

**ASYMPTOTIC AND NUMERICAL ANALYSIS OF A PREMIXED  
LAMINAR NITROGEN DIOXIDE - HYDROGEN FLAME**

by

**G.T. Linteris  
Building and Fire Research Laboratory  
National Institute of Standards and Technology  
Gaithersburg, MD 20899**

and

**F.A. Williams  
Department of Applied Mechanics and Engineering Sciences  
University of California, San Diego  
La Jolla, CA 92093-0310**

**Reprinted from COMBUSTION SCIENCE AND TECHNOLOGY, Vol. 105, Nos. 4-6, 1995.**

**Notes: This paper is a contribution of the National Institute of Standards and Technology  
and is not subject to copyright.**

## Asymptotic and Numerical Analysis of a Premixed Laminar Nitrogen Dioxide–Hydrogen Flame

G. T. LINTERIS *National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

F. A. WILLIAMS\* *Department of Applied Mechanics and Engineering Sciences University of California, San Diego; La Jolla, CA 92093-0310*

(In final form December 15, 1994)

**ABSTRACT**—A kinetic mechanism of eighty-some reactions for flames in mixtures of hydrogen and nitrogen dioxide is systematically reduced to twenty-four-, eleven-, seven-, two-, and one-step mechanisms. The numerically predicted burning rates for the full mechanism describing a near-stoichiometric burner-stabilized flame at a pressure of 25 torr, and final temperature of 2000 K are compared with the results using the reduced mechanisms, and the sources of inaccuracies are identified. The two reactions  $\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH}$  and  $\text{H}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{H}$  account for about 97% of the  $\text{NO}_2$  and  $\text{H}_2$  consumption and  $\text{NO}$  and  $\text{H}_2\text{O}$  production, and are the principal reactions involving  $\text{OH}$  and  $\text{H}$  atoms. The reactions  $2\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{O}$  and  $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$  are important for  $\text{OH}$  and  $\text{O}$ , while the reactions  $\text{NO}_2 + \text{M} \rightarrow \text{NO} + \text{O} + \text{M}$  and  $\text{NO}_2 + \text{H}_2 \rightarrow \text{HONO} + \text{H}$  serve as important initiation reactions. The reactions  $\text{O}_2 + \text{H} \rightleftharpoons \text{OH} + \text{O}$ ,  $\text{H}_2 + \text{O} \rightleftharpoons \text{OH} + \text{H}$ , and  $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$  are significant but of lesser importance. In reducing the mechanism, the steady-state assumptions for the intermediates  $\text{O}$ ,  $\text{H}$ , and  $\text{OH}$  are shown to be good; however, their use is limited because the  $\text{H}$  and  $\text{OH}$  balance relations are dominated by the same reactions. As a result of these limitations, an asymptotic description of the flame structure using a one-step approximation to the kinetics is only able to predict the burning rate within a factor of three of the numerical result using the full mechanism.

*Key Words:* Reduced mechanisms, laminar flames, premixed flames, flame chemistry

### INTRODUCTION

Many important insights are being obtained from the development of reduced mechanisms to describe the kinetics of combustion reactions. The methodology typically involves the elimination of minor reactions based on examination of reaction fluxes and the sensitivity coefficients, and the application of steady-state and partial-equilibrium assumptions to reduce the number of species and reactions that must be considered (Smooke, 1991). This research article applies these techniques to a representative full mechanism and shows the accuracy with which twenty-four-, eleven-, seven-, two- and one-step reaction mechanisms can predict the flame speed given by the full mechanism, determines the reasons for the limitations of each mechanism, and demonstrates subtle errors that can arise in an ostensibly correctly reduced model.

The kinetic system to be studied is based on a premixed, burner-stabilized flame of nitrogen dioxide and hydrogen at a final temperature of 2000 K and a pressure of 25 torr, with 18 mole percent argon diluent. Consideration is restricted to fuel-air

\* Work supported by National Science Foundation under contract number CTS92-14888.

equivalence ratios  $\phi$  between 0.76 and 1.08. A motivation for the study is that the kinetics of the nitrogen/hydrogen/oxygen system are important in the gas-phase reaction region for deflagration of some solid rocket propellants. In addition, experimental results for this flame (at  $\phi = 1.08$ ) have been reported by Volponi and Branch (1990, 1992). In these experiments, concentrations of stable species through the flame were determined from mass-spectrometric analysis of gas samples extracted by a quartz probe, and the relative OH concentration and the OH rotational temperature were provided by laser-induced fluorescence. The experimental stable species and the relative OH concentration profiles were found to be in good agreement with the results of numerical predictions. The calculated concentrations were obtained from solution of the species conservation equations using the experimental temperature profile together with the full kinetic mechanism described below. Volponi and Branch determined that the full mechanism employed in their analysis was dominated by only a few reactions. This finding prompted the present attempts to systematically reduce the full mechanism and examine the accuracy with which the reduced mechanisms can reproduce the burning velocity.

## THE FULL MECHANISM

A reaction mechanism which includes many of the important reactions in this flame is the full mechanism given in Table 1 (Volponi and Branch, 1990, 1992), composed of twenty-three species and eighty-two reversible reactions. The rate data in this table are from Miller and Bowman (1989), Tsang and Herron (1991), Kaskan and Hughes (1973), Westley *et al.* (1991), Slack and Grillo (1978), and Yetter (1992). The full mechanism in

TABLE 1

Full mechanism for demonstration of model reduction in  $\text{NO}_2/\text{H}_2$  flame. The modified Arrhenius rate parameters  $A$ ,  $b$ , and  $E$  correspond to a specific reaction-rate constant of the form  $k = AT^b e^{E/RT}$ , with the units of mole, J, s, cm, K. Enhanced third-body efficiencies are as noted.

Reaction	$A$	$b$	$E$
1. $\text{NO}_2 + \text{H} = \text{NO} + \text{OH}$	3.50E + 14	0.0	6276
2. $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$	1.17E + 09	1.3	15171
3. $2\text{OH} = \text{O} + \text{H}_2\text{O}$	6.00E + 08	1.3	0
4. $\text{NO}_2 + \text{M} = \text{NO} + \text{O} + \text{M}$	1.10E + 16	0.0	276144
5. $\text{NO}_2 + \text{O} = \text{NO} + \text{O}_2$	1.00E + 13	0.0	2510
6. $\text{O} + \text{OH} = \text{O}_2 + \text{H}$	4.00E + 14	-0.5	0
7. $\text{O} + \text{H}_2 = \text{OH} + \text{H}$	5.06E + 04	2.67	26317
8. $\text{H}_2 + \text{NO}_2 = \text{HONO} + \text{H}$	0.343E + 13	0.0	121336
9. $\text{OH} + \text{NO} + \text{M} = \text{HONO} + \text{M}$	5.10E + 23	-2.51	-285
10. $\text{NO}_2 + \text{NO}_2 = \text{NO} + \text{NO} + \text{O}_2$	1.63E + 12	0.0	112232
11. $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$	2.11E + 12	0.0	-2004
12. $\text{NO} + \text{HO}_2 = \text{HNO} + \text{O}_2$	2.00E + 11	0.0	8314
13. $\text{H} + \text{O}_2 + \text{M}^a = \text{HO}_2 + \text{M}$	3.61E + 17	-0.72	0
14. $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$	7.50E + 12	0.0	0
15. $\text{HNO} + \text{M} = \text{H} + \text{NO} + \text{M}^b$	1.50E + 16	0.0	203677
16. $\text{HNO} + \text{NO}_2 = \text{HONO} + \text{NO}$	6.00E + 11	0.0	8284
17. $\text{HNO} + \text{OH} = \text{NO} + \text{H}_2\text{O}$	3.60E + 13	0.0	0

