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Ignition Delays in MMH + CH_4 + O_2 + Ar Mixtures

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Ignition delays have been investigated for mixtures of monomethylhydrazine (MMH) + O_2 + CH_4 + Ar at high temperature (907–1360 K) in the pressure range 246–412 kPa. All measurements were performed in the reflected-shock region of a shock tube. Reaction progress was monitored via piezoelectric pressure transducers and UV absorption by MMH. In the composition range studied, the ignition delays τ can be correlated by the expression $\tau(\mu s) = 2.042 \times 10^{-2}[\mathrm{MMH}]^{-0.87}[O_2]^{-2.09}[CH_4]^{+0.68}[\mathrm{Ar}]^{1.24} \exp(8503/T)$ where the concentrations are expressed in moles m^{-3}. This study shows unambiguously that CH_4 inhibits MMH + O_2 (+Ar) ignition. This inhibiting effect depends on the mixture composition (equivalence ratio in MMH, [MMH]/[CH_4] ratio, etc.), on the temperature, and on the pressure. From a mechanistic point of view, methane is supposed to compete with MMH decomposition products for reaction with oxygen. The comparison between the CH_4/O_2/Ar and CH_4/MMH/O_2/Ar ignition delays leads to the conclusion that MMH can be used as a ignition promoter in CH_4/O_2 mixtures.

Introduction

INFORMATION on the self-ignition of fuel-oxygen mixtures is of basic importance as well for its potential implications to practical combustion and ignition processes as for the possibility to derive basic kinetic information from these data. Monomethylhydrazine (MMH) offers a wide variety of applications because the hypergolic bipropellant combination MMH/nitrogen tetroxide (NTO) is particularly important for spacecraft and rockets. Extensively used in the past,[1] it is nowadays used for the space shuttles, for numerous satellites, and for the European launcher Ariane 5. MMH is taken into consideration in a significant number of recent publications,[2–7] projects, and studies [High-Performance Apogee Engines, NASA's hazardous testing of toxic materials and explosive mixtures (MMH/liquid oxygen), etc.], associated mostly with NTO but, for a few cases, with O_2.

The study presented here is devoted to the ignition delays in MMH + CH_4 + O_2 + Ar mixtures with the purpose of investigating the effect of methane on the ignition delays in MMH + O_2 + Ar at high temperature. The experimental results and their analysis are of interest to the development of some hypersonic aircraft since methane has been suggested as a candidate fuel.[8] Introduction of promoters (or inhibiters) allows variation of the ignition delays and the creation of fuel systems suitable for use in real engines.

Several studies[9–15] concerning the oxidation and/or decomposition of MMH have been previously published. The major objectives of these studies are to provide experimental kinetic data for MMH + oxidant mixtures in various conditions allowing the validation of a detailed kinetic modeling of MMH oxidation. Such models are of importance to numerical modelers who wish to incorporate finite rate chemistry.

Experimental

MMH is a liquid at room temperature and atmospheric pressure. Gaseous mixtures of MMH + CH_4 + O_2 + Ar are prepared, in Pyrex vessels, according to the Dalton law by mixing the gases with the vapor pressure of liquid MMH at room temperature. Analysis by infrared spectroscopy of the prepared mixtures shows that the mixtures should be used shortly after their preparation.[15]

Briefly, the shock tube employed is a 38.4-mm-i.d. stainless-steel tube, with a 1-m-long driver section, filled with helium up to 700 kPa, and a test section, about 3 m long, in which the mixtures are introduced at room temperature at a precisely known pressure. Several diagnostics instruments are located in the second half of the driven section: four piezoelectric pressure transducers, mounted flush with the inside wall, for shock-wave velocity measurement and a pair of CaF_2 optical windows mounted at 5 mm from the end of the tube, associated with a monochromator, for following absorption by MMH at 220 nm, from which the ignition delays are deduced. For these experiments the ignition delays can also be derived from the pressure signals. However, the ignition delays derived from the pressure signals always agreed with the absorption-derived ones to within a few percent. This will be shown in the Results and Discussion section. The conditions behind the reflected shock wave were determined from the incident-shock velocity using the one-dimensional shock relations and thermodynamic data presented elsewhere.[13] The values of $\Delta T/T$ and $\Delta P/P$, behind the reflected shock wave, are about 1.5 and 2%, respectively.

