

Nitric Oxide Formation in Combustion

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A review of the current understanding of nitric oxide production in hydrocarbon/air and hydrogen/air combustion processes shows that the extended Zeldovich mechanism yields accurate nitric oxide predictions for fuel/air equivalence ratios from zero to infinity for hydrogen combustion and from zero to about 1.5 for hydrocarbon combustion. The theory cannot predict the fuel-rich hydrocarbon results because important, yet to be discovered reactions or reaction mechanisms are missing. The oxygen atom concentration exerts considerable influence on the nitric oxide production rate. It should be calculated by using a partial equilibrium assumption of the H_2-O_2-CO reactions: $H+O_2 \rightleftharpoons OH+O$, $O+H_2 \rightleftharpoons OH+H$, $H_2+OH \rightleftharpoons H_2O+H$, and $CO+OH \rightleftharpoons CO_2+H$. The nitric oxide emission predictions, when compared to experimental measurements, verify the theoretical analysis.

Introduction

THE following review is restricted to nitric oxide production in gas-fired combustion systems in which hydrogen-air and hydrocarbon-air processes are used. The basic chemical kinetics for these systems are similar to those that exist around a burning fuel droplet; however, because the detailed conclusions would be very different such cases are excluded from the review.

In order to take full advantage of the naturally clean nature of gaseous fuels, it will be necessary to understand the nitric oxide formation mechanism in gas-fired combustion systems. Because of the availability of coal in the United States, the use of coal-fired powerplants is currently increasing; however, coal gasification technology will develop rapidly in the future, and gas generated from coal will become a major source of energy.

In a wide variety of industrial combustion processes in which nitric oxides are produced, fuel and air are injected separately, mixed, and burned. Sometimes the fuel and air are premixed before being injected into the combustion chamber. In either case, the fuel-air reactions are usually rapid, and the active reaction volume of the flame is small compared to the visible volume of the flame. The reactions that produce nitric oxide are slow compared to the combustion reactions and occur over the entire flame volume. The fuel-air combustion usually is controlled by turbulent mixing, but the nitric oxide production rate is regulated by its chemical rate. In other words, the fuel and air react instantaneously as soon as the mixing process brings them together. In the nitric oxide production chemistry, the turbulent mixing process supplies the chemical kinetics with sufficient concentrations of reactants; however, the production rate also depends strongly on the local temperature.

The chemical kinetics of nitric oxide are very sensitive to temperature; high temperatures yield high nitric oxide production rates. Thus the nitric oxide production is coupled to the turbulence in the flowfield through the temperature fluctuations.¹ This implies that the past history of the flow influences the nitric oxide production rate at a given position in the flow. This coupling to the flowfield has made accurate

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predictions of nitric oxide concentration levels in real combustion systems difficult.

Turbulent flames serve as the operational basis for many combustion devices, such as domestic furnaces, oil and gas fired boilers, diesel engines, and gas turbine combustors. Practical advances in emission reduction have been made in these applications; however, the prediction of nitric oxide formation in multidimensional turbulent flow is not very accurate, because the turbulent temperature fluctuations significantly affect the formation rates.

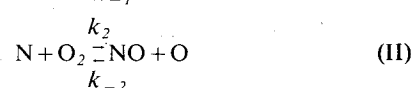
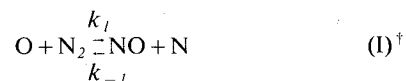
The chemical kinetics of nitric oxide formation in combustion processes has been extensively studied.²⁻⁹ Most of the studies involve either an over-simplification of the kinetics or an unnecessarily complex system of chemical reactions. In either case, the important aspects of the situation are obscured. It now appears that the essential features of the chemical kinetics required to predict nitric oxide production in combustion processes are reasonably well-known. Therefore, it is worthwhile to summarize the nitric oxide kinetics in a compact and useful form, while at the same time pointing out the limitations involved in the analysis.