Reaction	A	b	E
18. $H_2 + O_2 = 2OH$	1.70E + 13	0.0	199912
19. $H + HO_2 = 2OH$	1.40E + 14	0.0	4489
20. $O + HO_2 = O_2 + OH$	1.40E + 13	0.0	4489
21. $H + H + M^f = H_2 + M$	1.00E + 18	-1.0	0
22. $H + H + H_2 = H_2 + H_2$	9.20E + 16	-0.6	0
23. $H + H + H_2O = H_2 + H_2O$	6.00E + 19	-1.3	0
24. $H + OH + M^d = H_2O + M$	1.60E + 22	-2.0	0
25. $H + O + M^d = OH + M$	6.20E + 16	-0.6	0
26. $O + O + M = O_2 + M$	1.89E + 13	0.0	-7481
27. $H + HO_2 = H_2 + O_2$	1.25E + 13	0.0	0
28. $HO_2 + HO_2 = H_2O_2 + O_2$	2.00E + 12	0.0	0
29. $H_2O_2 + M = OH + OH + M$	1.30E + 17	0.0	190372
30. $H_2O_2 + H = HO_2 + H_2$	1.60E + 12	0.0	15899
31. $H_2O_2 + OH = H_2O + HO_2$	1.00E + 13	0.0	7531
32. $NH + O_2 = HNO + O$	1.00E + 13	0.0	50208
33. $NH + O_2 = NO + OH$	7.60E + 10	0.0	6402
34. $NH + NO = N_2O + H$	2.40E + 15	-0.8	0
35. $N_2O + OH = N_2 + HO_2$	2.00E + 12	0.0	41840
36. $N_2O + H = N_2 + OH$	7.60E + 13	0.0	63597
37. $N_2O + M = N_2 + O + M$	1.60E + 14	0.0	215894
38. $N_2O + O = N_2 + O_2$	1.00E + 14	0.0	117989
39. $N_2O + O = 2NO$	1.00E + 14	0.0	117989
40. $NH + OH = HNO + H$	2.00E + 13	0.0	0
41. $NH + OH = N + H_2O$	5.00E + 11	0.5	8368
42. $NH + N = N_2 + H$	3.00E + 13	0.0	0
43. $NH + H = N + H_2$	1.00E + 14	0.0	0
44. $NH_2 + O = HNO + H$	6.63E + 14	-0.5	0
45. $NH_2 + O = NH + OH$	6.75E + 12	0.0	0
46. $NH_2 + OH = NH + H_2O$	4.00E + 06	2.0	4184
47. $NH_2 + H = NH + H_2$	6.92E + 13	0.0	15272
48. $NH_2 + NO = NNH + OH$	6.40E + 15	-1.3	0
49. $NH_2 + NO = N_2 + H_2O$	6.20E + 15	-1.3	0
50. $NH_3 + OH = NH_2 + H_2O$	2.04E + 06	2.0	2368
51. $NH_3 + H = NH_2 + H_2$	6.36E + 05	2.4	42555
52. $NH_3 + O = NH_2 + OH$	2.10E + 13	0.0	37656
53. $NNH = N_2 + H$	1.00E + 04	0.0	0
54. $NNH + NO = N_2 + HNO$	5.00E + 13	0.0	0
55. $NNH + H = N_2 + H_2$	1.00E + 14	0.0	0
56. $NNH + OH = N_2 + H_2O$	5.00E + 13	0.0	0
57. $NNH + NH_2 = N_2 + NH_3$	5.00E + 13	0.0	0
58. $NNH + NH = N_2 + NH_2$	5.00E + 13	0.0	0
59. $NNH + O = N_2O + H$	1.00E + 14	0.0	0
60. $HNO + H = H_2 + NO$	5.00E + 12	0.0	0
61. $HNO + NH_2 = NH_3 + NO$	2.00E + 13	0.0	4184
62. $N + NO = N_2 + O$	3.27E + 12	0.3	0
63. $N + OH = NO + H$	3.80E + 13	0.0	0
64. $NO_2 + N = NO + NO$	4.00E + 12	0.0	0
65. $NO + N_2O = NO_2 + N_2$	1.00E + 14	0.0	207840
66. $N + O_2 = NO + O$	6.40E + 09	1.0	26276
67. $HNO + HNO = N_2O + H_2O$	3.95E + 12	0.0	20920
68. $NH + NO = N_2 + OH$	2.40E + 12	0.0	0
69. $N_2H_2 + M^e = NNH + H + M$	5.00E + 16	0.0	209200
70. $N_2H_2 + H = NNH + H_2$	5.00E + 13	0.0	4184
71. $NH_2 + N = N_2 + H + H$	7.20E + 13	0.0	0
72. $NH_2 + NH = N_2H_2 + H$	5.00E + 13	0.0	0
73. $NH + O = NO + H$	2.00E + 13	0.0	0
74. $NO_2 + NO_2 = NO + NO_3$	9.64E + 03	-0.7	87529
75. $NO_3 + NO_2 = NO + NO_2 + O_2$	1.40E + 11	0.0	13305

Reaction	A	b	E
76. $\text{NO}_3 + \text{NO}_3 = \text{NO}_2 + \text{NO}_2 + \text{O}_2$	2.60E + 12	0.0	32217
77. $2\text{NO}_2 + \text{M} = \text{N}_2\text{O}_4 + \text{M}$	1.70E + 13	0.0	-7196
78. $\text{NO} + \text{M} = \text{N} + \text{O} + \text{M}$	1.40E + 15	0.0	621031
79. $\text{NO}_2 + \text{O} + \text{M} = \text{NO}_3 + \text{M}$	1.50E + 28	-4.1	10326
80. $\text{HNO} + \text{O} = \text{OH} + \text{NO}$	1.80E + 13	0.0	0
81. $\text{HONO} + \text{O} = \text{OH} + \text{NO}_2$	1.20E + 13	0.0	24937
82. $\text{HONO} + \text{OH} = \text{H}_2\text{O} + \text{NO}_2$	1.30E + 10	1.0	565

<sup>a</sup> third body efficiencies: H<sub>2</sub>O, 18.6; H<sub>2</sub>, 2.86; O<sub>2</sub>, 0; N<sub>2</sub>, 0

<sup>b</sup> third body efficiencies: H<sub>2</sub>O, 10; O<sub>2</sub>, 2; N<sub>2</sub>, 2; H<sub>2</sub>, 2

<sup>c</sup> third body efficiencies: H<sub>2</sub>O, 0; O<sub>2</sub>, 0

<sup>d</sup> third body efficiencies: H<sub>2</sub>O, 5

<sup>e</sup> third body efficiencies: H<sub>2</sub>O, 15; O<sub>2</sub>, 2; N<sub>2</sub>, 2; H<sub>2</sub>, 2

Table 1 serves as a convenient test-case mechanism to demonstrate the methodologies of reducing mechanisms and to illustrate where inaccuracies can occur.

As a first step in reducing the full mechanism, the equations of species and energy conservation were solved numerically by currently available techniques (Smooke, 1982; Kee *et al.*, 1980, 1983). The conservation equations in the numerical solution assume isobaric, steady, planar, one-dimensional, laminar flow and neglect radiation and the Dufour effect (heat flux associated with concentration gradients). Thermal diffusion is included in the calculation; neglecting it increases the burning rate by about 5% in the present flames, probably by eliminating some withdrawal of H atoms out of the reaction zone to the hot boundary. The adopted boundary conditions, corresponding to a solution for a burner-stabilized flame, are a fixed inlet temperature of 431 K (the experimental condition) with specified mass flux fractions at the inlet, and vanishing gradients downstream from the flame.

Unlike a freely propagating flame for which the mass flow is an eigenvalue of the energy equation, the mass flow rate in the numerical solution for a burner-stabilized flame is a specified constant. The mass flow (or equivalently the burning rate) determines the flame thickness, and hence the distance of the high-temperature region of the flame from the burner surface, the rate of heat loss to the burner surface, and the final temperature (which is lower than that of a freely propagating flame). In the present analyses, the numerical solution is used to determine iteratively that value of the mass flow rate which provides a final temperature that matches the desired final temperature. A final temperature of 2000 K was used since it matches the OH rotational temperatures measured by Volponi and Branch (1990, 1992) for  $\phi = 1.08$  and their experimental mass flow rate. It is of interest, however, to examine the kinetic mechanism of this system over a range of equivalence ratio. For consistency, a final temperature of 2000 K was used for  $0.76 \leq \phi \leq 1.08$ , since typically there is little variation of the final temperature with equivalence ratio in experiments on burner-stabilized flames.