Results and Discussion

Ignition Delays in MMH + CH_4 + O_2 + Ar Mixtures

The ignition delays of MMH + CH_4 + O_2 + Ar mixtures have been measured behind a reflected shock wave, at reflected shock temperatures T_5 varying from 907 to 1360 K and pressures P_5 from 246 to 412 kPa. Experiments were carried out with mixtures of x MMH + w CH_4 + y O_2 + z Ar with molar fractions x from 0.024 to 0.0557, y from 0.0437 to 0.10 (y/x ratio varying from 1.16 to 2.92), w from 0.0054 to 0.0323, and z from 0.8347 to 0.9204. The ratio x/w is between 1.23 and 6.46. Some of the simultaneous recordings of pressure and absorption signals observed at 220 nm are shown in Figs. 1 and 2. Basically, the oxidation in this temperature range follows a two-stage mechanism. The reaction begins with the oxygen-induced thermal decomposition of MMH after the reflected shock arrival. At $T < 1000$ K one can observe an incubation period prior to the apparent thermal decomposition of MMH (see Fig. 1). This was also observed for the experiments done in MMH + Ar mixtures.[11] At temperatures higher than 1050 K, the incubation period is not observed (see Fig. 2). During MMH decomposition, absorption progressively decreases while pressure increases. This decomposition is followed by an explosive oxidation reaction, characterized by a sudden absorption decrease and a simultaneous

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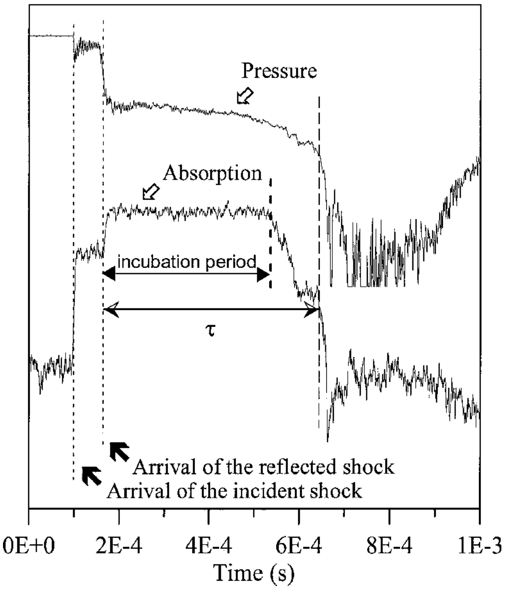

Fig. 1 **Simultaneous record of pressure and absorption signals at 220 nm for the mixture 5.24 mol% MMH + 9.39 mol% O_2 + 1.35 mol% CH_4 + 84.02 mol% Ar at reflected shock conditions $T = 907$ K and $P = 310.7$ kPa. $\tau_{exp} = 504$ μs.**

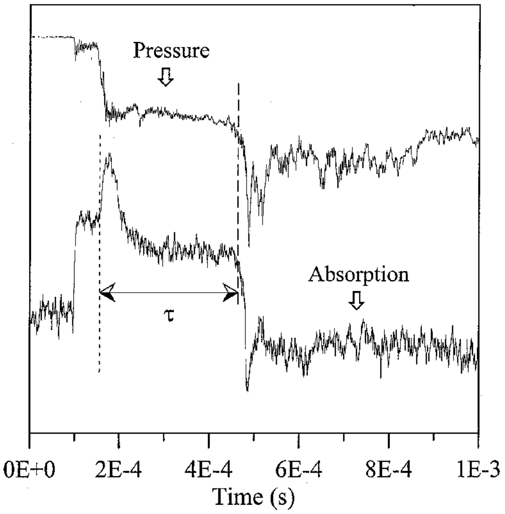

Fig. 2 **Simultaneous record of pressure and absorption signals at 220 nm for the mixture 3.74 mol% MMH + 7.38 mol% O_2 + 1.91 mol% CH_4 + 86.97 mol% Ar at reflected shock conditions $T = 1099$ K and $P = 254$ kPa. $\tau_{exp} = 323$ μs.**