Currently, there exists no complete model for the complex turbulent-reacting flow that occurs in most combustion systems. All of the currently accepted models involve empirical relationships for turbulent mixing and its influence on the chemical kinetics. These models have a practical value, but care must be taken not to be misled by fortuitous agreements between theory and experiment.

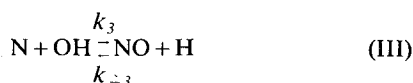
Most of the research on the kinetics of nitric oxide formation has been conducted in situations where the chemistry is uncoupled from the effects of fluid dynamics and turbulence. This is perfectly acceptable when determining rate constants, but it is not an acceptable approach to the accurate prediction of nitric-oxide emissions from combustion systems. In these systems, the kinetics and flowfield are coupled!

Kinetics

The extended Zeldovich mechanism generally is accepted as the method by which nitric oxide is formed in combustion processes; e.g., following the paper by Westenberg,³



[†]Throughout this paper reactions will be numbered with Roman numerals, in parentheses, on the right-hand side.



The Zeldovich reactions give the general rate for the NO production as

$$\begin{aligned} d(\text{NO})/dt = & k_1(\text{O})(\text{N}_2) - k_{-1}(\text{N})(\text{NO}) \\ & + k_2(\text{N})(\text{O}_2) - k_{-2}(\text{O})(\text{NO}) + k_3(\text{N})(\text{OH}) - k_{-3}(\text{H})(\text{NO}) \end{aligned} \quad (1)$$

The assumption of the steady-state approximation for the concentration of N is a standard procedure in treating a complex reacting mixture when the species is present in very small amounts as compared to the remaining species, and is true for the temperature of interest in ordinary combustion. This yields

$$(\text{N})_{ss} = \frac{(\text{O})\{k_1(\text{N}_2) + k_{-2}(\text{NO})\} + k_{-3}(\text{H})(\text{NO})}{k_{-1}(\text{NO}) + k_2(\text{O}_2) + k_3(\text{OH})} \quad (2)$$

By combining Eq. (2) with Eq. (1), one obtains the nitric-oxide formation rate,³

$$\frac{d(\text{NO})}{dt} = \frac{2k_1(\text{N}_2)(\text{O})}{1+A} - \frac{2A(\text{NO})}{1+A} \{k_{-2}(\text{O}) + k_{-3}(\text{H})\} \quad (3)$$

in which

$$A = k_{-1}(\text{NO}) / [k_2(\text{O}_2) + k_3(\text{OH})] \quad (4)$$

Equations (3) and (4) show that the formation of NO is influenced by N_2 , O_2 , O, H, OH, and NO. Usually A is much less than unity, because $(\text{NO})_{ss}$ is small; therefore;

$$d(\text{NO})/dt \approx 2k_1(\text{N}_2)(\text{O}) \quad (5)$$

and the (NO) is directly proportional to the atomic oxygen concentration. The simplified rate, as given by Eq. (5), has been used widely to predict (NO) , especially when NO is far from equilibrium.

In the past, it has been acceptable to assume that the NO formation rate is slow as compared to the combustion kinetics, so that the onset of NO production occurs in the secondary combustion zone after the combustion products have reached their equilibrium values. It also was standard to take (O) as its value in equilibrium with (O_2) . However, agreement with experiment was not good, even in constant temperature situations, such as reflected shocks and stirred reactors.

Fenimore¹⁰ was the first to report the finding of NO in the combustion or primary region of premixed flames. He found concentrations in quantities up to the equilibrium values of NO. This "prompt NO" implied production rates that greatly exceeded those given by the Zeldovich relations with equilibrium atomic oxygen. Fenimore,¹⁰ along with Iverach et al.,¹¹ attributed the high-formation rate of NO to an attack of carbon or hydrocarbon radicals on nitrogen molecules, i.e.,



because "prompt NO" did not appear for fuel-lean hydrocarbon flames or in H_2 or CO flames.

