Simplified Structure Models for Premixed n-Alkane Cool Flames

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Abstract

The chemical kinetics of cool flames in mixtures of normal alkanes, oxygen, and nitrogen recently have been reduced to obtain simplified asymptotic flame-structure models that can be used to compare theoretical predictions with experimental measurements. A key step that affects flame structures strongly, namely the abstraction of a hydrogen atom from the alkyl radical by an oxygen molecule, had not been taken into account in those models. This deficiency has now been remedied for diffusion flames. The present contribution reports the corresponding remedy for premixed-flame analyses. In the new model, non-zero chemical reaction rates are restricted to narrow regions in the vicinity of the maximum temperature, whereas previously they extended throughout the preheat zone. Comparisons of the new predictions with experimental burning-velocity measurements seem favorable.

Keywords: Premixed cool flames; n-alkanes; simplified chemistry; flame speed

Novelty and significance

A theoretical model for n-alkane premixed cool-flame deflagration is developed using a 7-step, simplified chemical kinetic model involving activation-energy asymptotics for a negative activation energy for the first time for premixed flames. The results are compared against existing, and newly measured experimental data for n-dodecane cool flames in varying oxygen concentrations. The theoretical results show the importance of hydrogen atom abstraction from the alkyl radical at low temperatures, which confines the chemistry to a small region around the peak flame temperature.

Authors contributions

The authors (VN and FAW) were equally involved in formulating the theoretical model, doing the calculations, and writing the paper. One of the authors (MB) performed the detailed chemistry calculations.

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1. Introduction

Over a small range of temperatures, called the negative-temperature-coefficient (NTC) range (which becomes less evident and increases in temperature with increasing pressure but always remains between 500 K and 1000 K), the heat-release rates of normal alkanes in oxygen-nitrogen mixtures decrease with increasing temperature. Cool flames, concerning which there is a sizable literature [1], have flame temperatures in the NTC range. Besides computational studies of cool-flame structures utilizing various degrees of detailed chemistry, as discussed in the cited review [1], theoretical investigations have been published, employing asymptotic analysis with greatly reduced chemistry, involving fewer than 10 elementary steps [2,3]. The motivation for the latter work was enhancement of our physical understanding of the flame structures, sacrificing accuracy for the sake of exposing as clearly as possible the dominant and controlling mechanisms that are most important. The present contribution is of that simple-model type.

Four elementary steps are central to cool-flame structure in the present investigation. Conversion of the fuel F to an alkyl radical R through H-atom extraction by an hydroxyl radical occurs in the first step, after which there is addition of an oxygen molecule to R, in the second step, to form RO_2. The RO_2 then isomerizes to a radical that is denoted by QOOH in the literature, but (contrary to other investigations) at the present level of accuracy (as was tested by comparing predictions of the San Diego Mechanism [4] with and without that approximation) the isomerization is fast enough that RO_2 can be eliminated in terms of QOOH, which is denoted simply by I in our previous and present work. The third essential step in the present description is the second addition of O_2, this time to I, to produce OH and an alkylketohydroperoxide, denoted by K. These products actually arise only after a further internal isomerization, but, again, it is fast enough to be considered to occur instantaneously in the present approximation (as well as in the San Diego Mechanism, in which the intermediate radical was eliminated through its steady state). The fourth essential step is the unimolecular decomposition of K to liberate another OH, thereby creating branching through that chain carrier. The additional products of the fourth step, denoted below by P_4, are reactive, for example in heat generation (the chemistry of which is not addressed in this work) but they do not play any role in the present description and so are simply treated as products.

In our previous premixed-flame publication [3], a fifth elementary step (with rate parameters extracted from the literature) was needed, the unimolecular decomposition of I to form species that did not participate in the chemistry and that therefore could be treated as stable products, which will be denoted by P_5 here. That step was required to slow down the chemistry at the higher temperatures by reducing the concentration of an essential intermediary; otherwise predicted burning velocities were too large in comparison with those computed employing detailed chemistry, and the high-temperature termination of the NTC range was lost. Experimental data on cool-flame laminar burning velocities had become available and were reported in that paper; although the experimental results in the figure published there are correct, the comparison with predictions shown, along with the associated discussion, is wrong because of an error in units and so should be ignored. A sixth step