Table 1 **Experimental ignition delays in MMH + O_2 + CH_4 + Ar mixtures (τ_{exp}) for different conditions of composition (see text), temperature and pressure, corresponding calculated ignition delays without methane τ_c and ratio τ_{exp}/τ_c showing the inhibiting effect of methane on MMH + O_2 + Ar ignition. The overall uncertainty in τ_{exp} is estimated at ± 10 μs. x_i are mole fraction of species i**

x_{MMH}	x_{O_2}	x_{CH_4}	x_{Ar}	P, kPa	T, K	τ_{exp}, μs	τ_c, μs	τ_{exp}/τ_c
0.024	0.0469	0.0087	0.9204	269.4	1146	623	380	1.64
0.024	0.0469	0.0087	0.9204	376.6	1159	348	225	1.55
0.024	0.0469	0.0087	0.9204	363.7	1324	139	93	1.49
0.0265	0.0773	0.0215	0.8747	268.3	998	788	568	1.39
0.0265	0.0773	0.0215	0.8747	383.3	1008	504	326	1.55
0.0265	0.0773	0.0215	0.8747	271.5	1099	537	247	2.17
0.0303	0.053	0.0096	0.9071	408.1	1051	536	292	1.84
0.0303	0.053	0.0096	0.9071	267.6	1097	508	357	1.42
0.0303	0.053	0.0096	0.9071	370.5	1161	272	150	1.81
0.0335	0.0693	0.0146	0.8826	367.7	996	370	339	1.09
0.0335	0.0693	0.0146	0.8826	376.4	1108	258	134	1.92
0.0335	0.0693	0.0146	0.8826	412.2	1276	80	42	1.90
0.0349	0.0437	0.0054	0.916	363.7	1085	440	284	1.55
0.0349	0.0437	0.0054	0.916	270.2	1246	220	149	1.48
0.0349	0.0437	0.0054	0.916	255.1	1360	111	90	1.23
0.0366	0.0632	0.0198	0.8803	274.3	973	1120	628	1.78
0.0366	0.0632	0.0198	0.8803	286	1107	514	197	2.61
0.0366	0.0632	0.0198	0.8803	373.9	1159	279	97	2.88
0.0366	0.0632	0.0198	0.8803	256.9	1186	329	134	2.45
0.0374	0.0738	0.0191	0.8697	352	1179	137	74	1.85

Table 2 **Experimental ignition delays in MMH + O_2 + CH_4 + Ar mixtures (τ_{exp}) for different conditions of composition (see text), temperature and pressure, corresponding calculated ignition delays without methane τ_c and ratio τ_{exp}/τ_c showing the inhibiting effect of methane on MMH + O_2 + Ar ignition. The overall uncertainty in τ_{exp} is estimated at ± 10 μs. x_i are mole fraction of species i**

