Ignition Delay Time of Small Hydrocarbons-Nitrous Oxide(-Oxygen) Mixtures

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1 Introduction

Numerous propellants and energetic materials are characterized by chemical structures with one or several nitro and/or nitrate groups [1]. Their combustion is a complex process which involves various physico-chemical phenomena occuring both in the solid and gas phases as well as at their interface [1, 2]. Nitro and nitrate based compounds are also attractive as auto-ignition promoters in diesel engine [3]. In addition to different practical propulsion applications, the chemistry of nitrogen dioxide is relevant to more fundamental subjects for a number of mixtures such as CH_3NO_2(-O_2), H_2-NO_2/N_2O_4, CH_4-NO_2/N_2O_4 and C_2H_6-NO_2/N_2O_4, which exhibit a double cellular structure when detonating [4–6]. Nitrous oxide has been identified as an important intermediate during the combustion of many solid propellants [7, 8]. Consequently, it is important to properly describe the chemistry of hydrocarbons with N_2O in order to accurately model the gas phase kinetics of solid propellant combustion. However, there is a limited number of data concerning the high temperature oxidation of hydrocarbons by nitrous oxide. The purposes of the present study are to experimentally measure the auto-ignition delay time of some small hydrocarbon-nitrous oxide(-oxygen) mixtures using the shock tube technique and to test the validity of several recent detailed reaction models.

2 Materials and methods

2.1 Materials

The experimental setup used is a shock tube composed of three parts separated by two diaphragms. The driver section and the driven section are 6.19 and 11.28 m long, respectively, with a 15.24 cm inner diameter. The test section is 2.44 m long and has a 7.62 cm inner diameter. A 2.03 m long with a 7.62 cm inner diameter cookie-cutter is used to drive the shock wave from the driven to the test section. The test section is equipped with 3 pressure transducers and a photomultiplier tube mounted in front of a quartz window located 13 mm from the end wall. The uncertainty on the incident shock wave velocity is less than 2%. The thermodynamic state behind the reflected shock was calculated from the incident shock velocity assuming frozen chemistry and translational-vibrational-rotational equilibrium. An optical fiber was employed to collect the light emission from the reacting mixture and a narrow passband filter centered around 307 nm was used to select the emission originating from the ($A^2\Sigma^+$-$X^2\Pi$) OH radical electronic transition. The ignition delay time was studied behind reflected shock waves. The uncertainty on this parameter is estimated to be on the order of 20 % [9]. Figure 1 shows an example of experimental records and illustrates the definition of the two characteristic times of reaction used, that is the times to 50% and 100% of the emission peak. Gaseous mixtures were prepared from research grade gases in a 9.25 liter mixture vessel, using the partial pressure method, and were mixed with a brushless fan mounted inside the vessel. The Ar dilution was 96%. Table 1 gives the mixture compositions and

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experimental conditions. The equivalence ratio was defined as follows:

$$\Phi = \frac{2 \cdot X_C + 0.5 \cdot X_H}{X_O} \tag{1}$$

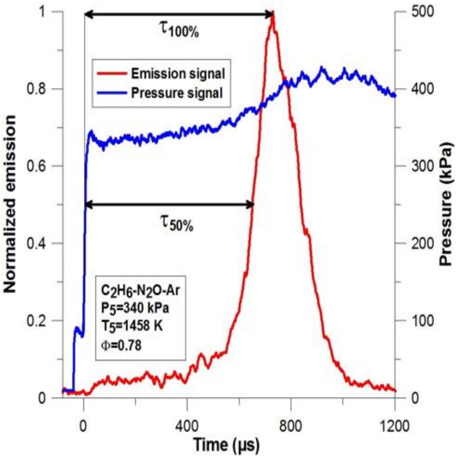


Figure 1: Typical experimental signals and definitions of the two characteristic times of reaction.

