

# Kinetic Modeling and Sensitivity Analysis of Nitrogen Oxide Formation in Well-Stirred Reactors\*

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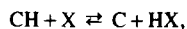
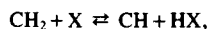
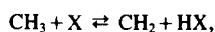
and

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We have modeled the experimental data of Bartok et al. and Duterque et al. on methane combustion in stirred reactors. A method to calculate the first-order sensitivities of the mole fractions and temperature with respect to the rate constants is discussed and applied to nitric oxide production. We have thus been able to evaluate the nitrogen chemistry in the presence of hydrocarbons under stirred conditions. We find the extended Zeldovich mechanism to be the major source of NO under lean conditions, while the prompt-NO formation is dominant under fuel-rich conditions. The important features of the model under fuel-rich conditions are the following:

1. The reaction  $\text{CH} + \text{N}_2 \rightleftharpoons \text{HCN} + \text{N}$  is the only important initiating step in the prompt-NO formation.
2. The CH concentration is established through the sequence



where X is H or OH.

3. Nitric oxide is recycled back to CN and HCN through reactions with C, CH, and  $\text{CH}_2$ . This results in the exhaust of significant quantities of HCN from the reactor.

## I. INTRODUCTION

In recent years great efforts have been made to explain the chemical mechanisms responsible for

forming nitrogen oxides in combustion processes. Three mechanisms have been identified: thermal-NO, prompt-NO, and fuel-NO. Through modeling the experimental data of Bartok et al. [1] and Duterque et al. [2] on methane combustion in jet-stirred reactors, we evaluate the different routes to NO formation. An important reason for modeling this stirred reactor data is our interest in the

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interaction between the hydrocarbon and the nitrogen chemistry. Because of the intense backmixing, the interaction between the hydrocarbon species and the nitrogen species is more significant in a jet-stirred reactor than in flames. Furthermore, the short residence times obtainable in such reactors tend to suppress the thermal NO formation, thus making other routes more significant.

Early chemical kinetic models for NO formation in methane combustion in stirred reactors (e.g., [3, 4]) used the Zeldovich mechanism as the only source of NO and failed to explain the experimental data, especially under fuel-rich conditions. More recent attempts [5-7] included mechanisms for prompt-NO formation and obtained good agreement with the measurements. However, for some of the most significant reactions, these models relied on reaction rates that conflict with recent direct measurements. Furthermore, none of the previous models included the C<sub>2</sub>-chemistry, which is known to be an important part of the methane oxidation scheme. In this exploratory work we have incorporated recent results in areas such as the conversion of NH<sub>i</sub>-species to NO and N<sub>2</sub> (e.g., [8]), the HCN-chemistry [9], the C<sub>2</sub>-chemistry (e.g., [10-12]), and the reactions of CH<sub>2</sub> [13] and CH [14, 15].

The stirred reactor experiments we simulate cannot by themselves be used to validate our chemical kinetic model, partly because the only species measured is NO, and partly because the temperature in the experiments is uncertain. Our primary objective in this paper is to evaluate the nitrogen chemistry as it occurs in the presence of hydrocarbons. As an aid in interpreting the significance of competing pathways we have incorporated a method to calculate the first order sensitivity coefficients of the mole fractions and temperature with respect to the rate constants. This tool has enabled us to point out the rate-determining steps in the formation and consumption of NO under well-stirred conditions, and to identify areas that need further examination.

## II. GOVERNING EQUATIONS AND COMPUTATIONAL PROCEDURE

We have developed a perfectly stirred reactor (PSR) computer model [16]. It runs in conjunction

the CHEMKIN program [17], which handles the chemical reaction mechanism and the thermodynamic properties. The numerical method used is one recently developed and used for the solution of premixed flame problems [18].

In the formulation of the PSR model a well-defined volume is assumed to receive reactants at a steady rate, mix them homogeneously with the contents of the reactor, and eject the products at a steady rate. The governing equations describe a mass balance for each of the  $K$  species,

$$\dot{m}(Y_k - Y_k^*) - \dot{\omega}_k V W_k = 0, \quad (1)$$

and a heat balance for the reactor,

$$\dot{m} \sum_{k=1}^K (Y_k h_k - Y_k^* h_k^*) + Q = 0. \quad (2)$$

In these equations  $Y_k$  is the mass fraction of the  $k$ th species (there are  $K$  species);  $W_k$ , the molecular weight of the  $k$ th species;  $V$ , the reactor volume;  $\dot{\omega}_k$ , the molar rate of production by chemical reaction of the  $k$ th species per unit volume;  $h_k$ , the specific enthalpy of the  $k$ th species; and  $Q$ , the reactor heat loss. The superscript (\*) indicates the inlet conditions.

The nominal residence time is related to the reactor volume and the mass flow rate by

$$\tau = \frac{\rho V}{\dot{m}}, \quad (3)$$

where the mass density  $\rho$  is calculated from the ideal gas equation of state,

$$\rho = \frac{P \bar{W}}{RT}. \quad (4)$$

Here  $P$  is the pressure,  $R$  the universal gas constant, and  $\bar{W}$  the mixture's mean molecular weight. The residence time is often used as a characteristic parameter of the reactor instead of the mass flow rate. When this is the case  $\dot{m}$  is computed from Eq. (3).

The net chemical production rate  $\dot{\omega}_k$  of each species results from a competition between all the chemical reactions involving that species. We presume that each reaction proceeds according to the law of mass action and the forward rate

coefficients are in the modified Arrhenius form

$$k_f = AT^\beta \exp\left(\frac{-E_A}{RT}\right). \quad (5)$$

The governing equations form a set of  $K + 1$  nonlinear algebraic equations, the solution of which is the vector of temperature and the mass fractions,  $\phi = (T, Y_1, \dots, Y_k, \dots, Y_K)^T$ . We solve the system by a modified Newton method. The system of Eqs. (1) and (2) can be represented in vector form as  $F(\phi) = 0$ , where

$$F(\phi) = \left( \dot{m} \sum_{k=1}^K (Y_k h_k - Y_k^* h_k^*) + Q, \right. \\ \left. \dot{m}(Y_1 - Y_1^*) - \dot{\omega}_1 V W_1, \right. \\ \left. \dots, \dot{m}(Y_K - Y_K^*) - \dot{\omega}_K V W_K \right)^T. \quad (6)$$

In these terms the Newton method can be written as

$$\frac{\partial F}{\partial \phi} \Delta \phi = -F(\phi^{(n)}), \quad (7)$$

where  $\partial F/\partial \phi$  is the  $K + 1$  by  $K + 1$  Jacobian matrix,  $\Delta \phi = \phi^{(n+1)} - \phi^{(n)}$ , and  $n$  is an iteration index. Newton's method determines a sequence of iterations or approximate solutions that approach the true solution. Provided the initial estimate  $\phi^{(0)}$  of the solution is sufficiently good, Newton's method produces a sequence  $\{\phi^{(n)}\}$  that converges to the solution.

However, if during the course of the iteration the Newton algorithm fails to converge, the solution estimate is conditioned by a time integration. This provides a new starting point for the Newton algorithm that is closer to the solution, and thus it is more likely to be in the domain of convergence for Newton's method. Ultimately the problem is solved by convergence of the Newton iteration.

The transient problem is a nonlinear ordinary-differential-equation initial-value problem. The analogous time-dependent equation for mass conservation of each species is

$$\frac{dY_k}{dt} = -\frac{1}{\tau} (Y_k - Y_k^*) + \frac{\dot{\omega}_k W_k}{\rho}. \quad (8)$$

The energy balance for the reactor (assuming constant pressure) leads to

$$\frac{dh}{dt} = -\frac{1}{\tau} \sum_{k=1}^K (Y_k h_k - Y_k^* h_k^*) - \frac{Q}{\rho V}. \quad (9)$$

We find it convenient to rewrite the energy equation in terms of temperature rather than enthalpy. Since  $h = \sum_{k=1}^K Y_k h_k$  and  $c_p = \sum_{k=1}^K Y_k c_{pk}$ ,

$$\frac{dh}{dt} = c_p \frac{dT}{dt} + \sum_{k=1}^K h_k \frac{dY_k}{dt}, \quad (10)$$

where  $c_p$  is the mass-weighted mean specific heat. Combining Eqs. (8)–(10) leads to the form of the transient energy equation that we actually solve,

$$c_p \frac{dT}{dt} = \frac{1}{\tau} \sum_{k=1}^K Y_k^* (h_k^* - h_k) \\ - \sum_{k=1}^K \frac{h_k \dot{\omega}_k W_k}{\rho} - \frac{Q}{\rho V}. \quad (11)$$

We solve this system of ordinary differential equations using the backward-Euler method. The modified damped Newton's method, the calculation of the Jacobian matrix, and the procedure used for the timestepping are described in detail in the manual for the code [18].

In addition to solving the governing equations we incorporate a method to compute the first-order sensitivity coefficients of the mass fractions and temperature with respect to the rate constants. The vector  $F(\phi)$  is a function of the dependent variables and various input parameters  $\alpha$ , which include the  $I$  reaction rate constants. We may therefore write the equation system as

$$F(\phi(\alpha), \alpha) = 0. \quad (12)$$

Differentiating this equation with respect to  $\alpha$ , one obtains

$$\frac{\partial F}{\partial \phi} \frac{\partial \phi}{\partial \alpha} + \frac{\partial F}{\partial \alpha} = 0, \quad (13)$$

where  $\partial F/\partial \phi$  is the Jacobian of the original system,  $\partial \phi/\partial \alpha$  is the  $K + 1$  by  $I$  matrix of linear

sensitivity coefficients, and  $\partial F/\partial\alpha$  is the  $K + 1$  by  $I$  partial derivative matrix of the function  $F$  with respect to the rate constants. The Jacobian and its LU factorization are already available from solving the original system by Newton's method, and the parameter derivatives are easily computed by finite differences. Therefore, the linear system of equations (13) is readily solved for each column of the sensitivity matrix, corresponding to the sensitivities of the solution to each of the  $I$  reaction rates. The sensitivity coefficients are normalized in the form of logarithmic derivatives, i.e.,

$$\frac{\partial \ln Y_k}{\partial \ln \alpha_i} = \frac{\alpha_i}{Y_k} \frac{\partial Y_k}{\partial \alpha_i} \quad (14)$$

or

$$\frac{\partial \ln T}{\partial \ln \alpha_i} = \frac{\alpha_i}{T} \frac{\partial T}{\partial \alpha_i} \quad (15)$$

Furthermore, as in tables shown later, they are written in terms of mole fraction. Specifically,

$$\frac{\alpha_i}{X_k} \frac{\partial X_k}{\partial \alpha_i} = \frac{\alpha_i}{Y_k} \frac{\partial Y_k}{\partial \alpha_i} - \alpha_i \bar{W} \sum_{j=1}^K \frac{1}{\bar{W}_j} \frac{\partial Y_k}{\partial \alpha_i}, \quad (16)$$

where  $X_k$  are the mole fractions and  $\bar{W}$  is the mean molecular weight.

It is appropriate to make some points on how to interpret the sensitivity coefficients. A first-order sensitivity coefficient of (for example) 0.24 for the  $k$ th species with respect to the  $i$ th reaction can roughly be interpreted to mean that if the rate of the  $i$ th reaction were made twice as fast, it would cause a 24% increase in the concentration of the  $k$ th species. The sensitivity coefficients thus provide information about the rate-limiting steps in the production and consumption of particular species. However, the sensitivity coefficients depend strongly on the reaction mechanism used and can only be interpreted in terms of that particular mechanism. Furthermore, the sensitivity analysis does not necessarily provide information about the actual pathways for production and destruction of species. Such information must be derived from a rate-of-production analysis [18]. Clearly such an analysis also depends on the choice of mechanism.

### III. CHEMICAL KINETICS

The reactions and rate coefficients used in our calculations are shown in Table I along with appropriate references. They are largely derived from previous work of Miller and coworkers. The oxidation mechanism of methane, described by reactions 1–134, is drawn mainly from the work on acetylene and methane flames [10, 57]. The HCN mechanism (reactions 176–198) was developed in a study of HCN-doped hydrogen flames [9], and the reactions describing the conversion of  $\text{NH}_i$ -species to NO and  $\text{N}_2$  (reactions 135–175) are a subset of the mechanism developed to analyze ammonia flames and the thermal De- $\text{NO}_x$  process [8]. However, because the objective of this work is to understand the interaction between the hydrocarbon and the nitrogen chemistry in methane combustion, additional reactions had to be included in the mechanism. The most important of these are discussed in the following paragraphs.

The interaction between the hydrocarbon and the nitrogen chemistry is believed at least globally to follow the scheme shown in Fig. 1. There is still some controversy on which reaction is the initiating step in the prompt-NO formation. Many short-lived hydrocarbon radicals might conceivably attack  $\text{N}_2$ . However, the number of plausible candidates has been reduced to two [96]:



Blauwens et al. [97] found from flame experiments that the production of prompt-NO could be represented by either (R205) or (R206). In another flame study Matsui and Nomaguchi [98] found the amount of prompt-NO to be proportional to the CH concentration and favored (R205). This was supported by Benson [99], who on structural

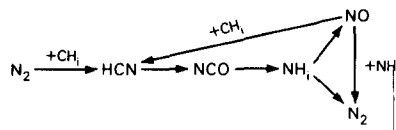


Fig. 1. The interaction between the hydrocarbon and the nitrogen chemistry under fuel-rich conditions.

