

Elementary reaction kinetics studies of interest in H₂ supersonic combustion chemistry

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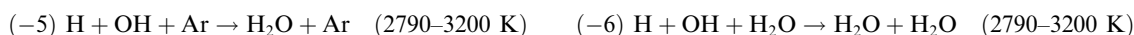
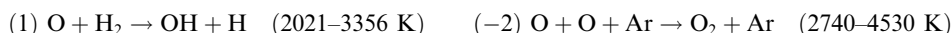
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Abstract

Elementary reactions of interest in H₂ supersonic combustion chemistry have been investigated using a shock tube technique connected to an atomic resonance absorption spectrophotometer. The rate constants for the reactions:



have been specified in the temperature range quoted respectively. The following rate coefficients were found:

$$k_1 = 7.1 \times 10^6 T^{2.1} \exp(-4140/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad k_{-2} = 1.8 \times 10^{17} T^{-1} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

$$k_{-3} = 3.6 \times 10^{17} T^{-1} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \quad k_{-4} = 6.75 \times 10^{18} T^{-1} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

$$k_{-5} = 3.75 \times 10^{21} T^{-2.1} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1} \quad k_{-6} = 6.75 \times 10^{22} T^{-2.1} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}.$$

The overall uncertainties in these expressions have been estimated by considering experimental parameters which contributed to uncertainties in the rate constants evaluation. These rate constants are compared to those reported previously in the literature. The effect of the studied reaction rate constants accuracy improvement on the H₂ supersonic combustion modeling has been investigated.

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Keywords: Elementary chemical kinetics; Supersonic combustion; High temperatures; Shock tube; Atomic resonance absorption spectrophotometry

1. Introduction

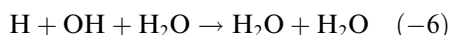
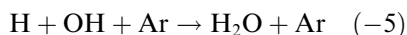
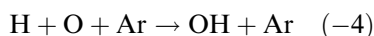
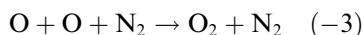
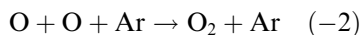
For years, propulsion systems more efficient than conventional aircraft or rocket engine have been sought. The effort to develop advanced propulsion systems capable to reach hypersonic speeds, greater than Mach 6, are induced by the requirement for cheaper and less pollutant vehicles. In supersonic combustors, such as supersonic combustors ramjets or scramjets, hydrogen

fuel is injected and burned into a supersonic flow of air. Due to the very short residence times of gases in combustors, the efficiency of this process is limited by fuel–air mixing dynamics and slow free-radical or atom recombination rates in nozzles. To simulate the combustion process, it is necessary to increase the accuracy of the chemical kinetics data. In particular, additional studies are required on (i) the two-body chain-branching and chain-propagating reactions responsible of the important atoms and radicals concentration in the combustor section and (ii) the atom and radical recombination reactions responsible for the chemical kinetic limitations in nozzles.

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Accordingly, we report here the results of new rate coefficient determinations for the reactions:



and the overall uncertainties in their corresponding expression.

Resonance absorption spectroscopy has been used to measure O-atom concentration behind reflected shock waves. The first to apply the atomic resonance absorption spectrophotometry (ARAS) method coupled to a shock tube to precise elementary reaction rate coefficients were Myerson and Watt [1]. They showed that resonance absorption is a very sensitive technique for measuring selected atoms at high temperatures. In particular, this technique allows to use low initial molar fractions of reactants, which improves the accuracy of the experiment (adiabatic conditions and reduced secondary reactions influence). Oxygen atom concentration was calculated from experimental O-atom absorption profiles and a calibration curve. Once, the reaction mechanism and the optimal experimental conditions were chosen in order to isolate the studied reaction, by using sensitivity analysis, its rate constant was deduced from the comparison between experimental O-atom profiles and computed simulations (SENKIN II [2]). The termolecular recombination rates are calculated from the equilibrium constant and the dissociation rates. After plotting the inferred experimental constants versus $1/T$ (or $\ln T$ for termolecular recombination reactions), rate constant expressions are determined by least-squares fitting all points.

