Laminar Burning Velocities of Formic Acid and Formic Acid/Hydrogen Flames: An Experimental and Modeling Study

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ABSTRACT

Laminar flame speed of formic acid and formic acid/hydrogen (4/1) flames was studied both experimentally and numerically. Experiments with flames of pure formic acid were performed at temperatures of 373 and 423 K while for formic acid/hydrogen flames the temperature value was 368 K. All the experiments were performed under atmospheric pressure, equivalence ratio range was 0.5-1.5. To measure laminar flame speed heat flux balance technique was applied. Three detailed chemical-kinetic mechanisms were tested on experimental data. Experiments showed that addition of 20% of hydrogen enables to increase laminar burning velocity of formic acid, for example in around 1.5 for stoichiometric flames. The comparison of experimental and numerical data showed that all models tend to overestimate laminar burning velocities of studied flames,

especially in the case of rich flames. The obtained results indicate that further improvement of existing chemical-kinetic models of formic acid oxidation is highly required.

KEY WORDS: formic acid, hydrogen, laminar flame speed, chemical-kinetic mechanisms

INTRODUCTION

The depletion of fossil fuel energy sources, and the environmental problems caused by the use of such fuels, motivate the urgent need for alternative fuel sources.[1] Because of its high gravimetric energy density and combustion that produces only water, hydrogen is one of the most promising candidates, applicable as a fuel in internal combustion engines and gas turbines.

However, wide utilization of hydrogen is not currently possible until technologies are developed for its safe and efficient transportation, storage and handling. Hydrogen can be stored as a compressed gas in cylinders at 100-700 atm, or as a liquid at -253 °C,[2] so, practical use of hydrogen entails several problems, especially for application in transportation systems. Hydrogen storage in cylinders under high pressure, or in cryogenic tanks, is followed by significant energy loss (H_2 compression, liquefaction and evaporation) and low volumetric energy capacity, and because they are severely limited in temperature and pressure range, physical adsorption approaches are not suitable.

Chemical hydrogen carriers, which include formic acid, have recently been proposed. Unlike hydrogen, the production and storage of formic acid has been performed for many years, and existing power systems can be adapted for formic acid use[1] Formic acid is a large capacity chemical industry, with a yearly global production of more than 500,000 tons; it decomposes at relatively low temperatures, forming CO in low concentrations, as well as other small organic

2

molecules.[3] However, the combustion chemistry of formic acid is poorly understood, and the study of formic acid oxidation has been very limited.

Bone and Gardner[4] studied formic acid oxidation in a static thermal reactor under temperatures between 613-743K. They observed that formic acid oxidation is followed by a relatively slow pressure rise, indicating low reactivity. Carbon oxides, water and free hydrogen were among the gaseous products of formic acid oxidation. Gaydon and Wolfhard[5] presented data on the spectroscopic study of formic acid oxidation at low pressure (~0.012 atm). Only the CO spectrum and several bands from the OH spectrum were registered; no bands indicating the presence of C_2, CH and HCO were observed. Laminar burning velocity under 433K and atmospheric pressure were measured for formic acid/O_2/N_2 blends in work by de Wilde and van Tiggelen.[6] The equivalence ratio was varied from 0.6 to 1.2. To calculate the values of laminar flame speed, the authors used the total flame area method. Due to the low combustion heat of formic acid the blends studied contained a low fraction of nitrogen.

There are several works on formic acid monomolecular decomposition in reactions $HOCHO=CO_2+H_2$ and $HOCHO=CO+H_2O$. At low temperatures and low pressures rate constants of these reaction were measured in works by Blake and Hinshelwood[7] and Blake, Davies, and Jackson,[8] and measured under high temperatures in works by Hsu et al.[9] and Saito et al.[10-13] $HOCHO=CO+H_2O$ was revealed to be the predominant reaction, while the reaction $HOCHO=CO_2+H_2$ made a much smaller contribution. Klatt, Rohrig, and Wagner[14] proved in experiments that reactions $HOCHO=H+HOCO$, $HOCHO=CO_2+2H$, $HOCHO=HCO+OH$ and $HOCHO=H+OCHO$ made a negligible contribution to formic acid monomolecular decomposition. The theoretical work of J. M. Anglada[15] presented data on rate constants for reactions of formic

acid with OH; it was shown in this work that the reaction with acidic hydrogen abstraction was predominant.