TABLE I

Reaction Mechanism Rate Coefficients in Form  $k_j = AT^\beta \exp(-E_0/RT)$  (units are moles, cubic centimeters, seconds, Kelvins and calories/mole; values of  $E_0$  in parentheses are in joules/mole)

	Reaction	A	$\beta$	$E_0$	References
1.	$H + O_2 \rightleftharpoons O + OH$	5.10E+16	-0.820	16510. (69078.)	[19]
2.	$H_2 + O \rightleftharpoons H + OH$	1.80E+10	1.000	8830. (36945.)	[20]
3.	$H_2 + OH \rightleftharpoons H_2O + H$	1.20E+09	1.300	3630. (15188.)	[21]
4.	$OH + OH \rightleftharpoons H_2O + O$	6.00E+08	1.300	0.	[22]
5.	$H + OH + M \rightleftharpoons H_2O + M^a$	7.50E+23	-2.600	0.	[20]
6.	$O_2 + M \rightleftharpoons O + O + M$	1.90E+11	0.500	95560. (399823.)	[19]
7.	$H + H + M \rightleftharpoons H_2 + M^f$	1.00E+18	-1.000	0.	[23]
8.	$H + H + H_2 \rightleftharpoons H_2 + H_2$	9.20E+16	-0.600	0.	[23]
9.	$H + H + H_2O \rightleftharpoons H_2 + H_2O$	6.00E+19	-1.250	0.	[23]
10.	$H + H + CO_2 \rightleftharpoons H_2 + CO_2$	5.50E+20	-2.000	0.	[23]
11.	$H_2 + O_2 \rightleftharpoons OH + OH$	1.70E+13	0.000	47780. (199912.)	[20]
12.	$H + O_2 + M \rightleftharpoons HO_2 + M^b$	2.10E+18	-1.000	0.	[24]
13.	$H + O_2 + O_2 \rightleftharpoons HO_2 + O_2$	6.70E+19	-1.420	0.	[24]
14.	$H + O_2 + N_2 \rightleftharpoons HO_2 + N_2$	6.70E+19	-1.420	0.	[24]
15.	$HO_2 + H \rightleftharpoons H_2 + O_2$	2.50E+13	0.000	700. (2929.)	[25]
16.	$HO_2 + H \rightleftharpoons OH + OH$	2.50E+14	0.000	1900. (7950.)	[25]
17.	$HO_2 + O \rightleftharpoons OH + O_2$	4.80E+13	0.000	1000. (4184.)	[25]
18.	$HO_2 + OH \rightleftharpoons H_2O + O_2$	5.00E+13	0.000	1000. (4184.)	[25]
19.	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	2.00E+12	0.000	0.	[26]
20.	$H_2O_2 + M \rightleftharpoons OH + OH + M$	1.20E+17	0.000	45500. (190372.)	[27]
21.	$H_2O_2 + H \rightleftharpoons HO_2 + H_2$	1.70E+12	0.000	3750. (15690.)	[27]
22.	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	1.00E+13	0.000	1800. (7531.)	[27]
23.	$CO + O + M \rightleftharpoons CO_2 + M$	3.20E+13	0.000	-4200. (-17573.)	[28]
24.	$CO + O_2 \rightleftharpoons CO_2 + O$	2.50E+12	0.000	47700. (199577.)	[29]
25.	$CO + OH \rightleftharpoons CO_2 + H$	1.50E+07	1.300	-760. (-3180.)	[30]
26.	$CO + HO_2 \rightleftharpoons CO_2 + OH$	5.80E+13	0.000	22930. (95939.)	[31]
27.	$CH_4 + M \rightleftharpoons CH_3 + H + M^c$	1.00E+17	0.000	88000. (368192.)	[32]
28.	$CH_4 + H \rightleftharpoons CH_3 + H_2$	2.20E+04	3.000	8750. (36610.)	[33]
29.	$CH_4 + O \rightleftharpoons CH_3 + OH$	1.20E+07	2.080	7630. (31924.)	[34]
30.	$CH_4 + OH \rightleftharpoons CH_3 + H_2O$	3.50E+03	3.080	2000. (8368.)	[35]
31.	$CH_4 + CH_2 \rightleftharpoons CH_3 + CH_3$	1.30E+13	0.000	9500. (39748.)	[36]
32.	$CH_3 + M \rightleftharpoons CH_2 + H + M$	1.90E+16	0.000	91600. (383254.)	[37]
*33.	$CH_3 + H \rightleftharpoons CH_2 + H_2$	9.00E+13	0.000	15100. (63178.)	[38]
34.	$CH_3 + O \rightleftharpoons CH_2O + H$	6.80E+13	0.000	0.	[39]
35.	$CH_3 + O \rightleftharpoons CH_2 + OH$	5.00E+13	0.000	12000. (50208.)	est
**36.	$CH_3 + OH \rightleftharpoons CH_2 + H_2O$	1.50E+13	0.000	5000. (20920.)	See text
37.	$CH_3 + OH \rightleftharpoons CH_2O + H_2$	1.00E+12	0.000	0.	est
38.	$CH_3 + O_2 \rightleftharpoons CH_2O + OH$	5.20E+13	0.000	34570. (144641.)	[40]
39.	$CH_3 + O_2 \rightleftharpoons CH_3O + O^e$	7.00E+12	0.000	25650. (107320.)	[40]
40.	$CH_3O + M \rightleftharpoons CH_2O + H + M^c$	1.00E+14	0.000	25000. (104600.)	[41]
41.	$CH_3O + H \rightleftharpoons CH_2O + H_2^e$	2.00E+13	0.000	0.	[42]
42.	$CH_3O + O \rightleftharpoons CH_2O + OH^e$	1.00E+13	0.000	0.	See [10]
43.	$CH_3O + OH \rightleftharpoons CH_2O + H_2O^e$	1.00E+13	0.000	0.	See [10]
44.	$CH_3O + O_2 \rightleftharpoons CH_2O + HO_2^e$	6.30E+10	0.000	2600. (10878.)	[43]
45.	$CH_2O + M \rightleftharpoons HCO + H + M$	3.30E+16	0.000	81000. (338904.)	[44]
46.	$CH_2O + H \rightleftharpoons HCO + H_2$	2.20E+08	1.770	10500. (43932.)	[45]
47.	$CH_2O + O \rightleftharpoons HCO + OH$	1.80E+13	0.000	3080. (12887.)	[44]
48.	$CH_2O + OH \rightleftharpoons HCO + H_2O$	3.40E+09	1.180	-447. (-1870.)	[45]
49.	$HCO + M \rightleftharpoons CO + H + M$	1.60E+14	0.000	14700. (61505.)	[46]
50.	$HCO + H \rightleftharpoons CO + H_2$	4.00E+13	0.000	0.	[47]

Table I. Continued

	Reaction	$A$	$\beta$	$E_0$	References
51.	$\text{HCO} + \text{O} \rightleftharpoons \text{CO} + \text{OH}$	$3.00\text{E}+13$	0.000	0.	[48]
52.	$\text{HCO} + \text{O} \rightleftharpoons \text{CO}_2 + \text{H}$	$3.00\text{E}+13$	0.000	0.	[41]
53.	$\text{HCO} + \text{OH} \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	$5.00\text{E}+12$	0.000	0.	[49]
54.	$\text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2$	$3.30\text{E}+13$	-0.400	0.	[50]
**55.	$\text{CH}_2 + \text{H} \rightleftharpoons \text{CH} + \text{H}_2$	$7.30\text{E}+17$	-1.560	0.	See text
56.	$\text{CH}_2 + \text{O} \rightleftharpoons \text{CO} + \text{H} + \text{H}$	$3.00\text{E}+13$	0.000	0.	[51], [52]
57.	$\text{CH}_2 + \text{O} \rightleftharpoons \text{CO} + \text{H}_2$	$5.00\text{E}+13$	0.000	0.	[51], [52]
58.	$\text{CH}_2 + \text{O} \rightleftharpoons \text{CH} + \text{OH}$	$5.00\text{E}+13$	0.000	12000. (50208.)	est
59.	$\text{CH}_2 + \text{OH} \rightleftharpoons \text{CH}_2\text{O} + \text{H}$	$3.00\text{E}+13$	0.000	0.	est
**60.	$\text{CH}_2 + \text{OH} \rightleftharpoons \text{CH} + \text{H}_2\text{O}$	$4.50\text{E}+13$	0.000	3000. (12552.)	See text
61.	$\text{CH}_2 + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{H} + \text{H}$	$1.60\text{E}+12$	0.000	1000. (4184.)	See [10]
62.	$\text{CH}_2 + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2$	$6.90\text{E}+11$	0.000	500. (2092.)	See [10]
63.	$\text{CH}_2 + \text{O}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	$1.90\text{E}+10$	0.000	-1000. (-4184.)	See [10]
64.	$\text{CH}_2 + \text{O}_2 \rightleftharpoons \text{CO} + \text{OH} + \text{H}$	$8.60\text{E}+10$	0.000	-500. (-2092.)	See [10]
65.	$\text{CH}_2 + \text{O}_2 \rightleftharpoons \text{HCO} + \text{OH}$	$4.30\text{E}+10$	0.000	-500. (-2092.)	See [10]
66.	$\text{CH}_2 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{O}$	$2.00\text{E}+13$	0.000	9000. (37656.)	est
67.	$\text{CH}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{CH}_2\text{O}$	$1.10\text{E}+11$	0.000	1000. (4184.)	See text
68.	$\text{CH}_2 + \text{CH} \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}$	$4.00\text{E}+13$	0.000	0.	[53]
69.	$\text{CH}_2 + \text{CH}_2 \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}_2$	$3.20\text{E}+13$	0.000	0.	[53]
**70.	$\text{CH} + \text{H} \rightleftharpoons \text{C} + \text{H}_2$	$1.50\text{E}+14$	0.000	0.	est
71.	$\text{CH} + \text{O} \rightleftharpoons \text{CO} + \text{H}$	$5.70\text{E}+13$	0.000	0.	[54]
72.	$\text{CH} + \text{OH} \rightleftharpoons \text{HCO} + \text{H}$	$3.00\text{E}+13$	0.000	0.	est
73.	$\text{CH} + \text{O}_2 \rightleftharpoons \text{HCO} + \text{O}$	$3.30\text{E}+13$	0.000	0.	[15]
74.	$\text{CH} + \text{CO}_2 \rightleftharpoons \text{HCO} + \text{CO}$	$3.40\text{E}+12$	0.000	690. (2887.)	[15]
75.	$\text{CH} + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_3 + \text{H}$	$3.00\text{E}+13$	0.000	0.	est
76.	$\text{CH} + \text{CH}_4 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}$	$6.00\text{E}+13$	0.000	0.	[55]
77.	$\text{CH} + \text{C}_2\text{H}_2 \rightleftharpoons \text{C}_3\text{H}_2 + \text{H}$	$1.30\text{E}+14$	0.000	0.	[55]
78.	$\text{CH} + \text{C}_2\text{H}_4 \rightarrow \text{products}$	$1.30\text{E}+14$	0.000	0.	[55]
79.	$\text{CH} + \text{C}_2\text{H}_6 \rightarrow \text{products}$	$2.40\text{E}+14$	0.000	0.	[55]
80.	$\text{C} + \text{OH} \rightleftharpoons \text{CO} + \text{H}$	$5.00\text{E}+13$	0.000	0.	est
81.	$\text{C} + \text{O}_2 \rightleftharpoons \text{CO} + \text{O}$	$2.00\text{E}+13$	0.000	0.	See [56]
82.	$\text{C} + \text{CO}_2 \rightleftharpoons \text{CO} + \text{CO}$	$6.00\text{E}+08$	0.000	0.	See [56]
83.	$\text{C} + \text{CH}_4 \rightleftharpoons \text{CH} + \text{CH}_3$	$5.00\text{E}+13$	0.000	24000. (100416.)	est
84.	$\text{C} + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}$	$5.00\text{E}+13$	0.000	0.	est
85.	$\text{C} + \text{CH}_2 \rightleftharpoons \text{C}_2\text{H} + \text{H}$	$5.00\text{E}+13$	0.000	0.	est
86.	$\text{CH}_3 + \text{CH}_3(+\text{M}) \rightleftharpoons \text{C}_2\text{H}_6(+\text{M})^{\text{e}}$	$1.60\text{E}+13$	0.000	-306. (-1280.)	[57]
87.	$\text{C}_2\text{H}_5 + \text{H} \rightleftharpoons \text{CH}_3 + \text{CH}_3$	$4.00\text{E}+13$	0.000	0.	See [41]
88.	$\text{CH}_3 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$	$2.10\text{E}+14$	0.000	19200. (80333.)	[58]
89.	$\text{CH}_3 + \text{CH}_2 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}$	$3.00\text{E}+13$	0.000	0.	[59]
90.	$\text{C}_2\text{H}_6 + \text{H} \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}_2$	$5.40\text{E}+02$	3.500	5200. (21757.)	[33]
91.	$\text{C}_2\text{H}_6 + \text{O} \rightleftharpoons \text{C}_2\text{H}_5 + \text{OH}$	$2.50\text{E}+13$	0.000	6360. (26610.)	[60]
92.	$\text{C}_2\text{H}_6 + \text{OH} \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	$8.70\text{E}+09$	1.050	1810. (7573.)	[61]
93.	$\text{C}_2\text{H}_6 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_4$	$5.50\text{E}-01$	4.000	8280. (34644.)	[33]
94.	$\text{C}_2\text{H}_6 + \text{CH}_2 \rightleftharpoons \text{CH}_3 + \text{C}_2\text{H}_5$	$2.20\text{E}+13$	0.000	8660. (36233.)	[36]
95.	$\text{C}_2\text{H}_5 + \text{M} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H} + \text{M}$	$1.00\text{E}+17$	0.000	31000. (129704.)	[41]
96.	$\text{C}_2\text{H}_5 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4 + \text{HO}_2$	$3.20\text{E}+12$	0.000	5020. (21004.)	[62]
97.	$\text{C}_2\text{H}_4 + \text{M} \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}_2 + \text{M}$	$2.60\text{E}+17$	0.000	79350. (332000.)	[63]
98.	$\text{C}_2\text{H}_4 + \text{M} \rightleftharpoons \text{C}_2\text{H}_3 + \text{H} + \text{M}$	$2.60\text{E}+17$	0.000	96600. (404174.)	[63]
99.	$\text{C}_2\text{H}_4 + \text{H} \rightleftharpoons \text{C}_2\text{H}_3 + \text{H}_2$	$1.10\text{E}+14$	0.000	8500. (35564.)	[64]
100.	$\text{C}_2\text{H}_4 + \text{O} \rightleftharpoons \text{HCO} + \text{CH}_3$	$1.60\text{E}+09$	1.200	746. (3121.)	[41]
101.	$\text{C}_2\text{H}_4 + \text{OH} \rightleftharpoons \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	$4.80\text{E}+12$	0.000	1230. (5146.)	[65]

