

Kinetic Effects of Air Contamination on the Combustion of Hydrogen

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Introduction

Besides the possible future switch to a hydrogen-based economy, there are many interests in studying the kinetic of combustion, oxidation, and ignition of hydrogen, particularly in relation to the development of advanced air-breathing propulsion systems. A good knowledge of the kinetic of hydrogen oxidation in the presence of NO_x (NO and NO_2) is of particular importance since these species are commonly present in vitiated air streams used for supersonic combustion tests. Unfortunately very few data are available in the literature. This study presents new kinetic results (mole fractions of reactants and products) obtained for the oxidation of hydrogen in diluted conditions, and perturbed by the addition of various concentrations of NO or NO_2 . We used a jet-stirred reactor operating in the temperature range 700-1150K and for pressures of 1 to 10 atm, and equivalence ratios, Φ , from 0.1 to 2.5. A detailed kinetic modelling of the present data, of the ignition of hydrogen-air and hydrogen- NO_x -air mixtures, and of the burning velocities of hydrogen-air mixtures was performed.

Experimental

We used a spherical fused silica jet-stirred reactor (JSR) of 29.5 cm^3 surrounded by a regulated electrical oven (c.a. 3 kW) wrapped with ceramic wool and located inside a stainless-steel pressure resistant jacket allowing operation up to 10 atm [1]. The fuel, hydrogen, was 99.995 pure, oxygen was 99.995% pure, and nitrogen was of regular purity (<50 ppm of O_2 ; <1000 ppm of Ar; <5 ppm of H_2). The flow rates were measured and regulated by thermal mass-flow controllers. The reactants were diluted by a flow of nitrogen. The fuel and the mixture O_2 - N_2 were pre-heated and flowed separately up to the mixing point at the entrance of the injectors. The experiments were performed at fixed residence time, τ , and variable temperature. Previous residence time distribution studies showed that this reactor operates under macro-mixing conditions [1]. As before [1,2], a good thermal homogeneity was observed along the vertical axis of the reactor by thermocouple measurements. A Pt/Pt-Rh 10% thermocouple, located inside a thin-wall fused-silica tube, <0.5 mm, to prevent catalytic reactions on the metallic wires of 0.1 mm in diameter was used. Since a high degree of dilution was used, the temperature rise due to the reaction was generally < 30 K. Low pressure samples of the reacting mixtures were taken by sonic probe sampling and collected in 1 liter Pyrex bulbs at c.a. 50 mbar for immediate gas chromatography (GC) analyses. In order to improve the GC detection, these samples were pressurized at 0.8 bar before injection into the GC column, using a glass home-made piston. Capillary columns were used with a thermal conductivity detector (TCD). For hydrogen measurements, a GC operating with nitrogen as carrier gas and a TCD was used. On-line Fourier transform infrared (FTIR) analyses of the reacting gases were also performed by connecting the sampling probe to a temperature controlled (140 °C) gas cell (10 m path length) via a Teflon heated line (130 °C). The pressure sample in the cell was 200 mbar. This analytical system allowed the measurements of H_2 , O_2 , H_2O , NO, N_2O , and NO_2 . Table 1 summarizes the experimental conditions of the present study.

Table 1. Experimental conditions in the JSR study.

Initial mole fractions				Φ	τ/s	P/atm
H ₂	O ₂	NO	NO ₂			
0.01	0.003333 to 0.05	0.0002	0	0.1; 0.2; 0.5; 1.0; 1.5	1	10
0.01	0.002 to 0.05	0	0	0.1; 1.5; 2.5	1	10
0.01	0.003333 to 0.05	0	0.00005	0.1; 0.2; 0.5; 1.0; 1.5	1	10
0.01	0.0025 to 0.05	0.0002	0	0.1; 0.2; 0.5; 1.0; 1.5; 2.0	0.24	1
0.01	0.005 to 0.025	0	0	0.2; 0.5; 1.0	0.24	1
0.01	0.003333 to 0.025	0	0.00005	0.1; 1.0; 1.5	0.24	1