Since formic acid is an intermediate product of the oxidation of larger molecules, its sub mechanism is present in several mechanisms developed for ethanol,[16] dimethyl ether,[17] propane,[18] acetic acid,[19] butanoic and pentanoic acids.[20]

Only one work by Marshall and Glarborg[21] presents the theoretical study of formic acid oxidation reactions. Using quantum chemistry *ab initio* calculations, the authors obtained the parameters for rate constants of formic acid reactions with H, O and HO_2 radicals. Rate constants for the other reactions were adopted from the literature. The authors performed numerical simulations for conditions reported in the work by de Wilde and van Tiggelen.[6] The comparison of experimental and modeling results showed better agreement for lean blends, while in rich conditions the model tended to overestimate the value of laminar burning velocity. The increase in diluent concentration increased this difference.

A recent work by Sarathy et al.[22] presents experimentally measured laminar burning velocities of formic acid/air, formic acid/hydrogen/air and formic acid/hydrogen/carbon dioxide/air blends at atmospheric pressure. For formic acid/air blends, experiments were performed at 373 and 423K, for formic acid/hydrogen/air and formic acid/hydrogen/carbon dioxide/air blends, the temperatures were 373K and 358K respectively. A detailed chemical kinetic mechanism of formic acid oxidation was also proposed. Because the mechanism was intensively validated, reactions of hydrogen and C_1-C_2 hydrocarbons were taken from the Aramco 2.0.[23-27] Reactions of formic acid oxidation were adopted from a previously mentioned work by Marshall and Glarborg.[21] For formic acid/air blends at 373K the model agreed with measurements within the experimental uncertainty for lean blends, and it gave higher value to stoichiometric and rich blends. However, at 423K the

experimental values for lean and rich blends were higher than predicted by the model; for stoichiometric blends, agreement was within the bounds of experimental error. The work of Sarathy et al.[22] showed experimental data for only lean formic acid/hydrogen/carbon dioxide/air blends. The best agreement between experiments and modeling was achieved for near-stoichiometric blends. In the formic acid/hydrogen/air blend, the model underestimated the values of laminar flame speed for the near-stoichiometric blends and agreed well for lean and rich conditions.

Another recent paper by Yin et al.[28] experimentally examined the laminar burning velocity of formic acid at temperatures 423 and 453K, atmospheric pressure, and at an equivalence ratio between 0.4 and 1.6. Modeling results with the Aramco 3.0[29] and Glarborg et al.[21] mechanisms were also given. The mechanism from Glarborg et al.[21] agreed with the experimental data, within the bounds of uncertainty; this model provided good agreement for both lean and rich blends. Their observations differed from the work of Sarathy et al.[22] The Aramco 3.0 model overestimated the values of laminar flame speed by about two times. The main reason for this difference in performance of applied mechanisms appears to have been caused by different rate constants for the reactions of H abstraction from the formic acid molecule and the subsequent decomposition of formed radicals. The authors combined the mechanisms of the Aramco 3.0[29] and Glarborg et al.[21] The resultant mechanism slightly underestimated laminar burning velocity values, disagreeing with the work of Sarathy et al.[22] The work by Yin et al.[28] also showed that the increase of equivalence ratio and the increase of oxygen content in the blend resulted in higher diffusional-thermal instability. For lean blends, the decrease of flame thickness was observed, indicating that lean flames were less stable, than stoichiometric and rich flames.

