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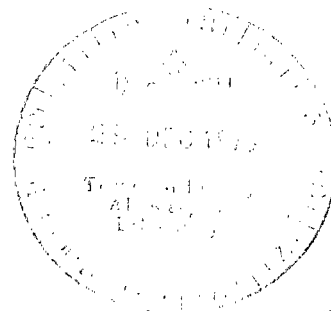
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ANALYTICAL STUDY OF MECHANISMS
FOR NITRIC OXIDE FORMATION
DURING COMBUSTION OF METHANE
IN A JET-STIRRED COMBUSTOR

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16. Abstract <p>The role of chemical kinetics in the formation of nitric oxide during the combustion of methane has been examined analytically by means of a detailed chemical mechanism for the oxidation of methane, for the reaction between hydrocarbon fragments, and for the formation of nitric oxide. By comparing predicted nitric oxide levels with values reported in the literature from jet-stirred combustor experiments, it was determined that the nitric oxide levels observed in fuel-rich flames cannot be described by a mechanism in which the rate of nitric oxide formation is controlled solely by the kinetics of oxygen atom formation. A proposed mechanism for the formation of nitric oxide in methane-rich flames reproduces the observed levels. The oxidation of HCN appears to be an important factor in nitric oxide formation.</p>		13. Type of Report and Period Covered Technical Note
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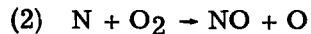
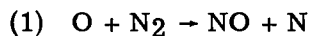
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SUMMARY

The role of chemical kinetics in the formation of nitric oxide during the combustion of methane has been examined analytically by means of a detailed chemical mechanism for the oxidation of methane, for the reaction between hydrocarbon fragments, and for the formation of nitric oxide. By comparing predicted nitric oxide levels with values reported in the literature from jet-stirred combustor experiments, it was determined that the nitric oxide levels observed in fuel-rich flames cannot be described by a mechanism in which the rate of nitric oxide formation is controlled solely by the kinetics of oxygen atom formation. A proposed mechanism for the formation of nitric oxide in methane-rich flames reproduces the observed levels. The oxidation of HCN appears to be an important factor in nitric oxide formation.

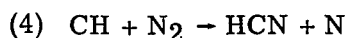
INTRODUCTION

Much attention has been paid recently to the development of analytical models that can predict quantitatively the amounts of nitric oxide emitted from combustion systems such as aircraft gas turbines. In most of these models, it is assumed that nitric oxide is formed primarily through the reactions



with the rate of nitric oxide formation being limited by the rate of reaction (1). The rate of reaction (1) is determined by the flame temperature and the level of oxygen atoms which, in turn, are determined by the kinetics of the fuel-oxygen reactions. This reaction scheme for nitric oxide formation is often called the Zeldovich mechanism.

In general, the current kinetic models are not able to adequately predict the observed nitric oxide levels, particularly for stoichiometric and fuel-rich hydrocarbon-air mixtures. For example, during an investigation of the formation of nitric oxide in hydrogen, carbon monoxide, and propane flames within a jet-stirred combustor, Engleman and co-workers (ref. 1) compared experimental nitric oxide concentrations with those predicted from a kinetic model of the appropriate system. Formation of nitric oxide in the nonhydrocarbon (H_2 and CO) systems was found to be adequately modeled at all equivalence ratios by reactions (1) to (3) and the appropriate fuel-oxygen kinetic reactions. However, the predicted levels in the propane flames greatly underestimated the observed concentrations (factors of 4 in fuel-lean and of 10 in fuel-rich flames). Similarly, Edleman and co-workers (ref. 2) compared experimental nitric oxide concentrations from methane-air flames in a jet-stirred combustor with those predicted from a kinetic model and found that the predicted levels underestimated the observed concentrations for stoichiometric and fuel-rich mixtures. It has been suggested (refs. 3, 4, and 5) that excess amounts ("superequilibrium") of oxygen atoms produced during the combustion of hydrocarbon fuels are responsible for the higher nitric oxide levels which are observed, and the current schemes do not adequately predict these oxygen atom levels. However, recent studies by Fenimore (ref. 6) and others (refs. 7 and 8) suggest that nitric oxide is produced by an additional reaction mechanism that only occurs in hydrocarbon-air flames. This nitric oxide is formed during the initial stages of the combustion reaction and is sometimes called "prompt" NO. It has been proposed that the reaction mechanism during early stages of combustion involves a hydrocarbon fragment which attacks molecular nitrogen, for example



Nitric oxide could then be produced by reaction (2) which is very fast compared with reaction (1).