Table I. Continued

	Reaction	A	$\beta$	$E_0$	References
102.	$C_2H_4 + OH \rightleftharpoons CH_2O + CH_3$	2.00E+12	0.000	960.	(4017.) [65]
103.	$C_2H_3 + M \rightleftharpoons C_2H_2 + H + M$	8.00E+14	0.000	31500.	(131796.) [66]
104.	$C_2H_3 + H \rightleftharpoons C_2H_2 + H_2$	4.00E+13	0.000	0.	[67]
105.	$C_2H_3 + O \rightleftharpoons CH_2CO + H$	3.30E+13	0.000	0.	[67]
106.	$C_2H_3 + OH \rightleftharpoons C_2H_2 + H_2O$	5.00E+12	0.000	0.	[10] est
107.	$C_2H_3 + O_2 \rightleftharpoons HCO + CH_2O$	4.00E+12	0.000	-250.	(-1046.) [68]
108.	$C_2H_3 + CH_2 \rightleftharpoons C_2H_2 + CH_3$	3.00E+13	0.000	0.	[10] est
109.	$C_2H_3 + C_2H \rightleftharpoons C_2H_2 + C_2H_2$	3.00E+13	0.000	0.	[10] est
110.	$C_2H_2 + M \rightleftharpoons C_2H + H + M$	4.20E+16	0.000	107000.	(447688.) [69]
111.	$C_2H + H_2 \rightleftharpoons C_2H_2 + H$	4.10E+05	2.390	860.	(3598.) See [10]
112.	$C_2H_2 + O \rightleftharpoons CH_2 + CO$	2.20E+10	1.000	2580.	(10795.) See [10]
113.	$C_2H_2 + O \rightleftharpoons HCCO + H$	3.60E+04	2.700	1390.	(5816.) [10]
114.	$C_2H_2 + O \rightleftharpoons C_2H + OH$	3.20E+15	-0.600	15000.	(62760.) [48]
115.	$C_2H_2 + OH \rightleftharpoons CH_2CO + H$	3.20E+11	0.000	200.	(837.) [70]
116.	$C_2H_2 + OH \rightleftharpoons C_2H + H_2O$	6.00E+12	0.000	7000.	(29288.) [48]
117.	$CH_2CO + M \rightleftharpoons CH_2 + CO + M$	3.60E+15	0.000	59300.	(248111.) [71]
118.	$CH_2CO + H \rightleftharpoons CH_3 + CO$	1.10E+13	0.000	3430.	(14351.) [72]
119.	$CH_2CO + H \rightleftharpoons HCCO + H_2$	7.50E+13	0.000	8000.	(33472.) [10] est
120.	$CH_2CO + O \rightleftharpoons CH_2O + CO$	2.00E+13	0.000	0.	[10] est
121.	$CH_2CO + O \rightleftharpoons HCCO + OH$	5.00E+13	0.000	8000.	(33472.) [10] est
122.	$CH_2CO + OH \rightleftharpoons CH_2O + HCO$	2.80E+13	0.000	0.	[70]
123.	$CH_2CO + OH \rightleftharpoons HCCO + H_2O$	7.50E+12	0.000	3000.	(12552.) [10] est
124.	$HCCO + H \rightleftharpoons CH_2 + CO$	1.10E+14	0.000	0.	[73]
125.	$HCCO + O \rightleftharpoons CO + CO + H$	1.10E+14	0.000	0.	[73]
126.	$HCCO + OH \rightleftharpoons HCO + CO + H$	1.00E+13	0.000	0.	[10]
127.	$HCCO + O_2 \rightleftharpoons CO + CO + OH$	1.50E+12	0.000	2500.	(10460.) See [10]
128.	$HCCO + CH_2 \rightleftharpoons C_2H + CH_2O$	1.00E+13	0.000	2000.	(8368.) [10] est
129.	$HCCO + CH_2 \rightleftharpoons C_2H_3 + CO$	3.00E+13	0.000	0.	[10]
130.	$HCCO + HCCO \rightleftharpoons C_2H_2 + CO + CO$	1.00E+13	0.000	0.	[10] est
131.	$C_2H + O \rightleftharpoons CH + CO$	5.00E+13	0.000	0.	[48]
132.	$C_2H + OH \rightleftharpoons HCCO + H$	2.00E+13	0.000	0.	[10] est
133.	$C_2H + O_2 \rightleftharpoons CO + HCO$	2.40E+12	0.000	0.	[74]
134.	$C_2H + O_2 \rightleftharpoons HCCO + O$	6.00E+11	0.000	0.	[74]
135.	$N_2H_2 + M \rightleftharpoons NNH + H + M$	5.00E+16	0.000	50000.	(209200.) [8] est
136.	$N_2H_2 + H \rightleftharpoons NNH + H_2$	5.00E+13	0.000	1000.	(4184.) [8] est
137.	$NNH + M \rightleftharpoons N_2 + H + M$	2.00E+14	0.000	20000.	(83680.) [75]
138.	$NNH + H \rightleftharpoons N_2 + H_2$	3.70E+13	0.000	3000.	(12552.) [76]
139.	$NNH + NO \rightleftharpoons N_2 + HNO$	5.00E+13	0.000	0.	[76]
140.	$NH_3 + M \rightleftharpoons NH_2 + H + M$	1.40E+16	0.000	90600.	(379070.) [76]
141.	$NH_3 + H \rightleftharpoons NH_2 + H_2$	7.00E+06	2.390	10171.	(42555.) [77]
142.	$NH_3 + O \rightleftharpoons NH_2 + OH$	2.10E+13	0.000	9000.	(37656.) [78]
143.	$NH_3 + OH \rightleftharpoons NH_2 + H_2O$	2.04E+06	2.040	566.	(2368.) [79]
144.	$NH_2 + H \rightleftharpoons NH + H_2$	6.90E+13	0.000	3650.	(15272.) [80]
145.	$NH_2 + O \rightleftharpoons NH + OH$	6.80E+12	0.000	0.	[81]
146.	$NH_2 + O \rightleftharpoons HNO + H$	6.60E+14	-0.500	0.	[81], [8]
147.	$NH_2 + OH \rightleftharpoons NH + H_2O$	4.50E+12	0.000	2200.	(9205.) [75]
148.	$NH_2 + N \rightleftharpoons N_2 + H + H$	7.20E+13	0.000	0.	[82]
149.	$NH_2 + NH \rightleftharpoons N_2H_2 + H$	5.00E+13	0.000	0.	[8]
150.	$NH_2 + NO \rightleftharpoons NNH + OH$	8.80E+15	-1.250	0.	[8]
151.	$NH_2 + NO \rightleftharpoons N_2 + H_2O$	3.80E+15	-1.250	0.	[8]
*152.	$NH + H \rightleftharpoons N + H_2$	3.00E+13	0.000	0.	[83]

Table I. Continued

	Reaction	$A$	$\beta$	$E_0$	References
153.	$\text{NH} + \text{O} \rightleftharpoons \text{NO} + \text{H}$	$2.00\text{E}+13$	0.000	0.	[8]
154.	$\text{NH} + \text{OH} \rightleftharpoons \text{HNO} + \text{H}$	$2.00\text{E}+13$	0.000	0.	[8]
155.	$\text{NH} + \text{O}_2 \rightleftharpoons \text{N} + \text{H}_2\text{O}$	$5.00\text{E}+11$	0.500	2000. (8368.)	See [76]
156.	$\text{NH} + \text{O}_2 \rightleftharpoons \text{HNO} + \text{O}$	$1.00\text{E}+13$	0.000	12000. (50208.)	[8]
157.	$\text{NH} + \text{O}_2 \rightleftharpoons \text{NO} + \text{OH}$	$1.40\text{E}+11$	0.000	2000. (8368.)	[8]
158.	$\text{NH} + \text{NO} \rightleftharpoons \text{N}_2\text{O} + \text{H}$	$4.30\text{E}+14$	-0.500	0.	[8]
159.	$\text{NH} + \text{N} \rightleftharpoons \text{N}_2 + \text{H}$	$3.00\text{E}+13$	0.000	0.	[8] est
160.	$\text{N} + \text{O}_2 \rightleftharpoons \text{NO} + \text{O}$	$6.40\text{E}+09$	1.000	6280. (26276.)	[84]
**161.	$\text{N} + \text{OH} \rightleftharpoons \text{NO} + \text{H}$	$3.80\text{E}+13$	0.000	0.	See [9]
**162.	$\text{N} + \text{NO} \rightleftharpoons \text{N}_2 + \text{O}$	$3.30\text{E}+12$	0.300	0.	See [9]
163.	$\text{N} + \text{CO}_2 \rightleftharpoons \text{NO} + \text{CO}$	$1.90\text{E}+11$	0.000	3400. (14226.)	[85]
164.	$\text{N} + \text{HCCO} \rightleftharpoons \text{HCN} + \text{CO}$	$5.00\text{E}+13$	0.000	0.	est
165.	$\text{NO} + \text{HO}_2 \rightleftharpoons \text{NO}_2 + \text{OH}$	$2.10\text{E}+12$	0.000	-480. (-2008.)	See [8]
166.	$\text{NO}_2 + \text{M} \rightleftharpoons \text{NO} + \text{O} + \text{M}$	$1.10\text{E}+16$	0.000	66000. (276144.)	[84]
167.	$\text{NO}_2 + \text{H} \rightleftharpoons \text{NO} + \text{OH}$	$3.50\text{E}+14$	0.000	1500. (6276.)	See [19]
168.	$\text{NO}_2 + \text{O} \rightleftharpoons \text{NO} + \text{O}_2$	$1.00\text{E}+13$	0.000	600. (2510.)	[84]
169.	$\text{HNO} + \text{M} \rightleftharpoons \text{H} + \text{NO} + \text{M}^d$	$1.50\text{E}+16$	0.000	48680. (203677.)	[84]
170.	$\text{HNO} + \text{H} \rightleftharpoons \text{H}_2 + \text{NO}$	$5.00\text{E}+12$	0.000	0.	[84]
171.	$\text{HNO} + \text{OH} \rightleftharpoons \text{NO} + \text{H}_2\text{O}$	$3.60\text{E}+13$	0.000	0.	[84]
172.	$\text{N}_2\text{O} + \text{M} \rightleftharpoons \text{N}_2 + \text{O} + \text{M}$	$1.60\text{E}+14$	0.000	51600. (215894.)	See [76]
173.	$\text{N}_2\text{O} + \text{H} \rightleftharpoons \text{N}_2 + \text{OH}$	$7.60\text{E}+13$	0.000	15200. (63597.)	[84]
174.	$\text{N}_2\text{O} + \text{O} \rightleftharpoons \text{NO} + \text{NO}$	$1.00\text{E}+14$	0.000	28200. (117989.)	[84]
175.	$\text{N}_2\text{O} + \text{O} \rightleftharpoons \text{N}_2 + \text{O}_2$	$1.00\text{E}+14$	0.000	28200. (117989.)	[84]
176.	$\text{HCN} + \text{O} \rightleftharpoons \text{CN} + \text{OH}$	$2.70\text{E}+09$	1.580	26600. (111294.)	[78]
*177.	$\text{HCN} + \text{O} \rightleftharpoons \text{NCO} + \text{H}$	$1.40\text{E}+04$	2.640	4980. (20836.)	See [86]
*178.	$\text{HCN} + \text{O} \rightleftharpoons \text{NH} + \text{CO}$	$3.50\text{E}+03$	2.640	4980. (20836.)	See [86]
179.	$\text{HCN} + \text{OH} \rightleftharpoons \text{CN} + \text{H}_2\text{O}$	$1.50\text{E}+13$	0.000	10929. (45727.)	[86], [87]
180.	$\text{HCN} + \text{OH} \rightleftharpoons \text{HOCN} + \text{H}$	$9.20\text{E}+12$	0.000	15000. (62760.)	[86], [87]
181.	$\text{HCN} + \text{OH} \rightleftharpoons \text{HNCO} + \text{H}$	$4.80\text{E}+11$	0.000	11000. (46024.)	[86], [87]
182.	$\text{HCN} + \text{CN} \rightleftharpoons \text{C}_2\text{N}_2 + \text{H}$	$2.00\text{E}+13$	0.000	0.	[88]
183.	$\text{CN} + \text{O} \rightleftharpoons \text{CO} + \text{N}$	$1.80\text{E}+13$	0.000	0.	[89]
*184.	$\text{CN} + \text{OH} \rightleftharpoons \text{NCO} + \text{H}$	$6.00\text{E}+13$	0.000	0.	[90]
185.	$\text{CN} + \text{H}_2 \rightleftharpoons \text{HCN} + \text{H}$	$3.00\text{E}+05$	2.450	2237. (9360.)	[91]
*186.	$\text{CN} + \text{O}_2 \rightleftharpoons \text{NCO} + \text{O}$	$5.60\text{E}+12$	0.000	0.	[89]
187.	$\text{CN} + \text{NO}_2 \rightleftharpoons \text{NCO} + \text{NO}$	$3.00\text{E}+13$	0.000	0.	est
188.	$\text{CN} + \text{N}_2\text{O} \rightleftharpoons \text{NCO} + \text{N}_2$	$1.00\text{E}+13$	0.000	0.	est
189.	$\text{NCO} + \text{M} \rightleftharpoons \text{N} + \text{CO} + \text{M}$	$3.10\text{E}+16$	-0.500	48000. (200832.)	[92]
*190.	$\text{NCO} + \text{H} \rightleftharpoons \text{NH} + \text{CO}$	$5.00\text{E}+13$	0.000	0.	See [9]
191.	$\text{NCO} + \text{O} \rightleftharpoons \text{NO} + \text{CO}$	$5.60\text{E}+13$	0.000	0.	[93]
192.	$\text{NCO} + \text{OH} \rightleftharpoons \text{NO} + \text{CO} + \text{H}$	$1.00\text{E}+13$	0.000	0.	[9] est
193.	$\text{NCO} + \text{H}_2 \rightleftharpoons \text{HNCO} + \text{H}$	$8.60\text{E}+12$	0.000	9000. (37656.)	See [9]
194.	$\text{NCO} + \text{N} \rightleftharpoons \text{N}_2 + \text{CO}$	$2.00\text{E}+13$	0.000	0.	See [9]
195.	$\text{NCO} + \text{NO} \rightleftharpoons \text{N}_2\text{O} + \text{CO}$	$1.00\text{E}+13$	0.000	-390. (-1632.)	[78]
196.	$\text{HOCN} + \text{H} \rightleftharpoons \text{HNCO} + \text{H}$	$1.00\text{E}+13$	0.000	0.	est
197.	$\text{HCNO} + \text{H} \rightarrow \text{HCN} + \text{OH}$	$5.00\text{E}+13$	0.000	12000. (50208.)	est
198.	$\text{HNCO} + \text{H} \rightleftharpoons \text{NH}_2 + \text{CO}$	$2.00\text{E}+13$	0.000	3000. (12552.)	[9] est
199.	$\text{C}_2\text{N}_2 + \text{O} \rightleftharpoons \text{NCO} + \text{CN}$	$4.60\text{E}+12$	0.000	8880. (37154.)	[89]
200.	$\text{C}_2\text{N}_2 + \text{OH} \rightleftharpoons \text{HOCN} + \text{CN}$	$1.90\text{E}+11$	0.000	2900. (12134.)	[94]
**201.	$\text{C} + \text{NO} \rightleftharpoons \text{CN} + \text{O}$	$6.60\text{E}+13$	0.000	0.	[95]
**202.	$\text{CH} + \text{NO} \rightleftharpoons \text{HCN} + \text{O}$	$1.10\text{E}+14$	0.000	0.	See text
**203.	$\text{CH}_2 + \text{NO} \rightarrow \text{HCNO} + \text{H}$	$1.40\text{E}+12$	0.000	-1100. (-4602.)	See text