x_{MMH}	x_{O_2}	x_{CH_4}	x_{Ar}	P, kPa	T, K	τ_{exp}, μs	τ_c, μs	τ_{exp}/τ_c
0.0374	0.0738	0.0191	0.8697	259.8	1011	429	382	1.12
0.0374	0.0738	0.0191	0.8697	254	1099	323	195	1.66
0.0374	0.0738	0.0191	0.8697	246.3	1208	196	99	1.98
0.0429	0.0559	0.0323	0.8689	258.5	1279	324	77	4.21
0.0431	0.0632	0.0142	0.8795	395.7	1042	275	176	1.56
0.0431	0.0632	0.0142	0.8795	282	1053	376	251	1.50
0.0438	0.0509	0.0113	0.894	279.4	1028	546	404	1.35
0.0438	0.0509	0.0113	0.894	395.3	1050	411	214	1.92
0.0438	0.0509	0.0113	0.894	282.3	1173	296	138	2.14
0.0484	0.0825	0.0203	0.8488	276.8	958	394	371	1.06
0.0484	0.0825	0.0203	0.8488	389.9	1013	222	142	1.56
0.0484	0.0825	0.0203	0.8488	279.4	1068	236	141	1.67
0.0524	0.0939	0.0135	0.8402	310.7	907	504	417	1.21
0.0524	0.0939	0.0135	0.8402	299.5	961	275	250	1.1
0.0524	0.0939	0.0135	0.8402	291.5	1021	173	150	1.15
0.0531	0.0996	0.0126	0.8347	299	913	372	374	1
0.0531	0.0996	0.0126	0.8347	274.5	958	216	263	0.82
0.0531	0.0996	0.0126	0.8347	403	1029	88	84	1.05
0.0557	0.068	0.0092	0.8671	396	1019	168	145	1.16
0.0557	0.068	0.0092	0.8671	399.1	1086	118	84	1.40

fast increase of pressure. For each experiment the ignition delay τ is defined as the time interval between the arrival of the reflected shock and the beginning of the explosive oxidation (see Figs. 1 and 2). All of the ignition delays τ determined experimentally for mixtures of $MMH + CH_4 + O_2 + Ar$ are given in Tables 1 and 2. They can be expressed, by least-squares multiregression, as

$$\tau(\mu s) = 2.042 \times 10^{-2}[\mathrm{MMH}]^{-0.87}[\mathrm{O_2}]^{-2.09}[\mathrm{CH_4}]^{+0.68}\mathrm{Ar}^{1.24}e^{8503/T} \tag{1}$$

with an average accuracy of about 12%. The concentrations are expressed in moles m^{-3}. The units of T and τ are degrees kelvin and microseconds, respectively. The corresponding best-fit linear correlation (full line) is given in Fig. 3 with the experimental values (points). Equation (1) is valid over the just-described experimental range. The exponent found on the molar fraction of methane equals +0.68. For $CH_4 + O_2$ + diluent mixtures Seery and Bowman[16] found an exponent of +0.4, Lifshitz et al.[17] +0.33, Tsuboi and Wagner[18] +0.32, and Cheng and Oppenheim[19] +0.48. Spadaccini and Colket[20] found +0.33, but in presence of additives (ethane, propane or butane) the exponent on methane concentration is +0.66. Eubank et al.[21] found $+0.4 \pm 0.2$. More recently, Petersen et al.[22] also found an exponent of +0.33. Although it is always hard to compare such correlations and sometimes meaningless because they are established in different experimental conditions, it is noteworthy to underline the rather good agreement observed here. MMH in these mixtures promotes its own ignition. This was also the case for the $MMH/O_2/Ar$ and $MMH/H_2/O_2/Ar$ mixtures. Kinetic explanations have been given elsewhere.[12] An interesting feature is the strong inhibiting effect of the diluent (here Ar) on the ignition of the $MMH/CH_4/O_2/Ar$ system. This was also the case for the $MMH/O_2/Ar$ and $MMH/O_2/H_2/Ar$ mixtures. Five other systems (ethylene oxide/oxygen/argon;