2. Experimental

The experimental arrangement was described in earlier papers [3–5]. Briefly, it is a 78-mm inner diameter stainless steel shock tube with a 0.9-m driver section and a 4-m long driven section evacuated to less than 2×10^{-7} mbar and with a typical leak-plus-outgassing rate of the order of 8×10^{-7} mbar/min or less. An ARAS coupled to the shock tube is used to monitor O-atom profiles at the emission line of the O triplet at 130.5 nm. It is made up of (i) a light source, (ii) a vacuum UV monochromator, (iii) a special blind photomultiplier. The absorption measurements are made behind a reflected shock front through two thin MgF_2 windows, close to the end of the shock tube driven section. Oxygen atom concentration profiles are deduced from experi-

mental O-atom absorption profiles and a calibration curve. Because of the ARAS technique high sensitivity, all gases used are of ultrahigh purity: Ar = 99.9999%, N_2 = 99.9999%, N_2O = 99.998%, H_2 = 99.9999% and O_2 = 99.998%. Distilled water, generally employed for HPLC (99.9997% purity), is used after outgassing cycles with Ar and freeze-pump-thaw cycles. The different gas mixtures are prepared by partial pressure measurements and stored in a 10 l glass bulb. The pressures of H_2O used in the mixture preparation are always much less than the saturation vapor pressure at room temperature. The H_2O adsorption possibility on the shock tube and glass preparation system walls are investigated by mass spectrometry analysis and by adsorption rate measurements, respectively.

3. Results and discussion

3.1. $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ rate constant

Our investigation was motivated by the scattering of the rate-constant values proposed in the literature experimental results and the lack of data for temperatures higher than 2700 K. This results have been already published for this rate constant in the 2690–3360 K temperature range [4]. Briefly, the mixtures of N_2O and H_2 were highly diluted in Ar, at total pressures of about 250 kPa. The rate constant for this reaction presented an Arrhenius dependence over our temperature range:

$$k_1 = 9.25 \times 10^{14} \exp(-9740/T(K)) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The overall uncertainty in this expression had been estimated to be much less than $\pm 20\%$. The literature experimental results obtained in a larger temperature range showed a non-Arrhenius behavior of the rate coefficient versus temperature. Accordingly, we used on one hand N_2 as bath gas (and He as driver gas) and on the other hand N_2 as driver gas (and Ar as bath gas) in order to extend our experiments at lower temperatures (2020–2640 K). In the temperature range 2020–3360 K, we obtained the three-parameters expression:

$$k_1 = 7.1 \times 10^6 T^{2.1} \exp(-4140/T(K)) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

with an overall uncertainty estimated to be about $\pm 20\%$. Fig. 1 compares the present rate-constant expression with those reported by earlier investigators at high temperature [6–17]. Our final result is in good agreement with the only study realized above 2800 K by Natarajan and Roth [6]. The difference between their expression and ours does not exceed 8%.

3.2. $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$ rate constant

The rate coefficients for the reactions $\text{O}_2 + \text{Ar} = \text{O} + \text{O} + \text{Ar}$ have been the subject of an earlier paper in

