Combustion and Flame 190 (2018) 327–336

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Experimental studies of nitromethane flames and evaluation of kinetic mechanisms

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ARTICLE INFO

Article history:
Received 16 August 2017
Revised 1 October 2017
Accepted 11 December 2017

Keywords:
Nitromethane
Oxy-fuel
Burning velocity
Kinetic modeling
Flame structure

ABSTRACT

The present work reports new experimental data for premixed flames of nitromethane, CH_3NO_2, at atmospheric pressure, and an evaluation of two contemporary kinetic mechanisms based on these new flame studies as well as previously published experimental data on laminar burning velocity and ignition. Flames of nitromethane + air at lean ($\phi = 0.8$) and rich ($\phi = 1.2$) conditions were stabilized on a flat-flame burner, where profiles of CH_2O, CO and NO were obtained using laser-induced fluorescence and temperature profiles using coherent anti-Stokes Raman spectroscopy. Laminar burning velocities for nitromethane + O_2 + CO_2 were measured using the heat flux method for $\phi = 0.8$–1.3 at 348 K and $\phi = 0.8$–1.6 at 358 K, and an oxidizer composition of 35% O_2 and 65% CO_2. In addition, the effect of the oxidizer composition was examined for a stoichiometric flame at 358 K by varying oxygen fraction from 30% to 40%. The mechanism by Mathieu et al. (*Fuel* 2016, 182, 597), previously not validated for flames, was able to reproduce experimental laminar burning velocities for nitromethane + air, but under predicted new results for $CH_3NO_2 + O_2 + CO_2$ mixtures. The mechanism by Brequigny et al. (*Proc. Combust. Inst.* 2014, 35, 703) under predicted experimental laminar burning velocities significantly at all investigated conditions. Previous studies have shown that none of the mechanisms can accurately predict ignition delay time over a wide range of conditions with respect to pressure, temperature, diluent and dilution ratio. The evaluation of the mechanisms reveals that the understanding of nitromethane combustion is at ~~the~~ present time not sufficient to produce a widely applicable mechanism.

1. Introduction

Nitromethane, CH_3NO_2, is the simplest fuel containing a nitro group and therefore considered a suitable model fuel to gain fundamental understanding of fuel-N chemistry. As a result of its dual fuel-oxidizer characteristics, nitromethane has potential as a monopropellant and is also used as a model compound to understand monopropellant combustion [1,2]. As a fuel by itself or as an additive in for example methanol or gasoline, nitromethane has several advantageous properties like its high lubricity and its effect to increase octane sensitivity [3]. The main combustion applications of nitromethane today, either pure or in mixtures with methanol, are in model prototype cars and race cars [4,5].

Since it is considered a model fuel for monopropellants, detonation characteristics and chemistry of nitromethane have been rather extensively studied [6–14]. Among combustion characteristics of nitromethane, thermal decomposition is the most studied process [15–29], whereas ignition, flame propagation and flame structure have not been sufficiently well characterized. Further efforts are thus required to achieve an exhaustive experimental characterization and accurate kinetic modeling.

Laminar burning velocities of nitromethane with oxidizer mixture of $O_2 + N_2$ have been examined in three previous studies. Already in 1959 De Jaeger and Van Tiggelen [30] estimated the laminar burning velocity using Schlieren imaging for nitromethane + O_2 + N_2 at various N_2 dilutions on a Bunsen burner. Using the spherical flame methodology, Brequigny et al. [31] measured the laminar burning velocity for nitromethane + air mixtures at 423 K in the pressure range 0.5–3 bar. They defined the equivalence ratio assuming N_2 as the final nitrogen product, and observed a maximum in laminar burning velocity at lean conditions, $\phi \sim 0.75$. However, by defining the equivalence ratio with NO as the final product, the maximum instead appears at rich conditions, $\phi \sim 1.2$, in line with many other fuels, as shown by Nauclér et al. [32]. In that work, laminar burning velocities for nitromethane + air in the temperature range 338–358 K at

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https://doi.org/10.1016/j.combustflame.2017.12.011
0010-2180/

atmospheric pressure, were determined using the heat flux method [32]. Based on the modeling results, it was shown that the width of the reaction zone of nitromethane + air flames needs to be considered when using the spherical flame technique [32]. Therefore, the experimental results obtained at 1 bar by Brequigny et al. [31] were reprocessed by Nauclér et al. [32], considering the predicted width of the reaction zone, which improved the agreement between the studies. The laminar burning velocities were further investigated by Faghih and Chen [33] using modeling with the mechanism of Brequigny et al. [31]. They showed that the modeling supported two-stage heat release and that this affects the evaluation of experimental data from spherical flames. A re-evaluation of the results of Brequigny et al. [31] using this new understanding, resulted in better agreement of the data with the predictions using a power-law expression suggested by Nauclér et al. [32].

Flame structure in premixed low-pressure nitromethane flames has been studied experimentally [34–36]. Modeling of flames of liquid nitromethane [1] indicated that the flames have a wide total reaction zone that can be divided into three distinct zones. Also, experimental and modeling studies of flames as well as ignition indicate that the nitromethane chemistry takes place in distinct zones or steps [1,10,12–14,34,37]. First the nitromethane is consumed, mainly by decomposition into CH_3 and NO_2, and the formed radicals and intermediates react in the zones that follow.