N	Φ	X_{CH4}	X_{C2H6}	X_{C2H4}	X_{C2H2}	X_{O2}	X_{N2O}	T_5 (K)	P_5 (kPa)
1	1.11	0.00867	-	-	-	-	0.03133	1527-1925	222-320
2	0.93	0.01066	-	-	-	0.01666	0.01266	1478-1945	249-321
3	0.78	-	0.00400	-	-	-	0.03598	1398-1730	282-359
4	1.12	-	0.00799	-	-	0.01798	0.01398	1272-1641	295-397
5	1.80	0.00532	0.00466	-	-	-	0.02994	1506-1862	241-334
6	1.11	0.00533	0.00466	-	-	0.01865	0.01133	1312-1693	279-361
7	1.37	-	-	0.00733	-	-	0.03200	1399-1773	254-348
8	1.41	-	-	0.01067	-	0.01600	0.01333	1269-1620	291-387
9	0.80	-	-	-	0.00549	-	0.03447	1436-1708	291-346
10	1.23	-	-	-	0.01000	0.01000	0.02050	1311-1545	330-378

Table 1: Mixture compositions and experimental conditions. In all cases, balance is Argon.

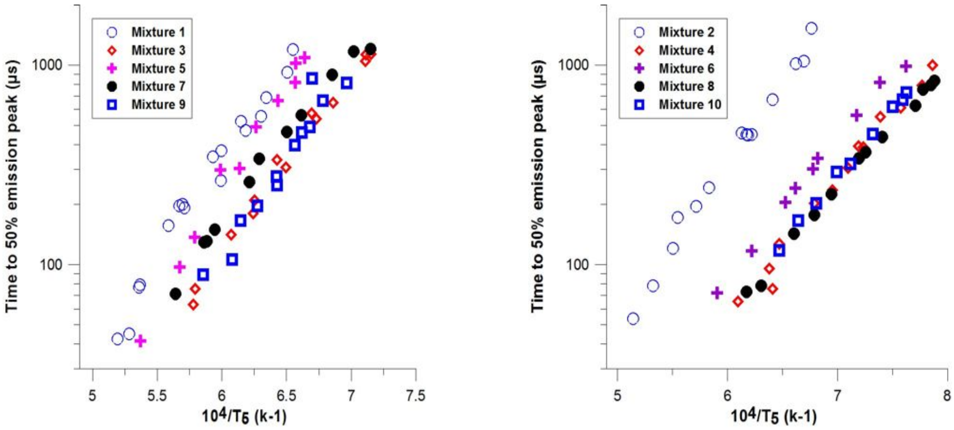
2.2 Modeling

Four modern reaction models have been evaluated with respect to the present experimental results: (i) the model of Konnov [10], 1200 reactions and 127 species, (ii) the model of Dagaut [11], 925 reactions and 128 species, (iii) the GRI-Mech 3.0 [12], 325 reactions and 53 species, and (iv) the Caltech mechanism assembled from [9, 11, 13, 14], 853 reactions and 110 species. In each case, the thermodynamic data supplied with each model were used. A sub-mechanism for the kinetics of excited OH radicals, OH*, from Hall and Petersen studies [15, 16] has been added in each model. The concentration of OH* is typically 6 orders of magnitude lower than that of OH radicals so that no significant modifications of the ground-state chemistry is expected by the inclusion of OH* chemical pathways. Modeling of the experimental results has been achieved by using the SENKIN code [17], assuming a constant volume reactor model.