Bowman¹² states, on the basis of methane/air shock-tube (constant temperature) data, that the extended Zeldovich reactions give the correct rates of formation in both the primary and secondary zones of flames if the (O) and (OH) are evaluated "correctly" (nonequilibrium chemistry). His experimental results show that the initial NO formation rate is

greater than it is at later times, and that NO in fuel-rich flames reaches equilibrium much faster than in fuel-lean flames.

Bowman used the extended Zeldovich mechanism for the theoretical NO formation rate, along with a methane-combustion scheme of 14 reactions. His analysis adequately predicts NO formation in lean to moderately rich methane-air mixtures behind reflected shock waves, provided that the radical concentrations and the temperature are "correctly evaluated." Because reflected shocks produce a constant temperature test volume, his NO chemistry proceeds isothermally. In addition, the shock temperatures (2900K) are high and favor the Zeldovich mechanism. Because of this difference between flames and reflected shock waves, there is a great need for detailed measurement of stable and unstable species in the combustion zone of flames, as opposed to measurements in a shock tube.

Sarofim and Pohl¹³ point out that oxidizing organic bound nitrogen, such as that found in HCN, is not limited by the $\text{N}_2 - \text{O}_2$ reaction scheme equilibrium constraint. Because Fenimore's data appear to be limited by this constraint, they feel Reaction (IV) is not the cause of "prompt NO." They believe that the combustion intermediates, O, OH, and H, and especially O, are not in equilibrium, and thus influence the NO-production rate. Sarofim and Pohl suggest using partial equilibrium of the $\text{H}_2 - \text{O}_2 - \text{CO}$ reactions to predict (O) and (OH) :



This essentially yields the maximum radical concentrations, because these reactions are assumed to equilibrate prior to removal of the radicals by the slow three-body reactions. Thus, one has

$$(\text{O}) = K_5 K_8 (\text{O}_2)(\text{CO}) / (\text{CO}_2) \quad (6)$$

$$(\text{OH}) = \{ [K_5 K_6 K_8 / K_7] [(\text{O}_2)(\text{CO})(\text{H}_2\text{O}) / (\text{CO}_2)] \}^{1/2} \quad (7)$$

$$(\text{H}) = \{ K_8 (\text{CO}) / (\text{CO}_2) \}^{3/2} \{ (K_5 K_6 / K_7) (\text{O}_2) (\text{H}_2\text{O}) \}^{1/2} \quad (8)$$

in which the equilibrium constant for reaction j is K_j . The substitution of Eqs. (6-8) into Eq. (5), or Eqs. (3) and (4), allows one to calculate (NO) at a given temperature and given major product species concentrations. Comparison of their experimental and theoretical results, as shown in Fig. 1, demonstrates that the Zeldovich mechanism, in which (O) from Eq. (6) is used, yields acceptable agreement with the experiments. The total amount of NO generated prior to the onset of equilibrium in the postflame gases (primary zone, "prompt NO") follows the behavior observed by Fenimore.

Sarofim and Pohl postulate that the "prompt NO" can be explained by the Zeldovich mechanism and that hydrocarbon species are not directly involved in the mechanism of NO production—at least for equivalence ratios less than 1.15. However, this results in a conflict, because these results do not explain why "prompt NO" was observed only by Fenimore in flames that contained hydrocarbons, and that the maximum "prompt NO" occurred at equivalence ratios of about 1.4.

Englman et al.¹⁴ used a jet-stirred reactor to investigate the formation of nitric oxide in H_2 , CO, and propane-air flames. Their experimental data, when compared to theoretical predicted NO concentrations using the Zeldovich mechanism, as modified to "correctly calculate (O) ," are in good agreement for the H_2 and CO flames; however, the theory predicts very low values (factor of 4 in fuel-lean to factor of

†Parentetical chemical notations, such as (N) , (NO) , and (O) , indicate concentrations.