The domain for the numerical calculation deserves discussion. The conversion of NO to N<sub>2</sub> is very slow, requiring about ten meters for completion, compared to the primary H<sub>2</sub> and NO<sub>2</sub> reactions which occur within about 1 cm at 2000 K. Conversion of NO to N<sub>2</sub> proceeds primarily by the reactions  $\text{H} + \text{NO} \rightarrow \text{OH} + \text{N}$ , and  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ ; since  $\text{H} + \text{NO}_2$  is a much stronger sink for H atoms, significant N<sub>2</sub> formation

is delayed until the  $\text{NO}_2$  is consumed. Consequently, reactions involving conversion of  $\text{NO}$  to  $\text{N}_2$  do not have a strong influence on the structure of the  $\text{NO}_2/\text{H}_2$  flame near the region of rapid temperature rise, although they do cause the temperature to rise very gradually beyond the primary reaction zone. Determination of the burning rate which produces the desired final temperature, 2000 K in this study, is somewhat ambiguous in the presence of a gradually rising temperature. One approach to avoid unrealistically large computational domains and to obtain more constant final temperatures is to eliminate entirely the slow  $\text{N}_2$ -formation chemistry from the full mechanism in Table 1. This was done when obtaining the burning rates for the full mechanism. In assessing the importance of the different reaction pathways, the nitrogen chemistry was included, but the domain of the numerical calculations was limited to about 0.5 cm beyond the region of rapid temperature rise. It may be possible in the future to develop a new procedure in which a revised formulation is devised by subtracting such slow steps at the beginning.

It should also be noted that for the leaner stoichiometries considered here,  $\phi = 0.82$  and 0.76, the overall reaction  $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$  (endothermic) causes the temperature to decrease slowly after the region of rapid temperature rise. For the purpose of determining the burning rate in these lean cases, the final temperature was taken as the peak temperature; that is, the slow endothermic reactions continuing downstream are considered not to affect significantly the temperature in the primary reaction zone.

The reaction  $\text{H}_2 + \text{NO}_2 = \text{HONO} + \text{H}$  is a potentially important initiation reaction in the full mechanism (Anderson, 1990; Volponi and Branch, 1992). The only available rate expression for this reaction is from Slack and Grillo (1978), obtained within the temperature range  $760 \text{ K} \leq T \leq 1000 \text{ K}$ . However, a lower specific reaction rate for this reaction may be appropriate. Not-yet-published results (Yetter, 1992) indicate that, in order to replicate recent flow-reactor data, the rate of this reaction must be lower by a factor of seven near 1000 K. As an additional test of the suitability of this lower rate expression, the experimental flame-structure measurements of Volponi and Branch (1992) can be compared to the flame structure calculated using the numerical techniques described below with the mechanism of Table 1. For a burner-stabilized flame with  $\phi = 1.08$  and the experimental reactant flow rates, the calculation yields a temperature profile which increases more rapidly than the experimental results of Volponi and Branch (1992) when the rate expression of Slack and Grillo is used. However, if the pre-exponential term in the specific reaction-rate constant is lowered by a factor of seven, then the predicted temperature profile agrees more closely with the experimental data. For these reasons, we adopt the lower rate for the reaction  $\text{H}_2 + \text{NO}_2 = \text{HONO} + \text{H}$  in the present paper. Considering the large uncertainty in the rate of Slack and Grillo (1987), (see Tsang and Herron, 1991), and the potential importance of this rate at 2000 K, additional data on the rate of this reaction at higher temperatures would be useful. Modifications to the activation energy rather than the pre-exponential of this rate expression could influence the importance of this reaction at 2000 K.

The numerical solution using the full mechanism of Table 1 allows calculation of the reaction fluxes and first-order sensitivity coefficients useful in making further simplifications, and it also provides the burning rate to be used as a basis for comparison with the numerical and asymptotic predictions of the reduced mechanisms. Figure 1 shows

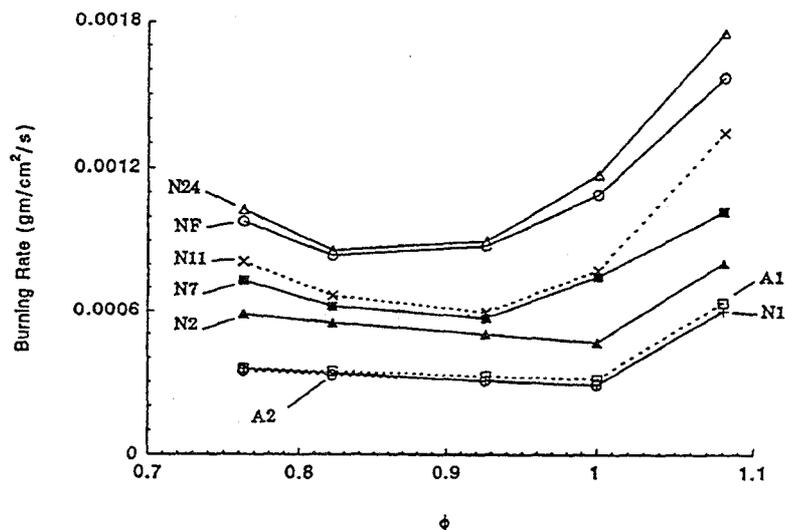


FIGURE 1 Burning rate as a function of fuel/oxidizer equivalence ratio  $\phi$  from numerical calculations using the full mechanism (NF), and reduced mechanisms with twenty-four (N24), eleven (N11), seven (N7), two (N2), and one (N1) reaction(s). Also shown for the one-step mechanism are the leading-order asymptotic results (A1) for  $0.76 \leq \phi \leq 1.08$  and the asymptotic solution to second order (A2) for  $0.76 \leq \phi \leq 1.00$ .

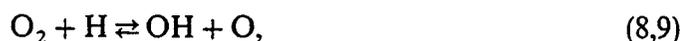
the numerically calculated burning rate as a function of the fuel/oxidizer equivalence ratio  $\phi$  obtained from the full mechanism. The burning rate has a minimum near  $\phi = 0.9$  and increases for leaner or richer mixtures. The increase in the burning rate away from  $\phi \approx 0.9$  may appear counter-intuitive at first glance. For these calculations, however, it must be remembered that the peak temperature was fixed at 2000 K; with first-order behavior in each reactant, a rich or lean mixture provides more of the abundant reactant in the reaction zone than a stoichiometric mixture and also lowers the effective heat release, both of which effects increase the burning rate for fixed final temperature  $T_x$  (Williams, 1985).

## THE STARTING MECHANISM

The next step is to obtain a smaller, algebraically more tractable starting mechanism from the full mechanism that can provide burning rates close to those of the full mechanism. Examination of the sensitivity coefficients and reaction fluxes from the numerical solution with the full mechanism indicates that only the first 17 reactions of Table 1 significantly influence the concentrations of major species. Considering only the second, third, sixth, seventh, eleventh, fifteenth, and seventeenth of these seventeen reactions to be reversible, and including the reverse of the ninth and thirteenth reactions and the forward rate of the remaining reactions yields a twenty-four-step reduced mechanism. Figure 1 shows the burning rate as a function of  $\phi$  obtained from the numerical calculation using the twenty-four-step mechanism for  $\phi$  from 0.76 to 1.08. As the figure indicates, the burning rates are within a few percent for  $\phi$  less than 0.92 and within about 10% for values of  $\phi$  up to 1.08. This slight increase in the burning

velocity for the richer flames is a consequence of neglecting reactions in the twenty-four-step mechanism, such as some additional reactions of HONO and HNO, which would tend to decrease the radical production rates.