The correct explanation for the discrepancy between predicted and observed nitric oxide levels in hydrocarbon flames is still a matter of controversy. However, it seems that a step toward resolving this controversy could be made if nitric oxide predictions are made by means of a hydrocarbon reaction model that reliably describes in a quantitative manner the combustion characteristics of the fuel, including the kinetics of oxygen atom formation. Comparison of these predictions with experimental data could then determine whether reactions (1) to (3) can adequately describe the nitric oxide formation process or whether an additional reaction mechanism must be used. Recently a study was made of the kinetics of oxygen atom formation during the oxidation of methane. (See ref. 9.) This

study resulted in a chemical kinetic scheme for methane oxidation which reasonably reproduced the reported combustion characteristics of methane-oxygen mixtures behind shock waves, including the kinetics of oxygen atom formation.

In this report the results of an analytical study of nitric oxide formation in methane-air flames within a jet-stirred combustor are presented. The purpose of the study was to compare predicted nitric oxide levels with experimental values by using the methane oxidation model reported in reference 9 coupled with reactions (1) to (3) and with a reaction mechanism which includes reaction (4).

SYMBOLS

H_i	enthalpy of species i , kJ/mol (kcal/mol)
ΔH_T	heat of reaction at temperature T , kJ/mol (kcal/mol)
k	rate coefficient, $\text{cm}^3/\text{mol}\cdot\text{sec}$ for bimolecular reactions, $\text{cm}^6/\text{mol}^2\cdot\text{sec}$ for termolecular reactions
\dot{m}	mass flow rate, g/sec
N	total number of species
p	pressure, atm (1 atm = 101.3 kPa)
Q	net heat loss from reactor, kilojoules (kilocalories) per gram of mixture
T	absolute temperature, K
V	reactor volume, cm^3
W_i	net rate of formation of species i , $\text{mol}/\text{cm}^2\cdot\text{sec}$
σ_i	concentration, moles of species i per gram of mixture
ϕ	equivalence ratio, $\frac{\text{Fuel-air ratio}}{\text{Stoichiometric fuel-air ratio}}$
$[\text{NO}], [\text{HCN}]$	concentration of nitric oxide and hydrogen cyanide, respectively, ppm

METHANE-AIR CHEMICAL KINETIC MODEL

The chemical kinetic reaction model and the rate coefficients used in this study are listed in table I. The rate coefficients selected for these reactions were obtained from the literature whenever possible. (See refs. 9 to 25.) Rate coefficients that could not be found in the literature were estimated. Reactions (1) to (3) describe the formation of nitric oxide, and reaction (4) describes the formation of atomic nitrogen as suggested by Fenimore in reference 6. The rate coefficient for reaction (4) was estimated by using Hirschfelder's rule (ref. 26) to determine the activation energy. A preexponential factor of 10^{13} cm³/mol-sec, common to most radical-molecule reactions, was selected for reaction (4). Reactions (5) to (23) describe the oxidation of methane. These reactions and rate coefficients provide a quantitative description of the kinetics of oxygen atom formation and the ignition characteristics of methane-oxygen mixtures. Further details on this reaction scheme are given in reference 9.

