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Autoignition of Methane Mixtures: The Effect of Hydrogen Peroxide

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The objective of this study was to estimate the efficiency of autoignition promotion for CH_4 combustible mixtures by H_2O_2. This was accomplished by computing ignition delays for $CH_4/O_2/Ar(N_2)$ mixtures for various compositions, additive concentrations, pressures, and temperatures. Ignition delay times for additive-free compositions were predicted in good agreement with available experimental data. A model demonstrates that replacing 5–10% (volumetric) of the fuel with H_2O_2 shortens the ignition delay by over one order of magnitude for all conditions examined. The effect of promotion is particularly pronounced at temperatures $T < 1500$ K.

Introduction

CONTROL of ignition processes by addition of promoters (additives reducing ignition delay time) to burn H_2 or HC fuels efficiently in air is an increasingly interesting method for improving the performance of airbreathing propulsion systems. Compounds used as promoters are free radicals, nitrogen oxides, peroxides, and others such as SiH_4. In looking for suitable promoters one should consider not only effectiveness in a general sense (i.e., dependence on combustor pressure, temperature, and air/fuel mixture ratio), but also availability, cost, impact on atmospheric chemistry (e.g., the ozone layer), toxicity, and many other technology-related factors.

The role played by nitrogen oxides introduced into a hydrogen–air system has been studied in detail by Laster and Sojka,[1] and Baranovskii et al.[2] A study of the effect of adding H_2O_2 to a supersonic H_2/air diffusion flame has been reported elsewhere.[3]

Since among HC fuels methane is most attractive because of its relatively large specific impulse and good cryogenic cooling properties for sustained hypersonic flight, but it is also least reactive, the selection of efficient promoters for methane may become an important issue, especially for wind-tunnel testing. Typical ignition delay for stoichiometric methane/air may reach upwards of $\mathcal{O}(10^{-2}–10^{-1})$ s at combustor $T_c \sim 1100$ K and $P_c \sim 1$ atm, thereby preventing stable flame anchoring unless a strong recirculating region is maintained at the expense of large pressure drop. Ignition itself may be an even more serious problem because of the narrow flammability limits of methane.

Systematic data on the effect of stable additives, higher HC fuels, and free radicals on methane ignition are summarized by Zamansky and Borisov.[4] Ramohalli et al.[5] observed experimentally the improved flame stability for fuel lean CH_4/air mixtures with 3% injection of H_2O_2 that suggests an important role of H_2O_2 in the ignition process.

The purpose of this study is to investigate the effects of hydrogen peroxide H_2O_2 as promoter on the ignition delay times for methane/air combustion. $CH_4/O_2/Ar$ mixtures were studied and simulated numerically, since reliable experimental data on ignition delay times for these (promoters-free) mixtures are available.[6,7] Lifshitz et al.[6] also considered H_2 and C_3H_8 as additives. Then CH_4/air mixtures were simulated. Numerical results indicate that moderate H_2O_2 addition reduces delay times by about one order of magnitude in the temperature range of 1525–2025 K and the pressure range of 2.55–13.01 atm of the experiments.[6] Substantial reduction of ignition delay time was obtained also for stoichiometric and nonstoichiometric CH_4/air mixtures at conditions of interest for designers of supersonic combustion chambers operation.

Model Description

The ignition delay time is related to a latent period in the combustion process of a premixed mixture, when the temperature stays nearly constant. During this period, however, the mixture components may experience essential changes. In this study a computer model was used to calculate the mixture parameters as a function of time,[8] and the ignition delay time was defined as the time at which the temperature gradient picks up (point of inflection of the temperature vs time profile).

The detailed reaction mechanism of methane oxidation for a set of 23 species (H_2, O_2, OH, H, H_2O, O, H_2O_2, HO_2, CH_4, CO, CO_2, HCO, CH_2O, CH_3, CH_2, CH, Ar or N_2, N, NO, N_2O, NO_2, HNO) was generated in an automatic way from the C/H/O/N chemical system database employed.[9] Each of N_r elementary chemical reactions involving N_s species is in the general form

$$\sum_{s=1}^{N_s} \nu'_{sr} X_s \underset{k_b^r}{\overset{k_f^r}{\rightleftharpoons}} \sum_{s=1}^{N_s} \nu''_{sr} X_s, \qquad r = 1, N_r \tag{1}$$

where X_s is the mole of s species, ν'_{sr} and ν''_{sr} are stoichiometric coefficients, and k_f^r and k_b^r are the rate coefficients for the forward and backward stages of the r reaction and are cast in the generalized Arrhenius form:

$$\begin{aligned} k_f^r &= a_f^r T^{\zeta_f^r} \exp(-E_{af}^r/T) \\ k_b^r &= a_b^r T^{\zeta_b^r} \exp(-E_{ab}^r/T) \end{aligned} \tag{2}$$

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Table 1 Reaction mechanism for $CH_4/O_2/Ar$ mixtures[a]