In order to greatly simplify the mechanism, we proceed further and neglect all but the first seven reactions in Table 1 to produce the eleven-step mechanism given by



The burning rate predicted by the eleven-step mechanism is also shown in Figure 1. The sources of the differences between the predictions of the twenty-four and eleven-step mechanisms are discussed below. The additional reactions



and



are listed here for convenience.

Reactions involving  $\text{HO}_2$  are not important in the range  $0.93 \leq \phi \leq 1.08$ . However, these reactions, the eleventh through the seventeenth reactions in Table 1, are important for  $\phi \leq 0.9$ . Under these lean condition, the molecular hydrogen concentration in the reaction zone is so low that the OH, formed rapidly from reaction of  $\text{NO}_2$  with H-atom, now reacts with  $\text{NO}_2$  instead of  $\text{H}_2$  to form  $\text{HO}_2$  and NO. The  $\text{HO}_2$  reactions have the overall effect of recombining H and OH to form  $\text{H}_2\text{O}$ , thereby slowing the burning rate. Eliminating the  $\text{HO}_2$  chemistry increases the burning rate about 30% for  $\phi$  from 0.76 to 0.82. This large increase is more than offset in the eleven-step mechanism because reaction (12) is also neglected. This reaction and the subsequent decomposition of HONO (13) are important sources of radicals for lean flames; eliminating these reactions from the twenty-four-step mechanism decreases the burning rate for leaner conditions slightly more than the increase from neglect of the  $\text{HO}_2$  reactions, so that neglect of the HONO and of the  $\text{HO}_2$  chemistry in the eleven-step mechanism approximately cancel for leaner flames. For richer flames, where the  $\text{H} + \text{O}_2$  branching reactions (8)–(11) become significant, neglect of the HONO reactions becomes less important, decreasing the burning rate by 14% at  $\phi = 0.93$  and only by 2% at  $\phi = 1.08$ . Finally, the reaction of  $\text{NO}_2$  with itself to form NO and  $\text{O}_2$  is neglected. This reaction is

endothermic and reduces the overall heat release, which increases the burning rate in the situation considered here; neglecting it decreases the burning rate by about 20% for  $0.93 \leq \phi \leq 1.08$ . The effect of endothermic reactions such as (14) can be incorporated into a one-step mechanism, in an approximate fashion, for some chemical systems, through the use of an effective heat release (Linteris and Williams, 1992); however, this approach was not adopted in the present study. The net result for this starting mechanism is that the eleven-step mechanism predicts a burning rate generally about 20 to 30% lower than that predicted by the eighty-two-step full mechanism and shows the proper variation of burning rate with  $\phi$ . We now proceed to further simplify the mechanism, with the aim of obtaining results convenient for analytical descriptions.

### THE SIMPLEST POTENTIAL GLOBAL MECHANISM

The eleven reactions discussed above were reduced to a two-step global mechanism following the methodology outlined by Peters (1991). The procedure begins with a balance equation for each particular species, which is

$$L([i]) = w_{i+} - w_{i-}, \quad (15)$$

where  $L([i])$  is the convective-diffusive operator on the concentration  $[i]$  of species  $i$ . With  $v_{ik+}$  and  $v_{ik-}$  denoting the appropriate stoichiometric coefficients of species  $i$  in reaction  $k$  for production and consumption of species  $i$ , respectively, and  $w_k$  the reaction rate of step  $k$ , the net production and destruction rates of species  $i$ ,  $w_{i+}$  and  $w_{i-}$ , are defined as  $\sum_{k=1}^r v_{ik+} w_k$  and  $\sum_{k=1}^r v_{ik-} w_k$  where  $r$  is the number of reactions.

The first step in reducing the mechanism is examination of the numerical results to determine which species can be considered to be in steady state. One indication of a steady state usually is that the steady-state species is present in concentrations much lower than that of the major species. To adjust for differences in the diffusion coefficients of the species, the numerically calculated concentrations are multiplied by the molecular-weight factors  $((\bar{W} + W_i)/(2W_i))^{1/2}$ , and the magnitudes of the resulting weighted concentrations are compared. Figure 2 shows the peak mole fractions of each species from the numerical solution obtained by using the seven-step mechanism (discussed below) for  $\phi$  from 0.76 to 1.08 and the peak mole fractions corrected as just described for diffusion effects. The corrected mole fractions for O are about four orders of magnitude lower than those of the major species, while OH is two orders of magnitude lower, and H varies from about two to three orders of magnitude lower. Consequently, the steady-state assumption should be good for O, OH, and H. A more precise way to test the validity of the steady-state assumption is to verify that  $(w_{i+} - w_{i-})/w_{i+} \ll 1$  at each position in the flame for the species in question. Figure 3 shows this parameter for O, OH, and H calculated from the numerical results using the seven-step mechanism. As shown, the magnitude of the parameter is less than 3, 6, and 14% for  $\phi = 0.76, 1.0$  and  $1.08$  respectively.

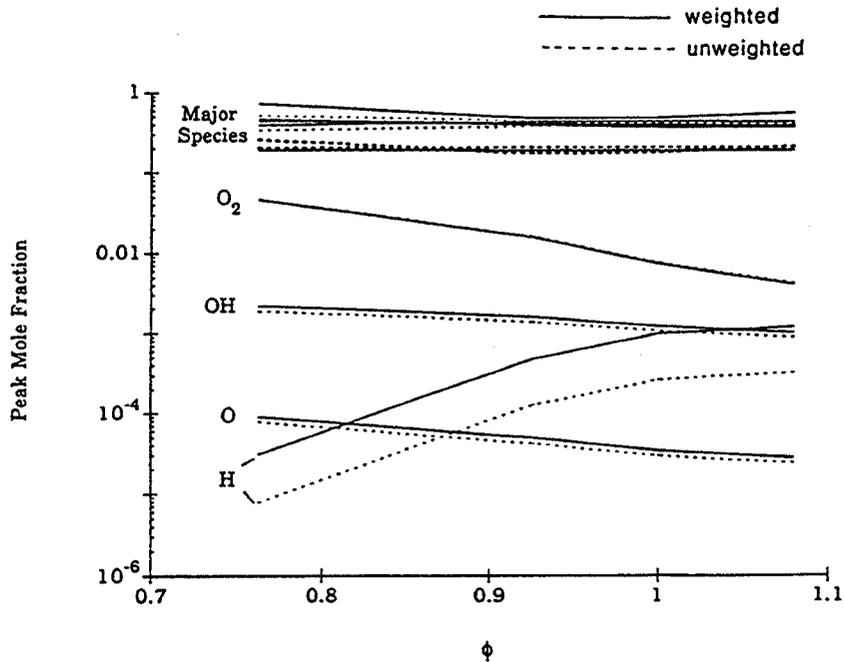
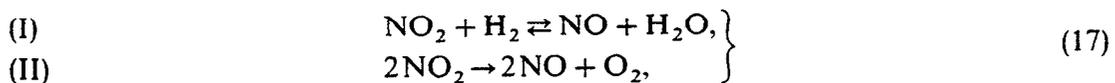


FIGURE 2 Numerically-calculated peak mole fractions using the seven-step reduced mechanism, and peak mole fractions multiplied by  $((\bar{W} + W_i)/(2W_i))^{1/2}$  to account for preferential diffusion.