The work by Osipova et al.[30] presented experimental data on the flame structure of atmospheric pressure premixed formic acid/hydrogen flames of different stoichiometry (φ=0.85, 1.1 and 1.3), and data on the laminar flame speed of formic acid flames (φ=0.5-1.5) at 368K. Three available mechanisms of formic acid oxidation were tested, those by Glarborg et al.,[21] Konnov et al.,[19] and the updated Aramco 2.0.[22] In general, all the mechanisms agreed satisfactorily with the experimental data, except in the case of formaldehyde, the reason being that mechanisms from works[19] and[22] had additional pathways of CH_2O formation from formic acid. However, the mechanism developed by Christensen and Konnov[19] overestimated the values of laminar burning velocities by around two times. The updated Aramco 2.0[22] provided the best agreement, but it still slightly overpredicted speed values in the rich region.

All the studies mentioned showed that in order to estimate the potential to implement formic acid as a fuel for real engines, experimental data from a wide range of conditions is imperative. Laminar burning velocity is an important combustion parameter. Currently, only four[6,22,28,30] have reported data on the laminar flame speed of formic acid flames, and these works predicted different behavior in such flames. Moreover, pure formic acid is known to have poor combustion properties; a possible solution is to add a small amount of hydrogen to improve combustion. There is only one experimental work on flame speed of formic acid/hydrogen fuel blends[22].

Since there is some scatter of the available data on formic acid laminar flame speed in the sense that different studies show different trends of agreement between experimental and numerical data, the objective of this work was, among other things, to determine which trend is correct and whether temperature and hydrogen addition influence on the agreement between experimental and numerical data. Our data shows that the change in temperature can not lead to a shift in the maximum laminar flame speed value, as well as change the trend of the agreement between

6

experimental and numerical data. Moreover, the addition of 10% [22] or 20% [30] of hydrogen does not change the fact that the main component of the fuel is formic acid which mainly determines oxidation process. Therefore, it is expected, that in terms of agreement between experimental and numerical data, the same trend will be observed as for pure formic acid flames, i.e. the increase of the fuel equivalence ratio leads to the increase of the discrepancy between the model and the experiment. At the same time, in the work [22] it turned out that the biggest discrepancy is observed for near-stoichiometric blends.

EXPERIMENTAL METHOD

The laminar burning velocity of $HOCHO/O_2/N_2$ flames was measured at temperatures 373 and 423K (T_0), and for $HOCHO/H_2/O_2/N_2$ the temperature value was 368K. Experiments were performed under atmospheric pressure; the equivalence ratio ranged from 0.5 to 1.5 and the O_2/N_2 ratio was 3/7, $HOCHO/H_2$ ratio – 4/1.

Figure 1 shows the scheme of experimental setup used in this work.

24 mm

Heating jacket
T_b =423K/453K/423K

thermocouples

Cooling jacket
T_0 =373K/423K/368K
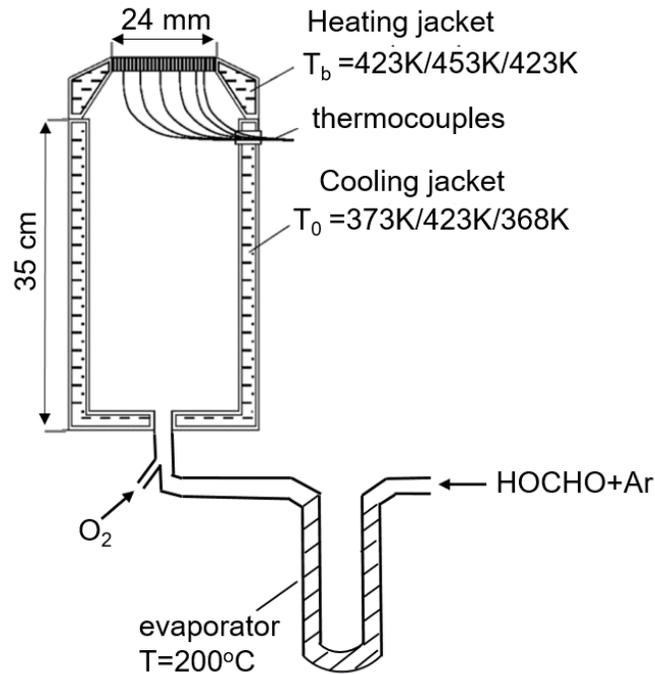
35 cm