Reactions (25) to (30) describe the formation of the hydrocarbon fragments CH₂ and CH by the systematic removal of hydrogen atoms by the radicals H, O, and OH. The rate coefficients for reactions (25) to (27) were estimated by using activation energies reported for similar reactions (reactions (6) to (8)) and preexponential factors that are smaller by a factor of about 10. These preexponential factors were chosen so that the rate of these reactions would not be larger than the rate of reaction (10) which together with reaction (9) is considered to be the primary process responsible for the destruction of methyl radicals. (See ref. 9.) Reactions (31) to (33) describe the destruction of the hydrocarbon fragments CH₂ and CH by reaction with molecular oxygen. Reaction (33) is very exothermic ($\Delta H_{2000\text{ K}} = -356$ kJ/mol (-85 kcal/mol)); therefore the activation energy was assumed to be zero. Since reaction (33) is similar to reaction (4), the same preexponential factor was chosen. Other reactions involving hydrocarbon fragments and molecular nitrogen are possible (ref. 27); however, they are highly endothermic and therefore would not be expected to be important compared with reaction (4).

JET-STIRRED COMBUSTOR MODEL

An ideal jet-stirred combustor consists of a combustion chamber with a well-defined volume into which the fuel-air mixture enters and instantaneously mixes with the reactor contents at a constant pressure. The mixture of reactants and products flows out continuously in a manner which results in a steady-state operation. In steady-state operation the species concentration within the reacting volume (combustion chamber) is determined from the balance between the net rate of production (or consumption) of each species by chemical reaction and the difference between the input and output flow rates of the species. This type of combustor is called a perfectly stirred reactor. A perfectly stirred reactor

is treated mathematically by formulating the equations for mass, species, and energy conservation as described by Jones and Prothero (ref. 28) in solving a system of simultaneous nonlinear algebraic equations.

Briefly, the conservation equations for a perfectly stirred reactor are formulated in the following manner. Consider a stirred reactor of volume V containing combustion gases at a pressure p and a uniform temperature T . For steady-state operation, conservation of mass is given by

$$\dot{m}^* = \dot{m}$$

where \dot{m}^* is the mass flow rate into the reactor and \dot{m} is the mass flow rate out of the reactor. The superscript $*$ always refers to incoming reactants. Conservation of species is given by

$$\frac{\dot{m}}{V}(\sigma_i - \sigma_i^*) = W_i \quad (i = 1, 2, 3, \dots, N)$$

where σ_i^* and σ_i are the input and output concentrations of species i , N is the total number of species, and W_i is the rate of formation of species i per unit volume because of chemical reactions. Conservation of energy is given by

$$\sum_{i=1}^N \sigma_i^* H_i^* - \sum_{i=1}^N \sigma_i H_i = Q$$

where H_i is the enthalpy of species i and Q is the heat loss from the reactor per unit mass because of radiation, thermal diffusion, and convection. For adiabatic operation, of course, Q is zero.

The stirred-reactor calculations presented in this report were made with a computer program described in reference 29. These calculations simulated the experiments made by Bartok and co-workers (ref. 30), who carried out experiments in a Longwell-Weiss jet-stirred combustor for fuel-lean, stoichiometric, and fuel-rich methane-air mixtures. Inlet temperature for these experiments was 463 K and reaction pressure was 1 atm. The nitric oxide data selected for comparison were from experiments with residence times of 2.3 msec. These data were selected because the residence times were short enough to increase chances that the reactor was nearly perfectly stirred, and also because a wide range of inlet equivalence ratio was used. Nitric oxide data were also reported for 1.8-msec residence times; however, the equivalence-ratio range was not as wide as the 2.3-msec data.

DISCUSSION OF RESULTS

The results presented in figure 1 are a comparison between the two processes describing nitric oxide formation. When the principal methane oxidation mechanism, reactions (5) to (24), is coupled with reactions (1) to (3), the calculated nitric oxide levels are in good agreement with the fuel-lean data only. For fuel-rich conditions, the predicted levels are up to a factor of 10 lower than the observed levels. Parametric studies with the methane oxidation scheme revealed that reactions (5), (9), and (10) had a large influence on the predicted oxygen atom levels, particularly the peak oxygen atom levels. (See ref. 9.) An attempt was made to adjust some of the rate coefficients for these reactions to provide better agreement between experimental and calculated results for the fuel-rich regime. However, a set of rate coefficients could not be found that would substantially increase the oxygen atom levels. It seems that some other chemical path is required for fuel-rich conditions.