In proceeding to derive a global mechanism, the balance equations are written as

$$\left. \begin{aligned}
 L([\text{H}]) &= -w_1 + w_2 - w_3 - w_8 + w_9 + w_{10} - w_{11}, \\
 L([\text{O}]) &= +w_4 - w_5 + w_6 - w_7 + w_8 - w_9 - w_{10} + w_{11}, \\
 L([\text{OH}]) &= +w_1 - w_2 + w_3 - 2w_4 + 2w_5 + w_8 - w_9 + w_{10} - w_{11}, \\
 L([\text{H}_2]) &= -w_2 + w_3 - w_{10} + w_{11}, \\
 L([\text{H}_2\text{O}]) &= +w_2 - w_3 + w_4 - w_5, \\
 L([\text{O}_2]) &= +w_7 - w_8 + w_9, \\
 L([\text{NO}_2]) &= -w_1 - w_6 - w_7, \\
 L([\text{NO}]) &= +w_1 + w_6 + w_7.
 \end{aligned} \right\} \quad (16)$$

Indiscriminate use of the algebraic relations for the rates obtained from  $L([i]) = 0$  for the intermediate radical species O, H, and OH (i.e. substitution of the balance relations for the radical species without consideration of the relative magnitude of each) produces balance equations corresponding to the two-step global mechanism



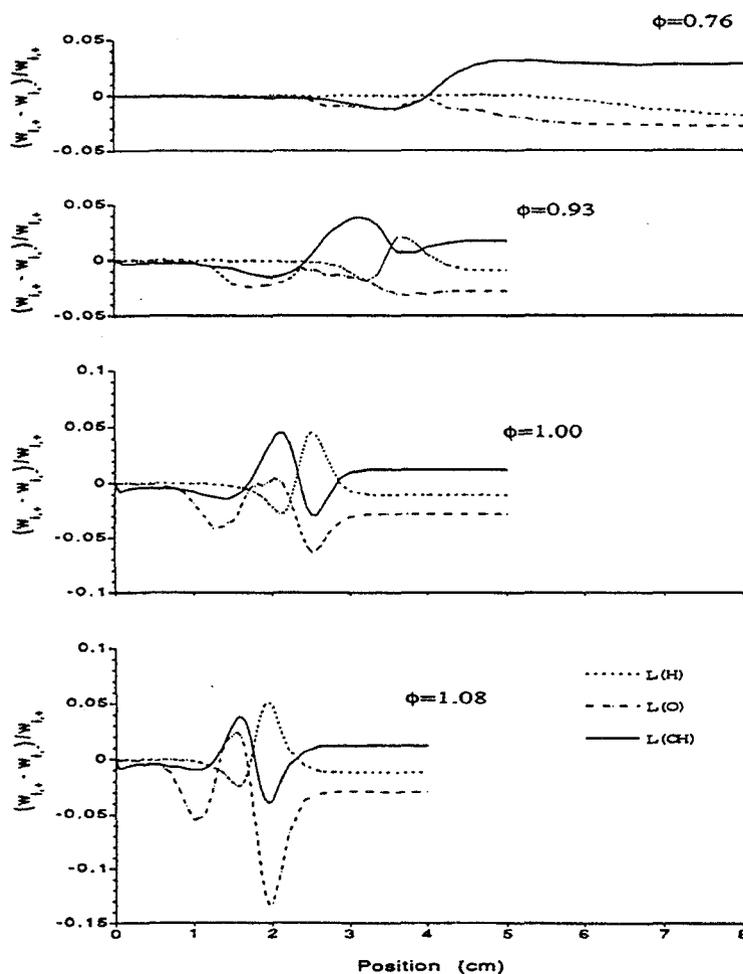


FIGURE 3 Accuracy of the steady-state relation for H, O, and OH given by the relation  $(w_{i+} - w_{i-})/w_{i+}$  as a function of position in the flame from numerical calculations using the seven-step mechanism for  $\phi = 0.76, 0.93, 1.00,$  and  $1.08$ .

with the corresponding rates

$$w_1 = w_1 + w_8 - w_9, \quad (18)$$

$$w_{11} = w_6. \quad (19)$$

These results suggest that, if the steady-state assumption is valid for O, H, and OH, and if the effect of  $\text{NO}_2$  decomposition (occurring in the eleven-step mechanism from reactions (6) and (7) is neglected, then the  $\text{NO}_2/\text{H}_2$  flame should be reducible to a one-step mechanism.

The importance of reaction (II) in the seven-step mechanism can be assessed by examining Figure 2. For near-stoichiometric ( $0.93 \leq \phi \leq 1.08$ ) flames  $\text{O}_2$  is a minor species, less than two mole percent, implying that reaction II consumes only a small fraction of the  $\text{NO}_2$ . Although reaction (II) is endothermic (heat of reaction of  $57.4 \text{ kJ}/(\text{mol NO}_2)$ ) compared to  $-194.3$  for reaction (I)),  $\text{NO}_2$  decomposition modifies

the effective heat release at most by only 5% for this range of  $\phi$ . At  $\phi = 0.76$  the global reaction II consumes about 8% of the  $\text{NO}_2$ , lowering the effective heat release is about 12%, and increasing the burning rate about 12%. For achieving greater simplicity, there is motivation to neglect reaction (II) and to accept the relatively small consequent penalty in accuracy. For near-stoichiometric flames, there should be relatively minimal sacrifice in accuracy; for equivalence ratios approaching 0.76, the error in neglecting global step (II) is about 10%.

To obtain the simplest potential global mechanism, it then becomes desired to express the rate of the global reaction (I)  $w_1$  in terms of major species concentrations and specific reaction-rate constants for the elementary reactions. To illustrate more clearly how to accomplish this task, it is helpful to simplify the problem further by neglecting some additional steps.

### THE SEVEN-, TWO- AND ONE-STEP MECHANISMS

Further examination of the reaction fluxes and sensitivity coefficients from the numerical solutions using the starting mechanism indicates that reactions (8)–(11) play only a minor role (although increasingly important for richer conditions). Ignoring these reactions leads to a seven-step mechanism consisting of reactions (1)–(7). Figure 1 shows the numerically predicted burning rate using the seven-step mechanism, which is within about 7% of the result of the eleven-step mechanism, except for rich flames where the chain-branching steps (8) and (10) become increasingly important. Since the burning rate for the worst condition predicted by the seven-step mechanism is still within about 38% of the result obtained by using the full mechanism, and elimination of reactions (8)–(11) provides significant algebraic simplification in the steady-state expressions for the concentrations of intermediates and for  $w_1$ , the seven-step mechanism is now adopted for further study. With these simplifications, the balance equations for H, O, and OH become

$$L([\text{H}]) = -w_1 + w_2 - w_3, \quad (20)$$

$$L([\text{O}]) = +w_4 - w_5 + w_6 - w_7, \quad (21)$$

and

$$L([\text{OH}]) = +w_1 - w_2 + w_3 - 2w_4 + 2w_5. \quad (22)$$

The steady states in Equation (20) and (21) readily enable us to write

$$[\text{H}] = \frac{k_2[\text{H}_2]}{k_3[\text{H}_2\text{O}] + k_1[\text{NO}_2]} [\text{OH}] \quad (23)$$

and

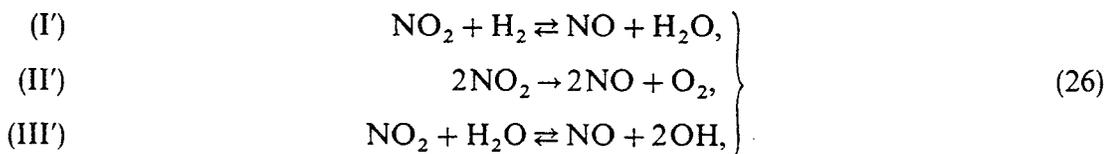
$$[\text{O}] = \frac{k_4[\text{OH}]^2 + k_6[\text{M}][\text{NO}_2]}{k_5[\text{H}_2\text{O}] + k_7[\text{NO}_2]}. \quad (24)$$

However, a difficulty arises in Equation (22) in that it is found that  $|2(w_4 - w_5)| \ll |(w_1 + w_3 - w_2)|$ . We therefore are not yet justified in going to a one-step mechan-

ism, and we proceed instead to develop a two-step mechanism by assuming that the intermediate species present at the highest concentrations, OH, is not a steady-state species, writing the balance relation for OH as

$$L([\text{OH}]) + L([\text{H}]) = 2[k_5[\text{H}_2\text{O}][\text{O}] - k_4[\text{OH}]^2], \quad (25)$$

in which Equation (23) is used (in principle) to evaluate  $L([\text{H}])$ . The balance relations for the stable species, together with Equation (25), correspond to the global mechanism



with the corresponding rates

$$\left. \begin{array}{l} w_{\text{I}} = w_2 - w_3, \\ w_{\text{II}'} = w_7, \\ w_{\text{III}'} = -w_4 + w_5. \end{array} \right\} \quad (27)$$