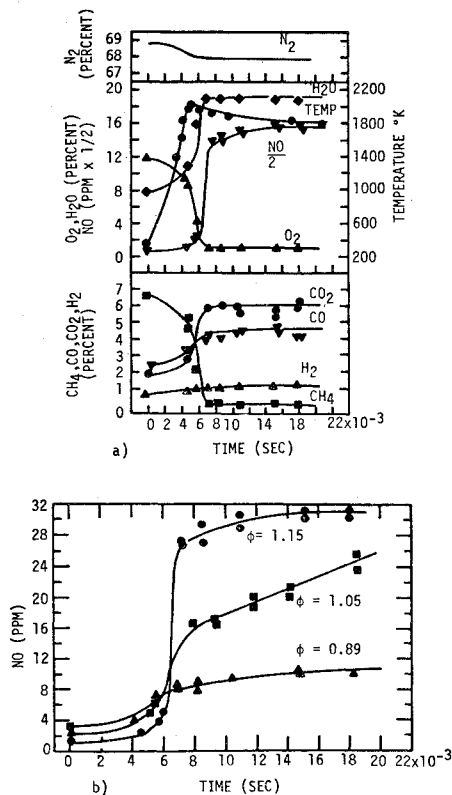


Fig. 1 Concentration, temperature, and nitric oxide profiles in laminar methane/air flames.¹³ Burner diameter = 2.5 cm, flow rate = 3500 cm³/min.: a) temperature and concentration for fuel/air equivalence ratio of 1.15, b) nitric oxide profiles for fuel/air equivalence ratios of 0.89, 1.05 and 1.15.

10 in fuel-rich) for propane flames. They modeled the propane combustion as a one-step global reaction to CO and H₂, and then used the CO-H₂ reaction mechanism to complete the combustion (eight reactions for H₂-air, three for CO-air). Seemingly, the global-propane reaction is in error. Figure 2 shows a comparison of predictions and experiment for temperature and (NO) for jet-stirred reactor burning of three gases: hydrogen, carbon monoxide, and propane.¹⁴ The figure clearly shows that the hydrocarbon predictions are very poor. The hydrocarbon predictions could be improved by a "proper" treatment of the oxygen-atom production mechanisms, as discussed previously.

Takagi et al.¹⁵ experimentally found, in agreement with Sarofim and Pohl¹³ and Iverach et al.,¹⁶ that the extended Zeldovich mechanism predicts reasonable values for NO concentration in hydrogen-air turbulent-diffusion flames if the oxygen-atom concentration is calculated by the partial equilibrium of the rapid reactions V and VII. However, better agreement was obtained when a 35-step kinetic mechanism was used for the H₂-O₂-N₂ system to predict (O). For propane-air flames, the extended Zeldovich mechanism failed to predict accurate results, either as a result of the high temperature required or as the result of the extremely large oxygen-atom overshoot that was required.

Iverach et al.¹¹ experimentally and theoretically showed that the Zeldovich mechanism predicts the concentrations of nitric oxide downstream from flat premixed lean-to-moderately fuel-rich ($\Phi < 1.15$) hydrocarbon flames in air if the oxygen-atom concentration is calculated carefully. They used a partial equilibrium composed of Reactions (V) and (VIII) to calculate (O), (OH), and (H). In addition, they obtained agreement between experiment and theory for all nonhydrocarbon flames.

Iverach et al.¹⁶ point out a questionable premise regarding the time-distance relationship in Fenimore's work. Fenimore