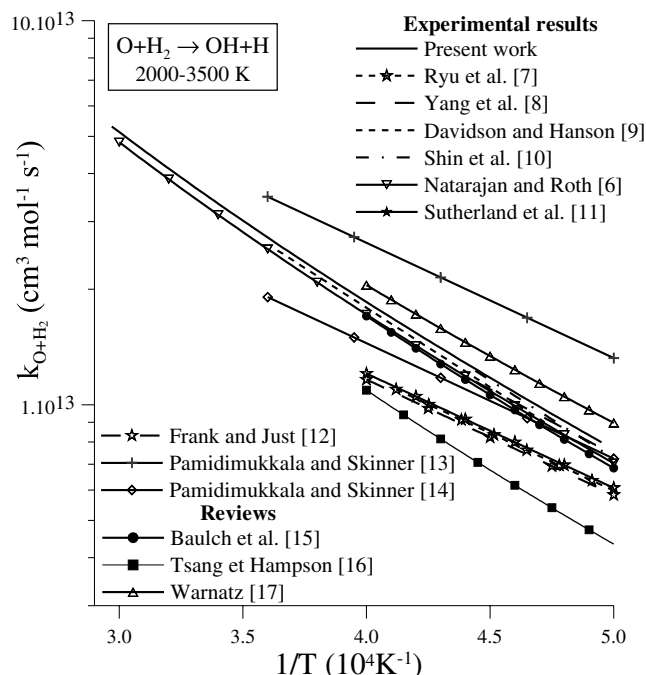


Fig. 1. Comparison between our determination and earlier rate-constant expressions for the reaction $O + H_2 \rightarrow OH + H$.

the temperature range 3000–4530 K [3]. Mixtures containing 26.5–146.6 ppm of O_2 in Argon had been shock-heated to a total pressure between 120 and 450 kPa. The following rate coefficients had been found:

$$k_2 = 3.4 \times 10^{14} \exp(-55,700/T(K)) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_{-2} = 1.8 \times 10^{17} T(K)^{-1} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1},$$

with overall uncertainties estimated to be about $\pm 30\%$.

Within the framework of the H_2 supersonic combustion chemistry study, it was interesting to study the reactions $O + O + N_2 = O_2 + N_2$, in order to precise the relative efficiency coefficient of N_2 with respect to argon as collision partner. Due to our too short shock-tube driver section which limits the observation time, O_2/N_2 mixtures could not be used directly. After verifying the validity of the earlier results of the $O_2 + Ar = O + O + Ar$ reaction rate constant in the temperature range 2740–3130 K and at total pressure of about 260 kPa, the rate constant for the reaction $O_2 + N_2 \rightarrow 2O + N_2$ has been specified using mixtures containing 300–10,000 ppm of O_2 diluted in N_2/Ar mixture, in the temperature range 2740–3460 K and at total pressure of about 190 kPa. The optimal percent ratio of N_2/Ar was 40/60. The relation between the dissociation rate, k_d , and the equilibrium constant K , $K = k_d/k_r$, was used to deduce the recombination rate of O-atoms by N_2 . In the studied temperature range, we found:

$$k_3 = 6.8 \times 10^{14} \exp(-55,700/T(K)) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_{-3} = 3.6 \times 10^{17} T(K)^{-1} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}.$$

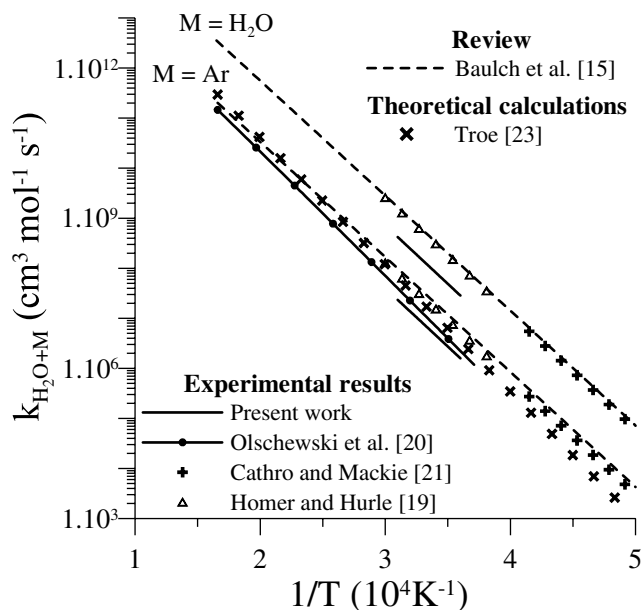


Fig. 2. Comparison between our determination and earlier rate-constant expressions for the reaction: $H_2O + M \rightarrow H + OH + M$.

