On the role of excited species in hydrogen combustion

Alexander A. Konnov*

Division of Combustion Physics, Lund University, Lund, Sweden

ABSTRACT

Recently updated hydrogen combustion mechanism was combined with ozone decomposition reactions 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 against commonly accepted sets of laboratory experiments. It was expected that new reactions incorporated into the model should not affect its predicting ability for "thermal" combustion of H_2, i.e. in the absence of excited species in the initial mixtures. 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 at all condition, 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. Kinetic role of $O(^1D)$ and $OH(^2\Sigma^+)$ in the "thermal" combustion of H_2 was found negligible. 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.

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1. Introduction

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 [1].

For the simplest hydrogen + air system it was demonstrated that ignition delays can be significantly shortened under the action of a high-voltage nanosecond discharge that was also successfully reproduced by the detailed kinetic model including electronically excited species [2]. Furthermore, direct current low pressure glow discharge was shown to substantially reduce induction length of the $H_2 + O_2$ mixture ignition in a flow reactor [3]. This experiment was simulated using one-dimensional [4] and 2D models [5] with the emphasis on the relative role of singlet states of oxygen and odd oxygen $(O + O_3)$. Indeed, the discharge generates not only excited singlet states of oxygen, $O_2(a^1\Delta g)$ and $O_2(b^1\Sigma g+)$, but also ozone and excited atomic oxygen $O(^1D)$. Depending on the distance from the generator to combustion zone, pressure, gas composition, and treatment of the surfaces, excited species may survive or not [5–7]. The only demonstration of the hydrogen flame acceleration caused by generation of active species in the low-pressure glow discharge was realized in the pioneering experiment of Basevich and Kogarko [8]. This effect was attributed to the enhanced chain branching in the reaction $H + O_2(a^1\Delta g)$ [8, 9].

Owing to very limited experimental evidences, the individual effects of exited species on hydrogen combustion were often analyzed numerically. Starik and co-authors extensively investigated different types of excitation, such as vibrational [10–13], electronic, caused by discharge [4, 13–18], resonant laser radiation [19–21], or laser-induced decomposition of ozone [22]. The effects of excited species were modeled at the conditions of ignition, detonation, and flame propagation. In all cases it was claimed that excited species may effectively shorten ignition delays [4, 13, 14, 22], accelerate burning velocities [16, 17], and improve stabilization of detonation waves in supersonic flows [11–15, 18–20].

Other relevant studies of hydrogen combustion affected by excited species are not so numerous, yet tackle photochemical ignition of premixed H_2 + air by excimer lasers [23], acceleration of detonation

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* Corresponding author.
  E-mail address: Alexander.Konnov@forbrf.lth.se

development by addition of ozone [24], decrease of ignition delays [25–29], and increase of the burning velocities in hydrogen + air mixtures [26].

The detailed kinetic models developed and implemented in these numerical works are fundamentally diverse both in the ground-state (thermal) hydrogen chemistry and in the reactions of excited species. Chukalovsky et al. [5] compared the MSU (Moscow State University) mechanism [25, 30], the mechanisms developed by Starik and Titova in 2003 [19], by Starik et al. in 2010 [13], and updated mechanism based on the works of Popov [27–29]. They found that at the conditions of experimental study of Smirnov et al. [3], the most important initiation reaction is

$$H_2 + O_2 = OH + OH \tag{X1}$$
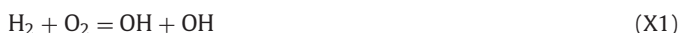
in the MSU mechanism, in the earlier model of Starik and Titova [19], and in their own model [5]. Admitted that this reaction is an artificial "brutto process" they argued that its inclusion is required for proper description of the thermal self-ignition of hydrogen. This and other reactions to be excluded from the hydrogen kinetic mechanism are discussed in the present work.

Most recent models of Starik et al. [13, 18, 31, 32] seem to properly incorporate reaction

$$H_2 + O_2 = H + HO_2 \tag{14}$$

as initiation step in the absence of excited species. However, overall performance of these mechanisms in hydrogen combustion modeling was shown to be unsatisfactory. Olm et al. [33] presented extensive analysis of the performance of 19 recent hydrogen combustion models in comparison with ignition measurements in shock tubes and rapid compression machines, burning velocity measurements and concentration–time profiles in jet-stirred and flow reactors, covering wide ranges of temperature, pressure and equivalence ratio. The analysis indicates that the performance of the mechanism of Starik et al. [31] is far from being satisfactory and cannot be recommended for the modeling of hydrogen combustion.