Reaction	a_f^r	ζ_f^r	E_{af}^r
1. $CH_3 + H + M^b \rightleftharpoons CH_4 + M$	8.00×10^{26}	−3.00	0
2. $CH_4 + O_2 \rightleftharpoons CH_3 + HO_2$	7.90×10^{13}	0.00	56,000
3. $CH_4 + H \rightleftharpoons CH_3 + H_2$	2.20×10^{04}	3.00	8,750
4. $CH_4 + OH \rightleftharpoons CH_3 + H_2O$	1.60×10^{06}	2.10	2,460
5. $CH_4 + O \rightleftharpoons CH_3 + OH$	1.02×10^{09}	1.50	8,604
6. $CH_4 + HO_2 \rightleftharpoons CH_3 + H_2O_2$	1.80×10^{11}	0.00	18,700
7. $CH_3 + O_2 \rightleftharpoons CH_2O + OH$	2.50×10^{11}	0.0	9,000
8. $CH_3 + O \rightleftharpoons CH_2O + H$	8.00×10^{13}	0.0	0
9. $CH_3 + OH \rightleftharpoons CH_2 + H_2O$	7.50×10^{06}	2.0	5,000
10. $CH_3 + H \rightleftharpoons CH_2 + H_2$	9.00×10^{13}	0.0	15,100
11. $CH_2 + H \rightleftharpoons CH + H_2$	1.00×10^{18}	−1.56	0
12. $CH_2 + OH \rightleftharpoons CH + H_2O$	1.13×10^{07}	2.0	3,000
13. $CH_2 + OH \rightleftharpoons CH_2O + H$	2.50×10^{13}	0.0	0
14. $CH + O_2 \rightleftharpoons HCO + O$	3.30×10^{13}	0.0	0
15. $CH + O \rightleftharpoons CO + H$	5.70×10^{13}	0.0	0
16. $CH + OH \rightleftharpoons HCO + H$	3.00×10^{13}	0.0	0
17. $CH + CO_2 \rightleftharpoons HCO + CO$	3.40×10^{12}	0.0	690
18. $CH + H_2O \rightleftharpoons CH_2O + H$	1.17×10^{15}	−0.75	0
19. $CH_2 + CO_2 \rightleftharpoons CH_2O + CO$	1.10×10^{11}	0.0	1,000
20. $CH_2 + O \rightleftharpoons CO + H + H$	5.00×10^{13}	0.0	0
21. $CH_2 + O \rightleftharpoons CO + H_2$	3.00×10^{13}	0.0	0
22. $CH_2 + O_2 \rightleftharpoons CO_2 + H + H$	1.60×10^{12}	0.0	1,000
23. $CH_2 + O_2 \rightleftharpoons CH_2O + O$	5.00×10^{13}	0.0	9,000
24. $CH_2 + O_2 \rightleftharpoons CO_2 + H_2$	6.90×10^{11}	0.0	500
25. $CH_2 + O_2 \rightleftharpoons CO + H_2O$	1.90×10^{10}	0.0	−1,000
26. $CH_2 + O_2 \rightleftharpoons CO + OH + H$	8.60×10^{10}	0.0	−500
27. $CH_2 + O_2 \rightleftharpoons HCO + OH$	4.30×10^{10}	0.0	−500
28. $CH_2O + OH \rightleftharpoons HCO + H_2O$	3.43×10^{09}	1.18	−447
29. $CH_2O + H \rightleftharpoons HCO + H_2$	2.19×10^{08}	1.77	3,000
30. $CH_2O + M \rightleftharpoons HCO + H + M$	3.31×10^{16}	0.0	81,000
31. $CH_2O + O \rightleftharpoons HCO + OH$	1.80×10^{13}	0.0	3,080
32. $HCO + OH \rightleftharpoons H_2O + CO$	1.00×10^{14}	0.0	0
33. $HCO + M \rightleftharpoons H + CO + M$	2.50×10^{14}	0.0	16,802
34. $HCO + H \rightleftharpoons CO + H_2$	1.19×10^{13}	0.25	0
35. $HCO + O \rightleftharpoons CO + OH$	3.00×10^{13}	0.0	0
36. $HCO + O \rightleftharpoons CO_2 + H$	3.00×10^{13}	0.0	0
37. $HCO + O_2 \rightleftharpoons HO_2 + CO$	3.30×10^{13}	−0.40	0
38. $CO + O + M_3{}^b \rightleftharpoons CO_2 + M_3$	6.17×10^{14}	0.0	3,000
39. $CO + OH \rightleftharpoons CO_2 + H$	1.51×10^{07}	1.30	−758
40. $CO + O_2 \rightleftharpoons CO_2 + O$	1.60×10^{13}	0.0	41,000
41. $HO_2 + CO \rightleftharpoons CO_2 + OH$	5.80×10^{13}	0.0	22,934
42. $CH_2 + O_2 \rightleftharpoons CO + OH + H$	3.00×10^{13}	0.0	0
43. $CH_2 + H_2 \rightleftharpoons CH_3 + H$	7.00×10^{13}	0.0	0
44. $CH_2 + OH \rightleftharpoons CH_2O + H$	3.00×10^{13}	0.0	0
45. $H_2 + O_2 \rightleftharpoons OH + OH$	1.70×10^{13}	0.0	47,780
46. $H_2 + OH \rightleftharpoons H_2O + H$	1.17×10^{09}	1.30	3,626
47. $O + OH \rightleftharpoons O_2 + H$	4.00×10^{14}	−0.50	0
48. $O + H_2 \rightleftharpoons OH + H$	5.06×10^{04}	2.67	6,290
49. $H + O_2 + M_2{}^b \rightleftharpoons HO_2 + M_2$	3.61×10^{17}	−0.72	0
50. $OH + HO_2 \rightleftharpoons H_2O + O_2$	7.50×10^{12}	0.0	0
51. $H + HO_2 \rightleftharpoons OH + OH$	1.40×10^{14}	0.0	1,073
52. $O + HO_2 \rightleftharpoons O_2 + OH$	1.40×10^{13}	0.0	1,073
53. $OH + OH \rightleftharpoons O + H_2O$	6.00×10^{08}	1.3	0
54. $H + H + M_1{}^b \rightleftharpoons H_2 + M_1$	1.00×10^{18}	−1.0	0
55. $H + H + H_2 \rightleftharpoons H_2 + H_2$	9.20×10^{16}	−0.6	0
56. $H + H + H_2O \rightleftharpoons H_2 + H_2O$	6.00×10^{19}	−1.25	0
57. $H + H + CO_2 \rightleftharpoons H_2 + CO_2$	5.49×10^{20}	−2.0	0
58. $H + OH + M \rightleftharpoons H_2O + M$	1.60×10^{22}	−2.0	0
59. $H + O + M \rightleftharpoons OH + M$	6.20×10^{16}	−0.6	0
60. $O + O + M \rightleftharpoons O_2 + M$	1.89×10^{13}	0.0	−1,788
61. $H + HO_2 \rightleftharpoons H_2 + O_2$	1.25×10^{13}	0.0	0
62. $HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	2.00×10^{12}	0.0	0
63. $H_2O_2 + M \rightleftharpoons OH + OH + M$	1.30×10^{17}	0.0	45,500
64. $H_2O_2 + H \rightleftharpoons HO_2 + H_2$	1.60×10^{12}	0.0	3,800
65. $H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	1.0×10^{13}	0.0	1,800
66. $H + HO_2 \rightleftharpoons O + H_2O$	3.10×10^{10}	0.0	3,590
67. $O + OH + M \rightleftharpoons HO_2 + M$	1.0×10^{16}	0.0	0
68. $H_2O_2 + H \rightleftharpoons H_2O + OH$	1.00×10^{13}	0.0	3,590
69. $H_2O_2 + O \rightleftharpoons H_2O + O_2$	8.40×10^{11}	0.0	4,260
70. $H_2O_2 + O \rightleftharpoons OH + HO_2$	2.00×10^{13}	0.0	5,900
71. $HO_2 + H_2 \rightleftharpoons H_2O + OH$	6.50×10^{11}	0.0	18,800

[a] Units are moles, cubic centimeters, seconds, Kelvins, and calories/mole.

[b] Third body concentrations M_i and the chaperon efficiencies were those of Miller and Bowman[9] database.