HOCHO+Ar

O_2

evaporator
T=200°C

Figure 1. Experimental setup

The heat flux balance technique was applied to determine the values of the laminar flame speed.[31,32] Details of this method are given in the work[33], here only a brief description is given. Since the temperature of the edges of the burner disk (T_b) is higher than the temperature of the fresh gas blend (T_0), after passing the burner orifices the fresh gas blend is heated. This temperature ratio allows us to stabilize the flame not only when the flow rate of the unburned gas blend is less than the laminar flame speed, but also when the flow has a slightly higher speed. In this case, there is a small temperature gradient on the burner surface, since the edges of the burner have slightly higher temperature than its center, and at the burner edges the local flame speed is slightly higher than that in the center. Figure 2 presents the scheme of the heat fluxes on the burner surface. Here q_+ is the uniform heat flux from the flame to the burner at height h, q_- is the uniform

heat flux from the burner to the fuel blend at x=0. Then the total heat flow (q) to the burner is determined by the difference between q_+ and q_- and is equal to $q = q_+ - q_-$.
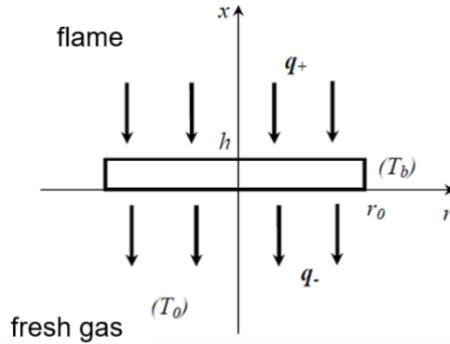

Figure 2. Scheme of the heat fluxes to the burner surface

Depending on the value of q, there can be three cases: q>0, q<0, and q=0. If q>0, the temperature of the burner disk center is higher than the temperature of its edges, and the flow rate of the fuel blend is lower than the laminar flame speed. If q<0, the opposite situation is observed: the temperature of the burner disk center is lower than the temperature at the edges, and the flow rate of the fuel blend is higher compared to the laminar flame speed. When q=0, the radial temperature distribution on the burner surface is uniform, and the flow rate of the fuel blend is equal to the laminar flame speed of the flame. The energy equation allows us to derive the relation between the temperature of the burner disk center and the temperature at some distance from the center. The detailed description of the procedure of energy equation solution is explained in the work. This relation is given by parabolic function:

$$T_p(r) = T_c \left(1 - \frac{1}{4} \alpha^2 r^2 \right)$$

9

$T_p(r)$-radial temperature distribution on the burner surface, T_c – temperature of the burner center, α^2– parabolic coefficient. The flow rate of gas blend is equal to laminar flame speed in the case of uniform temperature distribution on the burner surface, when $\alpha^2 = 0$.

In the experiments, flames were stabilized on a flat burner; the burner consisted of a 35 cm high tube and a perforated copper disk (diameter 24 mm, 3 mm thick). The diameter of the orifices was 0.5 mm; the distance between the orifices' centers was 0.7 mm. A copper disk and an unburned gas blend were heated with two thermostats pumping oil through the cavities in the burner body. The temperature value of the disk edges was 423K for experiments in which the unburned gas blend temperature was 373 and 368K. For experiments at the fresh gas temperature of 423K the temperature of the disk edges was equal to 448K. The radial temperature distribution on the surface of the copper disk was measured using six T-type thermocouples, whose junctions were pressed into the burner orifices at distances of 0, 2.4, 4.5, 7, 10, and 11.5 mm from the disk center.

The composition and flow rate of the studied blends were set with mass flow controllers (MKS Instruments), and by supplying liquid formic acid to the evaporator (a U-shaped tube filled with copper beads), using a syringe driven by a stepper motor. The evaporator temperature was maintained at 200°C.