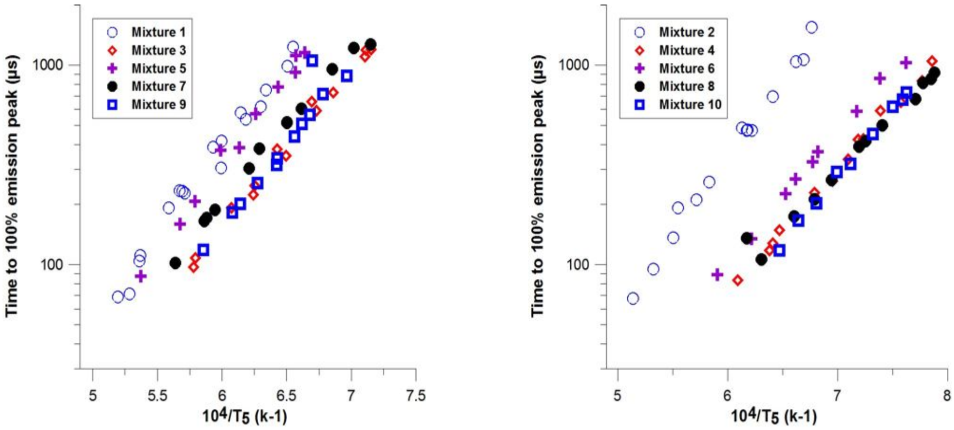
3 Results and discussion

3.1 Experimental results

Ignition delay time of CH_4-,C_2H_6-,CH_4-C_2H_6-,C_2H_4,C_2H_2-N_2O mixtures with and without O_2 were measured behind a reflected shock wave in the temperature and pressure ranges 1269-1945 K and 222-397 kPa, respectively. Figure 2 presents the data obtained for the 10 mixtures studied. Mixtures containing methane exhibit significantly longer ignition delay time, from 30% longer for mixtures with both CH_4 and C_2H_6, up to 5 times longer for mixture with CH_4 only. Mixtures with both O_2 and N_2O seem to demonstrate lower activation energies, 25% lower on average, compared to the mixtures with N_2O as the only oxidant. This observation is consistent with previous results obtained with H_2-O_2-(N_2O)-Ar mixtures [18].



(a) $\tau_{50\%}$ HC-N_2O mixtures (b) $\tau_{50\%}$ HC-N_2O-O_2 mixtures



(c) $\tau_{100\%}$ HC-N_2O mixtures (d) $\tau_{100\%}$ HC-N_2O-O_2 mixtures

Figure 2: Experimental ignition delay time of small hydrocarbons-N_2O(-O_2) mixtures.

For some of the mixtures studied, the OH* emission profiles demonstrated complex behaviours with emission starting just after the reflected shock, levelling off and finally strongly increasing as the main exothermic oxidation step takes place. This phenomenon was found to be both mixture and temperature dependent. Such profiles were never observed for the mixtures with CH_4 as the only fuel. For the mixtures containing C_2H_6, the pre-ignition emission was always observed at intermediate and higher temperature, except for the C_2H_6-N_2O-O_2-Ar mixture for which this feature was not present. The relative amplitude of the first emission peak ranged from 5-10% of the main peak at intermediate temperature to 30% at high temperature. At the highest temperature studied, the two peaks merge and only one peak is seen. For the mixtures containing C_2H_2 and C_2H_4, the pre-ignition emission was visible only in the high temperature range, irrespective of the presence or absence of oxygen. Figure 3 shows some typical exemples of the observed emission profiles. Such complex emissiom features have been already reported by Rotavera et al [19] during the oxydation of n-nonane by oxygen behind reflected shock wave.