Reaction rate parameters a^r, ζ^r, and E_a^r, listed in Table 1, are taken mainly from Miller and Bowman.[9] The parameters for the last two reactions in this table were taken from Wu et al.[10] The additional methyl-consuming reaction

$$CH_3 + O_2 \rightleftharpoons CH_2O + OH$$

which was not included in the compilation[9] is assumed to be important. The kinetics of this reaction derived from Tsuboi and Wagner[11] are proven to be necessary to reproduce the ignition delay times measured in shock-tube experiments. To reproduce correctly the equilibrium limit, the Arrhenius parameters for the backward reactions in Eqs. (2) were calculated with the help of a linear regression analysis to obtain the best-fit values of $k_b^r = k_f^r/K_c^r$, where K_c^r is the equilibrium constant for the r reaction. The equilibrium constants and species properties were calculated with the help of the well-known NASA polynomials.[12]

The high-temperature oxidation mechanism was not tuned for any particular composition, temperature, or pressure conditions, and does not contain C_2 chemistry.[13] The initial step of the ignition process is the fuel decomposition reaction

$$CH_4 + M \rightleftharpoons CH_3 + H + M \tag{3}$$

whose pressure-dependent falloff nature has been neglected. The N−O reactions used to simulate ignition processes in CH_4/air mixtures are listed in Table 2.

The mathematical zero-dimensional model that describes the time evolution of homogeneous mixtures parameters, in an adiabatic, constant pressure environment simulating that of an aerocombustor, is formulated as an initial value problem for the system of ordinary differential equations (ODEs)[14]

$$\rho \frac{dy_i}{dt} = f_i(c) = W_i \sum_{r=1}^{N_r} (\nu''_{ir} - \nu'_{ir})\dot{\omega}_r$$
$$(y_i)_{t=0} = y_i^0, \qquad i = 1, N_s \tag{4}$$

supplemented by the two algebraic constraints

$$\begin{aligned} H(t) &= \sum_{i=1}^{N_s} y_i h_i(T) = \text{const} \\ P(t) &= R_0 T \sum_{i=1}^{N_s} c_i = \text{const} \end{aligned} \tag{5}$$

Here, $c_i = \rho_i/W_i$ and y_i are the numbers of moles in cm^3 and mass fractions, respectively, t is the time, H and $h_i(T)$ are total enthalphy and enthalphies of i species, respectively, W_i and ρ_i are the i species molecular mass and density, T is the temperature, P is the pressure, R_0 is the universal gas constant, and the variable $\dot{\omega}_r$ is the rate of progress of the rth reaction defined in terms of Arrhenius kinetics.

Table 2 N−O Reactions[a]

Reaction	a_f^r	ζ_f^r	E_{af}^r
1. $CO_2 + N \rightleftharpoons NO + CO$	1.90×10^{11}	0.00	3,400
2. $HO_2 + NO \rightleftharpoons NO_2 + OH$	2.11×10^{12}	0.00	−479
3. $NO_2 + H \rightleftharpoons NO + OH$	3.50×10^{14}	0.00	1,500
4. $NO_2 + O \rightleftharpoons NO + O_2$	1.00×10^{13}	0.00	600
5. $NO_2 + M \rightleftharpoons NO + O + M$	1.10×10^{16}	0.00	66,000
6. $N_2O + OH \rightleftharpoons N_2 + HO_2$	2.00×10^{12}	0.00	10,000
7. $N_2O + H \rightleftharpoons N_2 + OH$	7.60×10^{13}	0.00	15,200
8. $N_2O + M \rightleftharpoons N_2 + O + M$	1.60×10^{14}	0.00	51,600
9. $N_2O + O \rightleftharpoons N_2 + O_2$	1.00×10^{14}	0.00	28,200
10. $N_2O + O \rightleftharpoons NO + NO$	1.00×10^{14}	0.00	28,200
11. $HNO + M \rightleftharpoons H + NO + M$	1.50×10^{16}	0.00	48,680
12. $HNO + OH \rightleftharpoons NO + H_2O$	3.60×10^{13}	0.00	0
13. $HNO + H \rightleftharpoons H_2 + NO$	5.00×10^{12}	0.00	0
14. $N + NO \rightleftharpoons N_2 + O$	3.27×10^{12}	0.30	0
15. $N + O_2 \rightleftharpoons NO + O$	6.40×10^{09}	1.00	6,280
16. $N + OH \rightleftharpoons NO + H$	3.80×10^{13}	0.00	0

[a] Units are moles, cubic centimeters, seconds, Kelvins, and calories/mole.

The steady state in such calculations corresponds to the equilibrium state. Since the time required to reach equilibrium generally exceeds the characteristic times associated with the most rapid reactions by several orders of magnitudes, the initial value problem for the so-called stiff ODEs [Eq. (4)] must be solved by appropriate methods. To integrate numerically the

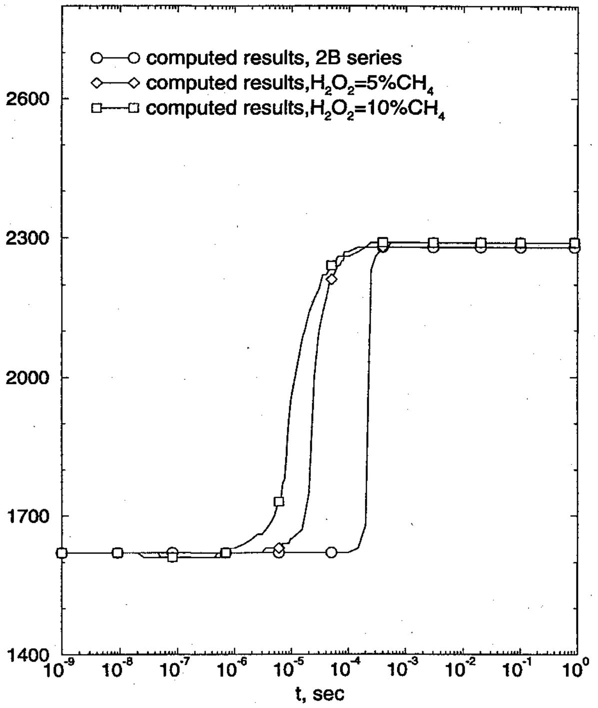

Fig. 1 Time history for temperature used to define ignition delay time.

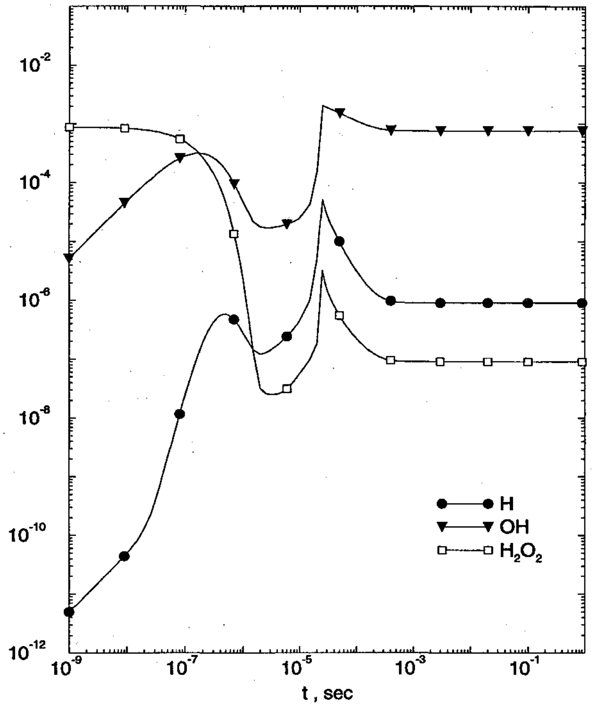

Fig. 2 Time history for radicals H and OH showing two maxima (equivalence ratio = 0.5, T = 1617 K, P = 8.6 atm, H_2O_2 = 5% CH_4).