When reaction (4) and reactions (25) to (33) are added to the principal methane oxidation scheme, the predicted nitric oxide levels are brought into fair agreement with the data, as shown in figure 1. However, the predicted nitric oxide levels are still smaller

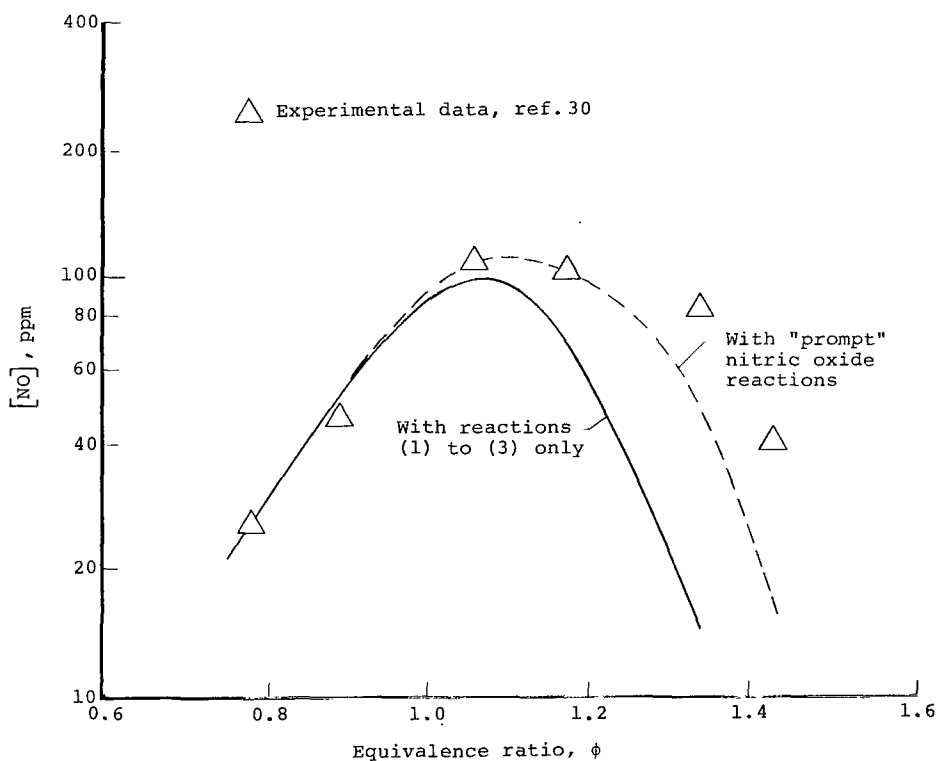


Figure 1.- Calculated and experimental nitric oxide levels for methane-air mixtures.
 $T_{\text{initial}} = 463 \text{ K}$; $p = 1 \text{ atm}$.

by a factor of about 2 for $\phi = 1.4$. The addition of these reactions did not substantially change the nitric oxide levels for the fuel-lean and near stoichiometric regime because the rates of reactions (31) to (33) are sufficiently fast to prevent the buildup of the CH_2 and CH hydrocarbon fragments, and thus the rate of nitrogen atom production by reaction (4) is reduced. An attempt was made to adjust the rate coefficients for the fragment-forming reactions and the fragment-consuming reactions to provide better agreement between the experimental and calculated nitric oxide levels. However, a set of rate coefficients could not be found that would significantly increase nitric oxide levels for the very fuel-rich regime ($\phi \approx 1.4$) without overpredicting the nitric oxide levels in the near stoichiometric region. For example, by decreasing the rate coefficient for the fragment-consuming reaction by a factor of 10, there is better agreement between experiment and prediction at $\phi \approx 1.4$; but at $\phi = 1.1$, the predicted value is about 50 percent larger than the measured level. This comparison is given in figure 2. It appears that the kinetic model presented in table I is not complete and other sources of nitric oxide must be found.