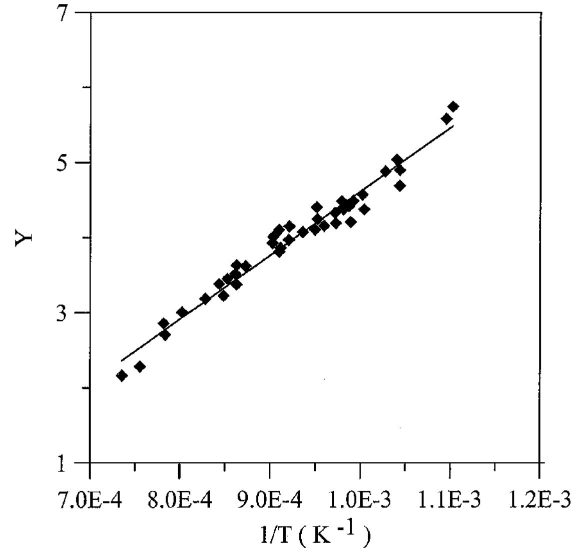

Fig. 3 Correlation fit (——) obtained for experimental MMH + O_2 + CH_4 + Ar ignition delays τ_{exp} (■). $Y = \ell n\,\tau\,[MMH]^{+0.87}\,[O_2]^{+2.09}\,[CH_4]^{-0.68}\,[Ar]^{-1.24}$ is given vs 1/*T*.

ethylene oxide/oxygen/nitrogen; propylene oxide/oxygen/argon; 1,2-epoxybutane/oxygen/argon; and 2,3-epoxybutane/oxygen/argon) also have been shown to exhibit high power dependencies (from 0.78 up to 1.48) on the diluent (argon or nitrogen) concentration.[23] Nevertheless, most of the systems studied generally exhibit no dependence, or a small positive power dependence, on the concentration of argon. This suggests that the ignition mechanisms for these systems ($CH_4/O_2/Ar$ for instance, among others) are primarily kinetic and not thermal over a wide range of conditions. For MMH/O_2 it has been shown by Gray and Sheerington[24] that the ignition mechanism is thermal. This means that relatively huge amounts of heat are liberated during the ignition delay time. As underlined by Lifshitz and Suslensky,[23] an increase in heat capacity (by increasing the diluent concentration) for the same amount of heat released depresses the temperature elevation and thus inhibits the progress of the reaction. This feature was also shown indirectly by the authors[12] of the present paper in a preliminary experimental study by substituting nitrogen to argon.

Effect of the Addition of Methane on Ignition Delays in MMH + O_2 + Ar mixtures

It was shown[12] that the ignition delays in MMH + O_2 + Ar can be expressed by the relationship

$$\tau(\mu s) = 1.891 \times 10^{-3}[\mathrm{MMH}]^{-1.08}[\mathrm{O_2}]^{-1.21}[\mathrm{Ar}]^{0.98}e^{10234/T} \qquad (2)$$

Expression (2) is valid over the following experimental ranges: equivalence ratio between 1 and 2.5, mole fractions of MMH from 0.0187 to 0.0826, oxygen from 0.0294 to 0.128, argon from 0.82 to 0.938, at reflected shock temperatures varying from 902 to 1341 K and pressures varying from 162 to 401 kPa with an average accuracy of 13%. The concentrations are expressed in moles m^{-3}. The units of T and τ are degrees kelvin and microseconds, respectively. By considering that the amount of methane present in the MMH + CH_4 + O_2 + Ar mixtures has been substituted to argon, it is possible to compare the experimental MMH + CH_4 + O_2 + Ar ignition delays with the ignition delays without methane, which can be evaluated with Eq. (3):

$$\tau(\mu s) = 1.891 \times 10^{-3}[\mathrm{MMH}]^{-1.08}[\mathrm{O_2}]^{-1.21} \times ([\mathrm{Ar}] + [\mathrm{CH_4}])^{0.98}e^{10234/T} \qquad (3)$$

