The Formation of Nitric Oxide and the Detection of HCN in Premixed Hydrocarbon-Air Flames at 1 Atmosphere

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The Formation of Nitric Oxide and the Detection of HCN in Premixed Hydrocarbon-Air Flames at 1 Atmosphere

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Abstract—The NO concentration profiles of premixed hydrocarbon-air flames were measured using probe sampling and ultraviolet absorption of NO. The flames were stabilized on a Meker-type burner of 7 cm diameter at a pressure of 1 atm. Investigated fuels were CH₄, C₂H₆, C₃H₈, C₅H₁₀, n-C₆H₁₄, i-C₅H₁₀, C₁₀H₂₂, C₁₀H₂₆, and gasoline. The measurements show the formation of nitric oxide according to the Zeldovich mechanism

\[ \text{O} + \text{N}_2 \xrightarrow{k_1} \text{NO} + \text{N} \]
\[ \text{N} + \text{O}_2 \xrightarrow{k_2} \text{NO} + \text{O} \]

with \( k_1 = 5 \times 10^{13} \exp(-75400/RT) \text{cm}^3\text{mol}\text{sec} \) in fuel lean flames. In fuel rich flames the NO formation due to the Zeldovich mechanism would require unreasonably high concentrations of O atoms and evidence is given for another way of NO formation in these flames. HCN has been found as an intermediate species and exceeds the NO concentration in very fuel rich flames.

1. INTRODUCTION

The formation of nitrogen oxide in combustion processes can be described in many cases by the mechanism suggested by Zeldovich (1946)

I \( \text{O} + \text{N}_2 \rightleftharpoons \text{NO} + \text{N} \)
II \( \text{N} + \text{O}_2 \rightleftharpoons \text{NO} + \text{O} \)

which may be extended by the reaction

III \( \text{N} + \text{OH} \rightarrow \text{NO} + \text{H} \)

But under conditions with small concentrations of oxygen the N atoms could react with oxygen containing compounds other than O₂ and OH. In addition there is the question of whether the N atoms react with hydrocarbons forming nitrogen containing compounds as intermediate species or as products. An additional NO formation process in, or close to, the main reaction zone of hydrocarbon-air flames has been discussed by Fenimore (1971), who suggested such reactions as

IV \( \text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N} \)
V \( \text{C}_2 + \text{N}_2 \rightarrow 2\text{CN} \)

with subsequent reactions to NO. Whereas Iverach et al. (1972) confirmed Fenimore's suggestion for fuel rich flames, Sarofim and Pohl (1972) were able to explain for methane flames the high rate of NO formation near to the main reaction zone by nonequilibrium concentrations of O-atoms.

2. EXPERIMENTAL

Figure 1 shows the experimental set-up schematically. The flameholder had a diameter of 7 cm and consisted of a bundle of copper tubes (2 mm inner diameter, 10 cm length). The copper tubes were surrounded by a double tube of steel, which could be cooled or heated by water. The air and the fuel flows were adjusted by needle valves and metered by rotameters. The gases were mixed in a mixing chamber and fed through a set of wire gauze into the copper tube matrix. Liquid fuels were metered with rotameters and then vaporized in a heated copper-capillary. This set-up allowed the vaporization of hydrocarbon mixtures as e.g. gasoline without disproportionating. Vaporized fuels were fed to the heated mixing chamber before
samples. The logarithmic absorption was nearly proportional to the NO concentration for the given set-up up to about 100 ppm. Figure 2 shows an absorption profile for 750 ppm NO concentration. The smallest detectable NO concentration was less than 1 ppm, the reproducibility was better than 5 per cent. The apparatus was calibrated with known test-mixtures of NO in pure nitrogen. This calibration could be checked by adding NO to the gasflow and probing in absence of combustion. The NO had to be admitted to the fuel flow, otherwise the NO would have been partially oxidized by the air. Oxidation of the NO in the gas samples at 110 torr was negligible. During 15 minutes residence time in the absorption cell no decrease of NO could be detected.

For the determination of the HCN concentrations two methods were used. For qualitative measurements, Draeger tubes (Leichnitz, 1969) were inserted between the quartz probe and a 500 cm³ evacuated bottle. The HCN concentration corresponding to 500 cm³ gas at NPT could be determined from the length of the discoloured sensitive material in the tube. This method is based on the reaction of HCN with HgCl₂, which produces HCl, and is described to be specific to HCN. The accuracy is of the order of 50 per cent, the sensitivity about 1 ppm. More accurate measurements were made by using a colorimetric method, which is based on the formation of a polymethin dye from halogenocyan and pyridine in the presence of an aromatic base (Einheitsverfahren, 1960). The HCN was absorbed by bubbling 2000 cm³ NPT of the probed gas through 50 ml 0.1 n NaOH, which resulted in a sensitivity of 0.1 ppm HCN. It was assumed as quoted in the literature that the reaction is specific to HCN or (CN)₂. In the presence of aqueous solutions of NaOH (CN)₂ would disproportionate to cyanide and cyanate. Both applied methods gave within the error limit the same results.