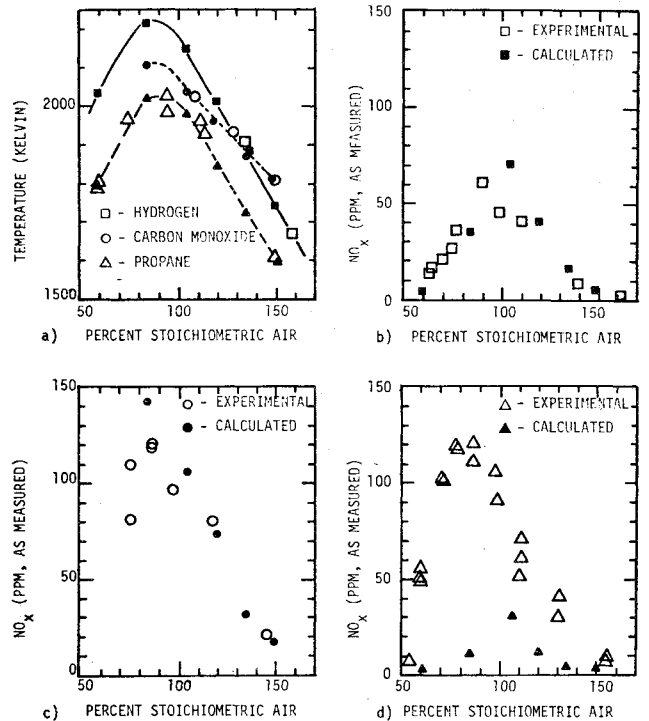


Fig. 2 Comparison of jet-stirred reactor experiment and theory - temperature and nitric oxide emission as a function of percent stoichiometric air¹⁴: a) temperature, b) hydrogen/air combustion, c) carbon monoxide/air combustion, d) propane/air combustion.

assumed that the tips of the flamelets on the Meker-type flat-flame burner corresponded to the flame front (the end of the primary flame zone). Because these flamelets are conical in shape, the true average position of the flame front is likely to be much closer to the base of the flamelets than to the tip; consequently, an error of as much as 5 msec may occur in the calculation of the residence time at any point in the postflame gas. This error is especially significant when it is close to the flame tip, where the rate of nitric-oxide production may be overestimated as a result of an underestimation of the dwell time.

In addition, Fenimore assumed that the oxygen atoms were in equilibrium with the oxygen molecules; however, the excess oxygen-atom concentrations, which are obtained by using the partial-equilibrium process discussed in the preceding (or a finite-rate process), lead to significant curvature of the nitric-oxide profile near the reaction zone. This accounts at least in part for the "intercept NO," which he observed. Whether or not this can explain fully the "prompt NO" is a matter of current controversy, and evaluation of the extended Zeldovich mechanism has become a matter of identifying the role of the nonequilibrium oxygen-atom concentration.

Further, shock-tube studies of the formation of nitric oxide favor the extended Zeldovich mechanism, because it is strongly temperature-dependent. Thus, at the high temperatures that are obtained in shock-tube experiments, the extended Zeldovich mechanism may mask completely any other nitric-oxide formation mechanism. The maximum temperature in a flame is approximately 2000K, whereas in shock-tube experiments, the test temperature is about 3000 K.¹²

Iverach et al.¹⁶ found that for rich hydrocarbon-air combustion the extended Zeldovich mechanism alone cannot model nitric-oxide kinetics. They suggested that nitrogen atoms can be produced by Reaction (IV) and



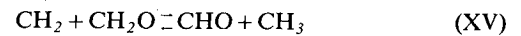
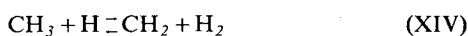
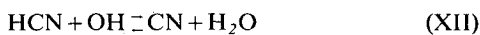
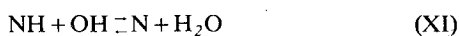
to feed the extended Zeldovich mechanism.

Table 1 Reaction rates

		k_f			Reference	
		A	n	B		
I	$O + N_2 \rightleftharpoons NO + N$	18	$X 10^{13}$	0	75.4	17
II	$N + O_2 \rightleftharpoons NO + O$	6.4	$X 10^9$	1	6.3	17
III	$N + OH \rightleftharpoons NO + H$	4.0	$X 10^{13}$	0	0	12
IV	$CH + N_2 \rightleftharpoons HCN + N$					
V	$OH + O \rightleftharpoons H + O_2$	2.5	$X 10^{13}$	0	0	17
VI	$OH + H \rightleftharpoons O + H_2$	8.0	$X 10^9$	1	7.0	17
VII	$H_2O + H \rightleftharpoons H_2 + OH$	2.5	$X 10^{13}$	0	5.2	17
VIII	$CO + OH \rightleftharpoons CO_2 + H$	5.6	$X 10^{11}$	0	1.08	17
IX	$C + N_2 \rightleftharpoons CN + N$					
X	$CH_2 + N_2 \rightleftharpoons HCN + NH$	2.04	$X 10^{13}$	0	41.7	17
XI	$NH + OH \rightleftharpoons N + H_2O$	5	$X 10^{11}$	0.5	2.0	17
XII	$HCN + OH \rightleftharpoons CN + H_2O$	2	$X 10^{11}$	0.6	5.0	17
XIII	$CN + O_2 \rightleftharpoons CO + NO$	3	$X 10^{11}$	0	0	17
XIV	$CH_3 + H \rightleftharpoons CH_2 + H_2$	2	$X 10^{11}$	0.7	3.0	17
XV	$CH_2 + CH_2O \rightleftharpoons CHO + CH_3$	1.50	$X 10^{11}$	0.7	4.0	17