Table I. Continued

	Reaction	<i>A</i>	$\beta$	<i>E</i> <sub>0</sub>	References
204.	C + N <sub>2</sub> O ⇌ CN + NO	1.00E+13	0.000	0.	See [56]
**205.	CH + N <sub>2</sub> ⇌ HCN + N	1.90E+11	0.000	13600. (56902.)	See text
206.	CH <sub>2</sub> + N <sub>2</sub> ⇌ HCN + NH	1.00E+13	0.000	74000. (309616.)	See text
207.	CH + NH <sub>2</sub> ⇌ HCN + H + H	3.00E+13	0.000	0.	est
208.	CH + NH ⇌ HCN + H	5.00E+13	0.000	0.	est
209.	CH <sub>2</sub> + NH ⇌ HCN + H + H	3.00E+13	0.000	0.	est
210.	CH + N ⇌ CN + H	1.30E+13	0.000	0.	[54]
211.	CH <sub>2</sub> + N ⇌ HCN + H	5.00E+13	0.000	0.	est
*212.	CH <sub>3</sub> + N ⇌ HCN + H + H	5.00E+13	0.000	0.	est
213.	CH <sub>4</sub> + N ⇌ NH + CH <sub>3</sub>	1.00E+13	0.000	24000. (100416.)	est

<sup>a</sup> Third body efficiencies:  $k_5(\text{H}_2\text{O}) = 20k_5(\text{Ar})$ .

<sup>b</sup> Third body efficiencies:  $k_{12}(\text{H}_2\text{O}) = 21k_{12}(\text{Ar})$ ,  $k_{12}(\text{CO}_2) = 5k_{12}(\text{Ar})$ ,  $k_{12}(\text{H}_2) = 3.3k_{12}(\text{Ar})$ ,  $k_{12}(\text{CO}) = 2k_{12}(\text{Ar})$ ,  $k_{12}(\text{O}_2) = 0$ ,  $k_{12}(\text{N}_2) = 0$ .

<sup>c</sup> Third body efficiencies:  $k_{27}(\text{H}_2\text{O}) = 5k_{27}(\text{Ar})$ .

<sup>d</sup> Third body efficiencies:  $k_{169}(\text{H}_2\text{O}) = 6k_{169}(\text{Ar})$ ,  $k_{169}(\text{H}_2) = k_{169}(\text{O}_2) = k_{169}(\text{N}_2) = 2k_{169}(\text{Ar})$ .

<sup>e</sup> No distinction is made between CH<sub>3</sub>O and CH<sub>2</sub>OH.

<sup>f</sup> Third body efficiencies:  $k_7(\text{H}_2\text{O}) = k_7(\text{H}_2) = k_7(\text{CO}_2) = 0$ .

<sup>g</sup> "Unimolecular" reaction in the fall-off region. Rate constant is calculated from the expression  $k = 1.67 \times 10^{13} \exp(306/RT)/(1 + 7.66 \times 10^{-7} \exp(-3032/RT)/[\text{M}])$ .

\*\* Most important reactions in NO formation from CH<sub>4</sub> in well-stirred reactors.

\* Important reactions in NO formation from CH<sub>4</sub> in well-stirred reactors.

grounds found (R206) unlikely to be the main candidate.

Direct rate measurements for these reactions at flame temperatures have not been carried out. Laufer and Bass [100] have determined a room temperature upper limit of 6.0E07 cm<sup>3</sup>/mole s for the CH<sub>2</sub> + N<sub>2</sub> reaction. We have estimated the rate coefficient for this reaction by considering its reverse. The addition of NH to the nitrogen end of hydrogen cyanide is isoelectronic with the analogous addition of oxygen atoms. In the latter case the addition complex lies about 20 kcal/mole above O + HCN [101]. We expect a similar result for NH + HCN. Using this number, assuming a normal value for the energy barrier of the 1,3 hydrogen shift from the nitrogen to the carbon (between 30 and 40 kcal/mole), and incorporating the appropriate endothermicity (24 kcal/mole), we deduce that reaction (R206) should have an activation energy between 74 and 84 kcal/mole. The rate of (R206) is determined by the transition state for the 1,3 hydrogen shift. Such transition states are normally very tight, and one consequently would

expect a low *A*-factor for  $k_{206}$ . Nevertheless, we have incorporated in our model a normal value of  $1 \times 10^{13}$  cm<sup>3</sup>/mole s. As a result we expect our rate expression,  $k_{206} = 1 \times 10^{13} \exp(-74,000/RT)$  cm<sup>3</sup>/mole s, to be systematically high, if anything.

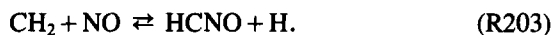
During the course of this work we found the CH + N<sub>2</sub> reaction to be rate-limiting for the prompt-NO formation under fuel-rich reactor conditions. Room temperature measurements of this reaction are not of direct use in establishing the appropriate rate coefficient, because the reaction at low temperatures is dominated by another product channel [14,102]. The rate has been inferred from flame experiments by Blauwens et al. [97] and by Matsui and Nomaguchi [98]. However, we find these rates to be much too high to be consistent with the stirred reactor data considered here. Instead, we derived a rate in the following way. We used the activation energy determined by Matsui and Nomaguchi of 13.6 kcal/mole. This value is in agreement with Benson's [99] estimate of 14 kcal/mole. We then adjusted the preex-

ponential factor to get the right peak value of NO in the modeling of the stirred-reactor data of Bartok et al. [1]. The rate obtained in this way,  $k_{205} = 1.9E11 \exp(-13,600/RT) \text{ cm}^3/\text{mole s}$ , at 2000K is a factor of 10 slower than the rate derived by Blauwens et al. and a factor of 6 faster than the rate estimated by Benson [103] and used in previous stirred-reactor modeling [5-7].

The recycle of NO to cyanide species by reaction with small hydrocarbon fragments has not yet been explained satisfactorily. We believe it to happen through the reactions



and

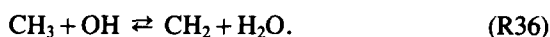


For the C + NO reaction we have used the rate  $6.6E13 \text{ cm}^3/\text{mole s}$ , determined at room temperature by Braun et al. [95] and confirmed by Husain and Kirsch [104]. The rate of the CH + NO reaction was measured recently by Berman et al. [15], who obtained a rate of  $1.1E14 \text{ cm}^3/\text{mole s}$ , independent of temperature. Several exothermic product channels are possible for this reaction, but the one written appears most probable. For the CH<sub>2</sub> + NO reaction we have assumed formation of HCNO, which is subsequently removed by H to form HCN and OH. These products and the rate coefficient for reaction (R197) are based on the isoelectronic sequence  $\text{NH} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{H}$ ,  $\text{H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH}$ . The rate for reaction (R203) is taken from experiments of Laufer [13] and Vinckier and Debruyne [105].

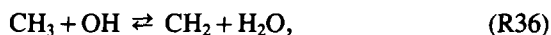
Because of the influence of the CH<sub>i</sub>-species on the nitrogen chemistry, we include a very detailed mechanism for the formation and consumption of CH<sub>2</sub> and CH. The formation of CH<sub>2</sub> in methane combustion proceeds through two different routes; the dominant route is determined by the equivalence ratio. In rich flames CH<sub>2</sub> is formed primarily through the C<sub>2</sub>-hydrocarbon channel [10, 11]. Under leaner conditions CH<sub>2</sub> is formed directly from CH<sub>3</sub>.

Peeters and Vinckier [106] found in their study

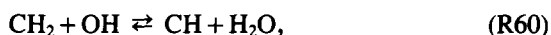
of stoichiometric and lean flames that CH<sub>2</sub> was formed by the reaction



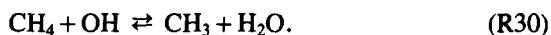
However, because of the lack of direct measurements on the CH<sub>3</sub> + OH reaction, both the rate and the product channels are controversial. We have estimated the rate coefficients for the reaction



and the similar reaction



by comparison with the rate coefficient for reaction (R30),



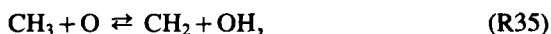
The general rule for such a set of abstraction reactions is that the more exothermic the reaction is, the more the transition state looks like the reactants [91]. The consequences of this general rule are that the more exothermic reactions in such a sequence usually have both larger preexponential factors and smaller energy barriers [91]. The more exothermic reactions also usually have more positive Arrhenius curvature. In the present case, reactions (R30) and (R60) are about equally exothermic. Therefore we have assigned (R60) an *A*-factor and activation energy that are essentially the same as those of (R30) at 2000K. Reaction (R36) is somewhat less exothermic; we have assigned its *A*-factor and activation energy accordingly (i.e., at 2000K). We have not tried to estimate the temperature dependence of the *A*-factors, since the present study involves only a limited range of temperatures.

Another potentially important CH<sub>2</sub>-forming reaction is



This reaction has been inferred from shock-tube experiments [40, 107], but not measured directly. We use a rate for this reaction of  $9.0E13 \exp(-15,000/RT) \text{ cm}^3/\text{mole s}$  [38].

The sequence





could possibly constitute a minor channel for  $\text{CH}_2$  and  $\text{CH}$  formation. The  $\text{CH}$ -forming product channel for the  $\text{CH}_2 + \text{O}$  reaction is negligible at room temperature [25, 26], but it has been suggested at higher temperatures from shock-tube experiments [108]. We include these reactions with estimated rates of  $5.0\text{E}13 \exp(-12,000/RT) \text{ cm}^3/\text{mole s}$ .

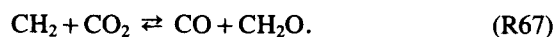
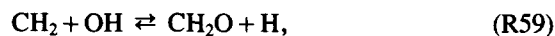
The routes for consumption of  $\text{CH}_2$  depend strongly on the equivalence ratio. Under stoichiometric and lean conditions  $\text{CH}_2$  reacts mainly with  $\text{O}_2$ . This reaction has several product channels, whose relative importance depends on temperature. We use the rates and pathways proposed by Miller et al. [10], with the addition of a  $\text{CH}_2\text{O} + \text{O}$  channel, which has recently been identified in shock tube experiments [52].

Under richer conditions a primary reaction is



The commonly used rate for this reaction,  $2.5\text{E}11 T^{0.67} \exp(-25,700/RT) \text{ cm}^3/\text{mole s}$  [109], conflicts with newer experimental data. Bohland and Temps [110] measured the rate directly at room temperature to be  $1.6\text{E}14 \text{ cm}^3/\text{mole s}$ . However, from shock-tube experiments Frank et al. [52] derived an upper limit of  $7.0\text{E}12 \text{ cm}^3/\text{mole s}$  for the temperature range 1650–2800K. This value is in agreement with an upper limit of  $1.0\text{E}13 \text{ cm}^3/\text{mole s}$  obtained at 2000K from flame experiments [106]. We combine these measurements to obtain a rate expression of  $7.3\text{E}17 T^{-1.56} \text{ cm}^3/\text{mole s}$ .

Other reactions of  $\text{CH}_2$  include



The rate of the  $\text{CH}_2 + \text{O}$  reaction has been measured recently at room temperature by Bohland et al. [51] to be  $8.1\text{E}13 \text{ cm}^3/\text{mole s}$ . We have adopted this rate together with the branching ratio  $k_{56}/k_{57}$  of 3 : 5 proposed by Frank et al [52].

