FORMATION OF NITRIC OXIDE IN PREMIXED HYDROCARBON FLAMES

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The formation was followed by probing flames of ethylene, methane, or propane with N2–O2 mixtures. The known kinetic laws of the well-understood N2–O2–NO system (limited by the rate of the reaction O + N2 → N + NO) described the growth of nitric oxide in the post-flame gas, after hydrocarbons were consumed, but could not describe a faster, transient formation of nitric oxide in the primary reaction zone. The transient formation did not occur in hydrogen or carbon monoxide flames, and therefore, may involve an attack of carbon or hydrocarbon radicals on nitrogen molecules (e.g., CH + N2 → HCN + N). At atmospheric pressure, the transient formation gave its greatest yield in flames containing 1.3 to 1.4 times the stoichiometric amount of fuel. Its yield increased somewhat with pressure, particularly in fuel-lean flames, so that at 3 atmos pressure the nitric oxide formed quickly in the primary reaction zone was about the same in flames of 0.8 as of 1.4 mixture strength. The transient formation possessed a relatively weak temperature dependence. Extrapolating the measurements, one can suggest that the new mechanism may contribute significantly to the emission of nitrogen oxides from a gas turbine, but the major contribution occurs by the known mechanism of the N2–O2 system.

Introduction

We know how to calculate the amount of nitric oxide formed in hydrocarbon–air flames if the formation follows the laws of the simpler N2–O2–NO system. We are less confident, however, that flames obey these laws. It is not clear, for example, that they can account for the build-up of nitric oxide to the concentrations observed in fuel-rich flames in internal combustion engines. The aim of the work reported here was to test whether hydrocarbon flames obey these laws.

We start by stating the law of growth in the N2–O2–NO system, under conditions of interest to us. The only reactions involving nitric oxide which we need consider are (1) and (2):

\[ O + N_2 \rightarrow N + NO \quad (1) \]

\[ N + O_2 \rightarrow O + NO. \quad (2) \]

Assuming a steady concentration of N atoms, we expect

\[ \frac{d[NO]}{dt} = \frac{2k_1[O][N_2]}{k_1} = 9.5k_1 \times \exp \left( -\frac{75.5 \text{kcal}}{RT} \right) [O][N_2]. \quad (3') \]

where \( K \) is the equilibrium constant \( k_1k_2/k_1k_2 + k_2 \).

Initially, (3) simplifies to (3'):

\[ \frac{d[NO]}{dt} = 2k_1[O][N_2] = 2k_1k_2[O][N_2]/k_1 = 9.5k_1 \times \exp \left( -\frac{75.5 \text{kcal}}{RT} \right) [O][N_2]. \quad (3') \]

The rate is put in terms of the temperature independent \( k_1 \) and the known equilibrium constant, \( k_1/k_1 \), in order to facilitate subsequent comparison of predicted with observed results. Accepted values for the rate constants are\(^2\):

\[ k_1 = 13 \pm 4 \times 10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}, \]

independent of temperature;

\[ k_2 = 15 \times 10^{12} \exp \left( -7.9 \text{ kcal}/RT \right). \]

Temperature is presumed to be measurable, \([N_2]\) is presumed known, and it is an acceptable approximation to set \([O]\) equal to the equilibrium concentration in the hot products—although this requires justification because we know that O atoms in rather low temperature flames may briefly attain a much larger than equilibrium concentration. The hotter the flame, however, the less does \([O]\) ever exceed the equilibrium concentration, and Eqs. (3) and (3') are only
appreciable in hot flames anyway, because they contain the factor exp \((-75.5\, \text{kcal}/RT\)). Thus, whenever the equations predict a significant rate (1 ppm or more per msec) the approximation is justified.

By comparing the experimental rate with that predicted by (3) or (3') one can decide whether the equations are applicable in flames, or if the additional species in flames change the law of growth. The additional species include carbon and hydrocarbon radicals in the primary reaction zone and H, OH, H₂, H₂O, CO, and CO₂ both in the primary zone and in the post-flame gas after the hydrocarbons are burned up.