$$k_f = AT^{+n} \exp(-B/RT) \text{ (cm}^3/\text{mole sec)}, B \sim \text{KCal}, T \sim \text{K}$$

Waldman et al.¹⁷ kinetically modeled methane-air combustion in a perfectly stirred reactor (PSR) and obtained reasonable nitric-oxide emission agreement for $0.7 \leq \Phi \leq 1.6$ by using a 33-reaction mechanism. In order to improve the nitric-oxide agreement, they adjusted the value of k_f . They noted that k_f was obtained from shock-tube experiments in which the vibrational state of N_2 did not have sufficient time to reach equilibrium. The much longer stay times in stirred reactors allowed the vibrational state of N_2 to reach equilibrium at the reaction temperature; hence, the value of k_f had to be increased slightly. This improved the agreement between theory and experiment. The fuel-rich alternate path used by Waldman et al.¹⁷ for NO included the following reactions:



The theoretical predictions of Waldman et al. compare well with the jet-stirred reactor data of Bartok and Engelman¹⁸ for which the stay time was 0.002 sec the pressure 1 atm, and the input temperature 375°F. The theoretical rates used for Reactions (X-XV) (see Table 1) are highly speculative, and although the theory of Waldman et al.¹⁷ agrees with one set of experiments, it may not agree with other data.

Figure 3 shows a comparison of predictions and experiment for (NO) in methane/air combustion in a jet-stirred reactor.¹⁹ The methane/air combustion was modeled by a 24-step process with an additional 8-step NO-production process. The agreement is very poor, probably because an important chemical species (possible formaldehyde) was neglected or the mixing in the combustor was inadequate. The experimental data appear to be suspect because the chemical rates should be proportional to the pressure squared, and the mixing rate should be proportional to pressure, yet the NO concentration is about the same for a rather large change in pressure.

Bachmaier et al.²⁰ detected HCN as an intermediate species in moderately rich propane-air flames and as a rather stable product in very rich flames. They could not be completely sure that CN_2 was measured instead of HCN; however, either probably can react to form NO.

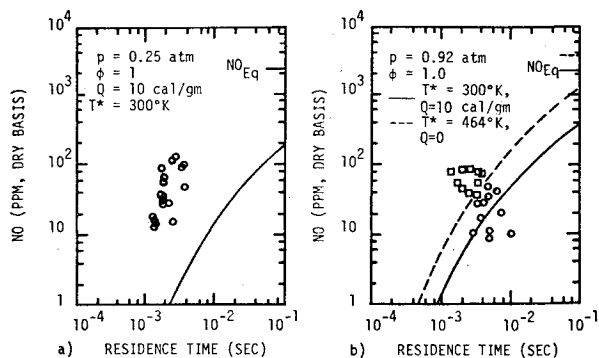


Fig. 3 Comparison of jet-stirred reactor nitric oxide predictions (solid and dashed lines) with experimental data (O, □) T^* = inlet temperature, Φ = fuel/air equivalence ratio, Q = heat loss, NO_{Eq} = theoretical nitric oxide equilibrium concentration¹⁹: a) $P = 0.25$ atm, b) $P = 0.92$ atm.