For the reaction between  $\text{CH}_2$  and  $\text{CO}_2$  we have combined the room temperature measurement of Laufer [13] with an estimated activation energy of 1 kcal/mole.

The role of  $\text{CH}$  as a precursor to prompt-NO has aroused increasing interest in the  $\text{CH}$ -reactions, and several of their rates have been determined recently. The rates measured recently include those of the reactions between  $\text{CH}$  and  $\text{O}_2$  [15],  $\text{CH}$  and  $\text{O}$  [54],  $\text{CH}$  and  $\text{CO}_2$  [15], and the reactions between  $\text{CH}$  and different  $\text{C}_1$  and  $\text{C}_2$  species [14, 55]. We incorporate these results directly in our mechanism.

The reaction between  $\text{CH}$  and  $\text{H}$  to form carbon atoms and  $\text{H}_2$  has been shown to be important, but its rate has not been measured directly. Peeters and Vinckier [106] found  $\text{CH}$  to be removed rapidly by  $\text{H}$  in rich methane and ethylene flames, evidenced by the presence of significant quantities of carbon atoms. The importance of this reaction was confirmed by Grebe and Homann [111] in their study of the chemiluminescence in the  $\text{C}_2\text{H}_2/\text{O}/\text{H}$  system. We have estimated the rate to be as fast as the room temperature rate of (R55), i.e.,  $k_{70} = 1.5\text{E}14 \text{ cm}^3/\text{mole s}$ . The reactions of  $\text{H}$ -atoms with  $\text{CH}$  and  $\text{CH}_2$  are discussed more extensively by Miller and coworkers in their paper on hydrocarbon/nitric oxide interactions in low-pressure flames [86].

$\text{CH}$ -producing pathways other than through  $\text{CH}_2$  have been proposed in the literature, e.g.,  $\text{CH}_3 + \text{O} \rightleftharpoons \text{CH} + \text{H}_2\text{O}$  [98] and  $\text{C}_2\text{H}_2 + \text{OH} \rightleftharpoons \text{CH} + \text{CH}_2\text{O}$  [112]. However, there is no experimental evidence for these reactions. Furthermore, they conflict with the findings of Peeters and Vinckier [106], and thus we do not include them.

#### IV. RESULTS AND DISCUSSION

We have used two sources of experimental data on methane combustion in jet-stirred reactors. Bartok et al. [1] did a series of experiments for methane/air combustion with and without the addition of fuel nitrogen. The  $\text{NO}$ -emissions were measured as a function of air/fuel equivalence ratio and residence time. Figures 2, 3, 6, 7 and 8 present comparisons between the Bartok data and our calculations for a perfectly stirred reactor with an

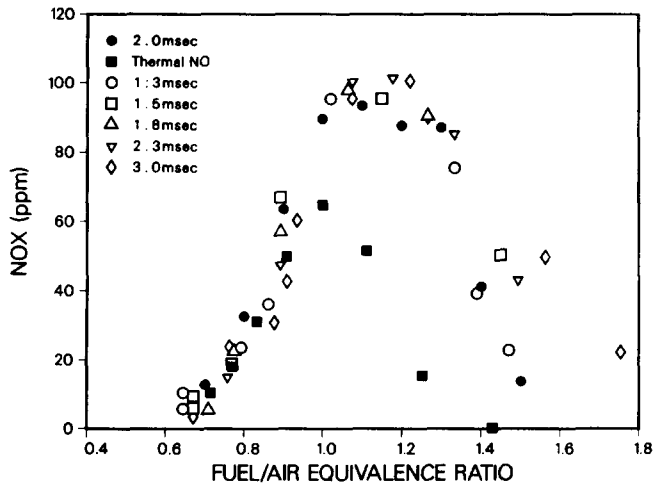


Fig. 2. Comparison between NO emissions data of Bartok et al. [1] on methane combustion in a stirred reactor and calculations for a perfectly stirred reactor with a nominal residence time of 2 ms. Open symbols denote experimental data, closed symbols denote calculated values. Reactor conditions: volume = 67.4 cm<sup>3</sup>, pressure = 1.0 atm,  $T_{inlet} = 464K$ . Residence time = 1.3-3.0 ms.

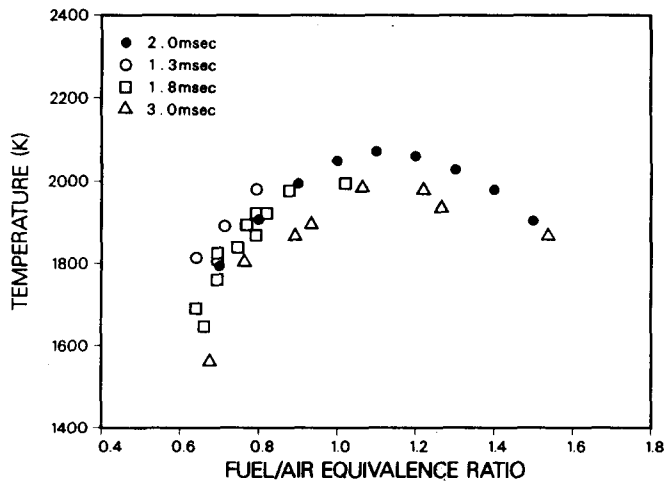


Fig. 3. Comparison between temperature data of Bartok et al. [1] on methane combustion in a stirred reactor and calculations for a perfectly stirred reactor with a nominal residence time of 2 ms. Open symbols denote experimental data, closed symbols denote calculated values. Reactor conditions: volume = 67.4 cm<sup>3</sup>, pressure = 1.0 atm,  $T_{inlet} = 464K$ . Residence time = 1.3-3.0 ms. Assumed heat loss in calculations: 130 cal/s.

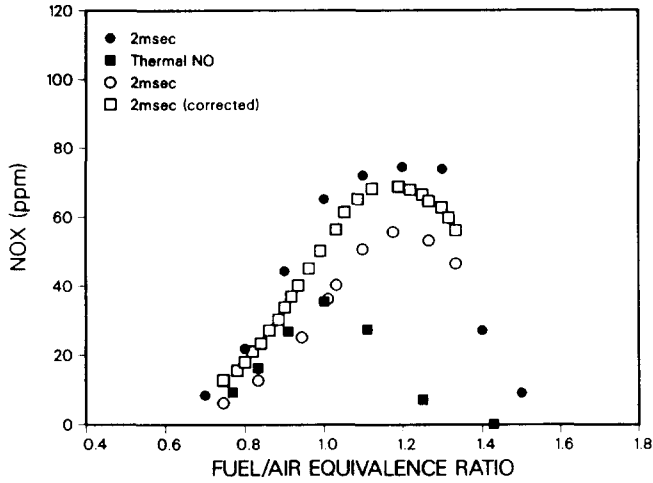


Fig. 4. Comparison between NO emissions data of Duterque et al. [2] on methane combustion in a stirred reactor and calculations for a perfectly stirred reactor with a nominal residence time of 2 ms. Open symbols denote experimental data, closed symbols denote calculated values. Reactor conditions: volume = 150 cm<sup>3</sup>, pressure = 1.0 atm,  $T_{inlet} = 353K$ . Residence time = 2.0 ms.

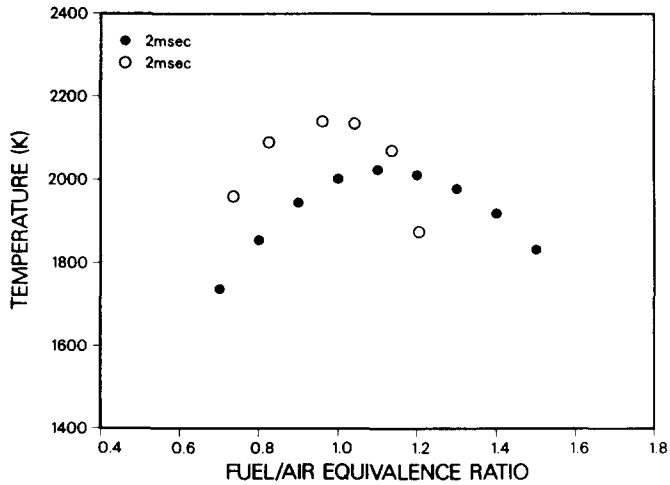


Fig. 5. Comparison between temperature data of Duterque et al. [2] on methane combustion in a stirred reactor and calculations for a perfectly stirred reactor with a nominal residence time of 2 ms. Open symbols denote experimental data, closed symbols denote calculated values. Reactor conditions: volume = 150 cm<sup>3</sup>, pressure = 1.0 atm,  $T_{inlet} = 353K$ . Residence time = 2.0 ms. Assumed heat loss in calculations: 200 cal/s.

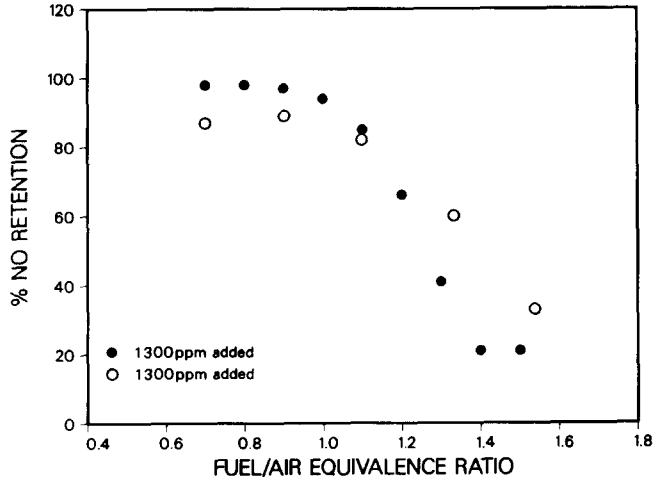


Fig. 6. Comparison between NO emissions of Bartok et al. [1] on methane combustion with NO added in a stirred reactor and calculations for a perfectly stirred reactor with a nominal residence time of 2 ms. Open symbols denote experimental data, closed symbols denote calculated values. Reactor conditions: volume = 67.4 cm<sup>3</sup>, pressure = 1.0 atm,  $T_{inlet}$  = 464K. Residence time = 2 ms.

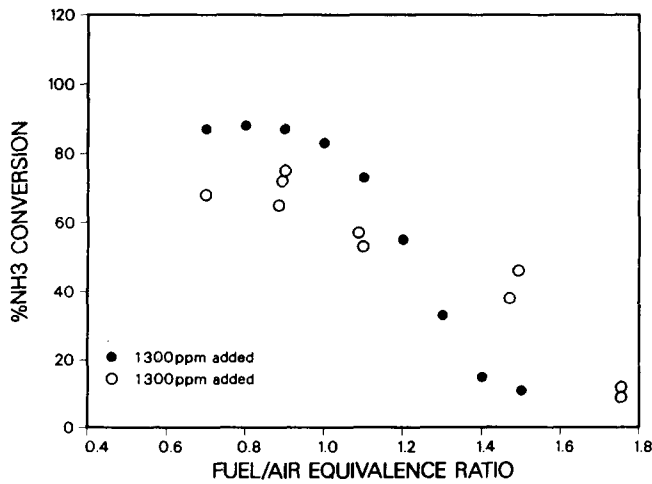


Fig. 7. Comparison between NO emissions data of Bartok et al. [1] on methane combustion with NH<sub>3</sub> added in a stirred reactor and calculations for a perfectly stirred reactor with a nominal residence time of 2 ms. Open symbols denote experimental data, closed symbols denote calculated values. Reactor conditions: volume = 67.4 cm<sup>3</sup>, pressure = 1.0 atm,  $T_{inlet}$  = 464K. Residence time = 2 ms.

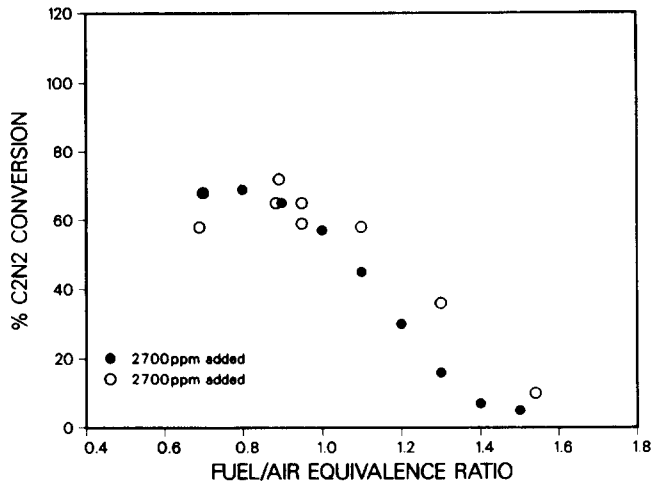


Fig. 8. Comparison between NO emissions data of Bartok et al. [1] on methane combustion with  $C_2N_2$  added in a stirred reactor and calculations for a perfectly stirred reactor with a nominal residence time of 2 ms. Open symbols denote experimental data, closed symbols denote calculated values. Reactor conditions: volume = 67.4 cm<sup>3</sup>, pressure = 1.0 atm,  $T_{inlet}$  = 464K. Residence time = 2 ms.

inlet temperature of 464K and a residence time of 2 ms.

In a more recent investigation Duterque et al. [2] made similar measurements on methane/air mixtures. Their experiments were performed with a lower inlet temperature (353K), but they had approximately the same residence time. Comparisons between their measurements and our calculations are shown in Figs. 4 and 5. The measured emissions of NO were corrected by Duterque et al. for NO-to-NO<sub>2</sub> conversion in the probe (Fig. 4). Our calculations show no significant quantities of NO<sub>2</sub> produced in the reactor; consequently, the predicted NO and the total nitrogen oxides are the same.