The NO formation in air-flames using the gaseous fuels methane, ethane, propane, n-butane, ethylene, acetylene and the liquid fuels n-hexane, i-octane, cyclohexane, benzene, and gasoline has been investigated. The equivalence ratios were varied between \( \lambda = 0.6 \) and \( \lambda = 1.6 \) (\( \lambda = (\text{fuel/air})/(\text{fuel/air})_\text{stoich} \)). Methane flames could be stabilized up to \( \lambda = 1.3 \), acetylene flames up to \( \lambda > 2.3 \). The cold gas velocity with respect to the burner area was always about 45 cm/sec, except for acetylene, where the velocity reached about 100 cm/sec. The flames were probed up to a height
of 5 cm above the burner. This height corresponds to a reaction time of ca. 15 msec, respectively ca. 7 msec for the acetylene flames.

3. EXPERIMENTAL RESULTS

Figures 3 and 4 show the NO profiles of propane and acetylene flames as characteristic examples of the flames investigated. The straight lines have been fitted through the data points measured between 10 and 40 mm height above the burner and do not necessarily represent the NO profile near zero height. The statement 'height above the burner' is not equivalent with height above the main reaction zone, since for some flames the main reaction zone is not a flat disc, but consists of many small flame cones above the copper tubes of about 5 mm height merging more or less together. In some very fuel rich flames the cones were open at the tip. It was shown in a separate experiment that the streamlines in the flame were practically parallel, which indicates that the model of the one-dimensional flame can be applied to the flames investigated and that a linear relationship between the height above the burner and the reaction time can be assumed. Except for acetylene flames the heat losses to the flameholder were less than 1 percent of the total heat liberated, which is equivalent to a temperature decrease of less than 20 K.

The NO profiles of all fuels show a qualitative similarity with respect to the air-fuel ratio. For fuel lean flames a small but in many cases a finite NO concentration was measured adjacent to the main reaction zone. Within a more or less small regime (10 to 20 mm) the NO grew commonly not linearly with distance, but further downstream an almost constant gradient was usually observed. A typical example is depicted in Figure 5. The slope of the NO profile of this propane flame (\(\lambda = 0.92\)) at a 10 mm height is three times larger than at 40 mm. The linear extrapolation to zero height (zero reaction time) of all NO profiles with varying slopes is rather arbitrary. For flames with an equivalence ratio \(\lambda > 1\) the initial gradient becomes greater, whereas the slope some centimeters downstream reduces to smaller values, and most of the NO is now formed shortly behind the main reaction zone. For flames with \(\lambda \approx 1.2\) and richer the
initial increase is so fast, that the rise of the NO profile cannot be resolved accurately. The NO concentration remains constant with height above the burner; however, this level decreases now with further increasing \( \lambda \). Acetylene air flames have been stabilized up to \( \lambda > 2.3 \) and in these very fuel rich flames \( (2.16 < \lambda < 2.3) \) a rather small amount of NO was found near to the flameholder, whereas in this particular case the NO concentration grew linearly with height above the burner.

As Fenimore (1971) has shown for several flames the NO formation may be divided into a part due to the Zeldovich mechanism with O atom equilibrium concentrations and into the remaining part, which may include the NO production due to the Zeldovich mechanism with the excess concentration of O atoms over the equilibrium value—if such concentrations appear—and due to other mechanisms. The NO profiles have been extrapolated linearly some centimeters downstream to zero height above the burner and the intercepts with the ordinate ("prompt NO") have been plotted as a function of the mixture strength as shown by Figure 6 for various fuels. For some mixture strengths this procedure is questionable as mentioned above (Figure 5) since the length of the NO profile, which can be used for linear extrapolation, may become rather short, but it might be useful for a more qualitative comparison of the behaviour of different hydrocarbons in the investigated range of mixture strengths. Saturated hydrocarbons show no significant differences with respect to the rates of NO formation. However, a certain tendency was observed insofar as the maximum of the "prompt NO" shifts to lower mixture strengths with increasing number of C atoms, and that the maximum of about 50 ppm for methane increases to 70 ppm for i-octane. The "prompt NO" starts at \( \lambda = 0.75 \) for methane and at \( \lambda = 0.6 \) for the other fuels. No "prompt NO" is found for \( \lambda > 1.6 \), which is near the soot formation limit. For fuels in the order ethane, ethylene, acetylene the maximum of the "prompt NO" profile raises from 50 to 80 to 100 ppm, and the fuel rich limit of "prompt NO" shifts from about \( \lambda = 1.6 \) to \( \lambda = 2.1 \). The results found for the cyclic hydrocarbons, cyclohexane and benzene, are somewhat different: the maximum for cyclohexane is 75 ppm NO and the limits are at \( \lambda = 0.8 \) and \( \lambda = 1.9 \), whereas for benzene the limits lie near \( \lambda = 0.7 \) and \( \lambda = 1.6 \) with a maximum at 110 ppm NO. Gasoline shows a maximum of 90 ppm NO and limits at \( \lambda = 0.7 \) and \( \lambda = 1.7 \).