A factor of 2 between the efficiencies of N_2 and Argon as collision partners was determined, which is in very good agreement with the result of Jerig et al. [18], who realized the first and last investigation on the $O_2 + N_2 \rightarrow 2O + N_2$ reaction. The overall uncertainty in the present expression is estimated to be about $\pm 35\%$, including the possible errors due to the uncertainties in

- (i) The calculated temperature and pressure behind reflected shock waves;

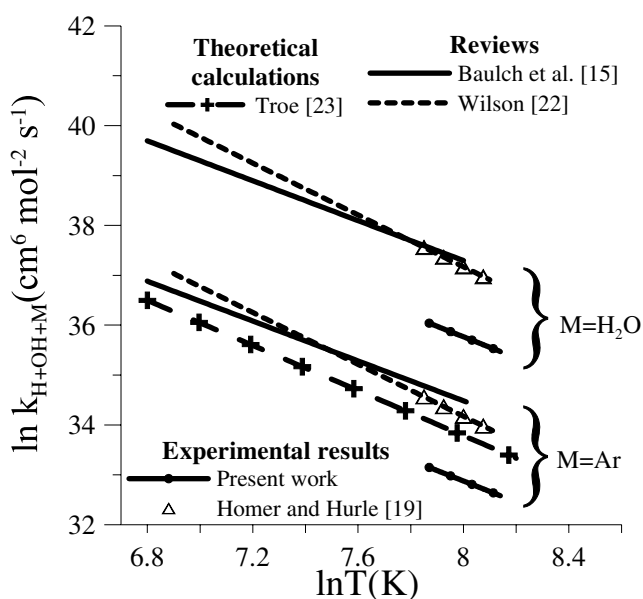


Fig. 3. Comparison between our determination and earlier rate-constant expressions for the reaction: $H + OH + M \rightarrow H_2O + M$.

- (ii) The mixture composition;
- (iii) The optical system calibration;
- (iv) The sensitive reaction mechanism rate coefficients;
- (v) The equilibrium constant estimate, for k_{-3} determination.

3.3. $H + O + M \rightarrow OH + M$ rate constant

The first experimental results for the $OH + Ar = H + O + Ar$ reaction have been presented in an earlier paper [5]. Experiments had been conducted in rich $H_2/O_2/Ar$ mixtures, at temperature between 2950 and