Because of uncertainty in interpreting the temperature measurements, we choose for both sets of experiments to apply a heat loss to the reactors and compute the temperature from a heat balance. The temperature measurements in Bartok's experiments seem to be the more reliable, since they were measured directly by thermocouples, while Duterque et al. determined the temperatures in their experiments from concentration and heat loss measurements using an energy balance. However, the temperature data from Bartok et al. are scarce in the fuel-rich region, and there is some scatter in

the lean region temperature data. The heat loss used in our calculations for Bartok's experiments was chosen to make the calculated temperature fit the measurements under lean conditions (Fig. 3).

By comparing the experimental data of the two sources one notices that in Bartok's experiments both the inlet temperature and the NO-emissions are considerably higher than in the similar experiments of Duterque et al.. Under lean conditions most of the NO is formed by the reaction of O-atoms with N<sub>2</sub>. Since this reaction has a high activation energy, the formation of NO under these conditions is very sensitive to the temperature. Thus, provided the NO-measurements are correct, it seems that the actual temperatures in the Duterque experiments must have been lower than the temperatures in the similar experiments by Bartok et al.. This means that the temperatures determined by Duterque et al. are probably too high. Trying to resolve this discrepancy, we did some adiabatic (no heat loss) calculations for the reactor at different residence times. These calculations indicated that to obtain the high temperatures reported by Duterque, the residence time would have to be approximately 5 times the value reported. However, there would still be discrepancies in the shapes of the temperature profiles.

Lowering the residence time to values of 0.3–0.5 ms increased the discrepancy both in the location and size of the temperature peak. Consequently, we have chosen to adjust the heat loss for Duterque's experiments in our calculations to make the calculated NO-emissions match the experimental data under lean conditions. The selected heat loss of 200 cal/s lowers the temperature 30–40K below the adiabatic result at the same residence time.

### The Methane/Air Combustion

Figures 2 and 4 show comparisons between the undoped methane/air data of Bartok and Duterque, respectively, and our calculations for the NO emissions. With the temperatures computed in the manner described above, the agreement between the measurements and the calculations is generally satisfactory.

Tables II and III show the results of the sensitivity analysis, corresponding to Figs. 2 and 4. From these tables and a rate-of-production analysis some conclusions can be drawn about the principal routes to NO-formation under well-stirred conditions. Under stoichiometric and lean conditions the main pathway to NO is the Zeldovich-mechanism, the rate determining step being



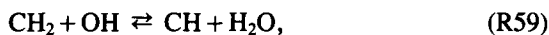
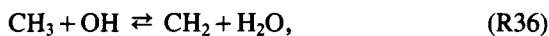
However, under lean conditions a significant contribution comes from the pathway through  $\text{N}_2\text{O}$ , initiated by



The importance of this reaction compared to (R162) increases with decreasing temperature. In fuel-rich situations the Zeldovich mechanism loses its significance due to the small O-atom concentrations. From Figs. 2 and 4 it is clear that the Zeldovich mechanism cannot describe the NO formation in this area; inclusion of a mechanism for prompt-NO formation is necessary to explain the experimental data.

From the sensitivity analysis one can see that the

formation of the small  $\text{CH}_i$ -species is a controlling step in the prompt-NO formation. The important reactions are



The abstraction reaction between  $\text{CH}_3$  and OH is the major source of  $\text{CH}_2$  under stirred conditions. Without this reaction it is very difficult to obtain agreement between our calculations and the experimental data. In its absence we compute an anomalous relative minimum in the NO produced in Fig. 2 at an equivalence ratio of approximately 1.2; a similar irregularity occurs in Fig. 4. Under fuel-rich conditions  $\text{CH}_2$  is also formed through reaction (R33) and to a lesser extent through the acetylene route. Near blowout a significant part of the oxidation process occurs through the  $\text{C}_2$ -species. In this area the NO-formation is sensitive to  $\text{C}_2$ -hydrocarbon reactions, not because they produce  $\text{CH}_2$  directly, but because these reactions begin to influence the active free radical concentrations.

We find the  $\text{CH} + \text{N}_2$  reaction to be the major source of prompt-NO under the present conditions. With our estimated rate for the  $\text{CH}_2 + \text{N}_2$  reaction this reaction is of secondary importance in our calculations. Since this estimate is expected to be an upper limit, this conclusion is a conservative one. However, the conclusion holds even with much larger values of  $k_{206}$  such as those used in some of our preliminary calculations [113].

The relative importance of the two chemical mechanisms forming NO under the present conditions, thermal-NO and prompt-NO, determines the shape of the curve for NO in Figs. 2 and 4. As seen in the figures the thermal-NO peaks just around stoichiometric conditions. However, because of the prompt-NO formation the overall NO peaks under fuel-rich conditions. As discussed above, we adjusted the rate of the  $\text{CH} + \text{N}_2$  reaction in order to predict the size of this peak



TABLE II

Linear Sensitivity Coefficients for NO for the Bartok Data

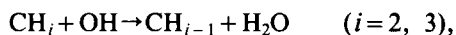
Reaction	Fuel/Air Equivalence Ratio								
	0.70	0.80	0.90	1.00	1.10	1.20	1.30	1.40	1.50
1. $H + O_2 \rightleftharpoons O + OH$	0.04	0.04	0.04	0.04	0.04	0.02	0.04	0.27	0.38
5. $H + OH + M \rightleftharpoons H_2O + M$	-0.02	0.01	0.05	0.09	0.12	0.16	0.05	-0.05	-0.01
12. $H + O_2 + M \rightleftharpoons HO_2 + M$	-0.09	0.02	0.09	0.10	0.08	0.06	0.02	-0.06	-0.06
25. $CO + OH \rightleftharpoons CO_2 + H$	0.11	0.08	0.05	0.03	0.01	0.01	0.00	-0.04	-0.04
27. $CH_4 + M \rightleftharpoons CH_3 + H + M$	0.00	0.00	0.00	0.00	0.01	0.03	0.04	-0.40	-0.42
33. $CH_3 + H \rightleftharpoons CH_2 + H_2$	0.02	0.02	0.03	0.05	0.08	0.14	0.10	0.02	0.00
34. $CH_3 + O \rightleftharpoons CH_2O + H$	-0.19	-0.18	-0.18	-0.22	-0.31	-0.44	-0.29	0.12	0.02
36. $CH_3 + OH \rightleftharpoons CH_2 + H_2O$	0.14	0.13	0.12	0.14	0.17	0.19	0.09	0.02	0.00
49. $HCO + M \rightleftharpoons CO + H + M$	0.02	-0.01	-0.02	-0.03	-0.03	-0.05	-0.02	0.06	0.03
50. $HCO + H \rightleftharpoons CO + H_2$	0.00	0.00	0.01	0.01	0.02	0.04	0.02	-0.06	-0.03
55. $CH_2 + H \rightleftharpoons CH + H_2$	0.02	0.01	0.02	0.02	0.05	0.10	0.11	0.04	0.04
59. $CH_2 + OH \rightleftharpoons CH_2O + H$	-0.05	-0.06	-0.07	-0.09	-0.15	-0.23	-0.18	0.05	0.00
60. $CH_2 + OH \rightleftharpoons CH + H_2O$	0.17	0.15	0.14	0.16	0.22	0.29	0.21	0.05	0.03
70. $CH + H \rightleftharpoons C + H_2$	-0.02	-0.03	-0.05	-0.10	-0.19	-0.33	-0.35	-0.35	-0.24
72. $CH + OH \rightleftharpoons HCO + H$	-0.01	-0.02	-0.02	-0.03	-0.05	-0.06	-0.04	0.00	0.00
73. $CH + O_2 \rightleftharpoons HCO + O$	-0.17	-0.13	-0.10	-0.08	-0.06	-0.05	-0.03	0.00	-0.03
74. $CH + CO_2 \rightleftharpoons HCO + CO$	-0.01	-0.02	-0.02	-0.03	-0.04	-0.07	-0.07	-0.01	-0.03
81. $C + O_2 \rightleftharpoons CO + O$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.06
88. $2CH_3 \rightleftharpoons C_2H_4 + H_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.07
90. $C_2H_6 + H \rightleftharpoons C_2H_5 + H_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.11
103. $C_2H_3 + M \rightleftharpoons C_2H_2 + H + M$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.25
104. $C_2H_3 + H \rightleftharpoons C_2H_2 + H_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.15	-0.26
112. $C_2H_2 + O \rightleftharpoons CH_2 + CO$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.06	-0.15
113. $C_2H_2 + O \rightleftharpoons HCCO + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.04	-0.10
152. $NH + H \rightleftharpoons N + H_2$	0.00	0.00	0.00	0.00	0.00	-0.01	-0.01	-0.03	-0.06
154. $NH + OH \rightleftharpoons HNO + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.06	0.08
158. $NH + NO \rightleftharpoons N_2O + H$	0.26	0.15	0.09	0.06	0.04	0.02	0.00	-0.01	0.00
160. $N + O_2 \rightleftharpoons NO + O$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.14
161. $N + OH \rightleftharpoons NO + H$	0.00	0.00	0.01	0.01	0.02	0.05	0.14	0.21	0.21
162. $N + NO \rightleftharpoons N_2 + O$	0.35	0.53	0.60	0.58	0.44	0.16	-0.11	-0.08	-0.02
172. $N_2O + M \rightleftharpoons N_2 + O + M$	0.39	0.23	0.14	0.09	0.06	0.03	0.01	0.00	0.00
173. $N_2O + H \rightleftharpoons N_2 + OH$	-0.27	-0.15	-0.09	-0.06	-0.04	-0.02	-0.01	-0.01	0.00
177. $HCN + O \rightleftharpoons NCO + H$	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.18	0.23
178. $HCN + O \rightleftharpoons NH + CO$	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.06	0.07
181. $HCN + OH \rightleftharpoons HNCO + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.06
184. $CN + OH \rightleftharpoons NCO + H$	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.15	0.08
186. $CN + O_2 \rightleftharpoons NCO + O$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.10
201. $C + NO \rightleftharpoons CN + O$	0.00	0.00	0.00	0.00	-0.01	-0.05	-0.19	-0.34	-0.24
202. $CH + NO \rightleftharpoons HCN + O$	0.00	0.00	0.00	-0.01	-0.01	-0.03	-0.09	-0.25	-0.33
203. $CH_2 + NO \rightleftharpoons HCNO + H$	0.00	0.00	0.00	0.00	0.00	-0.01	-0.02	-0.07	-0.15
205. $CH + N_2 \rightleftharpoons HCN + N$	0.23	0.22	0.23	0.28	0.42	0.67	0.78	0.89	0.97
212. $CH_3 + N \rightleftharpoons HCN + 2H$	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.19	-0.38

TABLE III

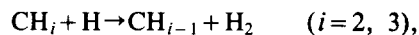
Linear Sensitivity Coefficients for NO for the Duterque Data

Reaction	Fuel/Air Equivalence Ratio									
	0.70	0.80	0.90	1.00	1.10	1.20	1.30	1.40	1.50	
1. $H + O_2 \rightleftharpoons O + OH$	0.05	0.04	0.04	0.04	0.04	0.01	0.07	0.33	0.64	
5. $H + OH + M \rightleftharpoons H_2O + M$	-0.02	0.00	0.05	0.10	0.15	0.18	0.00	-0.03	-0.01	
12. $H + O_2 + M \rightleftharpoons HO_2 + M$	-0.11	0.02	0.10	0.12	0.10	0.07	0.00	-0.07	-0.10	
25. $CO + OH \rightleftharpoons CO_2 + H$	0.13	0.09	0.06	0.03	0.01	0.01	-0.01	-0.06	-0.04	
27. $CH_4 + M \rightleftharpoons CH_3 + H + M$	0.00	0.00	0.00	0.01	0.02	0.05	0.00	-0.43	-0.52	
33. $CH_3 + H \rightleftharpoons CH_2 + H_2$	0.02	0.02	0.04	0.06	0.11	0.16	0.08	0.02	-0.02	
34. $CH_3 + O \rightleftharpoons CH_2O + H$	-0.23	-0.23	-0.24	-0.29	-0.39	-0.50	-0.20	0.09	0.02	
36. $CH_3 + OH \rightleftharpoons CH_2 + H_2O$	0.18	0.17	0.16	0.18	0.21	0.21	0.07	0.01	0.00	
49. $HCO + M \rightleftharpoons CO + H + M$	0.02	0.00	-0.02	-0.03	-0.04	-0.06	0.00	0.05	0.04	
50. $HCO + H \rightleftharpoons CO + H_2$	0.00	0.00	0.01	0.02	0.03	0.05	0.00	-0.05	-0.04	
55. $CH_2 + H \rightleftharpoons CH + H_2$	0.02	0.02	0.02	0.03	0.07	0.12	0.11	0.04	0.06	
57. $CH_2 + O \rightleftharpoons CO + H_2$	-0.05	-0.05	-0.05	-0.05	-0.05	-0.04	-0.02	-0.02	-0.01	
59. $CH_2 + OH \rightleftharpoons CH_2O + H$	-0.06	-0.07	-0.08	-0.12	-0.18	-0.25	-0.13	0.02	-0.01	
60. $CH_2 + OH \rightleftharpoons CH + H_2O$	0.20	0.19	0.18	0.21	0.27	0.32	0.16	0.04	0.04	
70. $CH + H \rightleftharpoons C + H_2$	-0.02	-0.04	-0.07	-0.13	-0.24	-0.38	-0.38	-0.35	-0.22	
72. $CH + OH \rightleftharpoons HCO + H$	-0.01	-0.02	-0.03	-0.04	-0.06	-0.06	-0.03	0.00	0.00	
73. $CH + O_2 \rightleftharpoons HCO + O$	-0.21	-0.17	-0.13	-0.10	-0.08	-0.05	-0.03	-0.01	-0.06	
74. $CH + CO_2 \rightleftharpoons HCO + CO$	-0.02	-0.02	-0.03	-0.04	-0.06	-0.08	-0.06	-0.02	-0.04	
80. $C + OH \rightleftharpoons CO + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.04	0.01	
81. $C + O_2 \rightleftharpoons CO + O$	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.07	0.07	
86. $2CH_3 \rightleftharpoons C_2H_6$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.05	
88. $2CH_3 \rightleftharpoons C_2H_4 + H_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.06	
90. $C_2H_6 + H \rightleftharpoons C_2H_5 + H_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.15	
103. $C_2H_3 + M \rightleftharpoons C_2H_2 + H + M$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.33	
104. $C_2H_3 + H \rightleftharpoons C_2H_2 + H_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.20	-0.36	
112. $C_2H_2 + O \rightleftharpoons CH_2 + CO$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.10	-0.18	
113. $C_2H_2 + O \rightleftharpoons HCCO + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.07	-0.12	
152. $NH + H \rightleftharpoons N + H_2$	0.00	0.00	0.00	0.00	0.00	-0.01	-0.01	-0.04	-0.06	
154. $NH + OH \rightleftharpoons HNO + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.07	0.06	
158. $NH + NO \rightleftharpoons N_2O + H$	0.31	0.19	0.11	0.07	0.05	0.02	-0.01	-0.01	0.00	
160. $N + O_2 \rightleftharpoons NO + O$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.20	
161. $N + OH \rightleftharpoons NO + H$	0.00	0.00	0.00	0.01	0.02	0.06	0.15	0.22	0.17	
162. $N + NO \rightleftharpoons N_2 + O$	0.24	0.42	0.51	0.50	0.35	0.08	-0.12	-0.05	-0.01	
172. $N_2O + M \rightleftharpoons N_2 + O + M$	0.45	0.28	0.17	0.11	0.07	0.03	0.00	0.00	0.00	
173. $N_2O + H \rightleftharpoons N_2 + OH$	-0.32	-0.19	-0.11	-0.07	-0.05	-0.02	-0.01	0.00	0.00	
174. $N_2O + O \rightleftharpoons 2NO$	0.05	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	
177. $HCN + O \rightleftharpoons NCO + H$	0.00	0.00	0.00	0.00	0.01	0.02	0.08	0.21	0.23	
178. $HCN + O \rightleftharpoons NH + CO$	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.07	0.07	
181. $HCN + OH \rightleftharpoons HNCO + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.05	
184. $CN + OH \rightleftharpoons NCO + H$	0.00	0.00	0.00	0.00	0.00	0.02	0.08	0.13	0.04	
186. $CN + O_2 \rightleftharpoons NCO + O$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.07	0.11	
201. $C + NO \rightleftharpoons CN + O$	0.00	0.00	0.00	0.00	-0.01	-0.06	-0.23	-0.33	-0.17	
202. $CH + NO \rightleftharpoons HCN + O$	0.00	0.00	0.00	-0.01	-0.01	-0.04	-0.11	-0.28	-0.31	
203. $CH_2 + NO \rightarrow HCN + H$	0.00	0.00	0.00	0.00	0.00	-0.01	-0.03	-0.09	-0.18	
205. $CH + N_2 \rightleftharpoons HCN + N$	0.28	0.28	0.29	0.35	0.52	0.74	0.81	0.93	0.97	
212. $CH_3 + N \rightleftharpoons HCN + 2H$	0.00	0.00	0.00	0.00	0.00	0.00	-0.02	-0.26	-0.40	