system [Eq. (4)], a linear, multistep method developed by Gear was used in the Kinetics code.[8] The Kinetics code uses computer-aided generation of the reaction mechanism, selects rate coefficients and species thermal properties by preprocessing the specialized databases, generates the numerical solution with an automatic choice of time steps and order of integration, and performs local sensitivity analysis based on the decomposed direct method.[15]

Results and Discussion

Comparison with Experiments

The ignition delays were at first computed and compared with experimental data for the additive-free $CH_4/O_2/Ar$ mixtures. Such a comparison was performed to assess the accuracy of the kinetic mechanism in the absence of additives. Some temperature vs time histories used to define the ignition delay times are plotted in Fig. 1. It is interesting to note that when H_2O_2 is added, H and OH radicals exhibit two maxima (see Fig. 2): the first one is caused by H_2O_2 decomposition, and the second is related to combustion of the main fuel. At the early stage of ignition H_2O_2 is rapidly decomposed via the reaction

$$H_2O_2 + M \rightleftharpoons OH + OH + M \qquad (6)$$

and thus H_2O_2 serves as the major radical source. At later times, i.e., during radical pool formation because of chain

Table 3 Composition of test gas mixtures (in volume %) and experimental[6] conditions

Series	CH_4	O_2	Ar	Additive	*T*, K	*P*, atm
1C	3.5	7	89.5	—	1752	10.95
	—	—	—	—	1805	10.97
	—	—	—	—	1832	11.43
	—	—	—	—	1587	8.43
2B	2	8	90	—	1617	8.60
	—	—	—	—	1749	9.47
	—	—	—	—	1712	9.42
	—	—	—	—	1677	9.33
4A	3.5	7	89.427	H_2 0.073	1722	10.47
	—	—	—	—	1760	10.55
	—	—	—	—	1698	10.53
	—	—	—	—	1630	10.00

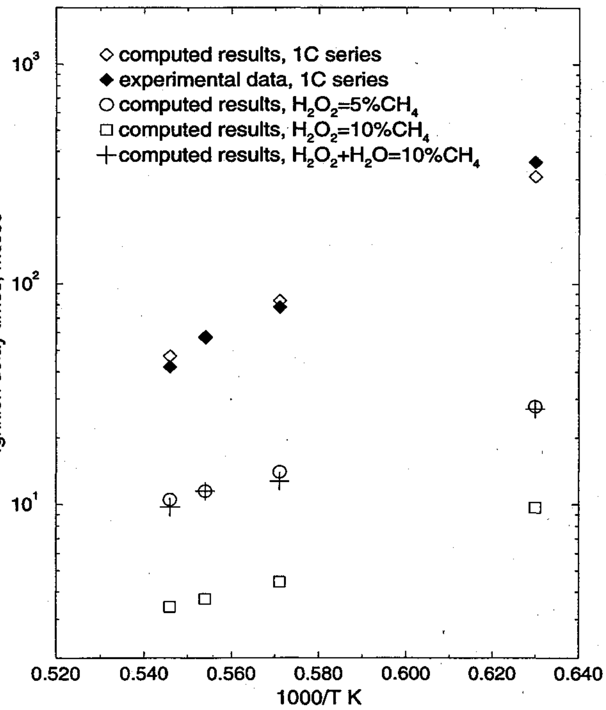

Fig. 4 Effect of H_2O_2 addition on $CH_4/O_2/Ar$ mixtures ignition delay times and comparison with experimental (additive-free) data (1C-series from Table 3).

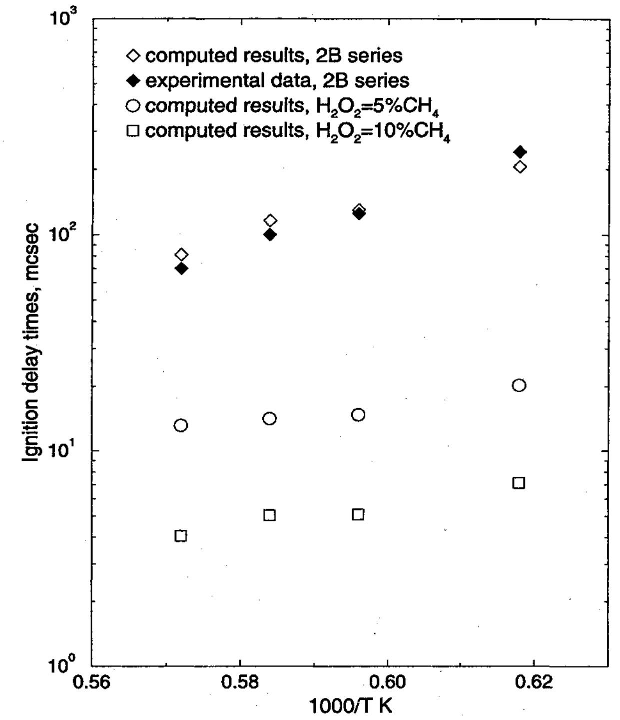

Fig. 3 Effect of H_2O_2 on $CH_4/O_2/Ar$ mixtures ignition delay times and comparison with experimental (additive-free) data (2B-series from Table 3).

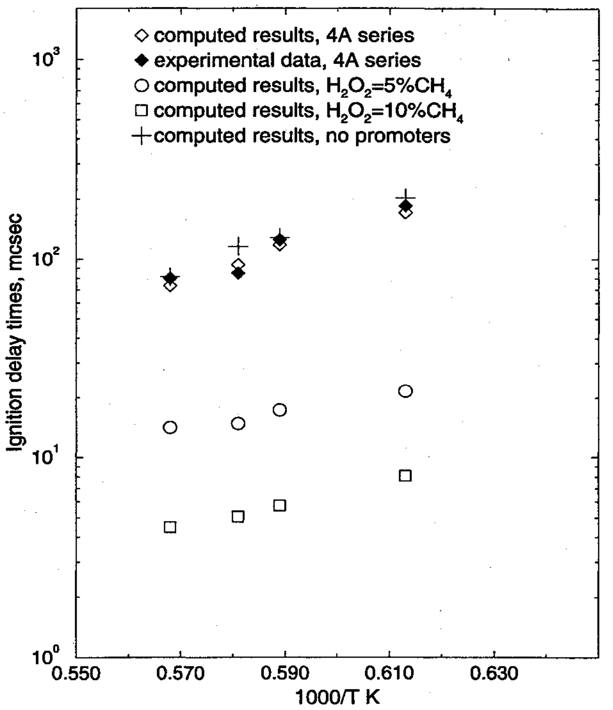

Fig. 5 Computed ignition delay times and comparison with experimental data when H_2 was used as additive (4A-series from Table 3).