MODELING

Numerical simulation of laminar flame speed was performed with the PREMIX code from a CHEMKIN PRO package. Three published mechanisms were applied, that of Glarborg et al.,[21] the updated Aramco 2.0,[22] and the mechanism that combined the Aramco 3.0[29] and that of Glarborg et al.[21] The number of species and reactions in these mechanisms is provided in Table 1. GRAD

and CURV parameters were set to equal 0.05. Multi-component and thermal diffusion options were considered in the simulation.

Table 1. Chemical-kinetic mechanisms applied in this work

Mechanism	Species Number	Reactions Number	Reference	Model №
Glarborg et al.	27	75	21	Model 1
Updated Aramco2.0	305	1761	22	Model 2
Aramco3.0 +Glarborg et al.	279	1739	21+29	Model 3

RESULTS

LAMINAR FLAME SPEED OF HOCHO/O_2/N_2 BLENDS

Figure 3 shows the dependence of the laminar flame speed of HOCHO/O_2/N_2 blends from the equivalence ratio. The uncertainty of the speed values obtained with the heat flux method was ~1 cm/s for near-stoichiometric flames, ~1.5 cm/s for rich; the lean flux was around 3 cm/s. The reason for increased uncertainty in lean blends is that lean flames are less stable than rich and near-stoichiometric flames. A similar trend was observed in the work of Yin et al.[28] According to the present results, under 373K the best agreement obtained between experimental and modeling values occurred in lean blends, whereas the increased equivalence ratio caused an increased discrepancy between experimental and numerical data. This observation agreed with the work of de Wilde and van Tiggelen[6] and Osipova el al.[30] and of Sarathy et al.[22] for the temperature of 373K (Figure 3a).

As previously noted, the base chemistry of Model 2 from the work of Sarathy et al.[22] (reactions of C_0-C_2 hydrocarbons) was adopted from the Aramco 2.0 mechanism[23-27] and the reactions of formic

11

acid from Marshall and Glarborg.[21] Such a replacement of the base chemistry allowed Model 2 to provide values of laminar flame speed which were slightly lower than those obtained with Model 1. As for Model 3, where reactions of hydrogen and light hydrocarbons were taken from the Aramco 3.0 mechanism,[29] its application produced slightly lower values of laminar burning velocity than in the case of Models 1 and 2. However, compared to the experimental data, all the mechanisms significantly overestimated the laminar flame speed values.

A similar trend was observed in the case when the temperature of the fresh gas blend was 423K. The best agreement between experimental and modeling data was achieved with lean blends. Model 2 gave a slightly lower value of laminar burning velocities than Model 1. Since it was expected that the use of Model 3 at 423K would produce a similar effect for the dependence of laminar burning velocity from equivalence as obtained from Models 1, 2 and 3 at 373K, the curve for Model 3 is not shown in Figure 3b.
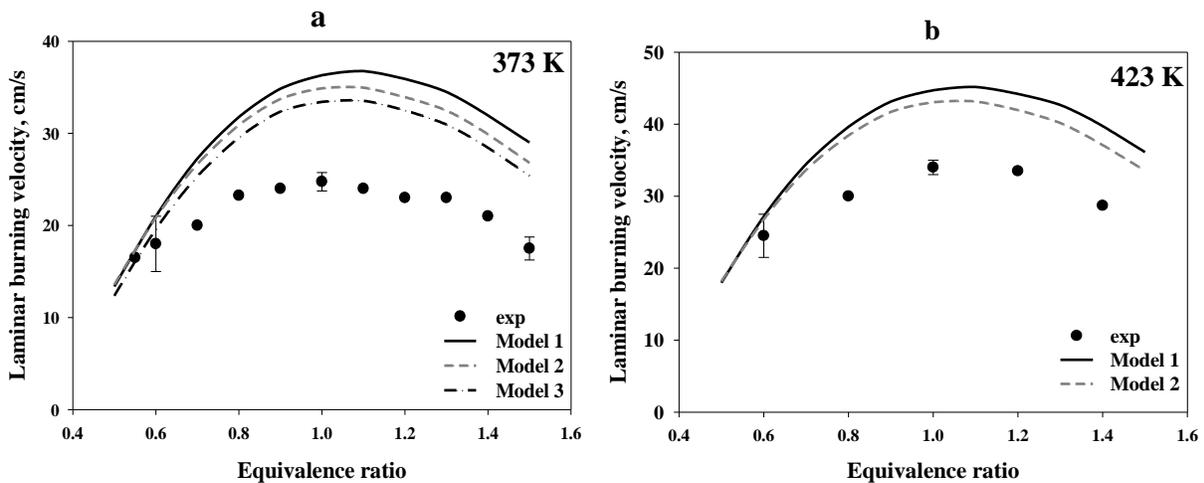