Equation (27) for  $w_{\text{III}'}$  with Equation (24) for  $[\text{O}]$ , provides a balance relation for OH, which is written as

$$\frac{1}{2} L([\text{OH}]) = w_{\text{III}'} = \frac{k_5[\text{H}_2\text{O}]k_6[\text{M}][\text{NO}_2] - k_4k_7[\text{OH}]^2[\text{NO}_2]}{k_7[\text{NO}_2] + k_5[\text{H}_2\text{O}]} \quad (28)$$

In this equation, the contribution from  $L([\text{H}])$  in Equation (25), although possibly important, has been neglected. With the effects of the  $\text{NO}_2$  decomposition route (II') again neglected, a two-step mechanism given by global reactions (I') and (III') is obtained. Using Equation (27) for  $w_{\text{I}'}$  with Equation (23), the rate of the global step (I') can be expressed as

$$-L([\text{H}_2]) = w_{\text{I}'} = \frac{k_1k_2[\text{NO}_2][\text{H}_2][\text{OH}]}{k_1[\text{NO}_2] + k_3[\text{H}_2\text{O}]} \quad (29)$$

The accuracy of this two-step approximation can be investigated by using Equations (28) and (29) to solve for the flame structure numerically and examining the results. Figure 1 shows the numerically predicted burning rate using the two-step mechanism. The burning rate has a linear dependence on  $\phi$  for both rich and lean flames with a minimum and discontinuity in the derivative of the burning rate with respect to the equivalence ratio at  $\phi = 1.0$ . This discontinuity stems from a discontinuity in the derivative of the heat release caused by the imposition of the steady state for O. The burning rate is about 12% lower than that predicted by the seven-step numerical results for  $\phi = 0.82$  and  $0.93$ , 38% lower at  $\phi = 1.00$ , and 20% lower at  $\phi = 0.76$  and  $\phi = 1.08$ .

Examination of the numerical results for the seven- and two-step mechanisms indicates three sources of disagreement. For rich flames, neglect of  $L([\text{H}])$  in Equation (25) is most important; in the hot part of the flame this term is negative and

consequently tends to increase  $[\text{OH}]$  and the rates, giving the seven-step mechanism the higher burning velocity. For lean flames, the presence of the  $\text{NO}_2$  decomposition route  $w_{\text{II}}$  causes a lower effective heat release in the seven-step mechanism compared to the two-step mechanism, thereby contributing to the lower two-step burning velocity. This effect becomes more important as  $\phi$  decreases. Also, for lean flames, inaccuracies in the O-atom steady-state relation, Equation (21), becomes important in the downstream part of the flame where reactions (4) and (5) achieve partial equilibrium. Examination of Equation (28) with  $w_{\text{III}} = k_5[\text{H}_2\text{O}][\text{O}] - k_4[\text{OH}]^2$  shows that, as  $(w_4 - w_5) \rightarrow 0$ , small errors in the O-atom concentration calculated from Equation (24) may cause large errors in  $L([\text{OH}])$ . The two-step formula in Equation (28) overestimates  $-L([\text{OH}])$  where OH is being consumed, leading to lower OH concentrations and a corresponding lower burning velocity in the two-step approximation. Since all three of these effects are in the same direction, the errors all add, instead of cancelling. The 20% discrepancy at  $\phi = 1.08$  and the 38% discrepancy at  $\phi = 1.0$  are due almost entirely to neglecting  $L([\text{H}])$ , and the 20% discrepancy at  $\phi = 0.76$  is due in roughly equal parts to neglect of step II' and O-atom steady-state inaccuracy.

It is worth emphasizing that the accuracies with which Equations (23) and (24) hold and with which step II' can be neglected are good enough that, in principle, there exists a two-step approximation for which burning-rate discrepancies from the seven-step prediction are less than 10%. The larger discrepancies appearing in Figure 1 are associated with the manner in which the two-step description was written. It has long been known (Williams, 1985, Appendix B) that steps like neglecting  $L([\text{H}])$  in Equation (24), instead of using the complicated expression for  $L([\text{H}])$  in terms of  $L([\text{OH}])$ ,  $L([\text{H}_2])$ ,  $L([\text{NO}_2])$ ,  $L([\text{H}_2\text{O}])$  and  $L(T)$ , obtained by substitution of Equation (23) for  $[\text{H}]$  into the operator  $L([\text{H}])$ , as required by a formal expansion procedure, can produce substantial errors. However, seldom have explicit examples of this, such as the present example for rich and stoichiometric flames, been encountered. Especially in view of the loss in accuracy in going from the twenty-four- to the seven-step mechanism, there is no reasonable justification at the present stage to proceed with the complexity involved in treating the  $L([\text{H}])$  term properly.

The difficulty with error arising from the need to evaluate  $[\text{O}]$  more accurately than can be done from the leading-order steady-state expression in Equation (24) does not seem to have been encountered before in the literature. This difficulty is associated with switching of relative accuracies of different steady states within the flame, and for this kinetic system, occurs for lean flames. The O-atom steady state, always good everywhere to better than 3% for  $\phi = 0.76$  and 0.93, is written in general as  $w_4 + w_6 = w_5 + w_7$ , which leads to Equation (24). The resulting formula for  $[\text{O}]$  is then used in Equation (28) to evaluate  $w_5 - w_4$ . This is perfectly proper in the upstream part of the flame, where O-atom steady-state relation is much more accurate than the approximation  $L([\text{OH}]) + L([\text{H}]) = 0$ , but in the downstream part of the flame, the partial equilibrium  $w_4 = w_5$  becomes almost as accurate as the O-atom steady state, and the further algebraic relation  $w_6 = w_7$  becomes applicable (within 8% for  $\phi = 0.76$ , which is also the accuracy of the relation  $w_4 = w_5$ ). A one-step approximation therefore applies in the downstream region, so that in this problem the inaccuracy is associated with the onset of a further simplification that holds as accurately as the overall simplification of Equation (24). A two-zone asymptotic analysis for this problem could be pursued. If

automatic procedures, such as the computational singular perturbation of Lam (1988), were available for two-point boundary-value problems involving systems of second-order equations, then this kind of difficulty could be approached with greater generality.

The one-step mechanism just identified as being reasonable in the downstream part of the flame is quite inaccurate in the upstream part, where the two-step mechanism is needed. Nevertheless, as a means for obtaining a simple, analytical expression for the burning rate, it is of interest to investigate the accuracy of a description in which the one-step mechanism is assumed to apply everywhere. This is achieved by explicitly introducing one further steady state from Equation (25),  $w_4 = w_5$ , as was previously done indiscriminately in deriving Equation (17). This leads to

$$[\text{OH}] = \{k_5/k_4 [\text{H}_2\text{O}] [\text{O}]\}^{1/2} \quad (30)$$

everywhere and, as indicated above, reduces Equation (24) to  $w_6 = w_7$ , which gives

$$[\text{O}] = (k_6/k_7) [\text{M}]. \quad (31)$$

Equation (30) then gives

$$[\text{OH}] = [(k_5/k_4)(k_6/k_7) [\text{M}] [\text{H}_2\text{O}]]^{1/2}, \quad (32)$$

which may be substituted into Equation (23) to obtain the needed explicit expression for  $[\text{H}]$ , which together with Equation (18) gives the rate of global reaction (I) as

$$w_1 = k_2 \left[ \frac{k_5 k_6 [\text{H}_2\text{O}]}{k_4 k_7 [\text{M}]} \right]^{1/2} \left[ \frac{1}{1 + k_3 [\text{H}_2\text{O}] / (k_1 [\text{NO}_2])} \right] [\text{H}_2] [\text{M}]. \quad (33)$$

The expression is approximately first order in  $\text{H}_2$  and zeroth order in  $\text{NO}_2$ , although for rich flames presumably  $[\text{NO}_2]$  approaches zero far downstream, so that the rate ultimately is first order with respect to  $\text{NO}_2$  as well. In fact, throughout most of the reaction zone,  $w_1$  is large compared with  $w_3$ —that is, the O abstraction from  $\text{NO}_2$  is a stronger H sink than the H abstraction from  $\text{H}_2\text{O}$ —so that the additive term in the denominator in Equation (33) remains small (of order 0.05 or less) and finally contributes nearly negligibly to the burning velocity. The next section describes prediction of the burning rate using the methods of activation-energy asymptotics (AEA) for this one-step mechanism. Comparisons of the accuracy of the one-step approximation will be given after the AEA formulas are summarized.