Table 1
Elementary reactions for modeling combustion of hydrogen in heated air

	Reaction		A	n	E/R	Ref.
1	$O + H_2 = OH + H$		3.72×10^6	2.17	4080	[6]
2	$H + O_2 = OH + O$		1.99×10^{14}	0	8460	[15]
3	$H_2 + OH = H_2O + H$		1.02×10^8	1.60	1660	[15]
4	$OH + OH = H_2O + O$		1.50×10^9	1.14	50	[15]
5	$H_2 + M = H + H + M$	$N_2/1.2/H/6/H_2/4/H_2O/15$	2.20×10^{14}	0	48,312	[24]
6	$H + O + M = OH + M$	$H_2O/5$	6.00×10^{16}	-0.60	0	[24]
7	$H + OH + M = H_2O + M$	$H_2O/6.3/H/2$	2.20×10^{22}	-2	0	[24]
8	$O + O + M = O_2 + M$	$H_2/3.67/N_2O/4.38$	1.00×10^{17}	-1	0	[24]
9	$O + O + N_2 = O_2 + N_2$		6.17×10^{15}	-0.50	0	[24]
10	$O + O + O_2 = O_2 + O_2$		7.98×10^{19}	-1.50	0	[24]
11	$H + O_2 + M = HO_2 + M$	$H_2/2.5/H_2O/16$	6.42×10^{18}	-1	0	[24]
12	$OH + OH + M = H_2O_2 + M$	$H_2O/6/H_2O_2/6/O_2/0.8$	1.30×10^{22}	-2	0	[24]
13	$H + HO_2 = OH + OH$		1.69×10^{14}	0	440	[15]
14	$H + HO_2 = H_2 + O_2$		6.62×10^{13}	0	1070	[16]
15	$H + HO_2 = H_2O + O$		1.18×10^{14}	0	1373	[25]
16	$H_2 + O_2 = OH + OH$		1.70×10^{13}	0	24,046	[26]
17	$HO_2 + O = O_2 + OH$		1.40×10^{13}	0	540	[27]
18	$HO_2 + OH = H_2O + O_2$		2.89×10^{13}	0	-250	[15]
19	$HO_2 + HO_2 = H_2O_2 + O_2$		2.00×10^{12}	0	0	[17]
20	$H_2O_2 + H = HO_2 + H_2$		4.80×10^{13}	0	4005	[16]
21	$H_2O_2 + H = H_2O + OH$		2.41×10^{13}	0	2000	[16]
22	$H_2O_2 + O = HO_2 + OH$		2.80×10^{13}	0	3220	[28]
23	$H_2O_2 + OH = HO_2 + H_2O$		1.00×10^{13}	0	905	[27]
24	$N_2 + O_2 = NO + NO$		9.10×10^{24}	-2.50	64,667	[29]
25	$O + N_2 = N + NO$		1.82×10^{14}	0	38,370	[30]
26	$NO + O = N + O_2$		3.80×10^9	1	20,834	[24]
27	$N_2 + M = N + N + M$	$N/6/H_2/2/H_2O/1.4$	3.72×10^{21}	-1.60	113,231	[24]
28	$NO + M = N + O + M$	$NO/20/O/20/N/20$	4.00×10^{20}	-1.50	75,487	[29]
29	$N_2O + M = N_2 + O + M$	$N_2/1.22/O_2/1.22/N_2O/5.56$	6.92×10^{23}	-2.50	32,711	[24]
30	$NO_2 + M = NO + O + M$	$H_2O/6.1/NO/2.9/N_2/1.4/N_2O/2.1$	1.10×10^{16}	0	33,013	[24]
31	$N_2O + O = N_2 + O_2$		1.00×10^{14}	0	14,091	[24]
32	$N_2O + O = NO + NO$		6.92×10^{13}	0	13,386	[24]
33	$NO_2 + O = NO + O_2$		1.00×10^{13}	0	302	[24]
34	$NO_2 + N = NO + NO$		4.00×10^{12}	0	0	[24]
35	$NO_2 + N = N_2O + O$		5.00×10^{12}	0	0	[24]
36	$N_2O + N = N_2 + NO$		1.00×10^{13}	0	10,015	[24]
37	$N_2O + NO = N_2 + NO_2$		1.00×10^{14}	0	25,011	[24]
38	$NO_2 + NO_2 = NO + NO + O_2$		2.00×10^{12}	0	13,487	[24]
39	$NO + H = N + OH$		2.63×10^{14}	0	25,364	[24]
40	$N + HO_2 = NO + OH$		1.00×10^{13}	0	1001	[24]
41	$HNO + O = NO + OH$		5.01×10^{11}	0.50	1001	[24]
42	$N_2O + OH = N_2 + HO_2$		6.31×10^{11}	0	4997	[24]
43	$OH + HNO = H_2O + NO$		1.26×10^{12}	0.50	1001	[24]
44	$HO_2 + NO = HNO + O_2$		1.99×10^{11}	0	1001	[24]
45	$NO + HO_2 = NO_2 + OH$		2.09×10^{12}	0	-240	[24]
46	$HNO + HO_2 = NO + H_2O_2$		3.16×10^{11}	0.50	1001	[24]
47	$NO_2 + H = NO + OH$		3.47×10^{14}	0	740	[24]
48	$N_2O + H = N_2 + OH$		7.59×10^{13}	0	7599	[24]
49	$HNO + H = H_2 + NO$		1.26×10^{13}	0	1998	[24]
50	$NO_2 + H_2 = H + HNO_2$		2.40×10^{13}	0	14,500	[31]
51	$H + NO + M = HNO + M$	$H_2/1.86/N_2O/2.21/H_2O/6.15$	2.92×10^{15}	0	-300	[24]
52	$HNO_2 + M = NO + OH + M$		5.00×10^{17}	-1	25,000	[31]

Rate coefficients are expressed in the modified Arrhenius form $k = AT^n \exp(-E/RT)$. Units are cm, mol, s and E/R in K.