An additional source of nitric oxide could be the hydrogen cyanide, HCN , that is produced in reaction (4). The kinetic model in table I does not provide any path by which

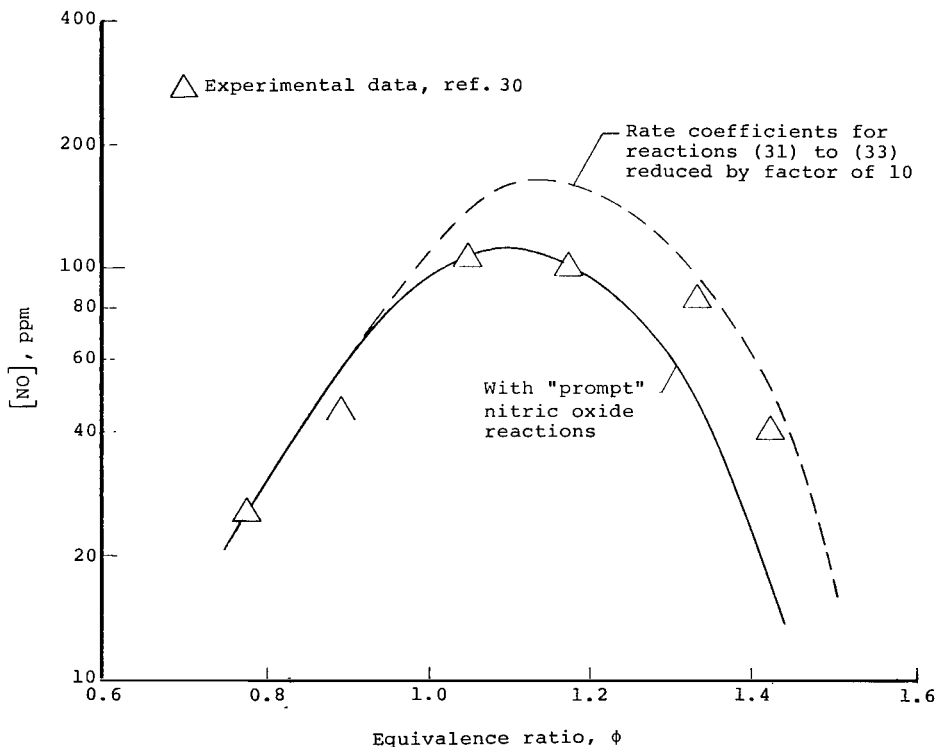
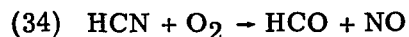


Figure 2.- Experimental and calculated nitric oxide levels using "prompt" NO reactions in table I and "prompt" NO reactions with adjusted rate coefficients for reactions (31) to (33).

HCN can be consumed and permits the HCN to accumulate. The accumulated HCN levels can be substantial and approach the nitric oxide levels as shown in figure 3. It is likely that significant amounts of HCN can be oxidized to nitric oxide, particularly in a stirred combustor where products are continually being mixed with fresh reactants. If it is assumed that all the HCN can be oxidized to nitric oxide, the predicted nitric oxide levels are in excellent agreement with the observed nitric oxide levels, as shown in figure 4. The conversion of hydrogen cyanide to nitric oxide could take place directly through a reaction such as



which is exothermic ($\Delta H_{2000 \text{ K}} = -63 \text{ kJ/mol}$ (-15 kcal/mol)) or through an indirect process leading to the formation of CN which then reacts directly with molecular oxygen by the very exothermic reaction ($\Delta H_{2000 \text{ K}} = -477 \text{ kJ/mol}$ (-114 kcal/mol))

