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Brief Communications

Cool-flame dodecane-droplet extinction diameters

Forman A. Williams[a], Vedha Nayagam[b,*]

[a] Department of Mechanical and Aerospace Engineering, University of California San Diego, La Jolla, California 92093, USA
[b] Department of Mechanical and Aerospace Engineering, Case Western Reserve University, Cleveland, OH 44106, USA

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ABSTRACT

Previously published simplified n-alkane cool-flame chemistry is re-evaluated for n-dodecane. Comparison with experimental results produces improved rate-parameter estimates for n-dodecane and indicates deterioration of the simplified chemistry with increasing pressure in predictions of droplet diameters at cool-flame extinction.

1. Introduction

In research directed towards developing an understanding of measurements of the combustion and extinction of normal-alkane droplets supported by cool-flame chemistry, performed in the International Space Station (ISS) [1], we employed a simplified chemical-kinetic description based on the San Diego mechanism [2]. The resulting reactions are shown in Table 1, where F denotes the normal alkane, R its alkyl radical, I the most relevant species resulting from the first oxygen addition to R (generally denoted as QOOH), and K the associated alkylketohydroperoxide, while P, Q, and S stand for collections of species that do not have to be tracked. In this simplified description, following hydrogen abstraction from the original fuel, the second step presumes rapid isomerization following the first oxygen addition and the third a steady state of the species formed by the second oxygen addition, maintaining partial equilibrium for its re-dissociation; I removal by decomposition to hydropreoxyl and the conjugate alkene, and alkyl removal by high-temperature chemistry, the fifth and sixth steps, were found to be essential quantitatively. The reader is referred to our previous publication [1] for further explanation and motivation producing this chemistry, which leads to a four-step formulation because OH and R maintain steady states.

2. Analysis and Discussions

The analysis [1] results in a description of the flame structure and predictions of the conditions at which the flame will extinguish. The cool flame persists until the droplet diameter has decreased to a point at which the residence time in the reaction zone of the gas-phase diffusion flame surrounding the droplet (at about three radii from the center) has been reduced to a value corresponding to which the cool flame becomes statically unstable and below which a quasi-steady flame structure with this cool-flame chemistry no longer exists. Predicted droplet diameters at this condition of cool-flame extinction were found to be in reasonable agreement with measurements for normal heptane droplets when use was made of the heptane chemistry that is present in the San Diego mechanism. Experimental data on droplet diameters at cool-flame extinction also were obtained in the ISS for normal dodecane droplets, but similarly short chemistry is not available for dodecane. Theoretical calculations therefore also were made employing the thermodynamic and transport properties of dodecane with the cool-flame chemical kinetics of heptane, instead, but it was found that the resulting predicted dodecane extinction diameters exceeded the measured values by more than a factor of three [1]. The purpose of the present communication is to estimate the differences between the rate parameters of heptane and dodecane, in the short description adopted by the San Diego mechanism, that would be needed to improve agreement between theory and experiment. The final resulting recommended rate parameters for dodecane are listed in Table 1; while they improve agreement, appreciable discrepancies remain.

There are detailed chemical-kinetic mechanisms that distinguish the different isomers in alkane combustion, properly consid-

* Corresponding author.
E-mail addresses: vedha.nayagam-1@nasa.gov, vedha.nayagam@case.edu (V. Nayagam).

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Table 1
The elementary reactions and their rate coefficients in Arrhenius form $k = A\exp(-T_a/T)$ with rate parameters in mol, s, cm^3, and K.

	Reaction	A	T_a
1	F+OH → R+H_2O	1.5 × 10^{12}	0
2	R+O_2 → I	3.7 × 10^{12}	0
3	I+O_2 → K+OH	6.4 × 10^{7}	−8360
4	K → P's+OH	1.6 × 10^{14}	19,840
5	I → Q's	3.0 × 10^{12}	12,090
6	R → S's	4.8 × 10^{13}	15,110

ering the possibility that different isomers may exhibit different rate parameters [3,4]. Those types of detailed descriptions, however, result in large mechanisms, which the San Diego mechanism purposely seeks to avoid. Apart from species in different electronic states, therefore, that mechanism lumps all isomers into a single species, the rate constants for which then become the sum of the rate constants of all isomers. The difference between heptane and dodecane (7 versus 12 carbon atoms, a larger number of isomers being associated with the latter) then produces a larger number of terms in the sum required in calculating rates of F, R, I, and K reactions for dodecane. If the rates are the same for all isomers, as they are considered to be for the I and K decompositions [3,4], steps 4 and 5, then the 6 dodecane isomers, compared with the 4 heptane isomers, result in the dodecane rates being larger by a factor of 1.5, as is the value listed in Table 1 for step 5 (step 4 being discussed further later). For the oxygen additions, the rates at interior sites are about twice the rates at the ends of the carbon chains [3,4], whence, with 5 interior locations for heptane and 10 for dodecane, interior and end rates each being the same for the two fuels, the resulting dodecane rate is 11/6 times that for heptane, as is given for steps 2 and 3 of Table 1. Step 1 also generally is assigned different rate parameters for interior and end abstractions, with the same values for the different normal alkanes [3,4], and the detailed chemistry for step 6 is appreciably different for dodecane than it is for heptane. In the absence of detailed hot-flame chemistry for dodecane in the San Diego mechanism, as conservative approximations that likely underestimate rates somewhat (but not to an extent likely to influence predictions strongly), the rates listed in Table 1 for steps 1 and 6 have been selected to be simply 3/2 those for heptane, just as for step 5. This serves to specify the rate parameters listed in the table for all of the steps except step 4, which is one of the steps to which predictions are most sensitive, uncertainties in values being roughly comparable for all of the steps. Activation energies for all steps are the same as for heptane, while prefactors are 3/2 those of heptane for steps 1, 5, and 6 and 11/6 those of heptane for steps 2 and 3.