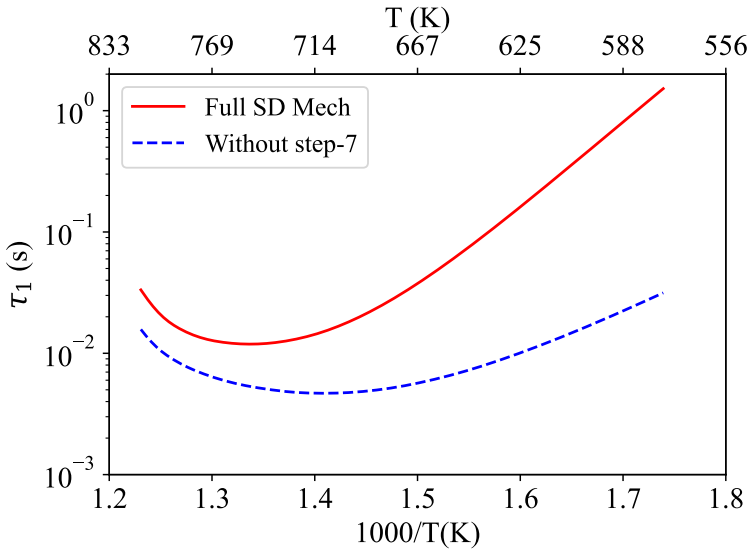


Figure 1: First induction time for stoichiometric n-heptane/air mixture calculated using the full San Diego mechanism, and with step-7 removed, for a homogeneous, isobaric reactor at 1 atm.

of a similar type, the unimolecular removal of R, forming non-participating species to be denoted by P_6, which had been needed for diffusion-flame extinction [2], was not included in the analysis because its effect is qualitatively similar to that of step 5 (which is simpler in that the resulting important influence on I is more direct), but it will be included here because it is found to be significant quantitatively.

Recent exploratory, premixed-flame computations, employing the detailed San Diego Mechanism [4], revealed that removal of R through H-atom extraction by oxygen molecules is an important step that decreases the predicted laminar burning velocity appreciably. Autoignition computations with the detailed chemistry, performed with and without this step, defining the ignition time as the first inflection point in the homogeneous, isobaric, adiabatic, temperature-time curve, exhibit a substantial influence of that step, as shown in figure 1, and that influence also was reflected in the exploratory burning-velocity computations in burner-stabilized flames. This seventh step had been overlooked in our original diffusion-flame and premixed-flame work because those investigations were based on previous studies that did not include this step [5], it being erroneously assumed (as had been claimed in some previous literature) that this step was too slow to be important. The modifications to the simplified model of diffusion-flame structure that are produced by inclusion of this seventh step has been explained recently [6], while the resulting changes to the premixed-flame structure are addressed here. The maximally reduced chemistry is the seven-step mechanism that is shown in Table 1 for convenience, along with the values employed for the rate parameters for n-dodecane. It should be noted that the kinetic and thermal parameters used in the calculations remain the same irrespective of the number of steps employed in a model.

Since the heat release, assumed to occur at the rate of step 4, is not included in this chemistry, it is treated as an undetermined parameter, which turns out to affect the flame

temperature and the burning velocity only through its influence on the oxygen concentration at the flame in the newly derived asymptotic analysis. Careful examination of the energetics of the mechanism shows that, to generate the heat needed to support a flame, step 4 must be exothermic, releasing enough heat to overpower the energetics of other steps. That step, however, in fact is endothermic, implying that, for the mechanism to work, P4 must be very unstable and rapidly produce radicals that quickly attack other species to liberate the required energy through various parallel paths. The species involved in those processes, however, will differ for different normal alkanes, complicating attempts to invent generally applicable, short, augmented mechanisms that account for the needed heat release. It is for this reason that the heat release is treated as an adjustable empirical parameter in the analysis. It is perhaps noteworthy that although this simple mechanism reasonably describes the low-temperature branching of the cool-flame chemistry, it cannot properly reproduce the correct energetics of the cool flame.