It is worth noting that not every new reaction need affect the applicability of (3). It is probable that the very fast reaction (4) intervenes in hot gases when water is a major constituent:

\[
N + OH \rightleftharpoons H + NO \tag{4}
\]

\((k_4 = 40 \times 10^{12} \, \text{cm}^3 \, \text{mole}^{-1} \, \text{sec}^{-1} \) at room temperature.\) But the inclusion of (4) in the mechanism, plus the assumption that H + O₂ = OH + O is equilibrated, only modifies Eq. (3) to (3''):

\[
\frac{d[\text{NO}]}{dt} = \frac{2k_3[O][N_2][1 - ([\text{NO}]K[N_2][\text{O}_2])]}{1 + k_{-1}[\text{NO}]/(k_4[\text{O}_2] + k_{4}[\text{OH}])}.
\]

(3'')

The modification leaves Eq. (3') applicable initially, and indeed extends its range of applicability to larger ratios of \([\text{NO}] / [\text{O}_2]\) than would be consistent with (3).

**Experimental**

Two different series of runs were carried out with different types of burners. In the first series, water cooled, porous plate burners of 10.2 or 27.5 cm² area were fed with metered flows of premixed reactants at atmospheric pressure. The thin primary reaction zone lay too close to the burner surface to be sampled, but downstream of this zone, at distances of a few mm to a few cm from the surface, the post-flame gas was sampled through a stout quartz probe into a previously evacuated flask of 5.54 liter volume. The sum of NO and NO₂ in the sample was determined by the phenol disulfonic acid method. The temperature of the flame gases was measured by sodium reversal and was constant over the region investigated.
In the second series of runs, a Meker-type burner mounted in a pressure vessel was used at 1, 2, and 3 atmos pressure. The surface area of the burner was 3.14 cm². Its flame consisted of many small cones whose flows merged into an approximately one-dimensional stream of burned gas 0.2 cm above the burner. The burned-gas temperature was not measured in the runs, but the flames were essentially adiabatic and the calculated temperature was expected to be approximately correct.

Results Obtained with Nonadiabatic Flames on Porous Burners

Figure 1 shows typical plots of the local concentration of nitrogen oxides against time. The concentration grows linearly with reaction time in the post-flame gas, but extrapolation of the curves back to zero time often gives positive intercepts. Since the reactants were free of nitric oxide, the intercepts mean that nitric oxide forms at a fast rate for a very short time in a region inaccessible to sampling—that is, in the primary reaction zone. Thereafter, nitric oxide continues to grow at a slower constant rate. In what follows, I consider the slopes of the curves and the intercepts separately.

If the slopes are determined by Eq. (3'), one can derive $k_-$ by substituting the observed rate and temperature, and the calculated equilibrium concentrations of O and N₂ into this equation. The $k_-$ found in this way from the three curves with appreciable slope in Fig. 1, and from similar curves in eleven other flames, are shown in Fig. 2. Five of these values come from C₂H₄-air flames, two from C₂H₄-O₂-N₂ (the O₂-N₂ mixtures used contained 21 to 30 per cent O₂), four from C₆H₆-O₂-N₂, one from CH₄-air, one from CH₄-O₂-N₂, and one from moist CO-air. The extreme rates of formation of nitric oxide were 1 and 49 ppm per msec. Gas temperatures ranged from 2112° to 2367°K, the mixture strengths of the flames from 0.8 to 1.2 of the stoichiometric amount of fuel. In all cases, the concentration of nitric oxide was small compared to the concentration appropriate to the equilibrium N₂ + O₂ → 2 NO.

The average $k_-$ = 14 ± 5 × 10¹² cm³ mole⁻¹ sec⁻¹. This agrees with the literature value in the introduction and I conclude that Eq. (3') applies in the post-flame gas of hydrocarbon flames after the hydrocarbon is burned up.

