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One-step reduced kinetics for lean hydrogen–air deflagration

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ABSTRACT

A short mechanism consisting of seven elementary reactions, of which only three are reversible, is shown to provide good predictions of hydrogen–air lean-flame burning velocities. This mechanism is further simplified by noting that over a range of conditions of practical interest, near the lean flammability limit all reaction intermediaries have small concentrations in the important thin reaction zone that controls the hydrogen–air laminar burning velocity and therefore follow a steady state approximation, while the main species react according to the global irreversible reaction $2H_2 + O_2 \rightarrow 2H_2O$. An explicit expression for the non-Arrhenius rate of this one-step overall reaction for hydrogen oxidation is derived from the seven-step detailed mechanism, for application near the flammability limit. The one-step results are used to calculate flammability limits and burning velocities of planar deflagrations. Furthermore, implications concerning radical profiles in the deflagration and reasons for the success of the approximations are clarified. It is also demonstrated that adding only two irreversible direct recombination steps to the seven-step mechanism accurately reproduces burning velocities of the full detailed mechanism for all equivalence ratios at normal atmospheric conditions and that an eight-step detailed mechanism, constructed from the seven-step mechanism by adding to it the fourth reversible shuffle reaction, improves predictions of O and OH profiles. The new reduced-chemistry descriptions can be useful for both analytical and computational studies of lean hydrogen–air flames, decreasing required computation times.

1. Introduction

Increased interest in the use of hydrogen has intensified needs for better understanding of its combustion behavior, for reasons of safety as well as in engine applications. Besides the necessity of being able to describe hydrogen–air ignition characteristics [1], it is especially desirable to focus on deflagrations in fuel-lean hydrogen–air mixtures, notably in hazard contexts, where release of low concentrations of hydrogen may lead to continued flame spread. As computational capabilities advance, increased use is being made of electronic computers to assess different combustion scenarios. With rare exceptions [2], full detailed hydrogen chemistry remains too complex to be used in related computational studies. Reliable reduced chemistry for lean hydrogen–air deflagrations therefore is needed for obtaining predictions computationally that can be applied ultimately for judging how to handle hydrogen in the built environment.

The hydrogen oxidation chemistry, involving only H_2, O_2, H_2O, H, O, OH, HO_2 and H_2O_2, from a global-reaction viewpoint is no more than a six-step mechanism, there being two atom (or element) conservation equations for the eight chemical species. In other words, although there are many more elementary chemical-kinetic reactions, there are only six independent differential equations for species conservation with nonzero chemical source terms. Various mechanisms that are reduced to fewer than six steps have been proposed and tested in the literature. These reductions evolved from pioneering investigations of steady-state and partial-equilibrium approximations by Dixon-Lewis [3] and others. A four-step mechanism with H_2O_2 and HO_2 assumed to be in steady state has been found to be accurate for laminar diffusion flames, for example [4]. For fuel-lean deflagrations, a three-step mechanism has been investigated in which H_2O_2 is absent and O and HO_2 are in steady states [5], and a two-step mechanism in which all reaction intermediates except H obey steady-state approximations has been shown to be reasonable [6] and has been employed to describe lean and stoichiometric hydrogen–air deflagration velocities through rate-ratio asymptotics [7].

It has long been believed that a one-step systematically reduced mechanism would be too inaccurate for any realistic application. However, it will be shown below that over a range of equivalence ratios adjacent to the lean flammability limit the concentrations of all chemical intermediates are small enough for them to follow

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Table 1
The 7-step mechanism with rate coefficients in the Arrhenius form $k = AT^n \exp(-T_a/T)$ as given in [9].

Reaction		A[a]	n	T_a [K]
1. $H + O_2 \rightleftharpoons OH + O$		3.52×10^{16}	-0.7	8590
2. $H_2 + O \rightleftharpoons OH + H$		5.06×10^{4}	2.67	3166
3. $H_2 + OH \rightleftharpoons H_2O + H$		1.17×10^{9}	1.3	1829
4f. $H + O_2 + M \rightarrow HO_2 + M$[b]	k_0	5.75×10^{19}	-1.4	0
	k_∞	4.65×10^{12}	0.44	0
5f. $HO_2 + H \rightarrow OH + OH$		7.08×10^{13}	0	148
6f. $HO_2 + H \rightarrow H_2 + O_2$		1.66×10^{13}	0	414
7f. $HO_2 + OH \rightarrow H_2O + O_2$		2.89×10^{13}	0	-250

[a] Units are mol, s, cm^3, and K.

[b] Chaperon efficiencies are 2.5 for H_2, 16.0 for H_2O, and 1.0 for all other species; Troe falloff with $F_c = 0.5$ [16].

accurately a steady state approximation, while the main reactants obey the overall irreversible reaction $2H_2 + O_2 \rightarrow 2H_2O$, with a global hydrogen-oxidation non-Arrhenius rate determined by those of the elementary reactions of the starting detailed mechanism, shown in Table 1. This one-step reduced mechanism is seen to provide reasonable predictions of limits for lean deflagrations as well as good results for deflagration velocities for conditions near the lean flammability limit. For richer mixtures, radical concentrations in the reaction layer increase, and their associated steady-state approximations, especially that of H, become less accurate, leading to the failure of the one-step reduced kinetics, which away from the flammability limit must be replaced by the two-step or three-step descriptions previously derived [5,6]. These limitations of the one-step mechanism are explored, and the simplifications of the chemistry that lead to the one-step approximation are evaluated. The one-step result is explicit and could readily be implemented in future codes for the calculation of lean hydrogen combustion in complex configurations.