Modelling

For the JSR modelling, we used the PSR computer code [3]. The kinetic reaction mechanism used here derives from the detailed chemical kinetic reaction mechanism previously used for the kinetic modelling of the hydrogen-enriched natural gas oxidation under atmospheric pressure conditions [4], of various fuels from methane to kerosene [2], and of the mutual sensitization of the oxidation of methane and NO in a JSR and flow reactors [5]. It includes 34 species and 56 reversible reactions. This kinetic reaction mechanism, including thermochemical data, is available from the authors (dagaut@cnr-orleans.fr). The pressure-dependencies of unimolecular reactions and of some pressure-dependent bimolecular reactions were taken into account when information was available (i.e., $k(P, T)$). The rate constants for the reverse reactions were computed from the forward rate constants and the appropriate equilibrium constants calculated using thermochemical data [5]. For the flame modelling, we used the Premix computer code [6]. A grid of 300 mesh points was used. The calculations were performed taking into account the Soret effect. Multi components diffusion coefficients were computed. The ignition delays were modelled using Senkin [7] assuming the validity of the constant volume approximation.

Results and Discussion

Examples of the present JSR results are given in Figs. 1-2. They show that both NO and NO₂ added at low levels of concentration favour the oxidation of the fuel. Also, Fig. 2 shows the mutual sensitization of the oxidation of H₂ and NO. These figures also serve to demonstrate the ability of the proposed scheme to represent the present data obtained in a broad range of conditions. Examples of the model validations for the ignition of H₂-air and H₂-NO-air and for flame speeds are given in Figs 3-4. A good agreement between these literature data and the proposed model was achieved.

Since we were confident in this proposed kinetic model, it was used to perform reaction paths analyses and first-order sensitivity analyses. The kinetic modelling indicates that the sensitization of the oxidation of hydrogen by NO in stoichiometric conditions is due to the following sequence of reactions. OH radicals are produced by $\text{NO} + \text{HO}_2 \Rightarrow \text{NO}_2 + \text{OH}$. The hydroxyl radicals are responsible for the oxidation of the fuel via the reaction $\text{H}_2 + \text{OH} \Rightarrow \text{H}_2\text{O} + \text{H}$. This reaction also serves to recycle HO₂ via $\text{H} + \text{O}_2 + \text{M} \Rightarrow \text{HO}_2 + \text{M}$. As a result, the oxidation of the fuel is favoured by the addition of NO. The last reaction participating to this mechanism is $\text{NO}_2 + \text{H} \Rightarrow \text{NO} + \text{OH}$ that recycles NO and contributes significantly to the production of OH radicals. The total pressure has no significant effect on the relative importance of these reactions over the pressure range 1-10 atm.

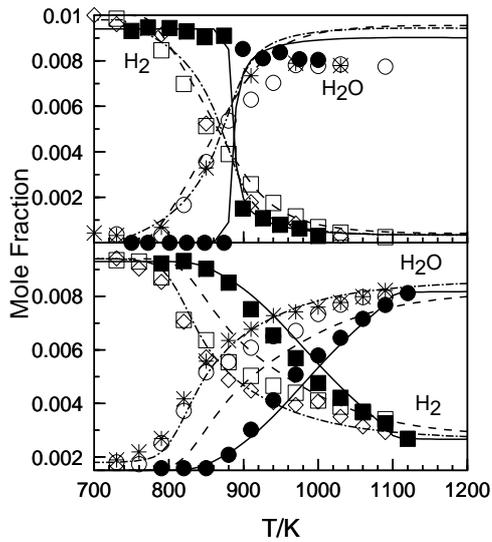


Fig.1 Sensitization of the oxidation of H_2 in a JSR at $\Phi=1$, 1 atm (top: 0.24s, 1000 ppm of H_2 , no NO_x : ■, ●, -; 200 ppm of NO : □, ○, - -; 70 ppm of NO_2 : ◇, *, -.-) and 10 atm (bottom: 1s, same symbols and lines as in the top figure).