Figure 7 depicts the HCN profiles of three fuel rich propane-air flames. At the equivalence ratio \( \lambda = 1.1 \) HCN is found only in the main reaction zone with a maximum concentration of 0.5 ppm. At \( \lambda = 1.35 \) HCN increases to 10 ppm, but disappears further downstream completely. At \( \lambda = 1.5 \) HCN is formed in the post reaction zone, reaches a value three times larger than the NO concentration and remains nearly constant between 15 and 45 mm above the burner. The measured HCN profiles near the burner might be influenced by interactions between the flame and the quartz probe and perhaps by the sampling method as the pressure drop across the probe orifice was only about 100 torr for these measurements; however this may affect the absolute HCN level more than the observed relative behaviour at different mixture strengths.

4. DISCUSSION

For many combustion processes with air, NO is the only important nitrogen containing product and its formation can be explained sufficiently by considering only the Zeldovich mechanism. In certain cases, however, our results in accordance with those of Fenimore (1971) and Iverach et al. (1972) led to the conclusion that other reactions than reactions (I) and (II) have to be taken into account. For all flames, which exhibit a major production of NO in the flow behind the main reaction zone, it seems reasonable and possible to use a simplified model for the NO production and to compare this with measurements. Assuming constant temperature, constant mole fractions of \( \text{O}_2, \text{N}_2 \) and
equilibrium concentration of O atoms and finally NO ≪ NO(equilibr.), it is easy to show that with the two forward reactions

\[ O + N_2 \rightarrow NO + N \]
\[ N + O_2 \rightarrow NO + O \]

and a steady concentration of N atoms the rate of NO production can be written as:

\[ \frac{d[NO]}{dt} = \alpha \cdot k_1 \cdot [N_2] \cdot [O]_{equil}. \quad \alpha = 2 \]

FIG. 6. "Prompt NO" as a function of mixture strength and fuel. The dotted lines show the uncertainty of the extrapolation at the determination of "prompt NO" in propane flames; similar curves were obtained for the other hydrocarbons.

Obviously the factor \( \alpha \) depends on the assumptions made. If for example it is assumed that the N atoms would also recombine to \( N_2 \), \( \alpha \) would be smaller than 2. The assumptions made above apply to fuel lean flames in many cases and Figure 8 shows the NO formation calculated with the simple model and \( \alpha = 2 \) for a characteristic reaction time of 5 msec in the postflame gases of various adiabatic hydrocarbon-air flames at 1 atm. In the fuel rich regime \( \lambda > 1.1 \), where the application of the Zeldovich mechanism is limited, the curves have been dotted. In fact here the measured values are
much higher than the predicted ones. The calculation of the thermal equilibrium was based on the enthalpies given by the JANAF TABLES (1960) and the reaction enthalpies for hydrocarbons given by the tables of Rossini et al. (1953). The formation of nitrogen compounds and hydrocarbons has been neglected in these calculations. A rate constant $k_1 = 5 \cdot 10^{13} \exp(-75400/RT) \text{cm}^3/\text{mol} \cdot \text{sec}$ consistent with the measurements under fuel lean conditions has been used. The calculated amount of NO in Figure 8 is simply proportional to the reaction time and also to the preexponential factor of the rate constant. A meaningful application of these results on a real combustion system is only possible, if the validity of the assumptions made above has been proved in each case.

A rise of the temperature from 2200 to 2300 °K increases the rate constant by a factor 2.1 and the O atom concentration in fuel lean flames by a factor 2. Thus the rate of NO formation increases by a factor 4. A variation of the equivalence ratio by only 10 per cent in the fuel lean region may alter the rate of NO formation by one order of magnitude.