Step-j	Reaction	A_j	T_j
1	F+OH $\rightarrow$ R+H_2O	1.5 10^{12}	0
2	R+O_2 $\rightarrow$ I	3.7 10^{12}	0
3	I+O_2 $\rightarrow$ K+OH	6.4 10^{7}	-8,360
4	K $\rightarrow$ P_4+OH	6.0 10^{13}	19,840
5	I $\rightarrow$ P_5	3.0 10^{12}	12,090
6	R $\rightarrow$ P_6	4.8 10^{13}	15,110
7	R+O_2 $\rightarrow$ P_7	7.5 10^{11}	1,760

Table 1: The elementary reactions and their rate coefficients in Arrhenius form $k_j = A_j \exp(-T_j/T)$ with rate parameters in mol, s, cm^3, and K, for n-dodecane.

2. Reaction Zones

As has been observed in all of this work [2,3,6], the species OH and R maintain accurate steady states, enabling them to be eliminated from the problem, so that the only intermediates that need to be considered are I and K. The two steady states result in a revised expression for the rate of production of I, which then becomes the rate of step 4 minus the sum of the rates of three steps, namely step 5 and the influences of steps 6 and 7 on I removal. Through the steady states, I is produced only by step 4, which occurs only in the hottest region. The influence of step 6 on I removal is the product of the rates of steps 6 and 3, divided by the rate of step 2, as a consequence of the applicable approximation for the steady state of R [2]. Moreover, since the steady-state expression for R (after use of the OH steady state) can accurately be expressed by equating the rate of step 2 to that of step 3 [6], the concentration of R in the rate expression for step 7 may be replaced by the concentration of I with the rate multiplied by $(A_3/A_2)e^{-T_3/T}$, resulting in a contribution to the rate of consumption of I having a negative activation energy, which can be described by an activation temperature to be denoted by $T_r = T_3 + T_7$ = -6,600 K. This seventh step

then effectively removes I from the preheat zone of the flame, thereby correspondingly eliminating K production from occurring in the preheat zone. This negates the previous flame structure [2], restricting all of the finite-rate chemistry to the vicinity of the hot boundary. The flame-structure analysis then can make use of activation-energy asymptotics (AEA) for a negative activation energy [6], I being absent at leading order (while K maintains a diffusive-convective balance) in the preheat zone.

The only fundamental change to the formulation of the problem is that, in the conservation equation for species I, an additional rate term, namely its destruction through step 7, now appears in the third equation of [3]. Since the equations (after addition of step 6) and boundary conditions otherwise are identical, there seems to be no point in repeating the formulation here. There is a downstream zone of I consumption, previously [3] only through step 5, the structure of which remains basically unchanged, as does the structure of the heat-release zone and that of the upstream I-consumption zone, the only revision being that now step 5 is augmented by step 6 everywhere, as indicated above. Additionally, the solutions for the temperature and oxygen mass fraction in the preheat zone remain the same, as does the burning-velocity formula obtained by addressing that zone. The only new aspect of the reaction-zone arrangement in the flame structure, then, is the presence of a zone of I destruction and K production just upstream from the upstream I-consumption zone, which, according to the AEA for negative activation energy, is thin but thicker than the upstream I-consumption zone. This reaction-zone arrangement is illustrated schematically in Fig. 2 where, unlike the profiles for the intermediates, for fuel, oxygen, and temperature only the outer solutions are exhibited.

The analysis of the structure of the new K-production zone is outlined below. The complete asymptotic analysis is quite extensive and therefore is included only as supplementary material, rather than lengthening the presentation in the main text substantially.

3. K-Production Zone

As indicated above, a consequence of the importance of step 7 is that K is produced only in a thin zone just upstream from the upstream I-consumption zone. The production occurs through step 3, which has a negative activation temperature of T_3 = -8,360 K. In that zone, I is consumed completely by a step having an activation temperature of T_r = -6,600 K. It is because these two activation temperatures are so close together that both of these steps can be approximated well as occurring in the same zone, in the context of AEA. In defining the size of that zone, a common average activation temperature of T_s = -7,500 K will be selected. This parallels the choice made in analyzing the structure of the corresponding zone for the diffusion flame [6]. The solutions for the mass fractions Y_I and Y_K of species I and K must satisfy downstream matching conditions for slopes at the upstream end of the upstream I-consumption zone; in addition, at the upstream end of this K-consumption zone the solution for Y_K must match the slope of the solution for Y_K in the preheat zone, while the solution for Y_I vanishes there, at leading order.