branching, some H_2O_2 is again formed through a propagation step

$$CH_4 + HO_2 \rightleftharpoons CH_3 + H_2O_2 \tag{7}$$

and also from the partial recombination of OH. The methyl, CH_3, and the hydrogen peroxy, HO_2, radicals are the most abundant in the radical pool. The oxidation of CH_3 proceeds via the sequence: $CH_3 \rightarrow CH_2O \rightarrow HCO \rightarrow CO$. The radical HO_2 is almost exclusively produced through the stages

$$\begin{aligned} H + O_2 + M &\rightleftharpoons HO_2 + M \\ H_2O_2 + O_2 &\rightleftharpoons HO_2 + HO_2 \end{aligned} \tag{8}$$

Compared to the first reaction, the second in Eq. (8) becomes important only if initial H_2O_2 is large. Therefore two independent paths forming HO_2 [and then H_2O_2 through Eq. (7)] exist. The first reaction of Eq. (8) depends on H, which peaks simultaneously with OH:

$$H_2 + OH \rightleftharpoons H + H_2O \tag{9}$$

Thus, the H and OH maxima become related. When H_2O_2 is added, therefore, the conventional ignition delay time definition based on H concentration maximum used by Meyer and Oppenheim[16] is no longer suitable. The criterium for the ignition delay time used by Schott and Kinsey,[17] $[OH] = 10^{-9}$ mole/cm^3, also does not work here because almost immediately OH concentrations exceeds this level by two orders of magnitude. This is why the definition of ignition delay time as that corresponding to the point of inflection of the temperature profile is employed in this study. In fact, the time so defined is well correlated to the second maximum of H concentration vs time profile and with the point at which the largest sensitivity coefficients occur.

The satisfactory agreement with the experimental data for selected series[6] (see Table 3): 1C (stoichiometric), 2B (lean, equivalence ratio equal 0.5), and 4A (stoichiometric, with H_2 as additive) are demonstrated in Figs. 3–5. The results for $CH_4/O_2/Ar$ mixtures when hydrogen peroxide is added (addition is reported as % volumetric) show an essentially monotonous reduction of ignition delay times. As H_2O_2 is practically available as aqueous solutions of various strengths, the efficiency of a 50% solution was also investigated. From the

Table 4 Composition of test gas mixtures (in volume %) and experimental[7,19] conditions

Series	CH_4	O_2	Ar	Air	*T*, K	*P*, atm
A	7.7	15.4	76.9	——	1476–1900	11.22–15.13
A1	2	20	78	——	1470–1850	——
A2	2	——	——	98	1450–1740	——
A4	4	——	——	96	1560–1700	——

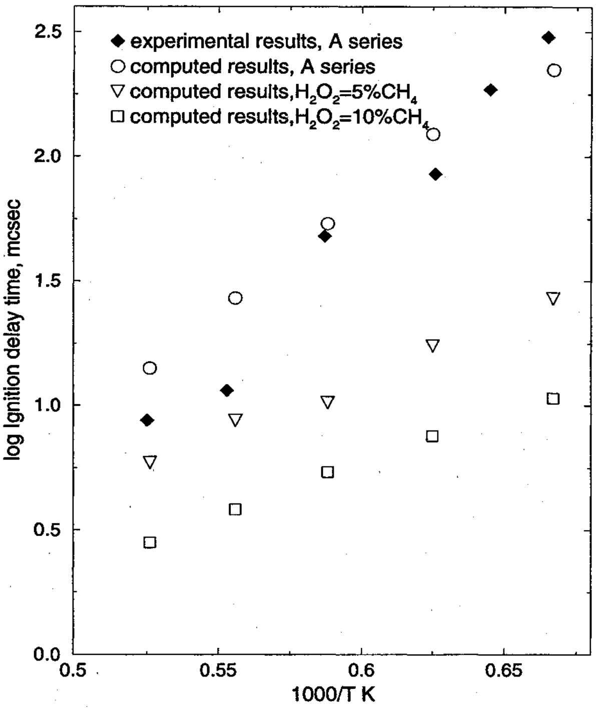

Fig. 6 Ignition delay times for A-series from Table 4.

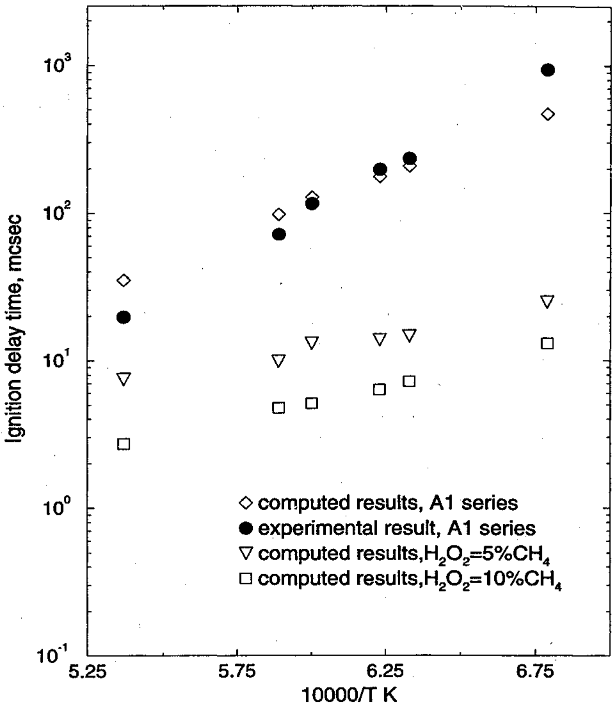

Fig. 7 Ignition delay times for A1-series from Table 4.

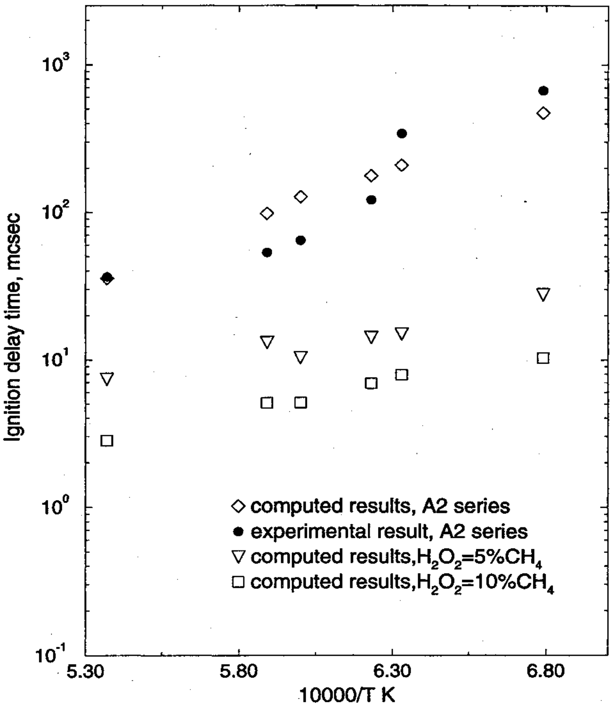

Fig. 8 Ignition delay times for A2-series from Table 4.