The measured NO concentrations can be compared with the calculated ones in those cases where a linear increase of NO concentrations with time was found. The "prompt NO" produced near the main reaction zone has to be subtracted from the total since this amount cannot be predicted by the model. Only those flames were evaluated for which it could be safely assumed that all mechanisms different from the Zeldovich mechanism are of negligible importance in the postflame zone. This was true at any rate for lean alkane flames, which have been evaluated with slightly corrected adiabatic flame temperatures due to heat losses. The averaged experimental rates of NO formation resulted in a rate constant $k_1 = 5 \cdot 10^{13} \exp(-75400/RT) \text{cm}^3/\text{mol} \cdot \text{sec}$. $1900 °K < T < 2250 °K$. The scatter of the data is within a factor 2. Up to an equivalence ratio of about 1.1, where the NO formation becomes too slow for evaluation, no systematic deviations from the computed results of Figure 8 have been found. Thus a preexponential factor of $5 \cdot 10^{13}$ may be adopted. This value is obviously smaller than the recommended value of...
Baulch et al. (1969) $k_1 = 1.36 \cdot 10^{14} \exp(-75400/RT) \text{cm}^3 \text{mol}^{-1} \text{sec}^{-1}$, but it agrees much better with the results obtained by Wray and Teare (1962) and other flame measurements. For evaluation of his experiments Fenimore (1971) used a temperature $T$ (inferred), which is equivalent to a preexponential factor of about $4 \cdot 10^{13}$. Livesey et al. (1971) derived from measurements in propane-oxygen flames a value of $4.6 \cdot 10^{13}$. An increase in accuracy of the measurements is feasible, but implies a considerable expense in the experimental set-up.

Figure 6 shows the amount of "prompt NO", which is formed in or near the main reaction zone of various adiabatic hydrocarbon-air flames. Of course this "prompt NO" may have different sources: (a) NO producing mechanisms, where reaction (I) is not the rate determining step, or (b) nonequilibrium concentrations of O atoms reacting via (I). It is known that in flames, especially at lower temperatures, the actual concentrations of radicals may in certain cases attain values some orders of magnitude above equilibrium (Bulewicz et al., 1956, Eberius et al., 1971, for example). According to the time, in which equilibrium is practically reached in the postflame gases, the excess concentration of O atoms contributes to the formation of "prompt NO". It has been shown recently that the super-equilibrium concentration of O atoms may explain the amount of "prompt NO" in shock-induced combustion of hydrogen-oxygen-nitrogen mixtures (Bowman, 1971) and in fuel lean and stoichiometric methane-air-flames (Sarofim and Pohl, 1972). But this hypothesis cannot explain the "prompt NO" in all flames in particular in very fuel rich hydrocarbon flames (Iverach et al., 1972). For example in the fuel rich propane-air flame ($\lambda = 1.41$) the NO concentration at 10 mm above the burner is 50 ppm and remains constant the following 40 mm in the postflame gases. To explain this NO formation by the reaction of O atoms with nitrogen about 0.2 per cent of atoms are needed along the first 10 mm with a sudden reduction at 10 mm height to a value at least 50 times smaller. This seems to be unreasonable and may give evidence that the NO may be formed in very fuel rich flames by others than the Zeldovich mechanism. These could be

$$
\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N} \\
\text{C}_2 + \text{N}_2 \rightarrow 2\text{CN}
$$

as suggested by Fenimore (1971), stressed by Iverach et al. (1972), and supported by the profiles of Figure 7, which show HCN as an intermediate species in moderate rich propane flames and as a rather stable product in the very rich flame. As the applied analytical methods are also sensitive to $\text{(CN)}_2$, at least in presence of water, it could not be precluded completely, that $\text{(CN)}_2$ was measured instead of HCN, but this would not alter the reasoning. Very probably the HCN or $\text{(CN)}_2$ found will react to NO, when air is admitted to the exhaust gases. It may be concluded, that, in lean flames, high O atom concentrations and, in very fuel rich flames, reactions as (IV) and (V) might be responsible for the "prompt NO". But a distinction of the different mechanisms for example at slightly rich flames seems impossible at present due to the lack of data.

In very fuel rich acetylene-air flames ($\lambda > 2.1$) NO formation shows a special behaviour. In these flames no "prompt NO" is observed, but a linear increase of the NO concentration with height above the burner is measured, as it is caused by the Zeldovich mechanism similar to that in lean flames. But it is unreasonable that the reaction of O atoms is responsible in this case for the NO formation. It has to be proved whether NO formation in these flames is due to a slow production of NO, similar to the "prompt NO" formation in fuel rich flames, or whether the NO was generated by a slow conversion to NO of rapidly formed nitrogen containing compounds which may have a rather high concentration. For example in an acetylene-air flame $\lambda = 2.3$ the HCN concentration was found to be 200 ppm at 25 mm above the burner. Further investigations are needed to resolve the mechanism of the NO formation in earlier and later states of the flame and to determine the influence of pressure and temperature as well as the influence of additives, for example inhibitors, which have a strong influence on the super-equilibrium concentrations of radicals in flames.

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