2. Short chemistry description

Among the different detailed hydrogen–oxygen kinetic mechanisms available in the literature, the so-called San Diego Mechanism [8] used in the following development has been tested recently and for most conditions was shown to give excellent predictions of laminar burning velocities v_l [9], as can be seen in Fig. 1, which compares numerical results obtained with the COSILAB code [10] with three different sets of experimental data [11–13]. The computations assume adiabatic isobaric planar-flame propagation with pressure $p = 1$ atm and initial temperature $T_u = 300$ K. The agreement between the experimental and numerical results is seen to be excellent when thermal diffusion is taken into account in the numerical description, except for very lean flames with equivalence ratio $\phi < 0.4$, where the numerical integrations tend to underpredict flame velocities, independent of cross-transport effects of thermal diffusion, suggesting that premixed combustion near the lean flammability limit does not occur in the form of a uniform planar front, a result to be anticipated from concepts of cellular instabilities.

A second set of computations, now with thermal diffusion excluded, is also shown in the figure. In agreement with earlier conclusions [14], the simplified transport description produces somewhat less satisfactory results, leading to overpredictions in flame velocities on the order of 10% for stoichiometric and moderately rich mixtures. This difference is attributable to Soret diffusion of H_2 out of the controlling reaction zone, towards the hot boundary, where the temperature is much higher at these near-stoichiometric conditions. For the fuel-lean mixtures of interest here, however, the temperature of the controlling reaction zone is not very different from the maximum temperature, so that the Soret effect is much less important for planar conditions, and it is seen in Fig. 1 that the resulting differences become negligible for lean flames. Since it is possible to focus most directly on the chemistry by excluding transport complexities, thermal diffusion will be omitted in the following development, and therefore the numerical results represented by the thin solid line in Fig. 1 will be taken as the basis for comparison with those to be obtained below. Since effects of nonplanar diffusion will not be investigated here, the lean-flame experimental results will not be considered further; they are, however, addressed elsewhere [15].

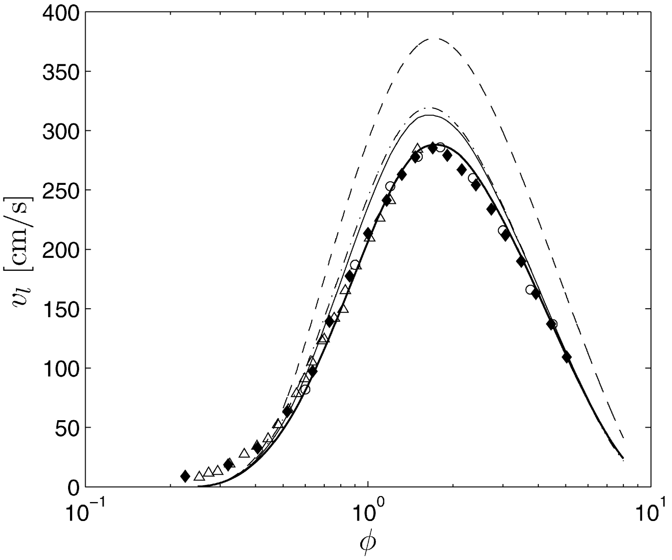

Fig. 1. The variation with equivalence ratio of the propagation velocity of premixed hydrogen–air flames for $p = 1$ atm and $T_u = 300$ K as obtained from experiments ([11]: diamonds; [12]: triangles; [13]: circles), from numerical integrations with the detailed chemistry and thermal diffusion included (thick solid curve) and with thermal diffusion excluded (detailed mechanism: thin solid curve; 9-step short mechanism: dot-dashed curve; 7-step short mechanism: dashed curve).

The San Diego Mechanism [8], of 21 reversible steps, is simplified further by noticing that, for hydrogen–oxygen systems, nine elementary reactions, only three of which are reversible, suffice to describe accurately hydrogen–air laminar burning velocities over the whole range of flammability conditions at pressures sufficiently below the third explosion limit of the hydrogen–oxygen system. This short mechanism includes the seven reactions shown in Table 1, together with the recombination reactions $H + H + M \rightarrow H_2 + M$ and $H + OH + M \rightarrow H_2O + M$, which become important for sufficiently rich mixtures, where the high temperatures lead to large radical concentrations, promoting two-radical reactions. Flame velocities computed with these 9 elementary reactions with thermal diffusion neglected are also included in Fig. 1, showing excellent agreement with the detailed-chemistry computations.

For mixtures that are very fuel lean, of interest in the present analysis, radical concentrations take on very small values, causing the direct recombination reactions $H + H + M \rightarrow H_2 + M$ and $H + OH + M \rightarrow H_2O + M$, which require three-body collisions involving two radicals, to become very slow compared with reaction 4f of Table 1 [7]. The chemistry description reduces then to the seven steps shown in Table 1, which include the three reversible shuffle reactions 1–3, the irreversible recombination reaction 4f, and the three irreversible HO_2-consuming reactions 5f–7f. The table shows the rate constants for all reactions, determining their dependence on the temperature T, except for the reverse of the shuffle reactions, whose rate constants must be obtained from the corresponding equilibrium constants. In calculating the pressure dependence of the reaction-rate constant $k_{4f} = Fk_0/(1 + k_0 C_M/k_\infty)$ we have evaluated the falloff factor F from the general expression derived in [16] and present in [10] and in