correctly. The *location* of the peak, however, is determined by the competing pathways leading to formation of  $\text{CH}_i$ -species. Increased rates for the reactions



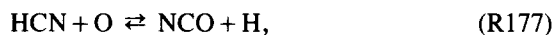
would move the peak closer to stoichiometric conditions, while increased influence of the sequence



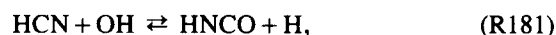
would move the peak toward even richer conditions, ultimately forming a pronounced double peak.

Under fuel-rich conditions the interaction between the hydrocarbon and the nitrogen chemistry results in a significant amount of cycling back and forth between NO and cyanide species. NO is recycled back to CN by the reaction  $\text{C} + \text{NO} \rightleftharpoons \text{CN} + \text{O}$  (R201), and to HCN by the reactions  $\text{CH} + \text{NO} \rightleftharpoons \text{HCN} + \text{O}$  (R202), and  $\text{CH}_2 + \text{NO} \rightleftharpoons \text{HCNO} + \text{H} \rightleftharpoons \text{HCN} + \text{OH}$  (R203, R197). Under fuel-rich conditions these reactions are rate-controlling. HCN is also formed through the reaction  $\text{CH}_3 + \text{N} \rightleftharpoons \text{HCN} + \text{H} + \text{H}$  (R212), which we have estimated to be very fast. These processes result in the exhaust of large quantities of HCN from the reactor under fuel-rich conditions.

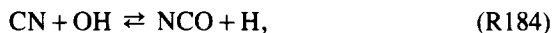
Under the present conditions there seems to be little interconversion between HCN and CN. In our mechanism the HCN formed is converted to NH through the reactions



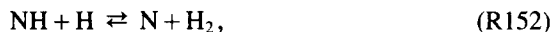
This sequence is in agreement with flame observations [9]. Under richer conditions this conversion also occurs through



Consumption of CN proceeds through



followed by (R190). The conversion of NH to NO occurs through

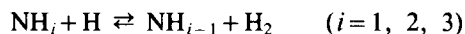


Under the conditions of these experiments the levels of NO and  $\text{NH}_i$ -species are relatively small. Therefore, conversion of NO to  $\text{N}_2$  is not significant.

### Addition of Fuel-NO

Figures 6–8 show comparison between Bartok's data and our calculations of the NO emissions for a methane/air mixture doped with NO,  $\text{NH}_3$ , and  $\text{C}_2\text{N}_2$ , respectively. Tables IV–VI contain the corresponding sensitivity coefficients. Comparison between these figures shows that the general behavior is the same whether the added compound is NO,  $\text{NH}_3$ , or  $\text{C}_2\text{N}_2$ . Under lean conditions the emission of NO corresponds to 60–100% of the added nitrogen compound. Under fuel-rich conditions the emission of NO is considerably lower, approaching zero at a fuel/air equivalence ratio of 1.6. The model predicts this general behavior. However, our calculations generally predict too high emissions of NO under lean conditions and too low NO-emissions under rich conditions.

The conversion of  $\text{NH}_i$ -species to NO in the  $\text{NH}_3$ -doped mixtures occurs through the sequence



followed by the reaction



In the  $\text{C}_2\text{N}_2$ -doped mixtures HCN and CN are rapidly formed from



Unlike the undoped experiments, here we find some interconversion between the HCN and CN

TABLE IV

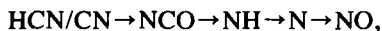
Linear Sensitivity Coefficients for NO for the Bartok Data with NO Added

Reaction	Fuel/Air Equivalence Ratio								
	0.70	0.80	0.90	1.00	1.10	1.20	1.30	1.40	1.50
1. $H + O_2 \rightleftharpoons O + OH$	0.00	0.00	0.00	0.01	0.01	0.02	0.04	-0.11	-0.57
2. $H_2 + O \rightleftharpoons H + OH$	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.03	-0.07
4. $2OH \rightleftharpoons H_2O + O$	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.03	-0.06
5. $H + OH + M \rightleftharpoons H_2O + M$	0.00	0.00	0.00	0.00	-0.01	-0.06	-0.10	0.00	0.01
12. $H + O_2 + M \rightleftharpoons HO_2 + M$	0.00	0.00	0.01	0.00	-0.01	-0.02	-0.03	-0.01	0.05
27. $CH_4 + M \rightleftharpoons CH_3 + H + M$	0.00	0.00	0.00	0.00	0.00	-0.01	-0.09	-0.03	0.41
33. $CH_3 + H \rightleftharpoons CH_2 + H_2$	0.00	0.00	0.00	-0.01	-0.02	-0.05	-0.08	-0.06	-0.01
34. $CH_3 + O \rightleftharpoons CH_2O + H$	0.01	0.01	0.02	0.03	0.07	0.15	0.27	0.14	0.01
36. $CH_3 + OH \rightleftharpoons CH_2 + H_2O$	-0.01	-0.01	-0.01	-0.02	-0.04	-0.06	-0.07	-0.04	-0.01
49. $HCO + M \rightleftharpoons CO + H + M$	0.00	0.00	0.00	0.00	0.00	0.02	0.05	0.01	-0.03
55. $CH_2 + H \rightleftharpoons CH + H_2$	0.00	0.00	0.00	0.00	-0.01	-0.03	-0.08	-0.09	-0.05
59. $CH_2 + OH \rightleftharpoons CH_2O + H$	0.00	0.00	0.01	0.01	0.03	0.08	0.16	0.12	0.05
60. $CH_2 + OH \rightleftharpoons CH + H_2O$	0.00	-0.01	-0.01	-0.02	-0.04	-0.09	-0.14	-0.11	-0.05
70. $CH + H \rightleftharpoons C + H_2$	0.00	0.00	0.00	0.00	-0.01	-0.03	-0.07	-0.09	-0.05
73. $CH + O_2 \rightleftharpoons HCO + O$	0.00	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.05
74. $CH + CO_2 \rightleftharpoons HCO + CO$	0.00	0.00	0.00	0.00	0.01	0.02	0.05	0.08	0.05
80. $C + OH \rightleftharpoons CO + H$	0.00	0.00	0.00	0.01	0.03	0.08	0.14	0.10	0.03
81. $C + O_2 \rightleftharpoons CO + O$	0.00	0.00	0.00	0.01	0.01	0.02	0.04	0.09	0.11
84. $C + CH_3 \rightleftharpoons C_2H_2 + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.05
103. $C_2H_3 + M \rightleftharpoons C_2H_2 + H + M$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	-0.24
104. $C_2H_3 + H \rightleftharpoons C_2H_2 + H_2$	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.01	0.24
112. $C_2H_2 + O \rightleftharpoons CH_2 + CO$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06
154. $NH + OH \rightleftharpoons HNO + H$	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.06	0.03
161. $N + OH \rightleftharpoons NO + H$	0.00	0.01	0.02	0.04	0.08	0.16	0.23	0.18	0.07
162. $N + NO \rightleftharpoons N_2 + O$	0.00	0.00	0.00	-0.02	-0.08	-0.17	-0.26	-0.19	-0.08
177. $HCN + O \rightleftharpoons NCO + H$	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.06	0.05
184. $CN + OH \rightleftharpoons NCO + H$	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.06	0.02
201. $C + NO \rightleftharpoons CN + O$	0.00	0.00	-0.01	-0.02	-0.04	-0.11	-0.20	-0.28	-0.21
202. $CH + NO \rightleftharpoons HCN + O$	-0.01	-0.01	-0.02	-0.03	-0.05	-0.07	-0.11	-0.22	-0.31
203. $CH_2 + NO \rightarrow HCNO + H$	0.00	0.00	0.00	-0.01	-0.01	-0.02	-0.03	-0.07	-0.14
205. $CH + N_2 \rightleftharpoons HCN + N$	0.00	0.00	0.01	0.01	0.02	0.03	0.05	0.08	0.03

species, mainly through



HCN and CN are then converted to NO by the sequence



described above.

The interaction between the nitrogen and the

hydrocarbon chemistry is similar to that in the undoped flames. Under rich conditions a major part of the NO in the doped flames is converted to CN and HCN through attack of C, CH and CH<sub>2</sub>. HCN and CN are then recycled back to NO through the sequence described above. Large quantities of nitrogen are thus continuously cycling back and forth between NO and cyanide species, most of it stored in the form of HCN. Only a small part of the NO on each cycle is converted to N<sub>2</sub> through reaction with the nitrogen

TABLE V

Linear Sensitivity Coefficients for NO for the Bartok Data with NH<sub>3</sub> Added

