Hydrogen combustion mechanism extended by reactions of excited species

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Overview

Macroscopic characteristics of fuel + oxidizer mixtures, such as ignition delays, flammability limits or laminar burning velocity, often impose constraints on efficiency and safety of practical combustion appliances. Enhancement and control of combustion processes is therefore highly important, especially if it can be achieved by modification of the mixture reactivity without changing the equivalence ratio or mass flow into a combustion device. Different scenarios, combined in a concept of plasma-assisted combustion, have been proposed, such as electrical discharge through the reacting mixtures or generation of active species, ozone, singlet oxygen, etc., upstream the oxidizer flow. Owing to very limited experimental evidences, the individual effects of exited species on hydrogen combustion are often analyzed numerically.

Model development

In the present study recently updated hydrogen combustion mechanism [1] was combined with ozone decomposition reactions [2] and extended by reactions of excited species: $O(^1D)$, $OH(^2\Sigma^+)$, and $O_2(a^1\Delta g)$. The reliability and the accuracy of the rate constants pertinent to these excited species were evaluated. Many reactions proposed in the literature and implemented in other kinetic schemes were found irrelevant or insignificant. The new mechanism for hydrogen combustion was then validated in comparison with commonly accepted sets of laboratory experiments. It was naturally expected that new reactions incorporated into the model should normally not affect its predicting ability for "thermal" combustion of H_2, i.e. in the absence of excited species in the initial mixtures. Contemporary detailed kinetic schemes silently ignore reactions of ozone and of excited species. For instance, reactions of ozone are not included since Dougherty and Rabitz [3] demonstrated that pertinent chemistry is not important over all conditions of hydrogen oxidation covering three explosion limits. Although possible channels of excited atomic oxygen formation were considered [4], their role remained uncertain.

Model validation

The model validation showed that predictions of ignition, oxidation, flame burning velocities and flame structure of hydrogen - oxygen - inert mixtures are indistinguishable or very close to those of the basic mechanism [1] at all conditions, except for hydrogen oxidation in a flow reactor close to explosion limit. It was further demonstrated that singlet oxygen formed in reaction $H_2 + O_2(1\Delta) = H + HO_2$ at ppm levels may notably accelerate the process. This finding certainly calls for revisiting this reaction both experimentally and with theoretical calculations. Kinetic role of $O(^1D)$ and $OH(^2\Sigma^+)$ in the "thermal" combustion of H_2 was found negligible.

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Flame enhancement

In addition, hydrogen + air flame enhancement by singlet oxygen was modeled. It was demonstrated that the burning velocity increase with 1% of $O_2(a^1\Delta g)$ seeded into the air is rather modest. Moreover, purely thermal effect due to additional enthalpy brought to the mixture exceeds chemical flame enhancement by the singlet oxygen. Thus, if the energy required for production of $O_2(1\Delta)$ is directly used for the mixture preheating, the flame acceleration would be more efficient. Model analysis, therefore, clearly demonstrates that some concepts of plasma-assisted combustion by $O_2(1\Delta)$ based on the predictions of earlier kinetic mechanisms could be over-optimistic.

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References

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