Figure 3. Laminar flame speed of HOCHO/O_2/N_2 flames vs. equivalence ratio at T_0=373 K (left) and T_0=423 K (right).

It is notable that the trend of agreement between experimental and modeling results presented in this work differs from that obtained in the work of Yin et al.[28], in which Model 1 provided equally good agreement between experiment and modeling in the entire range of equivalence ratios, whereas Model 3 slightly underestimated the values of laminar flame speed in the same range of equivalence ratio, compared to experimental results (for unburnt gas blends temperatures of 423K and 453K and oxygen fraction from 30 to 40%).

According to our data on laminar flame speed of $HOCHO/O_2/N_2$ flames at 373K and 423K, the increase in the initial temperature for 50K did not change the dependence of flame speed on equivalence ratio (peak position vs φ), either in experiments or in modeling. This data differs from the results presented in the work of Sarathy et al.,[22] in which the same temperature increase led to a shift in the peak value of the laminar flame speed to the rich zone, and the relative change of laminar burning velocity in the experiment was more significant than predicted by modeling. To explain such an effect, the sensitivity coefficients for the flame speed to the reaction of formic acid consumption and formation was analyzed. The major reactions were: $HOCHO+OH=OCHO+H_2O$, $HOCHO+OH=HOCO+H_2O$, $CO+OH=HOCO$, $HOCO(+M)=CO_2+H(+M)$, $HOCO+H=CO+H_2O$, $HOCO+O_2=CO_2+HO_2$. However, the values of the sensitivity coefficients remained almost constant when the temperature changed from 373K to 423K. From this perspective, the increase of the initial temperature for 50K was not expected to affect the agreement of the numerical data with the experiment; this was confirmed in the present work.

LAMINAR FLAME SPEED OF $HOCHO/H_2/O_2/N_2$ BLENDS

As previously noted, one way to increase the speed of formic acid flames was to add a small amount of hydrogen. The results from experiments and modeling of the laminar burning velocity of HOCHO/H_2/O_2/N_2 flames are shown in Figure 4.
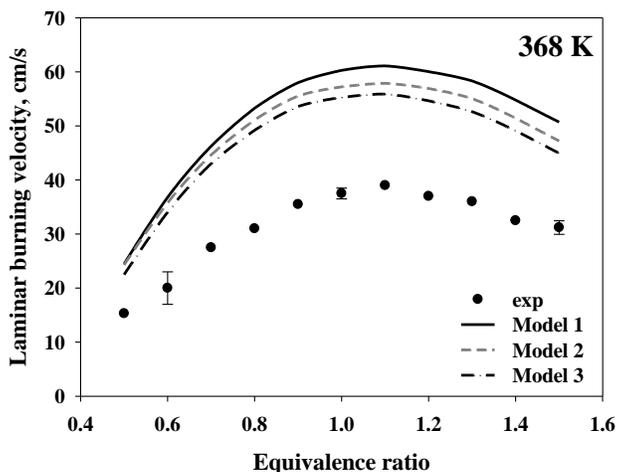

Figure 4. Laminar flame speed of HOCHO/H_2/O_2/N_2 flames vs. equivalence ratio, T_0=368 K.