Ignition of nitromethane in the presence of oxygen at lean, stoichiometric, and rich conditions has been investigated in two recent studies, by Mathieu et al. [38] with Ar as diluent and by Nauclér et al. [39] with N_2 as diluent, in temperature and pressure ranges 875–1595 K, 2–35 atm and 947–1333 K, 8–32 atm, respectively. For evaluation of earlier experimental studies [22,40,41] we refer to the discussion by Nauclér et al. [39].

Kinetic mechanisms for modeling of nitromethane + O_2 combustion in diluents Ar or N_2 are available in literature and the recent ones are outlined in the following. A mechanism for low-pressure nitromethane + O_2 + Ar flames was presented by Zhang et al. [36], with model predictions in satisfactory agreement with experimental results. Brequigny et al. [31] adapted the mechanism from Zhang et al. [36] to pressures in the range 0.5–3 bar, by updating selected rate constants. The mechanism was validated against laminar burning velocities for nitromethane + air at 423 K and 0.5–3 bar. The most recently published mechanism, from Mathieu et al. [38], was developed for self-ignition of nitromethane, and ignition delay times for nitromethane + O_2 + Ar at 2–34 atm were reproduced with satisfactory agreement. None of the mentioned mechanisms has been validated against experimental flame structures at atmospheric pressure and the mechanism of Mathieu et al. [38] has not been validated against laminar burning velocities. Reliable mechanism validation requires a wide range of experimental data and a validation including ignition, laminar burning velocities, and species profiles in flames, would give an indication on the overall ability of the two mechanisms to accurately represent nitromethane combustion.

Regarding laminar burning velocities, it has been shown that the diluent in the oxidizer mixture can have significant impact on the chemistry, and thus on the combustion characteristics [42]. For instance, in methanol flames, replacement of air with an $O_2 + CO_2$ oxidizer mixture was modeled using several contemporary kinetic mechanisms and it was evident that their abilities to incorporate the chemical and thermal effects of CO_2 were significantly different. It is therefore clear that experimental data on laminar burning velocities with $O_2 + CO_2$ as oxidizer is a way to further constrain kinetic model validation. It should be noted that carbon dioxide significantly changes chemical pathways, primarily by converting hydrogen atoms into hydroxyl radicals in reaction $CO_2 + H = CO + OH$, as discussed earlier [42]. The literature on the effect of carbon dioxide on nitromethane combustion is at present limited to a single study where the effect of CO_2 as a collision partner in the decomposition of nitromethane was investigated in a shock tube at 1050–1400 K and 0.2–40 atm [20]. Studies of CO_2-enriched gas mixtures are also of practical interest since the issue of increased atmospheric CO_2 levels has been suggested to be counteracted by carbon capture and sequestration (CCS) of high-CO_2 combustion exhaust [43]. Oxy-fuel combustion has the subordinate but important effect of reducing NO_x emissions, compared with combustion in air. This is partly because there is no N_2 present that can form NO_x at high combustion temperatures, but also a result of that the fate of fuel-nitrogen (fuel-N) under oxy-fuel conditions can be different than for combustion with air, as reviewed for combustion of fossil fuels [44,45].

In the present work, species profiles for CO, NO and CH_2O measured using laser induced fluorescence (LIF) are presented for premixed laminar atmospheric pressure nitromethane + O_2 + N_2 flames at lean and rich conditions, an important dataset for model validation. To improve knowledge on fuel-N conversion at CO_2-rich conditions, and to provide an additional constraint for model validation, the present study also includes new experimental data on the laminar burning velocity for nitromethane + O_2 + CO_2 flames. Two contemporary kinetic mechanisms for nitromethane combustion [31,38] are evaluated on their capability to accurately predict the measured combustion characteristics.

Table 1
Specifications for flames in the flame structure study.

ϕ	Gas velocity cm/s	Oxidizer composition	
		Air	N_2
0.8	20	0.82	0.18
1.2	22	0.74	0.26

2. Experimental details

2.1. Burner-stabilized flame for flame structure determination

2.1.1. Burner and flame conditions

Nitromethane + air + N_2 flames were stabilized on a heat flux burner [46] with the temperature of the burner head set at 363 K, using a thermostatic water bath. The studied flames had the properties given in Table 1, where flow velocities are chosen to be suitable to achieve a stable lifted flame. A stainless steel-plate was mounted 20 mm above the burner surface to further support flame stabilization. The burning velocity of the mixture and the flow velocity were matched by diluting the oxidizer with nitrogen. Liquid nitromethane from Sigma-Aldrich with a purity of 99.8% was stored in a fuel tank pressurized at 3 bars using argon to prevent it from reacting with air in the reservoir. The fuel flow was controlled using a mass-flow controller for liquid fuels (CORI-flow) and evaporated using a controlled evaporator mixer (CEM), both from Bronkhorst. The liquid nitromethane was mixed with air during evaporation and the mixture then passed through a heated hose set at the desired temperature of the unburnt gas, 363 K.

2.1.2. Rotational coherent anti-Stokes Raman spectroscopy

Coherent anti-Stokes Raman spectroscopy (CARS) [47] was used to measure flame temperature in the axial direction of the flames, and the experimental setup was designed for dual broadband pure rotational CARS [48,49]. In this approach, the CARS signal (ω_{CARS}) is generated by probing the Raman coherence driven by the pump (ω_1) and Stokes (ω_2) laser frequencies in a third-order non-linear process, i.e. $\omega_{CARS} = \omega_1 - \omega_2 + \omega_3$. The probe beam ($\omega_3$) was generated by a single-mode Nd:YAG laser (Quantel YG:98IE) operating at 532 nm with a FWHM of 0.003/cm and a pulse duration of ~8 ns.