Figure 1 compares calculated and measured cool-flame extinction diameters for dodecane droplets burning in air. Besides showing the previously published prediction employing the chemical-kinetic parameters for heptane, the figure shows the predictions stemming from the revised parameters reasoned above to be possibly applicable, identified in the figure as the "lumped" prediction, based on the same type of lumping for dodecane that had been selected for heptane. In this selection, then, the rate of steps 4 is 1.5 times that for heptane, just as for steps 1, 5, and 6, it having been reasoned above to be subject to the same factor as step 5. Although there is noticeable improvement in agreement with these selections, the predicted diameters are still larger than the measured diameters by more than a factor of two. This motivates further considerations.

It is widely accepted that significant uncertainties remain in values of the rate constant for K decomposition (as well as for other elementary steps) in the low-temperature chemistry of normal alkanes [5], and we estimate that the corresponding rate constant for the dodecane chemistry in this highly reduced description may be as much as an order of magnitude greater than that for the heptane chemistry. To fit the data better at a half atmosphere, the rate for step 4 for dodecane is therefore taken taken to be 10 times the previously employed value for the heptane case, while the previously reasoned factor of 3/2 is retained for step 5, which is somewhat less uncertain. This results in the prediction labeled "fit" in the figure. Although this prediction is seen in the figure to be close to experiment at low pressure, it decreases more slowly with increasing pressure than was observed in the measurements.

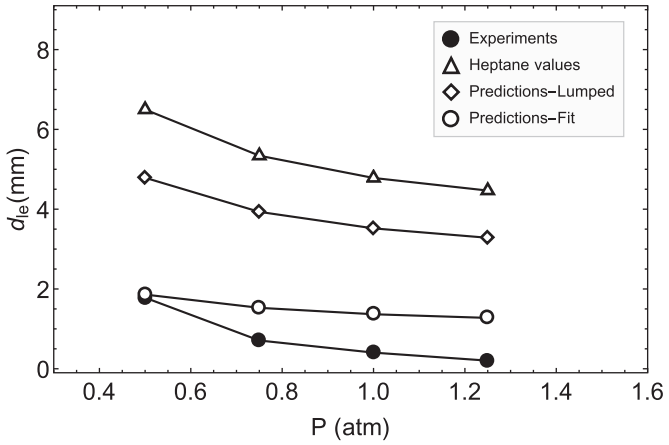

Fig. 1. The dependence of the droplet diameter at cool-flame extinction on pressure for n-dodecane droplets burning in 300 K air, according to experiment and to predictions with three different selections of chemical-kinetic parameters.

The predicted pressure dependence of extinction diameters, with chemistry like that in Table 1, in fact is found quite generally to be weaker than was observed in the ISS experiments. According to the previously derived and published formulas [1], when reasonable values are employed for the parameters that affect the predictions, for the data in the figure the extinction diameter varies inversely as the square root of the pressure, but experimentally the inverse power that best fits the data lies between 1.7 and 1.8, well above 0.5. One possibility is that this difference is caused by neglecting fuel-pyrolysis processes in the analysis, the rates of which increase rapidly with increasing pressure. Besides complicating the combustion mechanisms through absorption of pyrolysis products in the liquid, progressively modifying liquid properties, the gas-phase fuel decomposition may perpetuate gas-phase combustion by introducing additional chemistry there, which some have begun referring to as "warm flames" [6]. Some of these pyrolysis effects may be expected to persist at 0.5 atm, in which case the "true" ratio of the step-4 rate constant for dodecane to that for heptane may lie between the value 3/2 of the original estimate and 10 of the "fit"; perhaps the best choice would be a ratio of 4, which is the value selected for the entry listed in Table 1, a best-guess compromise between estimated uncertainties and fitting data. Since complicating pyrolysis-related effects are not taken into account in the present development, the simplified chemistry addressed here should be considered to apply best to droplet combustion of normal alkanes at sub-atmospheric pressures (if at all).

Given the best-estimate values of Table 1, the extinction diameters predicted by the theory remain greater than the measured values. An alternative to the possibility that the disagreements reflect influences of effects of fuel pyrolysis neglected in the theory is inaccuracy of the hypothesis in the analysis that the heat release per unit mass of oxygen consumed in the cool flame corresponds to conversion to products consisting only of CO and H_2O, independent of pressure. An increase in the heat release causes an increase in

the oxygen concentration at the cool flame according to the theory, which results in a reduction of the value of the predicted droplet diameter at extinction. The heat release is characterized by a parameter expressed through a temperature T_Q, the value of which, according to its definition, was estimated to be 4000 K for both heptane and dodecane [1]. If, instead, the value of T_Q for dodecane were to increase with pressure, then the predicted extinction diameter would decrease more rapidly with increasing pressure than is seen in the figure, in better agreement with experiment, and also the theoretical prediction of the limiting oxygen index [1], which corresponded to an oxygen mole fraction in the ambient atmosphere that is independent of pressure at a given flame temperature, would instead produce an ambient oxygen mole fraction that decreases with increasing pressure, closer to a fixed ambient oxygen concentration, instead. Although this additional possibility is attractive, it is found that to produce agreement between predictions and experiment through adjustment of values of T_Q would require a rate parameter for step 4 that is at least an order of magnitude larger than is reasonable, whence chemistry beyond that of Table 1, such as the pyrolysis phenomena suggested above, must be present for n-dodecane.

Declaration of Competing Interest

There are no conflict of interest declared by the authors.

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