results in Fig. 4, it follows that only H_2O_2 may be considered as a chemically active agent reducing ignition delay, the influence of the associated H_2O initial concentration being negligible. Hydrogen peroxide proved to be more effective than, for example, H_2, as shown in Fig. 5. This is of importance, because Taguchi et al.[18] used a methane–hydrogen mixture as fuel and injected it into a high-enthalpy supersonic airstream. Therefore ignition delays for series 4A were calculated also for additive-free conditions and compared with those including H_2. Hydrogen cannot be considered, strictly speaking, as a promoter, but rather an easily ignitable fuel. Its overall influence was found to be rather weak and was explained on a pure thermal basis, i.e., by increasing heat release and final products temperature, while H_2O_2 acts mainly as a gas catalyst, i.e., the mixture composition and temperature at final equilibrium remain unchanged. From these results we can conclude that moderate H_2O_2 addition reduces delay times by over one order of magnitude in the temperature range of 1525–2025 K and in the pressure range of 2.55–13.01 atm of the experiments.[6] The other experimental series used to compare theoretical and

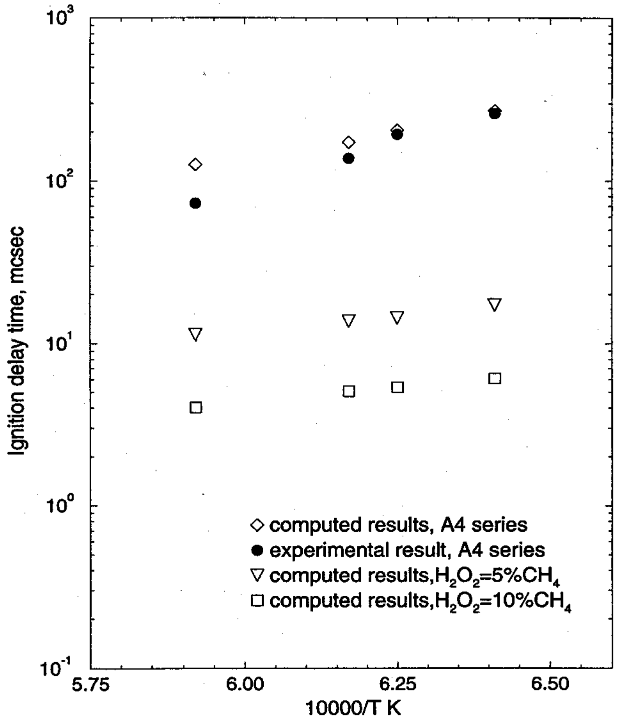

Fig. 9 Ignition delay times for A4-series from Table 4.

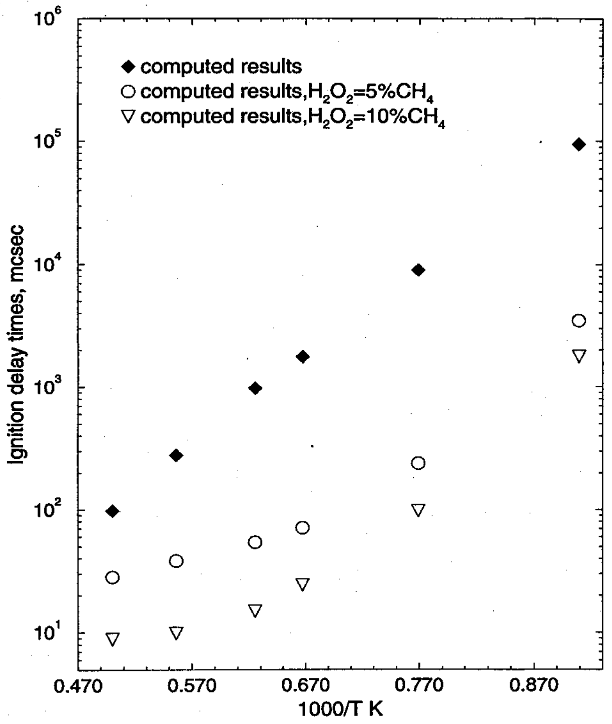

Fig. 11 Effect of H_2O_2 on CH_4/air mixtures ignition delay times (P = 1 atm, equivalence ratio = 0.5).

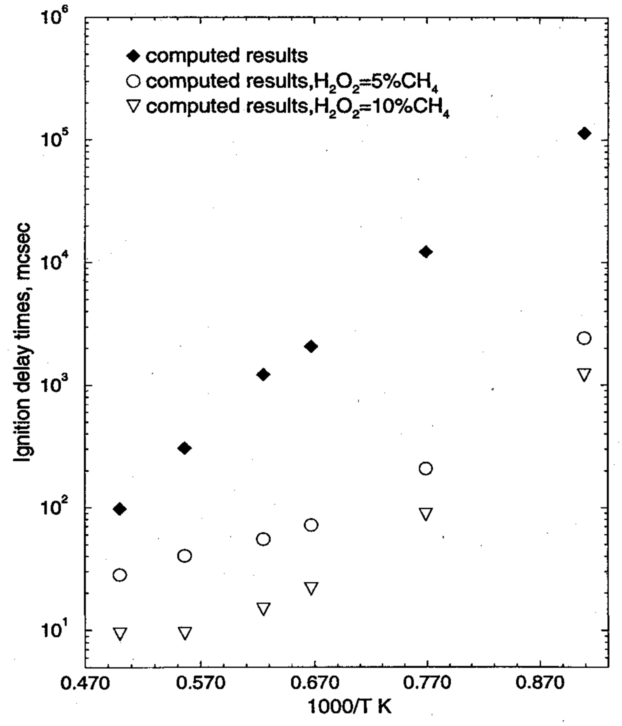

Fig. 10 Computational modeling (no experimental data) of the effect of H_2O_2 on CH_4/Air mixtures ignition delay times (P = 1 atm, equivalence ratio = 1).