## ASYMPTOTIC ANALYSIS

From Clarke (1975) and Mitani (1980), as summarized by Williams (1985), at leading order the square of the mass burning rate is

$$m^2 = \frac{2\lambda_\infty v'_{1,1} (v'_{2,1}/v'_{1,1})^{n_2} \rho_\infty^{(n_1+n_2)} B_{1,\infty} T_\infty^{b_1} Y_{1,0}^{(n_1+n_2-1)}}{c_{p,\infty} W_1^{(n_1+n_2-1)} \beta^{(n_1+n_2+1)} Le_1^{-n_1} Le_2^{-n_2}} e^{-E_1/(R^\circ T_\infty)} \\ \times \int_0^\infty y^{n_1} (y+a)^{n_2} e^{-y} dy, \quad (34)$$

where  $Y_i$ ,  $Le_i$ ,  $v'_{i,k}$  are the reactant mass fraction, Lewis number, and stoichiometric coefficient in reaction  $k$  for species  $i$ , respectively. The parameters  $B_{1,\infty}$  and  $E_1$  are the

pre-exponential factor and activation energy in the modified Arrhenius rate expression

$$w_i = W_i \sum_{k=1}^M (v''_{i,k} - v'_{i,k}) B_k T^{b_k} e^{-E_k/(R^0 T)} \prod_{j=1}^N \left( \frac{X_j p}{R^0 T} \right)^{v'_{j,k}}, \quad i = 1, \dots, N, \quad (35)$$

where  $N$  is the number of species in reaction  $k$ , and  $M$  is the total number of reactions;  $X_i$  and  $W_i$  are the mole fraction and molecular weight of species  $i$ ,  $p$  the pressure, and  $T$  the temperature. The subscripts 1 and 2 refer to the deficient and abundant reactants respectively, while 0 and  $\infty$  refer to the conditions in the unburned gas and at the final temperature. Single and double primes denote reactant and product species, and  $R^0$  is the universal gas constant. The parameter  $a$  is equal to  $(\beta/L_2)(\phi - 1)$ . The effective Lewis numbers are defined in terms of mole-fraction-weighted linear combinations of the Lewis numbers of all diffusion pairs (Chelliah and Williams, 1987). The Zel'dovich number is defined as  $\beta = \alpha E/(R^0 T_x)$  where the nondimensional heat release-parameter  $\alpha$  is  $h_0/(c_{p,\infty} T_x)$ , and  $h_0$  is the heat release per unit mass of initial mixture. Although the temperature exponent  $b_1 = b_2 + \frac{1}{2}(b_5 + b_6 - b_4 - b_7)$  in Equation (35) is small (0.65), it is included in the overall activation energy  $E$  (Peters and Williams, 1987). The Arrhenius pre-exponential factor  $A_1$  in the resulting reaction rate expression  $A_1 e^{-E/RT}$  is found from Equation (33) to be

$$A_1 = B_2 \left( \frac{B_5 B_6 [\text{H}_2\text{O}] [\text{M}]}{B_4 B_7} \right)^{1/2} \left( \frac{1}{1 + k_3 [\text{H}_2\text{O}]/(k_1 [\text{NO}_2])} \right) T_r^{b_1} e^{b_1}, \quad (36)$$

where  $T_r = 1600$  K.

The presence of the concentration terms for  $\text{H}_2\text{O}$  and  $\text{NO}_2$  in the additive term in the denominator of the rate expression, Equation (33), ordinarily would produce a more complicated integral in Equation (34), requiring numerical integration. For this kinetic system, however, this additive term is small, as described above, and  $[\text{H}_2\text{O}]$  in the reaction zone is near its final value. Consequently, good accuracy and convenient analytical solution of the integral in Equation (34) can be obtained by approximating the additive term in the pre-exponential factor in Equation (36) as a constant, using constant values for the  $\text{H}_2$ ,  $\text{NO}_2$ , and  $\text{H}_2\text{O}$  concentrations estimated from the asymptotic structure ( $[i] \approx \beta^{-1}([i]_0 - [i]_x) + [i]_x$ ) and constant values for  $k_1$  and  $k_3$  evaluated at  $T_x$ . The overall activation energy  $E$  for the one-step reaction (I) is given by

$$E = E_2 + \frac{1}{2}(E_5 + E_6 - E_4 - E_7) + b_1 R^0 T_r. \quad (37)$$

From Table 1,  $E = 202.5$  kJ/mol, and  $\beta$  ranges from 10.8 to 12.7, so AEA should be quite accurate for the one-step mechanism.

## RESULTS AND DISCUSSION FOR THE ONE-STEP MECHANISM

Figure 1 shows the leading-order asymptotically predicted burning rate from Equation (34) as a function of  $\phi$ , obtained by using the one-step mechanism in Equation (33). Also shown in Figure 1 are the results of a numerical solution for the burning rate using the one-step mechanism. These numerical results are about 5% lower than the leading-order asymptotic results. To improve the accuracy of the AEA prediction, the

solution was also obtained to second order in  $1/\beta$  for  $\phi = 0.76$  to 1.0, following the method of Chelliah and Williams (1987). These results, which explicitly include the effects of property variation and multicomponent diffusion, are about 5% lower than the leading-order asymptotic results and within 2% of the one-step numerical results. It is therefore seen that, as expected from the large values of  $\beta$ , the analytical asymptotic result provides an excellent approximation to the results of the one-step numerical mechanism for which they were derived.

These one-step descriptions, however, give burning rates about 50% lower than the numerical result for the seven-step mechanism and about a factor of 3 lower than those of the full-mechanism. The error in the two-step mechanism, compared to the seven-step mechanism, was discussed above. The further error in the one-step mechanism results from inaccuracies in the relation  $w_4 = w_5$ , which is poor upstream for all  $\phi$  and also increasingly poor downstream as  $\phi$  increases, and from inaccuracies in the subsequently derived relation  $w_6 = w_7$ , which is a good approximation at the center of the reaction zone but poor elsewhere for all  $\phi$ . Neglect of the chain-branching and recombination steps (8)–(11) affects the accuracy of the one- and two-step mechanisms to an extent comparable with the difference between the eleven- and seven-step mechanisms. These reactions can be included as perturbations in the AEA descriptions of the flames; however, considering the large differences between the seven- and one-step results, this does not seem warranted.