3700 K and in the pressure range of 220–310 kPa. The results expressed in the simple Arrhenius form were:

$$k_4 = 1.20 \times 10^{15} \exp(-48,100/T(K)) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_{-4} = 6.75 \times 10^{18} T(K)^{-1} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}.$$

These results were in good agreement with the ones given by Tsang and Hampson [16]. The overall uncertainty had been estimated to be about $\pm 30\%$, about three times lower than the rate coefficients error given by Tsang and Hampson [16].

3.4. $H + OH + M \rightarrow H_2O + M$ rate constant

The rate constant of the water decomposition reaction has been studied in the temperature range 2790–3200 K at total pressure of about 250 kPa and using mixtures containing 1200–4500 ppm of H_2O diluted in Ar. The rate constant of the termolecular recombination reaction between H, OH and Ar as collision partner was calculated from H_2O dissociation rate constant measurements and the equilibrium constant. The results from this study are

$$k_5 = 3.95 \times 10^{14} \exp(-53,690/T(K)) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_{-5} = 3.75 \times 10^{21} T(K)^{-2.1} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}.$$

The overall uncertainties in these expressions were estimated to be about $\pm 20\%$ and $\pm 25\%$ for reactions (5) and (–5) respectively, by considering experimental parameters which contributed to uncertainties in the evaluation of the rate constant for reaction (5). The influence of the equilibrium constant estimate has been taken into account for the k_{-5} overall uncertainty calculation too. The relative collision efficiency of H_2O collision partner with respect to argon was taken as 18 (common value between 16 and 20, in the literature for H_2/O_2 system). Then the following expressions were proposed:

$$k_6 = 7.10 \times 10^{15} \exp(-53,690/T(K)) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

$$k_{-6} = 6.75 \times 10^{22} T(K)^{-2.1} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1},$$

with overall uncertainties estimated to be about $\pm 25\%$ for reaction (6) and $\pm 30\%$ for reaction (–6). Compared to k_5 and k_{-5} overall uncertainty estimate, we also considered the uncertainty due to the chosen collision efficiency factor. Figs. 2 and 3 compare the present rate constant expressions with those reported by earlier investigators at high temperature, for the reactions $H_2O + M \rightarrow H + OH + M$ and $H + OH + M \rightarrow H_2O + M$ respectively. Homer and Hurle [19] noted that the very fast reaction: $H + H_2O \rightarrow H_2 + OH$ contributed to their recorded OH profile and then to the disappearance of water; but they did not take into account the $OH + M \rightarrow H + O + M$ dissociation reaction as a precursor of H-atoms for the $H + H_2O \rightarrow H_2 + OH$ reaction. Olschewski et al. [20]

Table 2
Initial combustor inlet conditions

Mach number	16
Equivalence ratio	1
Temperature	O_2 and N_2 : 1800 K H_2 : 325 K
Pressure	0.7 atm
Residence time	Combustor: 130 μs Nozzle: 320 μs

estimated that the decrease in water-concentration resulted only from the $H_2O + Ar \rightarrow H + OH + Ar$ reaction. Cathro and Mackie [21] considered the participation of the OH dissociation reaction, but they used a rate coefficient for this reaction of about nine times lower than the one specified above, which is in good agreement with the rate coefficient recommended by Tsang and Hampson [16]. Their experimental profiles showed significant and consistent deviations from the computed profiles in the early stages of reaction, always in the sense of a higher H concentration than computed. In the three cases [19–21], their considerations generate an overestimate of the rate constant for the reaction (5) and then for the reactions (–5), (6) and (–6). The values recommended by Baulch et al. [15] and Wilson [22] were derived from investigations of Homer and Hurle [19] and Olschewski et al. [20]. In its theoretical calculations, Troe [23] too, chose the collision efficiency in order to reproduce the rate constant of Homer and Hurle [19] and of Olschewski et al. [20]. This literature result analysis could justify the deviation found between the present results and those reported previously.