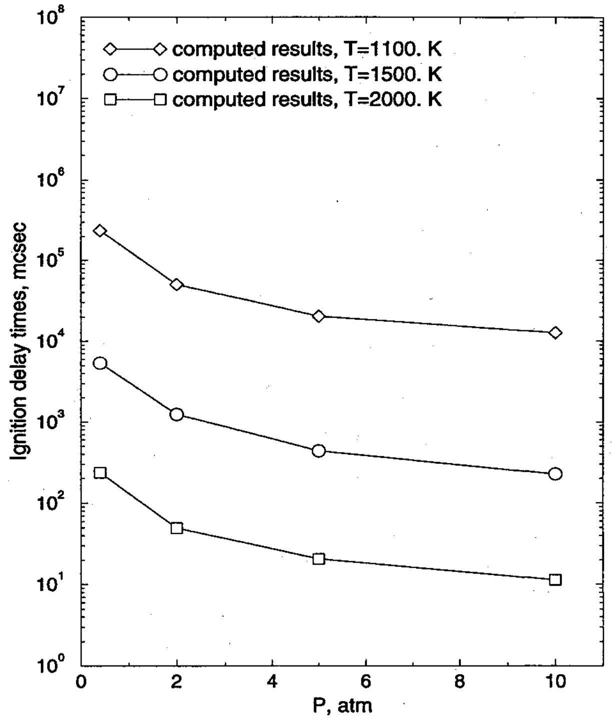

Fig. 12 Effect of pressure on CH_4/air mixtures ignition delay time (additive-free mixtures, equivalence ratio = 1).

experimental data are presented in Table 4.[7,19] The series A[19] refers to stoichiometric $CH_4/O_2/Ar$ mixtures with a reduced amount of diluent. The series A1[7] represents a fuel lean mixture with synthetic air ($O_2/Ar = 20/80$), and series A2–A4[7] correspond to fuel lean mixtures with raw laboratory air. To investigate the effect of the promoter addition for these cases, 5–10% of fuel was again substituted by H_2O_2. Not all initial conditions were explicitly stated in the information provided[7,19] for each experiment. In the experimental data by Burcat et al.[19] the pressure and temperature range and the condition of constant density were specified, whereas in those by Eubank et al.[7] the total density (3.0×10^{-5} mol/cm^3) and the temperature range were specified. Therefore, the parameters not explicitly specified were calculated through the thermal equation of state [Eq. (5)]. The results of calculations and comparison with experiments are plotted in Figs. 6–9. They again indicate reasonable agreement with the experimental data and the shortening of ignition delays when H_2O_2 was added.

Effect of H_2O_2 Addition

The validation of predictions by means of the experimental data implies that the chemical mechanism and its numerical solution should be considered sufficiently reliable to predict new results. Examples of such theoretical predictions, still using the scheme of Tables 1 and 2, refer to autoignition for CH_4/air stoichiometric (Fig. 10) and fuel lean (equivalence ratio equal 0.5, Fig. 11) mixtures at atmospheric pressure, for which experimental data are missing. The results for fuel-rich (equivalence ratio equal 2.0) mixtures are qualitatively the same and are not reported. These conditions would be of interest for practical supersonic combustion ramjets (SCRJ) and lean mixture gas-turbine applications, respectively. In this last application the difficulties associated with premixed, lean operation are well known: rough operation, vibrations, noise, and relighting problems. The positive effect of H_2O_2 is well pronounced, especially for low temperatures ($T < 1500$ K). The effect of pressure on ignition delay time has been also investigated. Predictions (Fig. 12) show that ignition delay time regularly decreases as pressure increases, in the range $P =$ 1100–2000 K, and this behavior is confirmed in the presence of H_2O_2 (Figs. 13–15). The data for temperatures $T < 1300$ K should be considered only as estimates, since at such temperatures C_2 chemistry may become important.

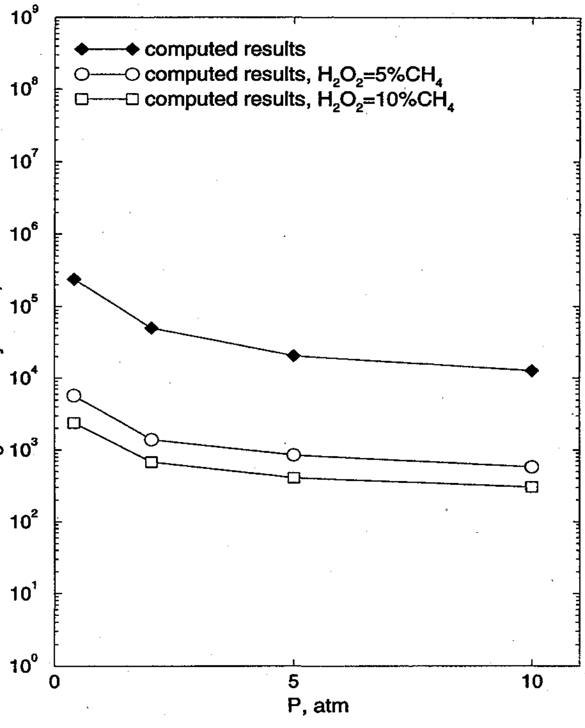

Fig. 13 Effect of pressure on additive-free and additive-added CH_4/air ignition delay time (To = 1100 K, equivalence ratio = 1).

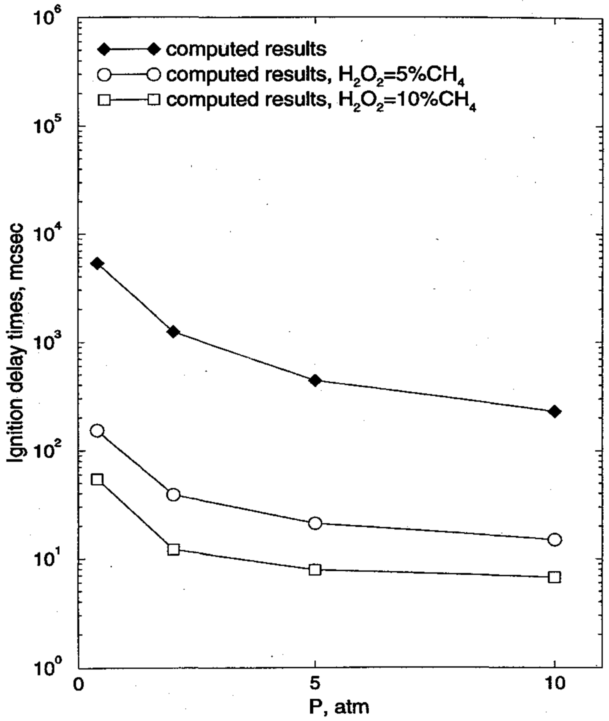

Fig. 14 Effect of pressure on additive-free and additive-added CH_4/air ignition delay time (To = 1500 K, equivalence ratio = 1).