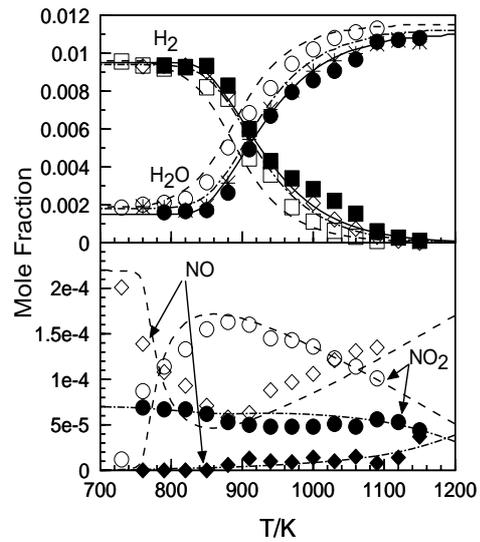


Fig. 2 Mutual sensitization of the oxidation of H_2 and NO at $\Phi=0.1$, 10 atm, 1000 ppm of H_2 , 1s (top: no NO_x : ■, ●, -; 200 ppm of NO : □, ○, - -; 70 ppm of NO_2 : ◇, *, -.-; bottom: with 200 ppm of NO , - - and open symbols; with 70 ppm of NO_2 , -.- and filled symbols).

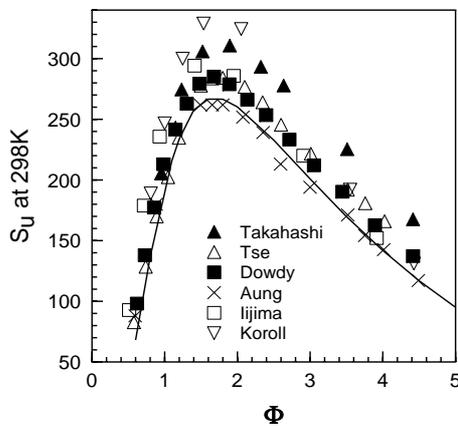


Fig. 3 Variation of the flame speed of H_2 -air mixtures at 298 K and 1 atm as a function of equivalence ratio. The data (symbols: ▲ [8], △ [9], ■ [10], × [11], □ [12], ▽ [13]) are compared to the modeling (line).

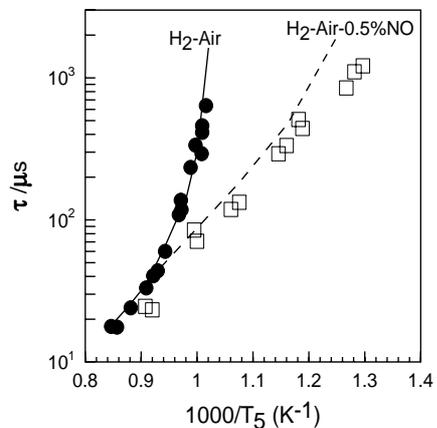


Fig. 4 Effect of the addition of 0.5% of NO on the ignition of a stoichiometric H_2 -air mixture at 2 atm. The data of [14] (symbols) are compared to the modelling (lines).

According to this modelling, the sensitization of the oxidation of hydrogen by NO_2 in stoichiometric conditions is due to the following sequence of reactions. As when NO was added, the fuel is mostly oxidized by reaction with OH radicals. It also reacts with atomic oxygen via $H_2 + O \Rightarrow OH + H$. The extra production of OH radicals is due to the reactions $NO_2 + H \Rightarrow NO + OH$ and $NO + HO_2 \Rightarrow NO_2 + OH$, whereas the main routes to OH are: $H + HO_2 \Rightarrow OH + OH$ and $H_2 + O \Rightarrow OH + H$. Finally, NO is recycled to NO_2 via $NO + HO_2 \Rightarrow NO_2 + OH$. As when NO

was added, the main reaction producing HO₂ is $H + O_2 + M \Rightarrow HO_2 + M$. The total pressure has no significant effect on the importance of these reactions over the pressure range 1-10 atm.

Whereas the effect of NO₂ on the oxidation of H₂ in the JSR, over the entire range of conditions of this study, is well predicted by this model using the rate constant of [15] for the reaction $NO_2 + H_2 \Rightarrow HONO + H$, a much higher rate constant would be necessary to reproduce the ignition delays of [14]. That would be incompatible with the present measurements and those of [15].

Conclusion

New experimental results were obtained for the oxidation of H₂ in diluted conditions in a JSR at 1-10 atm. The effect of the addition of NO and NO₂ was studied. A detailed kinetic model is proposed to interpret the results. This model was also validated against the available data for the ignition of hydrogen-air mixtures and H₂-air-NO_x mixtures, and for the flame speeds of hydrogen air mixtures. The proposed model allows a good representation of the set of data considered here. The present results confirm the rate constant of [15] for the reaction of NO₂ with H₂.

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