It seems impossible, however, that Eq. (3') can describe the fast formation of nitric oxide in

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Fig. 3. Upper plot: NO formed in or very near the primary reaction zone of ethylene flames. Lower plot: same data with NO expressed as a fraction of the equilibrium concentration in the final products.
primary reaction zone is not determined by the rate of Reaction (1).

The lower parts of Figs. 3 and 4 show that in rather fuel-rich flames, the nitric oxide formed in the primary reaction zone approaches the equilibrium amount in the hot products. In flames fed with less than about 1.3 times the stoichiometric fuel, the nitric oxide generated in the primary reaction zone is only a small part of the equilibrium amount.

Results Obtained with Adiabatic Flames at Variable Pressure

Seventeen ethylene-air flames (four with extra nitrogen or extra steam added) were burned on the Meker-type burner at various pressures. The experimental data for twelve of these are shown in Fig. 5, and the extrapolated intercepts (giving the nitric oxide formed quickly in the primary reaction zone) are plotted in Fig. 6 for all the
NITRIC OXIDE IN HYDROCARBON FLAMES

TABLE I
Calculations and measurements in adiabatic flames

<table>
<thead>
<tr>
<th>Mixture strength</th>
<th>(T(\text{calc})),* °K</th>
<th>(T(\text{inferred})),* °K</th>
<th>Intercept, ppm NO at (T(\text{inferred})), ppm</th>
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<tr>
<td>0.8</td>
<td>2170</td>
<td>2220</td>
<td>42</td>
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<tr>
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<td>2177</td>
<td>2220</td>
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<td>0.96†</td>
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<td>2200</td>
<td>40</td>
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<tr>
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<td>2175</td>
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<td>—</td>
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<td>—</td>
<td>92</td>
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<td>2257</td>
<td>—</td>
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</tr>
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<td>2190</td>
<td>—</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>2190</td>
<td>—</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>2190</td>
<td>—</td>
<td>69</td>
</tr>
</tbody>
</table>

* \(T(\text{calc})\) is the calculated adiabatic flame \(T\) with reactants at 298°K. \(T(\text{inferred})\) is calculated from the slopes of the NO-vs-time curves, assuming the applicability of Eq. (3'). \(T(\text{inferred})\) was arbitrarily called 2280° for 1.4 mixture strength, and 2220° for 1.5.

† This mixture contained extra \(N_2\) (equal to one-fifth of the initial air). Interpolating between the results at mixture strengths of 0.8 and 1.0, I conclude that the extra \(N_2\) lowered the temperature by about 160°, lowered the slope of the curves by about a factor of 6, and lowered the intercept by about a factor of 1.6.

‡ Mixture contained added steam (mole ratio steam/\(C_2H_4 = 1.23\) in reactants), which lowered \(T\) by about 90°, lowered slope of curve by a factor of 2.5, and lowered intercept by a factor of 1.6.

flames. Table I lists the calculated adiabatic flame temperatures (assuming reactants at 298°K) and the flame temperatures inferred from the slopes of the curves of NO-vs-time [assuming the applicability of Eq. (3') and the literature value of \(k_{-1}\)]. The inferred temperatures are higher—perhaps because the metal pressure vessel was heated some 50° by the flame within it and so the reactants were in fact hotter than 298°K.

One can see from Figs. 5 and 6 that the extrapolated intercepts increase somewhat with pressure, particularly in fuel-lean mixtures. This pressure dependence is additional evidence that the nitric oxide formed quickly in the reaction zone is not due to a brief excess of O atoms reacting in the sense of Reaction (1). Any such local excess should recombine faster the higher the pressure.

The lower part of Fig. 6 is consistent with the conclusion that the quickly formed nitric oxide, expressed as a fraction of the equilibrium concentration in the hot products, increases with the 0.5 ± 0.1 power of pressure. At mixture strengths of 1.4 and 1.5 times stoichiometric, the quickly formed nitric oxide seems to exceed the equilibrium concentration sometimes—but this is not necessarily a real phenomenon. The temperature and hence the equilibrium concentration is a little uncertain, the excess is not enormous, and the curves certainly flatten off as they approach the equilibrium concentration.