Just as for the diffusion flame [6], in terms of the flame temperature T_f (with the subscripts f and u identifying conditions at the flame and in the unburnt gas upstream, re-

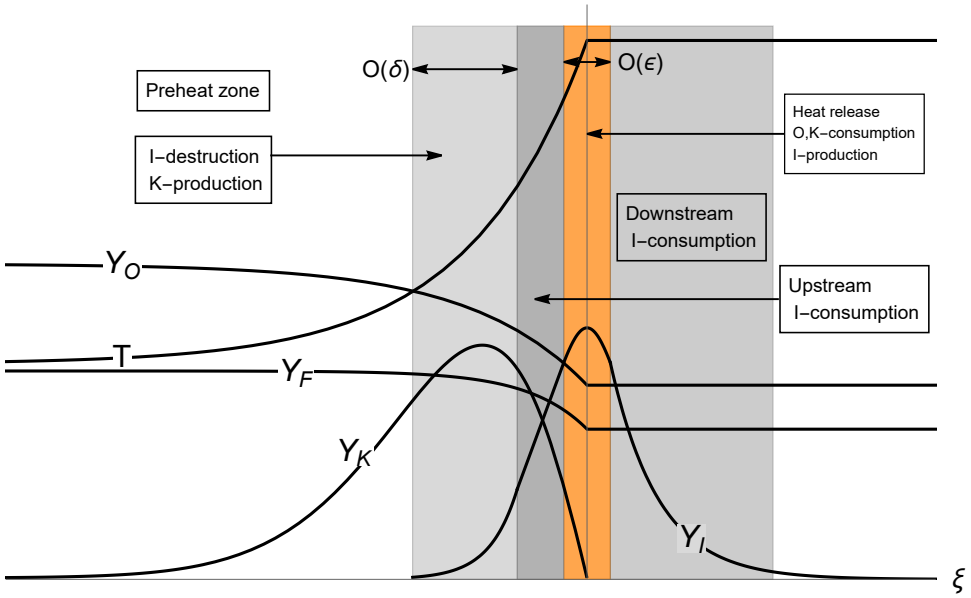


Figure 2: Schematic illustration of the flame structure.

spectively), the small parameter for the AEA expansion is taken to be $\delta = T_f/(-T_s)$. It becomes convenient here to employ the temperature T as the independent variable, selecting $x = (T_f - T)/(\delta T_f)$ as its non-dimensional measure of order unity in this zone. The diffusion-reaction balances for I and K then become $\mathrm{d}^2Y_I/\mathrm{d}x^2 = AY_I\mathrm{e}^x$ and $\mathrm{d}^2Y_K/\mathrm{d}x^2 = -BY_I\mathrm{e}^x$, respectively, in this zone, similar to what was found for the diffusion flame [6], where $A = L(T_f/T_s)^2[T_f/(T_f - T_u)]^2(D_f/S_f^2)(\rho_f Y_{Of}/W_O)(A_3A_7/A_2)\mathrm{e}^{-T_r/T_f}$ and, quite similarly, $B = L(T_f/T_s)^2[T_f/(T_f - T_u)]^2(D_f/S_f^2)(\rho_f Y_{Of}/W_O)(W_K/W_I)A_3\mathrm{e}^{-T_3/T_f}$. Here the Lewis number, taken to be the same for I and K, is written as L, ρ denotes the gas density, W_i stands for the molecular weight of species i, D is the thermal diffusivity of the mixture, and S_f represents the flame speed (burning velocity) measured in the burnt gas (the speed at which the flame recedes from an observer fixed in a coordinate system in which the burnt gas is at rest, which is the laboratory frame for a flame propagating from the closed end of a tube). These two differential equations are to be solved subject to the matching conditions imposed at $x = 0$ and as x approaches infinity.

Transformation to $t = 2A^{1/2}\mathrm{e}^{x/2}$ as the independent variable converts the differential equation for Y_I to a differential equation that is satisfied by modified Bessel functions. The solution that vanishes as x approaches infinity is proportional to the modified Bessel function of the second kind of order zero, which is denoted by $K_0(t)$; this function also arose in the diffusion-flame problem [6]. Use can profitably be made of the previously derived [3] expression $S_f^2 = 2L[T_f/(T_f - T_u)]^2(T_f/T_4)^2D_fA_4\mathrm{e}^{(T_4-T_f)}$ in the formula for A as is stated above to give $A = (1/2)(T_4/T_s)^2(A_3/A_2)(\rho_f Y_{Of}W_O^{-1}A_7/A_4)\mathrm{e}^{(T_4-T_r)/T_f}$. This last expression may be employed in the relationship obtained by matching the slope of the solution for the intermediate Y_I at $x = 0$ to derive an explicit formula for Y_I at the flame, to be denoted by