The concentrations are expressed in moles m^{-3}, T and τ with the same units as given before. In Table 1 we compare the experimental MMH + CH_4 + O_2 + Ar ignition delays, noted τ_{exp}, with those calculated with Eq. (3), noted τ_c. The ratio of τ with CH_4 to τ without CH_4, namely τ_{exp}/τ_c, is equal to one or greater than unity for 39 experiments. As a result, there is apparently no effect, below about 1000 K, or an inhibiting effect, above about 1000 K, of methane on ignition in MMH + O_2 + Ar. The ratio is lower than one for one experiment, but by considering the average accuracy of 13% as a result of the use of Eq. (3) and the average accuracy of 12% as a result of the use of Eq. (1), this result appears to be not significant because a promoting effect would be unambiguously evidenced only for τ_{exp}/τ_c ratio below 0.75. More generally, by comparing Eqs. (1) and (3), this conclusion has to be discussed in terms of the experimental conditions of temperature, pressure, equivalence ratio, and composition. The addition of 1 mol% CH_4 leads, in the range of validity of Eq. (1), to a maximum increase by a factor of 2.3 for the ignition delays of rich MMH + O_2 + Ar mixtures at high temperature and for the lower MMH molar fraction. This inhibiting effect should be little for stoichiometric mixtures at low temperatures, i.e., around 900 K, for a high molar fraction of MMH. In both cases the pressure influence on the inhibiting effect is of little importance, at least in our experimental pressure range. With the same procedure, in the validity range of expression (1), the addition of 2 mol% of methane is expected to increase τ between 1.2 and 3.6 times, depending on experimental parameters.

Kinetic Model

From a kinetic point of view, because the oxygen-induced thermal decomposition of MMH seems not to be influenced by the presence of methane (see Fig. 4), it is probable that methane (and/or its decomposition/oxidation products) competes with MMH decomposition products (N_2, CH_4, NH_3, H_2, HCN) for reaction with O_2.

The kinetics of methane oxidation has been the subject of a number of publications reporting experimental data and modeling results. A correlation of more than 500 ignition delay data, here noted t, in CH_4 + O_2 + diluent (mostly argon) is given by Spadaccini and Colket[20]:

$$t(s) = 2.21 \times 10^{-14}[\mathrm{O_2}]^{-1.05}[\mathrm{CH_4}]^{+0.33}e^{22659/T} \qquad (4)$$

The concentrations in Eq. (4) are expressed in mol cm^{-3}.

Because the higher the temperature, the more efficient the methane inhibiting effect is, one can suppose that the two ignition reactions, which are apparently uncoupled at low temperature, are more and more coupled as temperature increases. Consequently, this coupling, associated with the fact that the ignition delays in

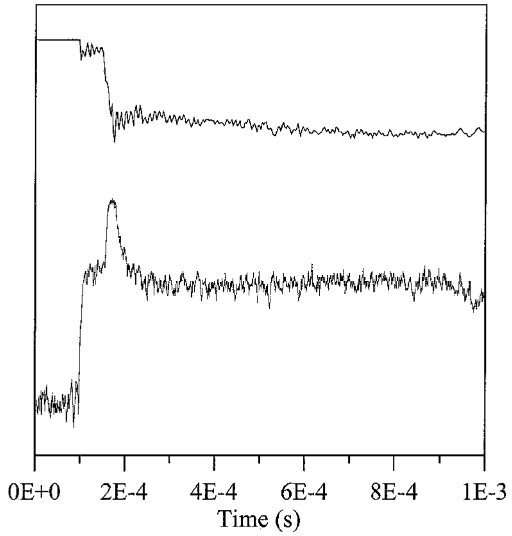

Fig. 4 Simultaneous record of the pressure and absorption signals at 220 nm for the mixture 4.29 mol% MMH + 5.59 mol% O_2 + 3.23 mol% CH_4 + 86.89 mol% Ar at reflected shock conditions T = 1124 K and P = 268.5 kPa. For these experimental conditions only the thermal decomposition of MMH is observed during the experiment time (about 800 μs). The ignition appears to be considerably delayed.

$MMH + CH_4 + O_2 + Ar$ are much lower than the corresponding ignition delays without MMH evaluated with Eq. (4), indicates that MMH can be used as a promoter for $CH_4 + O_2$ ignition.