Reaction	Fuel/Air Equivalence Ratio								
	0.70	0.80	0.90	1.00	1.10	1.20	1.30	1.40	1.50
1. H + O <sub>2</sub> ⇌ O + OH	0.01	0.01	0.01	0.01	0.02	0.03	0.06	-0.06	-0.44
2. H <sub>2</sub> + O ⇌ H + OH	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.04	-0.07
4. 2OH ⇌ H <sub>2</sub> O + O	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.04	-0.06
5. H + OH + M ⇌ H <sub>2</sub> O + M	0.00	0.00	0.00	0.00	-0.02	-0.07	-0.11	-0.01	0.01
27. CH <sub>4</sub> + M ⇌ CH <sub>3</sub> + H + M	0.00	0.00	0.00	0.00	0.00	-0.02	-0.12	-0.12	0.18
33. CH <sub>3</sub> + H ⇌ CH <sub>2</sub> + H <sub>2</sub>	0.00	0.00	0.00	-0.01	-0.02	-0.04	-0.07	-0.04	0.00
34. CH <sub>3</sub> + O ⇌ CH <sub>2</sub> O + H	0.01	0.01	0.01	0.03	0.06	0.14	0.27	0.15	0.03
36. CH <sub>3</sub> + OH ⇌ CH <sub>2</sub> + H <sub>2</sub> O	-0.01	-0.01	-0.01	-0.02	-0.03	-0.06	-0.06	-0.03	0.00
49. HCO + M ⇌ CO + H + M	0.00	0.00	0.00	0.00	0.01	0.02	0.06	0.02	-0.01
50. HCO + H ⇌ CO + H <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	-0.02	-0.06	-0.02	0.01
55. CH <sub>2</sub> + H ⇌ CH + H <sub>2</sub>	0.00	0.00	0.00	0.00	-0.01	-0.03	-0.07	-0.07	-0.04
59. CH <sub>2</sub> + OH ⇌ CH <sub>2</sub> O + H	0.00	0.00	0.00	0.01	0.03	0.07	0.16	0.12	0.04
60. CH <sub>2</sub> + OH ⇌ CH + H <sub>2</sub> O	0.00	0.00	-0.01	-0.02	-0.04	-0.07	-0.13	-0.08	-0.03
70. CH + H ⇌ C + H <sub>2</sub>	0.00	0.00	0.00	-0.01	-0.01	-0.03	-0.08	-0.10	-0.06
74. CH + CO <sub>2</sub> ⇌ HCO + CO	0.00	0.00	0.00	0.00	0.01	0.02	0.05	0.07	0.04
80. C + OH ⇌ CO + H	0.00	0.00	0.00	0.01	0.03	0.07	0.12	0.07	0.02
81. C + O <sub>2</sub> ⇌ CO + O	0.00	0.00	0.00	0.01	0.01	0.02	0.03	0.08	0.08
89. CH <sub>3</sub> + CH <sub>2</sub> ⇌ C <sub>2</sub> H <sub>4</sub> + H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.06
103. C <sub>2</sub> H <sub>3</sub> + M ⇌ C <sub>2</sub> H <sub>2</sub> + H + M	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	-0.12
104. C <sub>2</sub> H <sub>3</sub> + H ⇌ C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.05	0.11
152. NH + H ⇌ N + H <sub>2</sub>	-0.01	-0.01	-0.01	-0.02	-0.03	-0.03	-0.04	-0.05	-0.07
154. NH + OH ⇌ HNO + H	0.03	0.03	0.03	0.03	0.03	0.04	0.06	0.10	0.13
160. N + O <sub>2</sub> ⇌ NO + O	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.05	0.14
161. N + OH ⇌ NO + H	0.03	0.04	0.06	0.09	0.15	0.23	0.29	0.26	0.20
162. N + NO ⇌ N <sub>2</sub> + O	-0.05	-0.05	-0.06	-0.09	-0.15	-0.25	-0.32	-0.24	-0.17
177. HCN + O ⇌ NCO + H	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.08	0.10
184. CN + OH ⇌ NCO + H	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.07	0.03
201. C + NO ⇌ CN + O	0.00	0.00	0.00	-0.01	-0.04	-0.10	-0.19	-0.25	-0.17
202. CH + NO ⇌ HCN + O	-0.01	-0.01	-0.02	-0.03	-0.04	-0.06	-0.10	-0.20	-0.26
203. CH <sub>2</sub> + NO → HCNO + H	0.00	0.00	0.00	-0.01	-0.01	-0.01	-0.03	-0.07	-0.12
205. CH + N <sub>2</sub> ⇌ HCN + N	0.00	0.00	0.01	0.02	0.02	0.04	0.06	0.09	0.05
212. CH <sub>3</sub> + N ⇌ HCN + 2H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.10	-0.22

atom. Nevertheless, the NO emission is sensitive to this latter conversion.

Figures 9 and 10 show the fixed-nitrogen concentrations we calculate for conditions corresponding to Figs. 2 and 7, i.e., Bartok's stirred reactor experiments with mixtures of CH<sub>4</sub>/air and CH<sub>4</sub>/air/NO, respectively. The fixed nitrogen is stored in the form of NO and HCN; we calculate only small emissions of NH<sub>3</sub>. Figure 9 shows our calculations for the undoped experiment. Even

though the emissions of NO drop off under fuel-rich conditions, the total amount of fixed nitrogen peaks at a fuel/air equivalence ratio of 1.4. This is caused by the large quantities of HCN formed under fuel-rich conditions by attack of hydrocarbon species on NO and N<sub>2</sub>. Figure 10 shows the analogous calculations for the experiment doped with 1300 ppm NO. Here one can see that there is a minimum in the emission of fixed nitrogen at an equivalence ratio of 1.3. However, the precise

TABLE VI  
Linear Sensitivity Coefficients for NO for the Bartok Data with C<sub>2</sub>N<sub>2</sub> Added

Reaction	Fuel/Air Equivalence Ratio								
	0.70	0.80	0.90	1.00	1.10	1.20	1.30	1.40	1.50
1. H + O <sub>2</sub> ⇌ O + OH	0.01	0.01	0.01	0.02	0.03	0.04	0.07	-0.05	-0.32
2. H <sub>2</sub> + O ⇌ H + OH	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.04	-0.09
4. 2OH ⇌ H <sub>2</sub> O + O	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.04	-0.07
5. H + OH + M ⇌ H <sub>2</sub> O + M	-0.01	-0.01	-0.01	-0.02	-0.05	-0.10	-0.10	-0.01	0.00
27. CH <sub>4</sub> + M ⇌ CH <sub>3</sub> + H + M	0.00	0.00	0.00	0.00	-0.01	-0.03	-0.15	-0.13	0.07
33. CH <sub>3</sub> + H ⇌ CH <sub>2</sub> + H <sub>2</sub>	0.00	0.00	-0.01	-0.01	-0.03	-0.06	-0.08	-0.04	0.00
34. CH <sub>3</sub> + O ⇌ CH <sub>2</sub> O + H	0.02	0.03	0.04	0.07	0.11	0.20	0.30	0.13	0.03
36. CH <sub>3</sub> + OH ⇌ CH <sub>2</sub> + H <sub>2</sub> O	-0.01	-0.02	-0.03	-0.04	-0.06	-0.07	-0.06	-0.03	0.00
49. HCO + M ⇌ CO + H + M	0.01	0.00	0.00	0.01	0.01	0.04	0.06	0.02	-0.01
50. HCO + H ⇌ CO + H <sub>2</sub>	0.00	0.00	0.00	0.00	-0.01	-0.03	-0.06	-0.02	0.01
55. CH <sub>2</sub> + H ⇌ CH + H <sub>2</sub>	0.00	0.00	0.00	-0.01	-0.02	-0.04	-0.09	-0.07	-0.04
59. CH <sub>2</sub> + OH ⇌ CH <sub>2</sub> O + H	0.00	0.01	0.01	0.03	0.05	0.11	0.18	0.10	0.04
60. CH <sub>2</sub> + OH ⇌ CH + H <sub>2</sub> O	-0.01	-0.01	-0.02	-0.04	-0.07	-0.11	-0.15	-0.08	-0.03
70. CH + H ⇌ C + H <sub>2</sub>	0.00	0.00	0.00	0.00	-0.01	-0.02	-0.06	-0.08	-0.05
74. CH + CO <sub>2</sub> ⇌ HCO + CO	0.00	0.00	0.00	0.01	0.01	0.03	0.06	0.07	0.04
80. C + OH ⇌ CO + H	0.00	0.00	0.00	0.01	0.03	0.07	0.09	0.05	0.01
81. C + O <sub>2</sub> ⇌ CO + O	0.00	0.00	0.00	0.01	0.01	0.02	0.03	0.06	0.06
89. CH <sub>3</sub> + CH <sub>2</sub> ⇌ C <sub>2</sub> H <sub>4</sub> + H	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.06
103. C <sub>2</sub> H <sub>3</sub> + M ⇌ C <sub>2</sub> H <sub>2</sub> + H + M	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.05	-0.05
104. C <sub>2</sub> H <sub>3</sub> + H ⇌ C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	-0.02	-0.06	0.04
152. NH + H ⇌ N + H <sub>2</sub>	-0.01	-0.02	-0.02	-0.03	-0.05	-0.05	-0.05	-0.05	-0.06
154. NH + OH ⇌ HNO + H	0.04	0.04	0.04	0.05	0.05	0.07	0.09	0.13	0.14
158. NH + NO ⇌ N <sub>2</sub> O + H	-0.01	-0.01	-0.01	-0.01	-0.02	-0.02	-0.03	-0.05	-0.07
160. N + O <sub>2</sub> ⇌ NO + O	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.06	0.15
161. N + OH ⇌ NO + H	0.05	0.07	0.10	0.15	0.23	0.31	0.34	0.28	0.20
162. N + NO ⇌ N <sub>2</sub> + O	-0.07	-0.10	-0.13	-0.19	-0.26	-0.34	-0.40	-0.33	-0.24
177. HCN + O ⇌ NCO + H	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.09	0.17
178. HCN + O ⇌ NH + CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.05
184. CN + OH ⇌ NCO + H	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.07	0.06
186. CN + O <sub>2</sub> ⇌ NCO + O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.08
191. NCO + O ⇌ NO + CO	0.12	0.10	0.08	0.07	0.05	0.03	0.02	0.01	0.01
195. NCO + NO ⇌ N <sub>2</sub> O + CO	-0.15	-0.12	-0.09	-0.08	-0.06	-0.05	-0.04	-0.04	-0.04
201. C + NO ⇌ CN + O	0.00	0.00	-0.01	-0.02	-0.05	-0.10	-0.15	-0.18	-0.13
202. CH + NO ⇌ HCN + O	-0.01	-0.02	-0.03	-0.04	-0.05	-0.07	-0.10	-0.17	-0.21
203. CH <sub>2</sub> + NO → HCNO + H	-0.01	-0.01	-0.01	-0.01	-0.01	-0.02	-0.03	-0.06	-0.10
212. CH <sub>3</sub> + N ⇌ HCN + 2H	0.00	0.00	0.00	0.00	0.00	0.00	0.01	-0.04	-0.15

location of this minimum probably changes with the residence time.

These calculations have some implications for the use of staged combustion [114]. The idea of this combustion modification technique is to operate the first stage fuel-rich in order to lower the formation of NO and to convert the NO formed to

N<sub>2</sub>. In the second stage secondary air is added to complete the combustion. This technique has proved successful in limiting the NO-emissions from the combustion of nitrogen-containing fuels such as coal and oil. This corresponds to the calculations of Fig. 10. However, from Fig. 9 one can see that the technique should be used with

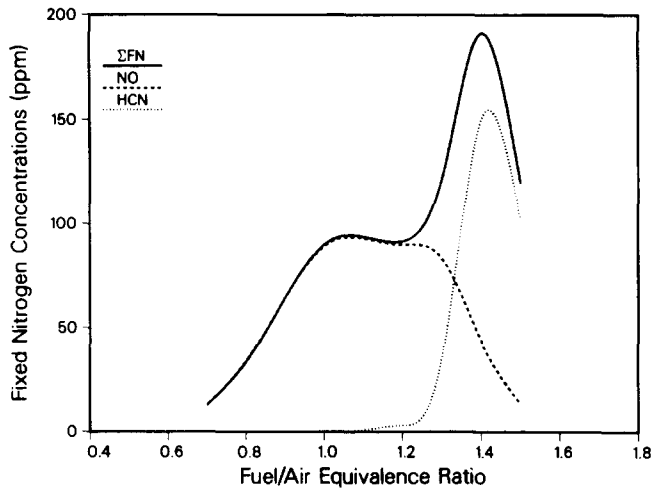


Fig. 9.  $\text{CH}_4/\text{air}$ , calculated fixed nitrogen emissions for methane combustion in a perfectly stirred reactor with a nominal residence time of 2 ms. Reactor conditions: volume =  $67.4 \text{ cm}^3$ , pressure = 1.0 atm,  $T_{\text{inlet}} = 464\text{K}$ .

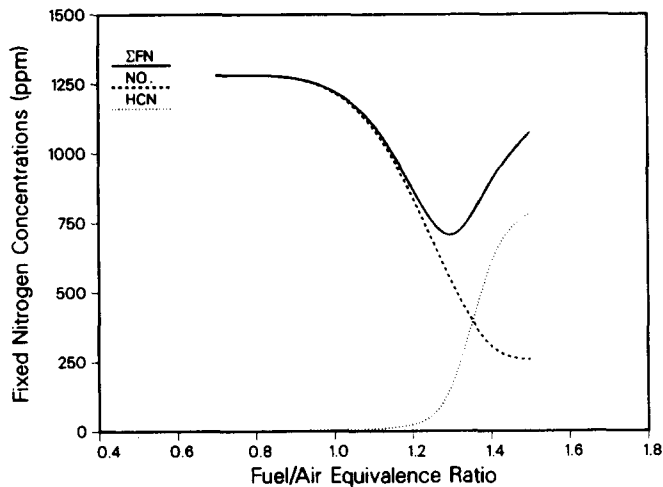


Fig. 10.  $\text{CH}_4/\text{air}$ , calculated fixed nitrogen emissions for methane combustion with 1300 ppm NO added in a perfectly stirred reactor with a nominal residence time of 2 ms. Reactor conditions: volume =  $67.4 \text{ cm}^3$ , pressure = 1.0 atm,  $T_{\text{inlet}} = 464\text{K}$ .

caution for fuels like natural gas, which do not contain fuel-nitrogen. The large quantities of HCN, which could be formed in the first stage, would be converted to NO during the lean combustion in the second stage.

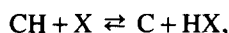
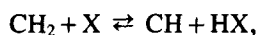
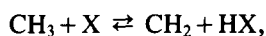
## V. CONCLUDING REMARKS

We have compared experimental data on NO emissions from stirred reactors with calculations for a perfectly stirred reactor. From the calcula-

tions some important points can be made:

1. While the Zeldovich mechanism is the major source of NO under fuel-lean conditions, inclusion of a mechanism for prompt-NO formation is necessary to explain the NO formation in rich situations. Controlling steps in the prompt-NO formation are the formation of CH followed by the attack of CH on N<sub>2</sub> to form HCN. Only CH + N<sub>2</sub> ⇌ HCN + N, not CH<sub>2</sub> + N<sub>2</sub> ⇌ HCN + NH, is important in breaking the N-N bond for prompt-NO.

2. The CH concentration is established by the sequence



where X may be H or OH. Some of these reactions are secondary product channels at low temperature for the specified set of reactants. Partly for this reason, and because they are radical-radical reactions, their rate coefficients are poorly known and require further investigation.

3. The rate constant we use for CH + N<sub>2</sub> ⇌ HCN + N is considerably lower than that inferred from flame measurements, but it is higher than that used in previous modeling.
4. Reactions of C, CH, and CH<sub>2</sub> with NO play an important role in limiting the NO formed under rich conditions. However, these reactions produce cyanide species, which result in the exhaust of large quantities of HCN from the reactor.

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