Y_{If} and given by the expression

$$\frac{2W_I(T_f-T_u)}{T_QW_K}\left(\frac{4(-T_s)\sqrt{A}K_1(2\sqrt{A})}{LT_f^2K_0(2\sqrt{A})/(T_f-T_u)}+\frac{(T_f-T_u)T_4^2R}{LT_f^2T_5}+\sqrt{1+\frac{2T_4^2(T_f-T_u)^2R}{L^2T_f^4}}-1\right)^{-1} \tag{1}$$

where the influences of steps 5 and 6 (the latter evaluated as in [2] and [6], a zone of I consumption through step 6 having been added to the upstream I-consumption zone of [3]) are accounted for through $R=(A_5\mathrm{e}^{-T_5/T_f}+A_6A_3A_2^{-1}\mathrm{e}^{-(T_6+T_3)/T_f})/(A_4\mathrm{e}^{-T_4/T_f})$, and T_Q is a temperature measuring the heat release under the assumption of a constant specific heat at constant pressure, as previously defined [3]. Here K_1 denoted the modified Bessel function of the second kind of order one, and to obtain this expression use has been made of the fact that the derivative of K_0 is -K_1, that derivative appearing from the first integral of the reaction rate across this zone, as is needed for the slope matching.

The leading-order solution $Y_I=Y_{If}K_0(t)/K_0(2\sqrt{A})$ provides the functional form of the source term in the differential equation for Y_K, which then may be integrated from $x=0$ to $x=\infty$ to derive a relationship between the slopes $\mathrm{d}Y_K/\mathrm{d}x$ at the boundaries of this zone. From matching to the preheat-zone solution, namely $Y_K=Y_{Kp}[(T-T_u)/(T_f-T_u)]^L$, where Y_{Kp} denotes the leading-order value of Y_K in this production zone, this slope at infinity is $-LY_{Kp}\delta T_f/(T_f-T_u)$. Matching to the solution downstream provides the slope $L\delta T_f/T_Q$ at $x=0$. The integration then produces the leading-order solution, simply $Y_K=Y_{Kp}$ in this zone, involving Y_{If} and resulting in

$$Y_{Kp}=\frac{Y_{If}W_K(-T_s)(T_f-T_u)A_2\sqrt{A}K_1(2\sqrt{A})}{W_ILT_f^2A_7\mathrm{e}^{-T_7/T_f}K_0(2\sqrt{A})}-(T_f-T_u)/T_Q, \tag{2}$$

after solving for Y_{Kp}. As before [3], it is assumed that Y_K is small compared with Y_I in the zone where K is produced, so that, in a first approximation, Y_{Kp} becomes negligible in (2). The resulting expression can be solved for Y_{If} and then used in (1) to obtain a formula that determines T_f from the experimental conditions and the rate and energetic parameters. Iteration is needed to find T_f from that result, after which the burning velocity S_F can be calculated from the formula given previously.

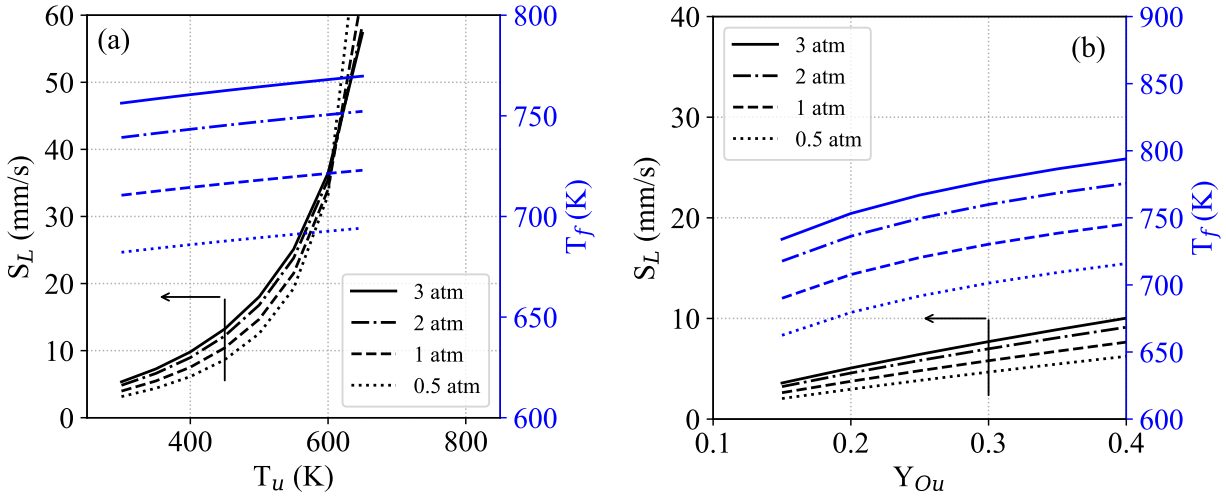
In the resulting formula that determines T_f, the first term inside the parentheses in (1) turns out to be negligible in comparison with the term arising from (2), so that the equation becomes simply