Catoire et al.[13,14] developed a kinetics model, which was shown to predict conveniently the $MMH/O_2/Ar$ and $MMH/O_2/H_2/Ar$ ignition delays. In this mechanism a methane oxidation submechanism is still introduced because methane is a product of the thermal decomposition of MMH. This kinetic model is based, on one hand, on the CH_4/O_2 reaction mechanism of Dagaut et al.[25] and, on the other hand, on the CH_4/O_2 oxidation mechanism of Hunter et al.[26] For this study the mechanism has been refined and updated to predict correctly the methane/oxygen/argon ignition delay set presented by Frenklach et al.[27] This set is composed of 11 ignition delays from studies performed in shock tubes by Lifshitz et al.,[17] Frenklach and Bornside,[28] and Gardiner et al.[29] The ignition delay time has been numerically defined as the time at which the rate of OH concentration increases suddenly. It also can, for the less diluted mixtures, be defined as the time at which the rate of pressure (or temperature) rise reaches its maximum. These three criteria lead to the same ignition delay values. The agreement between the numerical simulation and experiments is good (see Table 3) at high temperature. The agreement is also good at low temperature (below 1500 K). This is particularly important here as the inhibiting effect of CH_4 on $MMH/O_2/Ar$ ignition and the promoting effect of MMH on $CH_4/O_2/Ar$ ignition are observed or deduced at relatively low temperature (up to about 1300 K). However, the two low-temperature ignition delays of Table 3 are highly concentrated, and, as the CH_4 mole fraction is up to 0.03 here, this model has to be tested with experiments performed at relatively low temperature and simultaneously with relatively low methane concentration. Such experiments can be found in Spadaccini and Colket[20] or Seery and Bowman.[16] Table 4 shows that, below 1500 K, the model predicts ignition delays, which are too long by about a factor 2 to 3. The RAMEC mechanism of Petersen et al.[30,31] also predicts too long ignition delays, but the agreement is better with this model than with the CH_4/O_2 submechanism presently implemented in the $MMH/O_2/Ar$ kinetic model (see Table 4). It is questionable whether or not these models are able to predict correctly the methane/oxygen ignition chemistry in the 900–1300 K temperature range. Petersen et al.[30,31] noticed that most of the rate constants of important reactions in the 1000–1200 K temperature range are not experimentally well established and that these reactions need further study. This is the case particularly for the reaction

$$CH_4 + HO_2 \rightarrow CH_3 + H_2O_2$$

which has been shown to be important for ignition below 1500 K.[20]

Table 3 Experimental ignition delays (τ_{exp}) in mixtures of $CH_4/O_2/Ar$ compared with computed values (τ_{comp}). Experimental points from Lifshitz et al.[17] or Frenklach and Bornside[28] or Gardiner et al.[29]

P, kPa	T, K	mol% CH_4	mol% O_2	τ_{exp}, μs	τ_{comp}, μs
823.1	1650	3	6	268	214
997.7	2000	3	3	46	31
997.7	2000	1.5	6	18	18
823.1	1650	1.5	3	436	424
902.9	1810	2.12	4.24	99	73
225.7	1810	8.84	16.97	99	65
232.8	1400	9.5	19	1512	1788
249.4	1500	9.5	19	550	571
266.0	1600	9.5	19	226	217
397.6	1690	5	10	205	153
418.8	1780	2	4	210	174

Table 4 Experimental ignition delays (τ_{exp}) in mixtures of $CH_4/O_2/Ar$ compared with computed values (τ_{comp}). Experimental points from Spadaccini and Colket[20] or Seery and Bowman[16]

P, kPa	T, K	mol% CH_4	mol% O_2	τ_{exp}, μs	τ_{comp},[a] μs	τ_{comp},[b] μs
382	1336	3.46	15.25	1570	3620	2162
457	1461	3.5	5.6	1730	2710	2330
929.1	1464	6	12	166	573	474
497.5	1512	3.5	5.6	598	1420	1240
403.3	1348	4.8	19.1	1350	2293	1448
391.1	1388	4.8	19.1	800	1439	964
162.1	1464	4.8	19.1	1080	1177	856

[a] CH_4/O_2 kinetic model used here. [b] RAMEC[30,31].