The influence of the previously neglected HONO reactions (12) and (13) on the flame structure can be estimated by including these reactions in the one-step reduced mechanism and examining the asymptotically predicted burning rates. We proceed by adding reactions (12) and (13) back into the seven-step mechanism and assume a steady state for HONO,  $L(\text{HONO}) = w_{12} - w_{13} = 0$ . Again making indiscriminate use of the steady-state relations for O, H, OH, and also for HONO, we obtain the same two-step global mechanism of Equation (17), where the rate of the global step (II) is  $w_{11} = w_6 + w_{12}$  and now includes the contribution from Equation (12). Equations (30) and (31) for  $[\text{OH}]$  and  $[\text{O}]$  then become

$$[\text{OH}] = \left( \frac{k_5}{k_4} [\text{H}_2\text{O}] [\text{O}] + \frac{k_{12}}{k_4} [\text{NO}_2] [\text{H}_2] \right)^{1/2} \quad (38)$$

and

$$[\text{O}] = \frac{k_6 [\text{M}] + k_{12} [\text{H}_2]}{k_7} \quad (39)$$

Again neglecting the effects of the global step (II) and also the effects of  $w_8$  and  $w_9$  on  $w_1$  in Equation (18), the rate of the one-step reaction (I) is found to be

$$w_1 = k_2 \left( \frac{1}{1 + k_3 [\text{H}_2\text{O}] / (k_1 [\text{NO}_2])} \right) \times \left( \frac{k_5 k_6 [\text{H}_2\text{O}]}{k_4 k_7 [\text{M}]} + \frac{k_5 k_{12} [\text{H}_2] [\text{H}_2\text{O}]}{k_4 k_7 [\text{M}]^2} + \frac{k_{12} [\text{NO}_2] [\text{H}_2]}{k_4 [\text{M}]^2} \right)^{1/2} [\text{H}_2] [\text{M}], \quad (40)$$

which can be compared with Equation (33). The second and third additive terms in the second bracketed expression of Equation (40) account for the increase in O and OH concentrations produced by reactions (12) and (13). Again approximating the reaction-zone concentrations of the stable species as in Equation (36), we find that these additional two terms increase  $w_1$  by 12%, which increases the burning rate by about 6% for  $0.76 \leq \phi \leq 1.08$ . For comparison, it may be observed that adding reactions (12) and (13) to the seven-step mechanism increases the numerically calculated burning rate by 10–40% for  $0.93 \leq \phi \leq 1.08$  and 80% for  $\phi = 0.82$ . Because of their important contribution to the H and OH production, the HONO reactions are too important to be incorporated in this approximate fashion; however, these simple modifications do indicate an increase in the burning rate.

## CONCLUSIONS

For a burner-stabilized  $\text{NO}_2/\text{H}_2$  flame at 25 torr and 2000 K, a twenty-four-step starting mechanism is found to reproduce the numerically calculated burning rate within about 10% of the results using the eighty-two-reaction kinetic mechanism given in Table 1 for  $0.76 \leq \phi \leq 1.08$ . For these conditions, an eleven-step mechanism exists which produces burning rates about 30% lower than the full mechanism for  $0.76 \leq \phi \leq 1.08$ . About two thirds of this difference is due to neglect of the reaction of  $\text{NO}_2$  to NO and  $\text{O}_2$ , while the remaining third is due to neglect of the HONO reactions. For  $\phi = 0.76$ , the HONO reactions are even more important, their neglect decreasing the burning rate by 30%; neglect of  $\text{HO}_2$  reactions compensates for this, increasing the burning rate by about the same amount.

A seven-step approximation, which neglects the  $\text{H}_2$  and  $\text{O}_2$  branching reactions (8)–(11), yields a burning rate close to that of the eleven-step result for all but the richest condition, where the burning rate is 23% lower. Since the steady-state approximations for the intermediates O, H, and OH are good, reduction of the seven-step mechanism through use of the steady-state approximations may at first glance appear to be straightforward. The balance equation for H and OH, however, are dominated by the same reactions, reducing the usefulness of one equation. Thus, there exists a reasonably accurate two-step approximation which, however, develops further burning-rate errors on the order of 20% when simplified for convenient explicit numerical integration. Introduction of one further, rather poor approximation produces a one-step mechanism amenable to a simple analytical approximation for the burning rate based on the methods of activation-energy asymptotics that is still able to reproduce the burning rate within a factor of about three of the result obtained numerically using the eighty-two-step full mechanism.

## ACKNOWLEDGEMENTS

The authors are grateful to J. V. Volponi and M. C. Branch for providing pre-publication drafts and additional information, and for many helpful discussions. This work was supported by the National Science Foundation under contract number CTS92-14888.

## REFERENCES

- Anderson, W. R. (1990). Detailed Chemical Modeling of Propellant Flames. *JANNAF Combustion Meeting*, Cheyenne, WY, Nov.
- Chelliah, H. K. and Williams, F. A. (1987). Asymptotic Analysis of Two-reactant Flames with Variable Properties and Stefan-Maxwell Transport. *Combust. Sci. and Tech.*, **51**, 129.
- Clarke, J. F. (1975). The Pre-mixed Flame with Large Activation Energy and Variable Mixture Strength: Elementary Asymptotic Analysis. *Combust. Sci. and Tech.*, **10**, 189.
- Kaskan, W. E. and Hughes, D. E. (1973). Mechanism of Decay of Ammonia in Flame Gases from  $\text{NH}-\text{O}_2$  Flames. *Combustion and Flame*, **20**, 381.
- Kee, R. J., Miller, J. A. and Jefferson, T. H. (1980). CHEMKIN: A General-purpose, Transportable, Fortran Chemical Kinetics Code Package. Sandia National Laboratories Report, SAND80-8003.
- Kee, R. J., Warnatz, J., and Miller, J. A. (1983). A Fortran Computer Code Package for the Evaluation of Gas-phase Viscosities, Conductivities, and Diffusion Coefficients. Sandia National Laboratories Report, SAND83-8209.
- Lam, S. H. and Goussis, D. A. (1988). Understanding Complex Chemical Kinetics with Computational Singular Perturbation. Twenty-Second Symposium (International) on Combustion, The Combustion Institute, Pittsburgh. pp. 931.
- Linteris, G. T. and Williams, F. A. (1992). Asymptotic and Numerical Predictions of Carbon Monoxide-Nitrous Oxide Flame Structure. Twenty-Fourth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh. pp. 803.
- Miller, J. A., and Bowman, C. T. (1989). Mechanism and Modeling of Nitrogen Chemistry in Combustion. *Progress in Energy and Combustion Science*, **15**, 287.
- Mitani, T. (1980). Propagation Velocities of Two-Reactant Flames. *Combust. Sci. and Tech.*, **21**, 175.
- Peters, N. and Williams, F. A. (1987). The Asymptotic Structure of Stoichiometric Methane-Air Flames. *Combust. and Flame*, **68**, 185.
- Peters, N. (1991). Reducing Mechanisms. In *Reducing Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, M. D. Smooke (Ed.), Springer-Verlag, New York, pp. 48.
- Slack, M. W. and Grillo, A. R. (1978). Rate Coefficients for  $\text{H}_2 + \text{NO}_2 = \text{HONO} + \text{H}$  Derived from Shock Tube Investigations of  $\text{H}_2-\text{O}_2-\text{NO}_2$  Ignition. *Combust. Flame*, **31**, 275.
- Smooke, M. D. (1982). Solution of Burner Stabilized Premixed Laminar Flames by Boundary Value Methods. *J. Comp. Phys.*, **48**, 72.
- Smooke, M. D. (Ed.) (1991). *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, Springer-Verlag, New York.
- Tsang, W. and Herron, J. T. (1991). Reactions Involving  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}$ ,  $\text{HNO}_2$ ,  $\text{HCN}$  and  $\text{N}_2\text{O}$ . *J. Phys. Chem. Ref. Data*, **20** (4), 609.
- Volponi, J. V. and Branch, M. C. (1990). Flame Structure of  $\text{H}_2-\text{NO}_2$ -argon Laminar Premixed Flames. Paper WSS-CI-90-02, *Western States Section Meeting of the Combustion Institute*, October, La Jolla, CA.
- Volponi, J. V. and Branch, M. C. (1992). Flame Structure of  $\text{H}_2-\text{NO}_2$ -Argon and  $\text{H}_2-\text{O}_2$ -Argon Laminar Premixed Flames. *Combust. Sci. and Tech.*, in review.
- Westley, F., Herron, J. T., Cvetanovic, R. J., Hampson, R. F. and Mallard, W. G. (1991). NIST Standard Reference Database 17, NIST Chemical Kinetics Database Version 3.0, National Institute of Standards and Technology, Gaithersburg MD.
- Williams, F. A. (1985). *Combustion Theory*, 2nd. ed. Benjamin/Cummings, Menlo Park, CA. pp. 163.
- Yetter, R. A. (1992). Personal communication, Princeton, NJ.