$$\frac{2(T_f-T_u)(-T_s)A_2\sqrt{A}K_1(2\sqrt{A})}{LT_f^2A_7\mathrm{e}^{-T_7/T_f}K_0(2\sqrt{A})}=\frac{(T_f-T_u)T_4^2R}{LT_f^2T_5}+\sqrt{1+\frac{2T_4^2(T_f-T_u)^2R}{L^2T_f^4}}-1. \tag{3}$$

After solving this equation iteratively for T_f and then calculating the burning velocity S_F from its previous formula, the velocity of laminar propagation of the flame into the fresh mixture, S_L, is calculated as $S_f(T_u/T_f)$.

4. Aspects of the Predicted Flame Temperature and Burning Velocity

The assumption that the heat release occurs only in the thinnest reaction zone led to the flame temperature, T_f, obtained from equation (3), exhibiting no explicit dependence on the heat-release parameter T_Q. That parameter enters indirectly, only through the oxygen mass fraction, as given previously in equation (11) of [3], which appears in the parameter A. This absence of an explicit dependence is due to the fact that the flame temperature is determined by the chemical kinetics, not by the heat release, which affects only the outer solutions, and it also extends to the burning velocity S_f, according to its formula. This is quite different from that of a hot-flame deflagration where the downstream flame temperature is determined by thermodynamics (the heat of combustion) independent of the chemical kinetics. Moreover, the predicted burning velocity and flame temperature are entirely independent of the fuel mass fraction Y_{Fu}, which may affect the results only to the extent that it modifies the value of T_Q, that is, only through its possible influence on the oxygen concentration profile. If oxygen depletion by the flame is negligible, then the burning velocity cannot depend on the initial fuel concentration (or on the heat release) according this chemistry. These results imply that the theory cannot be correct if the initial fuel concentration is too small. Further considerations of additional chemistry would be needed to address the question of when this failure occurs.



(a) Dependence on ambient temperature for $Y_{Ou} = 0.23$.

(b) Dependence on Y_{Ou} at a T_u of 300 K.

Figure 3: Predicted values of flame temperatures and laminar burning velocities.

Representative predictions of the theory are shown in Fig. 3. These calculations were made for the fuel n-dodecane in nitrogen-oxygen mixtures, employing the values listed in Table 1 for the rate parameters, but results would be similar for other normal alkanes. Since the predictions are independent of the fuel and inert concentrations, only the ambient temperature T_u and ambient oxygen mass fraction Y_{Ou} need to be specified, along with the value of T_Q. The computations were made with $T_Q = 1000$ K. Although the flame

temperature T_f increases with increasing pressure, the S_L changes are small because its inverse proportionality to pressure largely offsets its increase with T_f. Predicted flame temperatures and burning velocities are somewhat higher for larger values of T_Q, especially at the lower pressures, but the differences are not large, no matter how large T_Q is; there is a value above which changes become imperceptible. At smaller values of T_Q, predicted values of flame temperatures and burning velocities are noticeably lower, especially for values below 500 K and for the lower pressures, but it is unlikely that values encountered in experiments would be that small. The results shown in the figure thus are the most reasonable predictions to be expected.