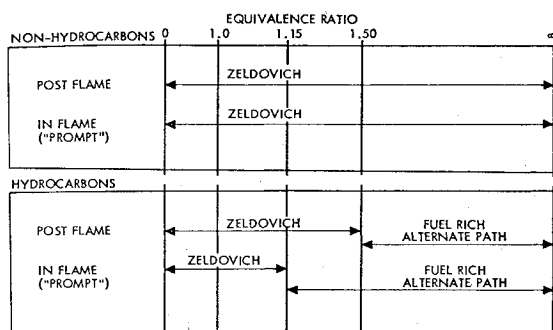


Fig. 4 Equivalence-ratio regions, where the Zeldovich mechanism holds for nitric-oxide production provided the oxygen atoms are carefully evaluated by partial equilibrium analysis as discussed in the text.

Myserson²¹ recently has observed that nitric oxide concentrations can be significantly reduced in the fuel-rich combustion product mixture by the introduction of molecular oxygen. The exact mechanism is not certain, but it is thought to occur as follows: the addition of O_2 to the hydrocarbon, nitric oxide, combustion product mixture produces effective nitric oxide reducing radicals, such as CH and CH_2 , by removing hydrogen atoms from the hydrocarbon. These free radicals react with the NO at temperatures between 1200K and 1700K and produce N_2 along with small concentrations of HCN . If the residence time is long enough, the HCN is recycled back through the process, and the ultimate final product becomes only N_2 .

The presence of nitrogen-containing species, such as CN and HCN in fuel-rich hydrocarbon flames, raises the question of whether techniques, which are derived to reduce nitric-oxide formation, can produce other pollutants. Haynes et al.²² investigated the kinetic relationships for the formation of toxic-nitrogen compounds, such as cyanide, CN , and the amine species, NH , and NH_2 , and NH_3 . The results indicate that, although fuel-rich operation methods aimed at reducing nitric-oxide emissions can result in a temporary formation of other toxic-nitrogen compounds, the consumption rates of CN species, after the hydrocarbons have been consumed, imply that their lifetimes are not long enough to allow them to be emitted from the combustion system.^{22,23} The amine species have a higher probability of being emitted, but they probably are all consumed by oxygen in the downstream sections of the furnace.

When a fuel containing chemically bound nitrogen is burned, the fuel nitrogen is partially converted to nitric oxide and partially to molecular nitrogen. It is known that the flame characteristics greatly affect the percentage of fuel nitrogen converted to nitric oxide.²⁴ Bituminous coals generally con-

tain 1 to 2% nitrogen by weight, and crude oils less than 1%. This nitrogen can represent a significant contribution to nitric-oxide emissions from stationary combustion systems, because 1% nitrogen by weight in a typical hydrocarbon fuel results in nitric-oxide levels of about 1200 ppm at 100% conversion.²⁵ Because the probability of nitrogen being bound to gaseous fuels is very low, the fuel-nitrogen problem will not be discussed further.

Conclusions

The kinetics of nitric oxide can be modeled as shown in Fig. 4. The extended Zeldovich reactions will predict accurate NO concentrations for all equivalence ratios for nonhydrocarbon combustion and for lean to moderately fuel-rich hydrocarbon combustion, if the oxygen-atom concentration is calculated carefully. It appears that partial equilibrium of the $H_2 - O_2 - CO$ reactions [Reactions (V-VIII)] can be used to predict (O).

The nitric oxide production rate is not completely known for hydrocarbon combustion in the fuel-rich region. The inability of the extended Zeldovich mechanism to make accurate nitric oxide predictions for fuel-rich hydrocarbon combustion implies that this method does not account for important reactions, or reaction mechanisms. Thus, the level of understanding of fuel-rich hydrocarbon combustion needs to be increased.

It must be understood that accurate predictions of nitric oxide concentration levels are coupled to the fluid mechanics of the combustion system. Thus, even with accurate chemical kinetics, the predictions may be in error because of inaccurate fluid mechanics.

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