Discussion

It is not surprising that Reactions (1), (2), and probably (4) describe the growth of nitric oxide in the post-flame gas. Evidence existed already that they described the decay of nitric oxide when \([NO]\) is large compared to the equilibrium concentration. For that case, Eq. (3'') rearranges to (5),

\[
-\frac{d[NO]}{dt} = \frac{2k_2[O_2](1 + [k_{-1}[NO] / (k_3[O_2] + k_4[OH])])}{k_2[O_2] + k_4[OH]}
\]

(5)
TABLE II

<table>
<thead>
<tr>
<th>Wt. ratios fed</th>
<th>Properties of adiabatic, locally stoichiometric flame</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$, °C</td>
</tr>
<tr>
<td>$H_2O$/fuel</td>
<td>Fuel/air</td>
</tr>
<tr>
<td>0</td>
<td>0.0183</td>
</tr>
<tr>
<td>0.025</td>
<td>0.0192</td>
</tr>
</tbody>
</table>

* Supposed to correspond to intercepts shown in Figs. 1 and 5.
† Corresponds to slopes of Figs. 1 and 5, calculated by Eq. (3').

Whatever its mode of formation, nitric oxide is generated in or near the primary reaction zone of sufficiently fuel-rich hydrocarbon flames until its concentration is of the order of the equilibrium amount, and this can happen when the concentration of $O$ atoms is so small that little or no nitric oxide is formed by Reaction (1).

The concentration of $N$ atoms is determined by equilibrated Reactions (2) or (4) which are indistinguishable if $H + O_2 = OH + O$ is also equilibrated.

Zeldovich found that (5') expressed the decay in post-flame gas containing $[NO] \ll [O_2]$. Fenimore and Jones found that it also applied even when $[NO]$ was about the same as $[O_2]$ and occasionally much larger than $[O_2]$; in their gases, $[OH]$ was of the order of $[NO]$ and it seems likely that Eq. (5) reduced to (5') because $k_4[OH]$ exceeded $k_4[NO]$. The $k_{-1}$ from these studies ($k_{-1} \approx 22 \times 10^{12}$ cm$^3$ mole$^{-1}$ sec$^{-1}$ from Zeldovich, $k_{-1} \approx 7 \times 10^{12}$ from Fenimore and Jones) agree within their possible errors with the value listed in the introduction.

It is more surprising, or at least new, to find a swift but brief formation of nitric oxide in the primary reaction zone. Because this formation requires hydrocarbon fuel, it may involve reactions like

$$ CH + N_2 \rightleftharpoons HCN + N, \quad \Delta H \approx 2 \text{ kcal} $$

$$ C_2 + N_2 \rightleftharpoons 2 \text{CN,} \quad \Delta H \approx 7 \text{ kcal.} $$

The significance of the quickly formed nitric oxide is likely to be in a practical combustion device? Some feel for this problem is given by Table II, which lists results of calculations for a hypothetical gas turbine. We are interested in the peak flame temperature in the head end of the combustor, before extensive dilution of the hot gas occurs, and suppose that this is a stoichiometric, adiabatic flame with temperature and equilibrium concentration of $O$ atoms given in the table. The equilibrium concentration of nitric oxide is also listed—but it is not expected to be attained. Instead, one expects the nitric oxide to be the sum of a quickly formed contribution plus the more slowly formed contribution predicted by Eq. (3').