5. Comparisons of Predictions with Experiment

In the previously mentioned experiment [3], a droplet of n-dodecane, supported by a fiber, is quickly inserted into an oven maintained at a fixed elevated temperature between 558 K and 703 K at 3 atm under normal gravity. The liquid begins to vaporize, and the vapor, being heavier than the surrounding gas, forms a downward moving plume. Cool-flame ignition first occurs in the lower part of the plume, where the residence time has been longest, and a premixed cool flame propagates upward. The upward propagation velocity initially is constant, and that initial upward velocity may be considered to be the difference between the theoretically calculated burning velocity and the downward velocity of the fluid in the plume. That propagation occurs in a mixture having a temperature equal to that at the position of ignition, which is uncertain but which will be less than the oven temperature because of natural convection currents in the chamber and the need for conductive heating of the downward-moving plume. These uncertainties, discussed previously [3], led to employing there values of T_u less than the oven temperature but larger than the values selected herein where, as a rough limiting estimate, that temperature is considered to be the arithmetic mean of the oven and droplet temperatures. Figure 4 shows the measured initial upward flame velocities and the calculated laminar burning velocities as functions of this assumed temperature.

It is seen from this figure that the agreement of the predictions with experiment is excellent if the heat-release parameter T_Q is in the range of 500 K to 1000 K. Flame-speed predictions for larger values of T_Q lie above the data, but the differences are not large, as the curves for T_Q approaching infinity show, so larger values might be acceptable. Since the selection of the temperature T_u is, however, uncertain, and in principle it could well be larger than shown, then the data would fall noticeably below these predictions. If that is indeed the case, and the previously assumed temperatures [3] are correct, then agreement would be improved by selecting a smaller value of T_Q, but that would lead to a stronger dependence of S_L on T_u than is observed, thereby still indicating a significant disagreement of the predictions with experiment. The comparisons shown in the figure therefore seem to be the best, the present choice made for T_u perhaps being the most realistic.

As indicted in the introduction, the predictions previously compared with experiment in [3] are incorrect, and when they are corrected it is found that predicted flame temperatures are higher, approaching 800 K, and, correspondingly, the predicted laminar burning velocities

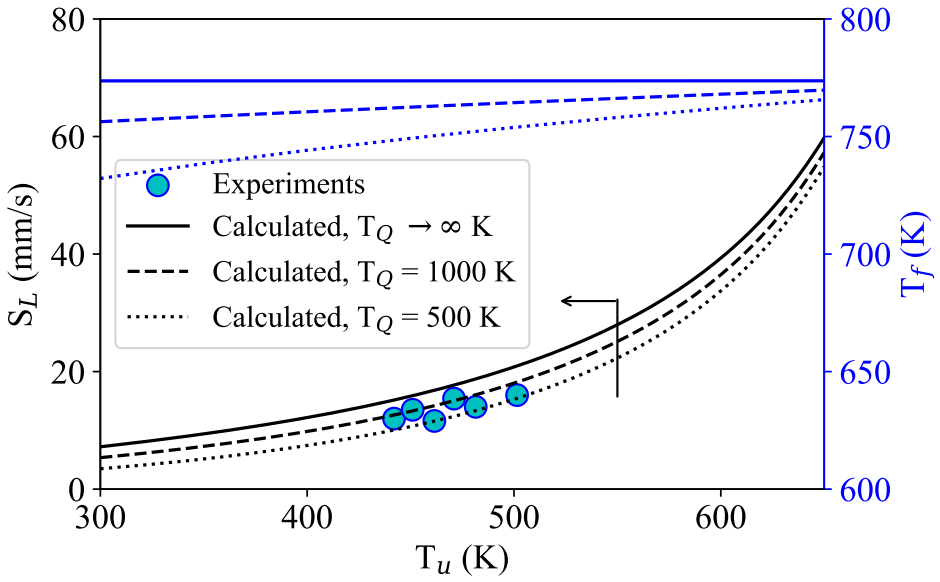


Figure 4: Theoretical and experimental dependence of the burning velocity on the initial temperature at 3 atm for cool flames of n-dodecane in air.

are much larger, resulting in S_L exceeding 80 mm/s, too high to be shown in Fig. 4. This remains true even after the addition of step 6, which reduces the burning velocity but was not included previously [3]. The effect on predictions of omitting step 7 thus is substantially more pronounced for premixed flames than for diffusion flames. That is due to the region of K production extending all the way to the cold boundary for the premixed flame in the absence of step 7 (while it never extends to a boundary of a diffusion flame), resulting in much larger concentrations of K and therefore much greater rates of heat release in the heat-release zone.