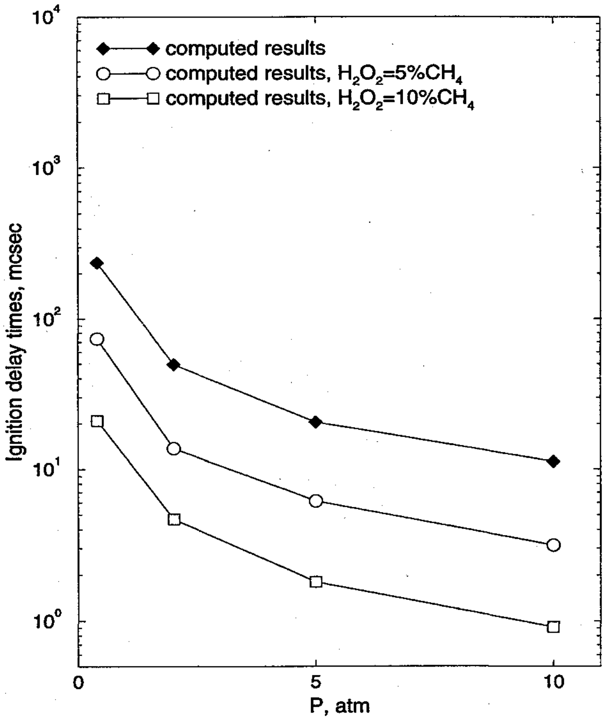

Fig. 15 Effect of pressure on additive-free and additive-added CH_4/air ignition delay time (To = 2000 K, equivalence ratio = 1).

To explain the effect of H_2O_2 on oxidation process acceleration, it is necessary to consider the dominant role of stage Eq. (6) in the reactions (6–9), in accordance with Chen et al.[20] To support this assumption, local sensitivity analysis based on the decomposed direct method was performed. The sensitivities of temperature to small changes in reaction rates were calculated via $s_j = \partial T/\partial k_j$ (j is the reaction index), and the 12 most important reactions are listed in Table 5 at two particular

Table 5 Absolute reaction sensitivities[a]

Reaction	$t = 0.5$ μs	$t = 44.5$ μs
$H_2O_2 + M \rightleftharpoons OH + OH + M$	7.72	36.5
$CH_3 + OH \rightleftharpoons CH_2 + H_2O$	3.90	574
$CH_3 + H \rightleftharpoons CH_2 + H_2$	2.81	−1040
$CH_4 + OH \rightleftharpoons CH_3 + H_2O$	−2.71	304
$CH_3 + O \rightleftharpoons CH_2O + H$	1.55	−656
$CH_4 + OH \rightleftharpoons CH_3 + H_2O$	−1.41	−764
$CH_3 + O_2 \rightleftharpoons CH_2O + OH$	1.33	3070
$H + H + M \rightleftharpoons H_2 + M$	1.02	−0.327
$CH_3 + H + M \rightleftharpoons CH_4 + M$	0.86	1810
$CH_4 + O \rightleftharpoons CH_3 + OH$	−0.77	358
$O + H_2 \rightleftharpoons OH + H$	0.745	3720
$CH_2O + H \rightleftharpoons HCO + H_2$	0.662	532

[a] Case 2 of 1C series,[6] $H_2O_2 = 5\%$ CH_4.

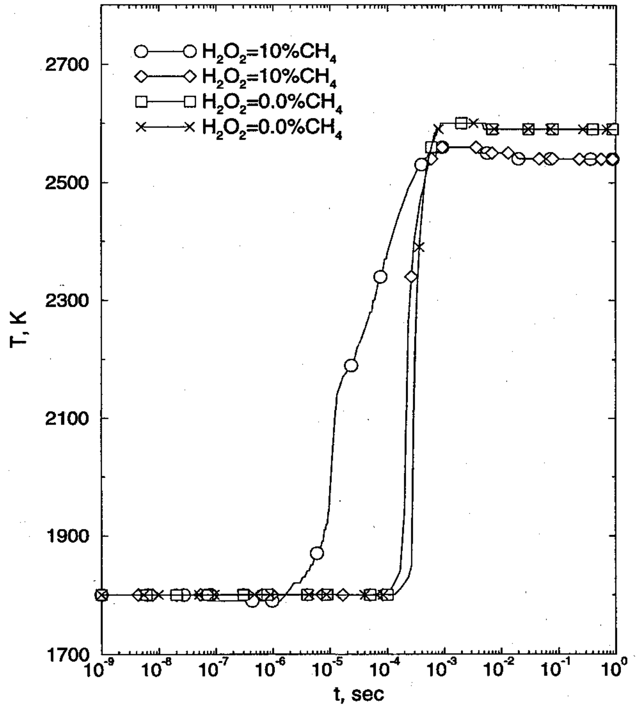

Fig. 16 Temperature vs time profiles for explanation of the mechanism of ignition acceleration. For regimes labeled by ◇ and × the reaction (6) is suppressed.

times. The key role of reaction (6) is shown during the initial phase of the ignition period ($t \leq 0.5$ μs). A numerical experiment was also performed to further validate this conclusion and some of its results are presented in Fig. 16. The temperature vs time curve for the fuel lean mixture ($T_0 = 1800$ K, $P_0 = 1$ atm, equivalence ratio = 0.5) with 10% of H_2O_2 added is labeled by ○. The temperature profile obtained for the same conditions, but with the reaction (6) suppressed is labeled by ◇. The profiles labeled by □ and × are the correspondent additive-free mixture cases. The nearly coincident last three temperature profiles illustrate the dominance of reaction (6) in the mechanism of acceleration for nonzero initial concentration of H_2O_2. This explanation was also found true by repeating sensitivity analysis and checking the effects of suppressing reaction (6), for stoichiometric and rich mixtures.

The practical advantage of H_2O_2 as a free radical promoter is its stability, until inside the high temperature zone. It can be quickly transported into the flame and after rapid decomposition it releases free radicals at the key location of the ignition process.

Conclusions

Methane autoignition promotion by hydrogen peroxide has been predicted using a computer model, emphasizing the detailed oxidation chemistry for $CH_4/O_2/Ar$ and CH_4/air mixtures. Numerical results are in good agreement with experimental data for all promoter-free compositions available in the literature. Hydrogen peroxide at concentrations below 10% (volumetric) significantly reduces the ignition delay for $CH_4/O_2/Ar$ mixtures in the pressure range of 2.55–13.01 atm in the temperature range of 1525–2025 K, and for CH_4/air mixtures in the pressure range of 0.4–10 atm and in the temperature range of 1100–2000 K, acting mainly as a gas catalyst in chain-branching reactions.

The mechanism of ignition acceleration is attributed to the dominant role of reaction (6) for all mixtures with nonzero initial concentrations of H_2O_2. Applications of those findings may include methane-fueled cruise SCRJ as well as advanced conventional ramjet and gas turbine combustors based on lean premixed combustion.

Acknowledgment

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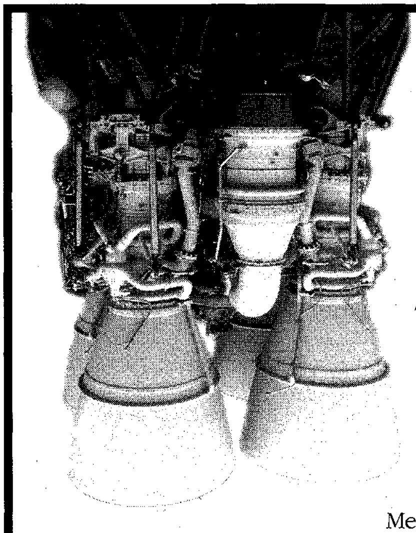

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