Assuming that kerosene follows the curves given in the lower part of Fig. 6 for ethylene, and supposing the quickly formed nitric oxide continues to increase with the 0.5 power of pressure, one expects the quickly formed contribution to be that listed in Table II as "prompt NO." The expected rate of the more slowly formed contribution is listed in the last column. If the mixing history in the combustor is equivalent to 2 msec at the stoichiometric temperature followed by instantaneous dilution and cooling, the hotter burning combustor would emit 178 ppm nitric oxide of which 27% is "prompt NO." The cooler...
combustor, burning with steam injection, would emit 106 ppm nitric oxide of which 37% is "prompt NO." These calculated levels are in the range of the nitric oxide actually observed from gas turbines. The calculation suggests that the quickly formed nitric oxide might be a significant part of the total, though not the major part. The decreased emission expected by lowering the peak flame temperature is due mostly to a slower rate of formation after hydrocarbons are consumed—as is shown experimentally by Fig. 5 and is discussed in the notes to Table I.

Acknowledgments

I am grateful to John Moore of our group for the equilibrium calculations listed in Table I, and to W. H. Day of the General Electric Gas Turbine Department for the calculations summarized in Table II.

C. T. Bowman, United Aircraft Corp. You have suggested that the "prompt NO," determined by extrapolating NO-concentration profiles measured in the post-flame zone to zero time, is evidence for the importance of reactions of the type \( \text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N} \) in NO-formation kinetics. In a shock-tube study of NO formation during combustion of \( \text{H}_2/\text{O}_2/\text{N}_2 \) mixtures, I have found that the experimental NO profiles exhibit substantial curvature. The NO-formation rates in the initial phases of reaction exceed those in the post-reaction zone. Complementary analytical studies have shown that this behavior can be accounted for by using only two reactions involving nitrogen: \( \text{O} + \text{N}_2 \rightarrow \text{N} + \text{NO} \) and \( \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} \). If NO profiles measured late in the reaction are extrapolated to zero time, then "prompt NO" is observed. However, as noted above, this "prompt NO" is consistent with a simple two-reaction scheme for the nitrogen chemistry. Hence, extrapolating NO profiles measured late in the reaction and observing "prompt NO" is not necessarily evidence for the importance of reactions of the type suggested by you. More definitive information would be obtained by probing low-pressure flames to measure NO profiles in the primary reaction zone.

Author's Reply. My NO profiles doubtless do bend downward toward zero concentration of NO at the origin. The intercepts obtained by linear extrapolation indicate only that in or near the primary reaction zone (in a region inaccessible to sampling at atmospheric or higher pressure) the rate of formation of NO must be much faster than it is in the post-flame gas. The question is whether this faster, transient rate is due to the reaction \( \text{O} + \text{N}_2 \rightarrow \text{N} + \text{NO} \), as is the slower, constant rate in the post-flame gas. If it is, one must suppose that more O atoms are present in the reaction zone of hydrocarbon flames than in hydrogen or carbon monoxide flames—and, in hydrocarbon flames, one must suppose that more O atoms are present in somewhat fuel-rich reaction zones than in somewhat fuel-lean ones. These requirements are improbable, so different mechanisms are suggested for the primary reaction zone and for the post-flame gas. I agree that one cannot be sure what happens in the primary reaction zone until this region is probed, and that studies at lower pressure would be valuable.

S. H. Bauer, Cornell University. You suggest that N atoms are formed in the region of the "prompt NO" by the reaction of CH radicals with \( \text{N}_2 \). In our laboratory, Dr. A. Bar-Nun studied the reactions between acetylene and elementary nitrogen in reflected shocks, and followed spectrophotometrically the CN, HCN, \( \text{C}_2 \), and (in a few cases) the \( \text{C}_1 \) production rates.
The data are complex and do not lead to a unique interpretation. However, the most consistent set of assumptions tells us that CN (and concomitant N) is formed by attack of C\textsubscript{1} and C\textsubscript{2} on N\textsubscript{2}. At the elevated temperatures of his studies, the equilibrium concentration of CH is very much less than the major species, C\textsubscript{2}H, C\textsubscript{4}, and C\textsubscript{8}. Attack by C\textsubscript{2}H may be ruled out, however, by the endothermicity of the reaction.

Author's Reply. I agree that the most important carbon or hydrocarbon radicals, supposed to form N atoms in the primary reaction zone, might be other than the CH radical.