Experiments also were performed in nitrogen-diluted air at 3 atm for ambient temperatures of 650 K. The experiments are described in [7], although that publication was focused on autoignition times, and the results for burning velocities, shown in Fig. 5 (with error bars indicating uncertainties) were obtained only through later analysis of the data. The comparisons of predictions of the present model, employing 1000 K for T_Q, with results of those experiments, as is shown in Fig. 5, demonstrate agreements well within the uncertainty bounds of the measurements. Although the experimental uncertainty is quite large, the predicted values and trend are seen to agree well with the measurements. This further bolsters the agreements seen in Fig. 4, favoring the applicability of the proposed reduced chemistry. Just as in the previous comparison, predicted burning velocities are much too large if step 7 is not included.

6. Conclusions

It may be concluded from these considerations that the seven-step reduced mechanism, along with the simplified structure model, presented herein, represents a definite improve-

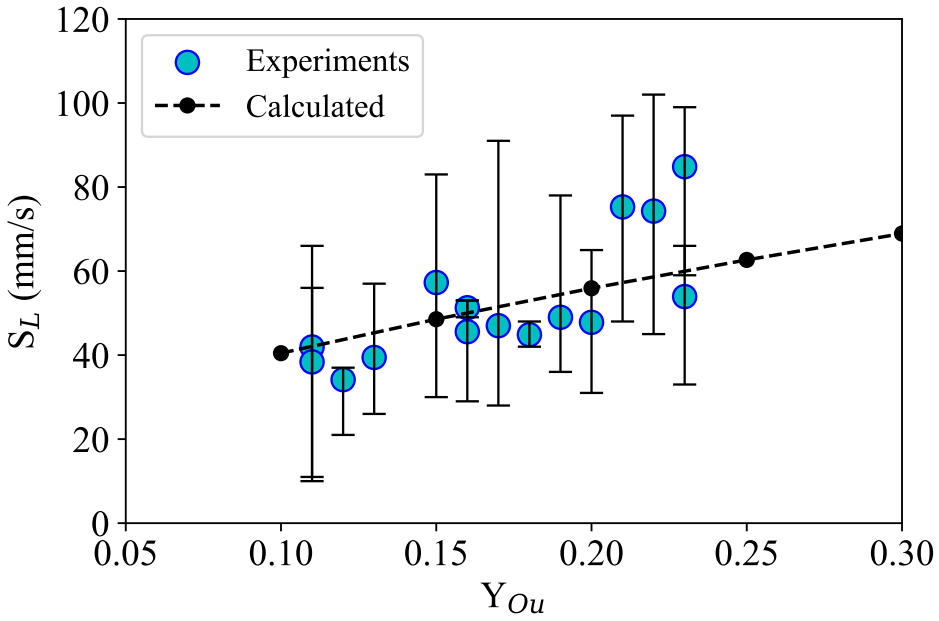


Figure 5: Theoretical and experimental dependence of the burning velocity on the oxygen mass fraction for n-dodecane in mixtures of nitrogen and oxygen at 3 atm with an initial temperature of 650 K.

ment over previous reduced-chemistry structures for premixed cool flames at levels of description below 10 elementary steps. For one of the reaction zones this structure model involves introduction of activation-energy asymptotics for a negative activation energy, never before done for premixed flames (although developed earlier for diffusion flames [6]). All seven steps of the reduced chemistry are needed if reasonable accuracy is to be obtained. Heat release corresponding to a temperature rise T_Q of about 1000 K is most reasonable for these experiments and is likely to apply rather broadly for n-alkane cool flames. That extent of heat release can occur with relatively small percentages of fuel and oxygen consumption, whence substantial leakage of reactants through the flame occurs. The chemistry is confined to relatively narrow regions in the vicinity of the position of attainment of the peak temperature (contrary to previous claims [3]). That flame temperature is determined entirely by the chemical kinetics, leading to concepts of flame temperatures being dependent upon equivalence ratios becoming irrelevant for these cool flames. The chemical-kinetic steps that actually produce this heat release have not been clarified at all here and are in need of further investigation.

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Supplementary materials

Supplementary material associated with this article can be found in the online version.

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