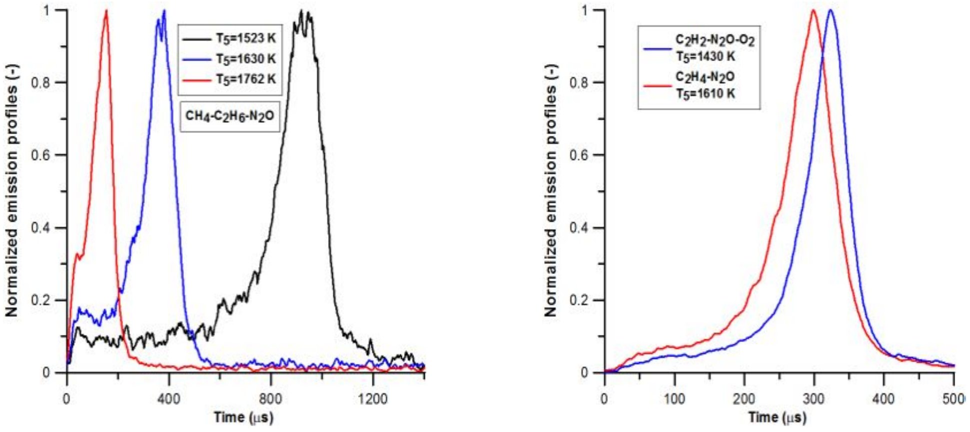


Figure 3: Experimental emission profiles of small hydrocarbons-N_2O(-O_2) mixtures.

3.2 Modeling results

The models of Konnov, Dagaut, Caltech and the GRI-Mech 3.0 were evaluated with respect to the present data assuming the constant volume reactor model. Table 2 shows the mean error for each model and mixture studied. The most accurate model is that of Konnov with a mean error around 20%. The model of Dagaut and the GRI-Mech 3.0 demonstrate much higher disagreement with the experimental values. The predictions of the Caltech model are close to those of the Konnov model as illustrated in Figure 4. However, its highest error is below that of the Konnov model and it reproduces better the shape of the emission profiles. Consequently, the model of Caltech has been used to interpret in detail the kinetics of the studied mixtures.

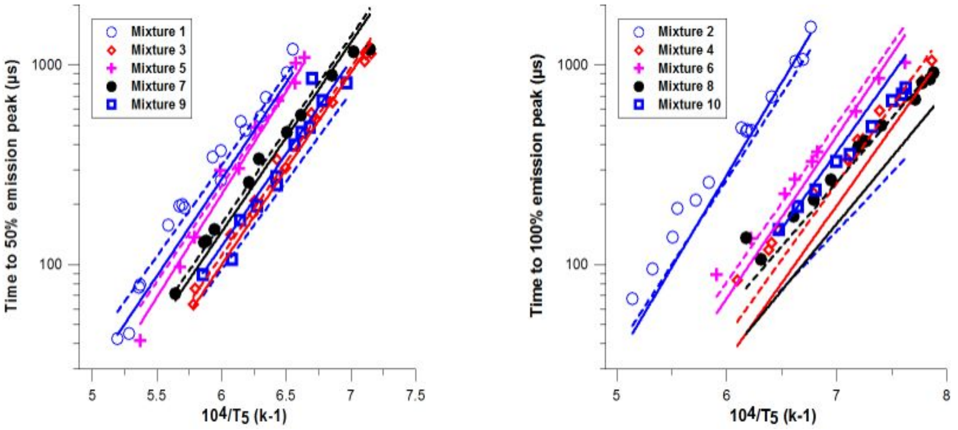
Mixure	Konnov	GRI-3.0	Dagaut	Caltech
1	15.6	18.1	16.1	22.6
2	21.7	17.2	16.8	20.2
3	12.1	35.1	68.6	15.1
4	19.1	26.6	37.3	31.2
5	11.7	30.2	48.4	13.2
6	16.0	15.5	73.7	20.0
7	13.4	25.1	72.7	17.7
8	12.8	87.3	48.2	43.2
9	22.7	65.9	34.0	12.4
10	60.7	73.2	70.7	24.4
Mean	19.5	37.9	45.9	22.1
Max	80.7	126.3	204.4	65.9
Min	0.9	0.1	0.6	0.1

Table 2: Relative error (%) for each of the reaction models used in the present study.

The analysis of the OH* rates of production (ROP) shows that for the mixtures containing N_2O

only, the formation of OH* is mainly due to R1: N_2O+H=N_2+OH*, with a smaller contribution of R2: CH+O_2=CO+OH*. For the mixtures containing both N_2O and O_2, the formation of OH* is exclusively due to R2. For all mixtures, the destruction of OH* is dominated by R3: H+O+M=OH*+M.

