

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COMMENTS

F. Tamanini, Factory Mutual Research, USA. Can you comment on the usefulness of a multi-equation (21 or 44) kinetic model in view of the fact that the theoretical predictions are only marginally better than those from the simple Zeldovich mechanism?

Author's Reply. A 21-reaction model was used to calculate the oxidation of CO as well as the production of thermal NO_x. This detailed model provides some quantitative improvement over the Zeldovich model, particularly for equivalence ratios of less than 0.7 and greater than 1.0. Also, it provides a test of the postulates of the various Zeldovich models, such as the assumption of local equilibrium for O.

A. Tewarson, Factory Mutual Research Corp., USA. In equivalence ratio calculations, additives need to be considered. What is the N-atom balance in cases where NO_x is increasing or decreasing? Also, Flame radiation is expected to change by the additives.

Author's Reply. The equivalence ratio in the plots is a nominal value neglecting the slightly reduced oxygen demand due to doping the hexane with

nitrogen compounds. The resulting maximum error in the equivalence ratio is less than 0.3%.

The concentrations of all nitrogen-containing species other than N₂ and NO were calculated to be less than 1 ppm for fuel-lean conditions. Therefore, the NO_x increases or decreases primarily at the expense of N₂.

Emission and absorption of radiation by the gas stream is negligible for the beam lengths encountered in the 9.5 mm tube, and is presumed to remain negligible with the nitrogen-doped fuels.

P. Schug, DFVLR Inst. fur Physikalische, West Germany. Under fuel rich conditions the chemistry of N-containing species is strongly influenced by the presence as well as absolute concentrations of hydrocarbon radicals, which your global model of fuel depletion is unable to predict. How useful is the combination of the three step global model and the detailed kinetic model under rich conditions and what assumptions on the O, OH, and H radical concentration are being applied, when you switch from the global to the detailed model?

Author's Reply. Our model is not expected to be valid for very high conditions ($\phi > 1.3$) for which

hydrocarbon radicals are formed. We postulated zero concentrations of O, OH and H in the preflame region. However, the postulate of equilibrium values at the flame front does not change our results significantly.

The computational work was described in our oral presentation, but was not completed in time for inclusion in the manuscript for the Symposium volume.

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H. G. Semerjian, National Bureau of Standards, USA. Comparison of your NO vs ϕ results with your model showed a substantial disagreement. Your axial temperature profiles showed a measurable

delay time, and yet you assume a complete and fast conversion of hexane to carbon monoxide. As a result, the NO production starts immediately at the inlet of the passage. Could this explain part of the disagreement you have observed?

Author's Reply. The agreement of our computed and experimental measurements of NO were good for lean mixtures, but were only fair for rich mixtures owing to the postulate of direct oxidation of the fuel to CO and H₂O whereas hydrocarbon fragments are known to be formed by decomposition of the fuel under rich conditions. NO formation began at the flame front, both experimentally and computationally.