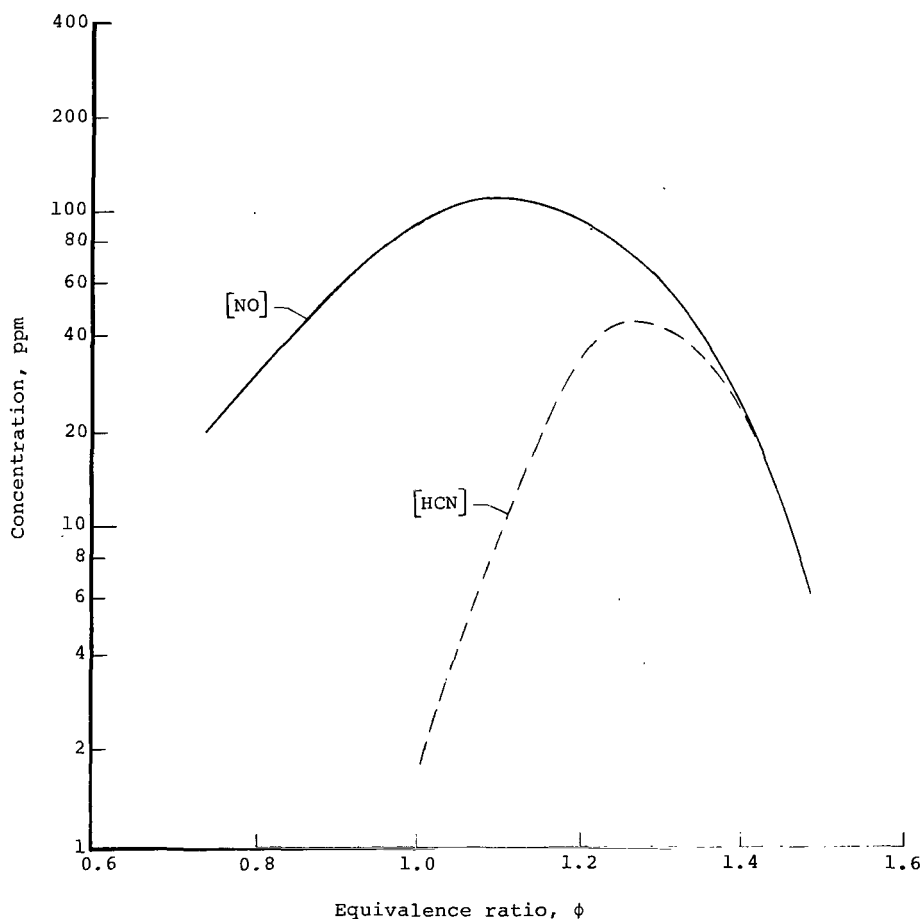
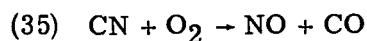


Figure 3.- Calculated NO and HCN levels for methane-air mixtures.

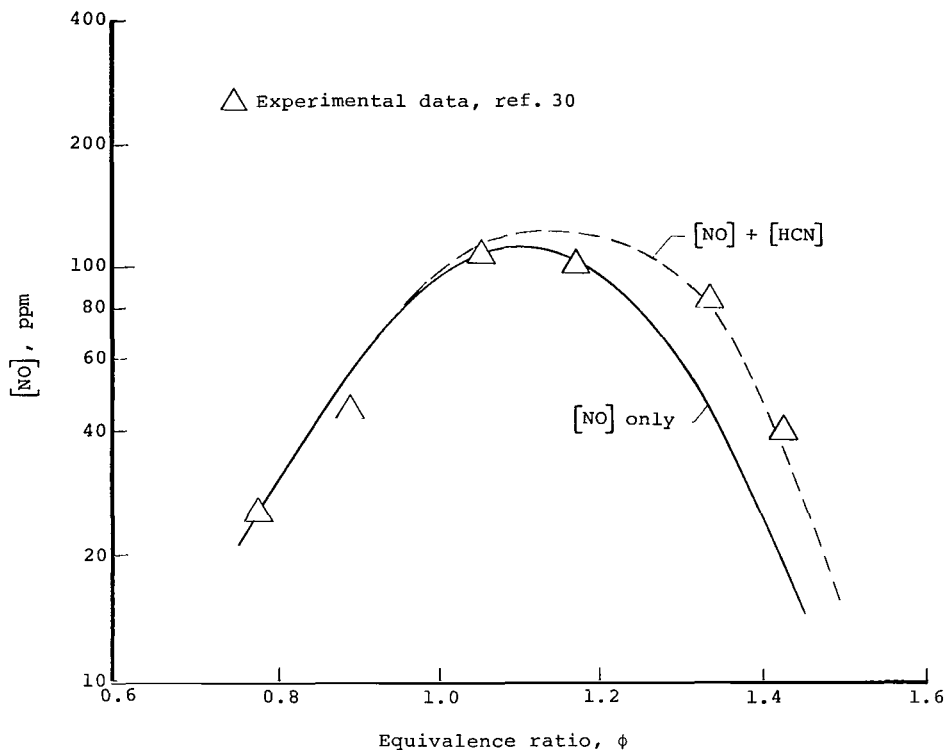
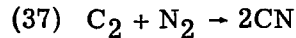
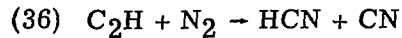