Reactions pertinent to excited singlet states of oxygen and ozone implemented in the most recent models of Starik et al. [13, 32], of Popov [5, 29], and in the MSU mechanism [25, 30] are most often inconsistent and largely different in rate constants as well. The inconsistency is manifested in the irreversibility of many reactions with excited species. It was demonstrated [34] that due to the incompleteness of the MSU mechanism (absence of many reverse reactions) it predicts an incorrect balance between O atoms, excited and ground state oxygen in ozone flames. It should be noted, however, that ozone reactions from the MSU mechanism [25, 30] excluding excited oxygen species are mostly balanced, and their implementation in the recent studies of combustion enhancement by ozone [6, 35–39] is justified. Yet, conclusions based on the complete set of reactions taken from the MSU mechanism by Ombrello et al. [7], and by Bourig et al. [26], should be treated cautiously.

In the present study recently updated hydrogen combustion mechanism [40] is combined with ozone decomposition reactions [34] and extended by reactions of excited species: $O(^1D)$, $OH(^2\Sigma^+)$, $O_2(a^1\Delta g)$. The goal of the present work was to evaluate the reliability and the accuracy of the rate constants pertinent to these excited species, and to validate and analyze kinetic mechanism predictions at high temperatures. A possible role of excited species in hydrogen combustion is evaluated and analyzed.

2. Reaction mechanism

2.1. Species, thermodynamic and transport parameters

Coherent laser radiation may excite molecular oxygen to $O_2(a^1\Delta g)$ or $O_2(b^1\Sigma g+)$ singlet states of oxygen that could individually affect

combustion chemistry [19, 20, 41]. However, the $O_2(b^1\Sigma g+)$-state is very short lived and due to physical quenching relaxes quickly to the lowest lying excited state, $O_2(a^1\Delta g)$. Collisional deactivation prevails at temperatures relevant to atmospheric chemistry (up to 370 K) [42–44] with negligible importance of chemical reactions. Kozlov et al. [45] demonstrated that the physical deactivation dominates in the collision of $O_2(a^1\Delta g)$ and $O_2(b^1\Sigma g+)$ with H_2 up to temperatures of 780–790 K. One may conclude that in the modeling of any technological combustion concept with upstream generation of $O_2(b^1\Sigma g+)$-state, such as premixed flames, it can be represented by $O_2(a^1\Delta g)$-state. Thus in the present mechanism only the $O_2(a^1\Delta g)$-state is included and in the following referred to as singlet oxygen. The triplet ground state of oxygen, $O_2(X^3\Sigma g-)$, is always termed O_2. Likewise vibrationally excited species are not considered in the model. Hydrogen polyoxides, HOOOH, HOOOOH and radical HO_3 are not included as well. Although these species have recently received some attention as possible temporary reservoir of OH in atmosphere [46, 47], they were never considered in combustion models, except in [48].

Thermodynamic data were taken from the recent database of Goos et al. [49]. All reactions in the mechanism are reversible. Rate constants of the reverse reactions are calculated from the forward rate constants and thermodynamic data.

The choice of the transport parameters implemented in the Chemkin package [50] for flame modeling was discussed by Alekseev et al. [40]. Following recommendations of Brown et al. [51] recently measured diffusion coefficients for OH, HO_2, and ozone [52] are adopted in the present model. Transport properties of excited species were assumed equal to those of corresponding ground-state species.

2.2. Reactions

The detailed reaction mechanism developed in this study is listed in Table 1. The rate coefficients in the present work are given in cm^3 mol s units, while activation energies are in cal/mole. In the following, the sources of the rate constants are outlined and particular choices are discussed. Also temperature ranges over which the rate constants were determined and associated uncertainties are presented. An estimated uncertainty factor, UF, implies that the rate constant is expected to be in the range $k/UF < k < k*UF$.

Reactions comprising updated hydrogen combustion mechanism as well as ozone decomposition reactions and associated rate constants have been discussed recently [34, 40], therefore they are only mentioned here if alternative product channels were proposed in in the most recent models of Starik et al. [13, 32], of Popov [5, 29], and in the MSU mechanism [25, 30]. The numbering of the reactions included in the present mechanism corresponds to Table 1, while reactions excluded from the model are listed in Table 2 with numbers (X1), (X2), etc.

2.2.1. Reactions of initiation
Reaction

$$H_2 + O_2 = H + HO_2 \tag{14}$$

is adopted as the main initiation step of hydrogen oxidation in all contemporary models including those of Hong et al. [53], Burke et al. [54] and Keromnes et al. [55]. The second channel of initiation in hydrogen–oxygen mixtures

$$H_2 + O_2 = OH + OH \tag{X1}$$

is of negligible importance as discussed elsewhere, e.g., [54, 56], and can be excluded from the model. Chukalovsky et al. [5] had to implement reaction (X1) with unrealistically high rate constant to increase reactivity of their model at the conditions of experiments of