3.5. Effects of the studied reaction rate constants accuracy improvement on the H_2 supersonic combustion modeling

The effect of the studied reaction rate constants accuracy improvement on the H_2 supersonic combustion modeling was estimated, by comparing the chemical energy yield uncertainty values before and after our

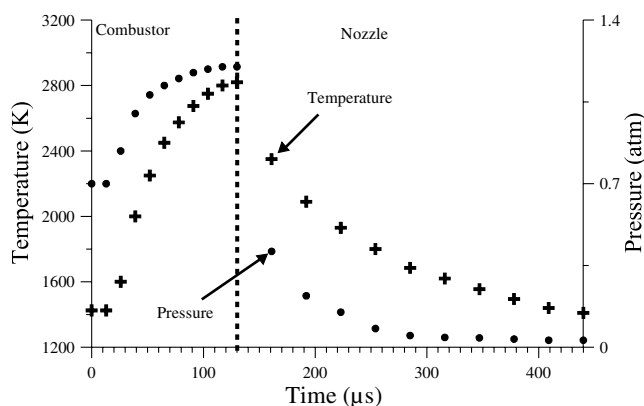


Fig. 4. Computed temperature and pressure profiles in the combustor and in the nozzle.

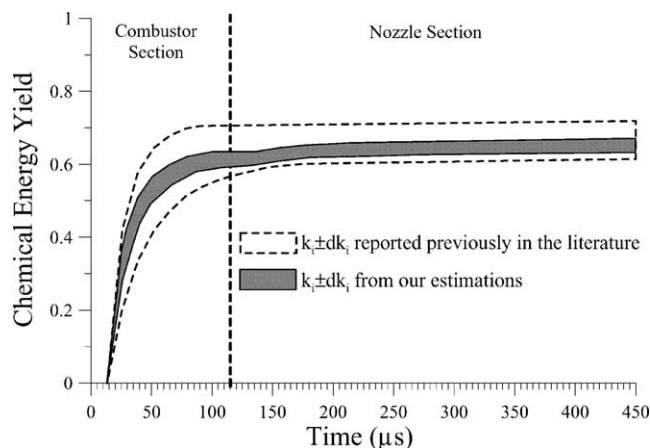


Fig. 5. Rate constant uncertainties effect of the reaction quoted in Table 3 on the energy yield.

Table 3

Rate coefficient uncertainties for sensitive elementary reactions in H_2 supersonic combustion

	Reaction	Uncertainty (%) from Ref.	Uncertainty (%) on our estimation
1	$O + H_2 = OH + H$	25 [6]	20
5	$H + H + M = H_2 + M$	50 (100 for $M = H_2O$) [15,16]	–
6	$H + O + M = OH + M$	100 [16]	30
7	$H + OH + M = H_2O + M$	50 [15]	30
8	$O + O + M = O_2 + M$	50 [17]	35
11	$H + O_2 + M = HO_2 + M$	50 [15]	–

estimations. The full reaction mechanism initially used for the computed simulations (SENKIN II [2]) is given in Table 1. The initial combustor inlet conditions are given in Table 2. The temperature and pressure profiles in the combustor and in the nozzle are presented in Fig. 4. Our calculations do not reproduce the realistic supersonic combustion conditions, because turbulent mixing and other factors may strongly influence the chemistry. However, these calculations permit to estimate qualitatively the influence of rate constant uncertainties on chemical energy yield reckoning. Fig. 5 presents the rate constant uncertainties effect of the reaction quoted in Table 3 on the range of chemical energy yield values. The improvement on the studied reaction rate constant accuracy generates an uncertainty on the chemical energy yield calculation about two times lower than with the rate constant uncertainties reported previously in the literature.

4. Conclusion and outlook

Resonance absorption measurements of O atoms, behind reflected shock waves, have been used to

precise the rate coefficients of elementary reactions which play major role in H_2 supersonic combustion chemistry. We showed the effect of the studied reaction rate constants accuracy improvement on the chemical energy yield uncertainty calculation. Additional kinetics studies are still needed. For example, more kinetic data on the effect of additives in combustor or nozzle section are necessary in order to increase the accuracy on the supersonic combustion energy yield calculation.

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