Figure 4.- Calculated NO and NO + HCN levels for methane-air mixtures.

It is not claimed that the reaction mechanism presented for nitric oxide formation is unique or corresponds to reality. However, some reaction process other than the direct formation of nitric oxide by reaction (1) appears necessary for fuel-rich conditions. The hypothesized kinetic mechanism contains reactions that probably do occur to some extent, and the ability of this set of reactions to reasonably reproduce the experimental observations requires that the assigned rate coefficients be reasonably correct. Nonetheless, experimental verification of the individual rate coefficients is still required. Also more information is required on the kinetics of HCN and CN oxidation. Hydrogen cyanide has been observed in hydrocarbon-air flames as an intermediate species and can exceed the nitric oxide levels in very fuel-rich flames. (See ref. 1.) Comparison of predicted HCN levels with levels measured in various stirred-reactor experiments with fuel-rich methane-air mixtures could provide a means to verify the reaction scheme proposed in this report. Other hydrocarbon-air mixtures should also be studied to determine whether other reactions can contribute to nitric oxide formation in fuel-rich mixtures. Different reactions may become important because the chemical structure of the fuel is different. For example, combustion of unsaturated hydrocarbons like ethylene, acetylene, and aromatics could result in larger HCN levels from reactions such as



As other sources of hydrocarbons, such as shale oil and various coal syncrudes, begin to be used in the production of hydrocarbon fuels, including jet fuels, the chemical composition of available fuels will vary even more. Any attempt to reliably predict nitric oxide levels as a function of chemical composition will require a greater understanding of the effect of fuel structure on nitric oxide production, particularly in fuel-rich mixtures.

CONCLUDING REMARKS

The purpose of this study was to examine the role of chemical kinetics in the formation of nitric oxide during the combustion of methane in a jet-stirred combustor. The results of the study revealed that nitric oxide formation in fuel-lean methane-air mixtures can be explained by a kinetic model in which the rate of nitric oxide formation is controlled by the kinetics of oxygen atom formation. However, for fuel-rich combustion another path for nitric oxide formation appears to be required. Fuel-rich predictions can be brought into fair agreement with the observed nitric oxide levels by assuming a reaction sequence that produces nitrogen atoms through a reaction between the hydrocarbon fragment CH and molecular nitrogen. Better agreement was obtained if the intermediate HCN was allowed to react completely to nitric oxide. The proposed reaction scheme is not necessarily unique, and therefore, further experimental studies, such as measurement of HCN levels in a jet-stirred combustor, should be made to verify the kinetic scheme. Also, studies of the kinetics of HCN oxidation are needed to determine the mechanism of HCN consumption. Studies of NO and HCN formation in hydrocarbons other than methane are also recommended to help determine whether other reaction paths can also lead to nitric oxide formation.