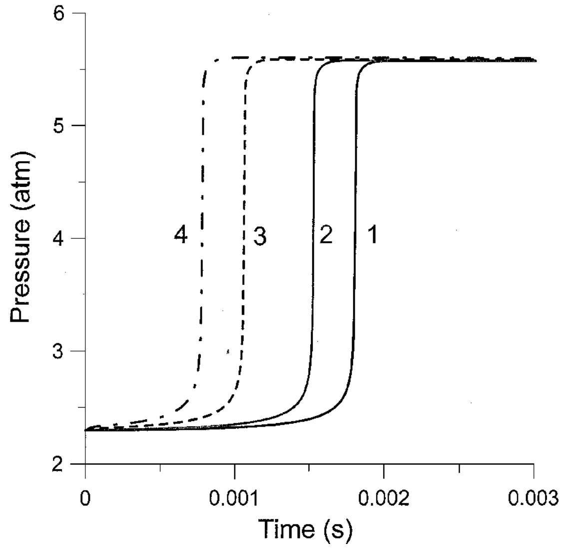

Fig. 5 Computed pressure profiles during the ignition of a $CH_4/O_2/Ar$ mixture, without or with a small amount of MMH added. Initial T = 1400 K; initial P = 232.8 kPa: 1, 9.5 mol% CH_4 + 19 mol% O_2 in Ar. τ = 1788 μs; 2, 9.5 mol% CH_4 + 19 mol% O_2 + 0.01 mol% MMH in Ar. τ = 1512 μs; 3, 9.5 mol% CH_4 + 19 mol% O_2 + 0.05 mol% MMH in Ar. τ = 1044 μs; and 4, 9.5 mol% CH_4 + 19 mol% O_2 + 0.1 mol% MMH in Ar. τ = 765 μs.

The identification of the important reactions at low temperature, and simultaneously at low pressure, (900–1200 K) for the CH_4/O_2 ignition is beyond the scope of the present paper as further improvements of the CH_4/O_2 kinetics model are needed. This work is in progress because the experiments presented here may allow indirectly these reactions to be identified.

Numerical Study of Effect of MMH on the Ignition of Methane/O_2/Diluent Mixtures

By considering the preceding arguments, it is not possible to expect that the kinetic model is able to reproduce the inhibiting effect of methane on $MMH/O_2/Ar$ ignition at low temperature. Nevertheless, as the $CH_4/O_2/Ar$ ignition delays are conveniently predicted at about $T > 1400$ K, the effect of the addition of small amounts of MMH can be numerically studied, at least qualitatively. Figure 5 shows that very small amounts of MMH are able to reduce significantly the CH_4/O_2 ignition delays. At lower temperatures (900–1300 K) MMH is predicted to be a very efficient promoter for CH_4/O_2 ignition. However, because the existing CH_4/O_2 kinetic models are probably not reliable, this has to be demonstrated.

Conclusions

This experimental study shows that methane inhibits $MMH + O_2 + Ar$ ignition. It is also preliminarily shown that MMH can be used as a promoter of $CH_4 + O_2 + Ar$ ignition. Although MMH has a considerably shorter ignition delay than methane, the two ignition reactions (i.e., that of MMH and that of CH_4) are not uncoupled. Nevertheless, the shortening of the $CH_4 + O_2 + Ar$ ignition delay is also an outcome of the heat released by MMH because the thermal decomposition of MMH is exothermic.

A correlation of the entire ignition delay data set obtained was established. A detailed kinetic model previously validated with $MMH/O_2/Ar$ and $MMH/O_2/H_2/Ar$ ignition delays is under consideration to simulate the MMH/CH_4/O_2/Ar ignition delays observed and to explain the additive effects deduced from these experiments. This work is in progress in order to make safer the production, handling, and use of MMH, and to enlarge the field of applications of this propellant.

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