The pre-ignition emission peak observed for some of the mixtures can be explained by a 2-step production of the main precursors of OH*. For the C_2H_6-N_2O mixtures with and without methane, the main precursor of OH* is H atom. Initially, the production of H is due to R4: C_2H_5(+M)=C_2H_4+H(+M). Subsequently, the formation of H is due to R5: OH+H_2=H_2O+H and R6: CO+OH=CO_2+H. For the mixtures containing C_2H_2 or C_2H_4, the main precursor is the CH radical. In both phases, CH is formed by R7: T-CH_2+H=CH+H_2, where T-CH_2 stands for the triplet form of the CH_2 radical. These features are illustrated in Figure 5 which shows typical experimental emission signals along with predicted OH*, H, CH, H and CH rate of production profiles.



(a) $\tau_{50\%}$ HC-N_2O mixtures (b) $\tau_{100\%}$ HC-N_2O-O_2 mixtures

Figure 4: Comparison between the prediction of the Konnov and Caltech models and the experimental delay times of small hydrocarbons-N_2O(-O_2) mixtures. Solid lines: Caltech. Dashed lines: Konnov.

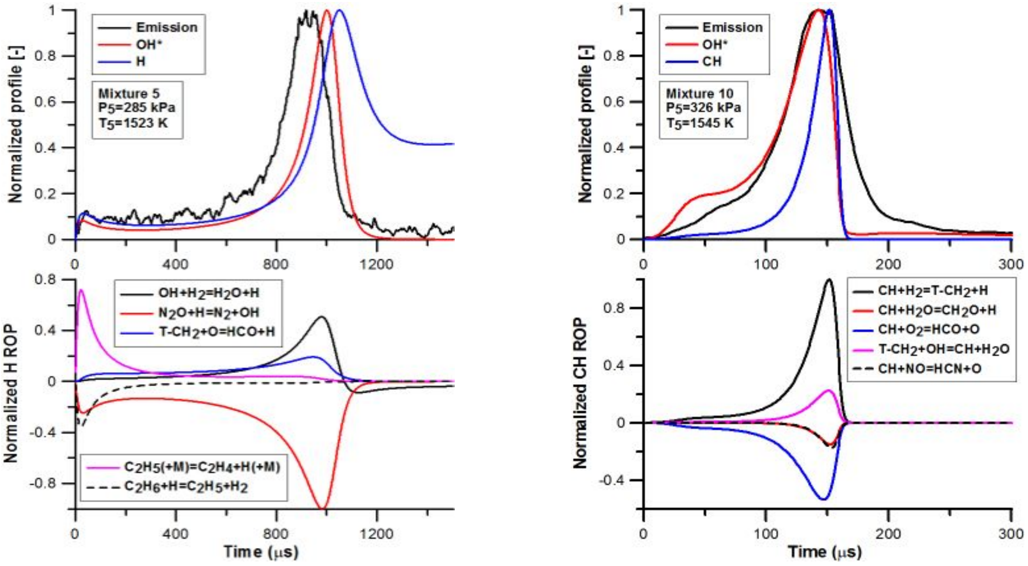


Figure 5: Experimental emission signals and predicted profiles of OH*, H, CH, H and ROP of H and CH.

4 Conclusion

In the present study, ignition delay times of CH_4-,C_2H_6-,CH_4-C_2H_6-,C_2H_4,C_2H_2-N_2O mixtures with and without O_2 were experimentally measured. The addition of oxygen induces a decrease of the activation energy of the oxidation process by 25% on average. Complex emission profiles have been observed for some of the mixtures. These profiles are characterized by pre-ignition emission peaks. Four detailed reaction models have been evaluated with respect to the present data. The model from Caltech was able to reproduce satisfactorilly both the ignition delay times and the emission profile shapes.
Future work will focus on the experimental and modeling study of the high temperature oxidation of nitro-alkanes and nitrate compounds in order to develop accurate reaction models for the gas phase kinetics of solid propellants.

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