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October 23, 1975

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TABLE I.- METHANE-AIR CHEMICAL KINETIC MODEL

Reaction	Rate coefficient, k (a)	Ref.
(1) $O + N_2 \rightarrow NO + N$	$1.36 \times 10^{14} \exp(-37946/T)$	10
(2) $N + O_2 \rightarrow NO + O$	$6.40 \times 10^9 T \exp(-3145/T)$	10
(3) $N + OH \rightarrow NO + H$	4.00×10^{13}	11
(4) $CH + N_2 \rightarrow HCN + N$	$1.00 \times 10^{13} \exp(-8052/T)$	Estimate
(5) $CH_4 + M \rightarrow CH_3 + H + M$	$4.00 \times 10^{17} \exp(-44500/T)$	9
(6) $H + CH_4 \rightarrow CH_3 + H_2$	$1.26 \times 10^{14} \exp(-5989/T)$	12
(7) $OH + CH_4 \rightarrow CH_3 + H_2O$	$3.00 \times 10^{13} \exp(-3020/T)$	13
(8) $O + CH_4 \rightarrow CH_3 + OH$	$2.00 \times 10^{13} \exp(-4630/T)$	14
(9) $CH_3 + O_2 \rightarrow CH_2O + OH$	$1.70 \times 10^{12} \exp(-745/T)$	9
(10) $CH_3 + O \rightarrow CH_2O + H$	$1.3 \times 10^{14} \exp(-1006/T)$	13
(11) $OH + CH_2O \rightarrow HCO + H_2O$	2.30×10^{13}	13
(12) $OH + HCO \rightarrow CO + H_2O$	1.00×10^{13}	9
(13) $HCO + M \rightarrow H + CO + M$	$2.00 \times 10^{12} T^{0.5} \exp(-14400/T)$	15
(14) $OH + CO \rightarrow CO_2 + H$	$4.00 \times 10^{12} \exp(-4026/T)$	16
(15) $CO + O_2 \rightarrow CO_2 + O$	$1.60 \times 10^{13} \exp(-20634/T)$	17
(16) $O + H_2 \rightarrow OH + H$	$2.07 \times 10^{14} \exp(-6920/T)$	18
(17) $OH + H_2 \rightarrow H_2O + H$	$5.2 \times 10^{13} \exp(-3271/T)$	16
(18) $H + O_2 \rightarrow OH + O$	$1.22 \times 10^{17} T^{-0.907} \exp(-8369/T)$	18
(19) $OH + OH \rightarrow H_2O + O$	$5.5 \times 10^{13} \exp(-3523/T)$	16
(20) $H + H + M \rightarrow H_2 + M$	1.00×10^{15}	19
(21) $H + OH + M \rightarrow H_2O + M$	$8.4 \times 10^{21} T^{-20}$	20
(22) $CO + O + M \rightarrow CO_2 + M$	6.0×10^{13}	21
(23) $O_2 + M \rightarrow O + O + M$	$1.32 \times 10^{21} T^{-1.7} \exp(-59400/T)$	22
(24) $N_2 + M \rightarrow N + N + M$	$4.98 \times 10^{18} T^{-0.75} \exp(-113200/T)$	22
(25) $H + CH_3 \rightarrow CH_2 + H_2$	$1.00 \times 10^{13} \exp(-6039/T)$	Estimate
(26) $O + CH_3 \rightarrow CH_2 + OH$	$1.00 \times 10^{12} \exp(-5032/T)$	Estimate
(27) $OH + CH_3 \rightarrow CH_2 + H_2O$	$1.00 \times 10^{12} \exp(-3020/T)$	Estimate
(28) $H + CH_2 \rightarrow CH + H_2$	$2.7 \times 10^{11} T^{0.67} \exp(-12934/T)$	23
(29) $O + CH_2 \rightarrow CH + OH$	$1.9 \times 10^{11} T^{0.68} \exp(-12934/T)$	23
(30) $OH + CH_2 \rightarrow CH + H_2O$	Obtained from $k_{30} = k_{28}$	24
(31) $O_2 + CH_2 \rightarrow HCO + OH$	$1.0 \times 10^{14} \exp(-1862/T)$	25
(32) $O_2 + CH \rightarrow CO + OH$	Obtained from $k_{32} = 0.4k_{28}$	24
(33) $O_2 + CH \rightarrow HCO + O$	1.00×10^{13}	Estimate

^aThe units for k are $\text{cm}^3/\text{mol}\cdot\text{sec}$ for bimolecular reactions and $\text{cm}^6/\text{mol}^2\cdot\text{sec}$ for termolecular reactions. Activation energies are expressed in kelvins. Subscripts to k correspond to reaction numbers.



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