From our data, the addition of 20% of hydrogen to the fuel blend significantly increased laminar flame speed, compared to flames of HOCHO/O_2/N_2 (~1.5 times for stoichiometric flames). The effect of flame speed increase was more pronounced for rich flames and appeared to be least for lean blends. This effect can probably be attributed to the fact that the maximum speed of hydrogen flames shifted more strongly to the region of rich blends than the maximum of flame speed of formic acid or, for example, light hydrocarbons.

Modeling results presented in Figure 4 indicate that the major discrepancy with the experiment occurred in rich flames. As in the case of pure formic acid flames, Model 1 produced the highest values of laminar flame speed of formic acid/hydrogen flames, and Model 3 predicted the lowest value. However, compared to the experiment, the simulation results in all the models significantly overestimated burning velocities throughout the entire range of the equivalence ratio.

14

In comparing the results of the numerical modeling of the laminar flame speed of HOCHO/O_2/N_2 mixtures (at T_0=373 K) and HOCHO/H_2/O_2/N_2 (at T_0=368 K), it was revealed that the relative difference between the simulation results for Model 1 and Model 3 was slightly greater for the HOCHO/H_2 fuel mixture ($\Delta U/U \approx 0.085$), compared to the numerical data for pure formic acid flames ($\Delta U/U \approx 0.072$). One possible explanation for this effect is that in Model 3, the part of this chemical-kinetic mechanism responsible for hydrogen oxidation reactions was more thoroughly tested, and optimized in a greater variety of experimental data than in Models 1 and 2.

Since the kinetics of hydrogen oxidation reactions significantly affected the laminar flame speed of HOCHO/H_2 fuel blends, the use of Model 3 for numerical simulation made it possible to achieve slightly better agreement for the flame speed of HOCHO/H_2 blends than in the case of pure formic acid flames. However, as the main component in the studied fuel blends was formic acid (80%), it was the acid that mainly determined the laminar flame speed value of such flames.

Summarizing all of the above, we would like to emphasize that there are several works in the literature presenting laminar flame speed of formic acids, but they were performed at conditions, which are different from those in the present work (temperature, fresh gas blend composition, dilution ratio). Therefore, we can only do qualitative comparison of the curves of laminar burning velocity vs equivalence ratio obtained and the agreement of experimental curves with numerical simulations. In previous works[21,30], a similar trend of agreement between experimental and numerical data obtained with Model 1 was observed: a better agreement is achieved for lean blends, while the increase of the equivalence ratio leads to an increase in the discrepancy between experimental and simulation data. If we compare with the work for pure formic acid[22], a similar trend is observed for the temperature of 373K, but for the higher temperature - 423K, there is a

discrepancy, which is as follows: according to the data presented in the work[22], laminar flame speed increases with the equivalence ratio increase, whereas according to the data obtained in the present work, the maximum speed is observed at equivalence ratio of 1.1. Firstly, formic acid is similar to hydrocarbons, and for hydrocarbons the maximum flame speed is around $\varphi \approx 1.0$, while for rich flames the speed value decreases. Also in the present paper, the sensitivity coefficients were analyzed. The detailed description of the sensitivity analysis will be given in the next section. It was found, that the increase in temperature does not lead to any change in the value of the sensitivity coefficients, which means that when the temperature changes by 50 K, there is no reason for the trend of agreement between experimental and numerical data to change. As for the work,[28] it was found that the temperature increase does not change the trend of agreement between experimental and numerical data. However, in the same work, it was revealed, that in the entire range of the equivalence ratio Model 1 provides good agreement between experimental and numerical data, while in our work we observed an increase in the discrepancy with an increase in the equivalence ratio. Moreover, the authors of the work[28] revealed that Model 3 slightly underestimates the values of laminar flame speed while in our work we observed the same effect as for Model 1. All available data on laminar flame speed of formic acid is presented in Supporting Information.
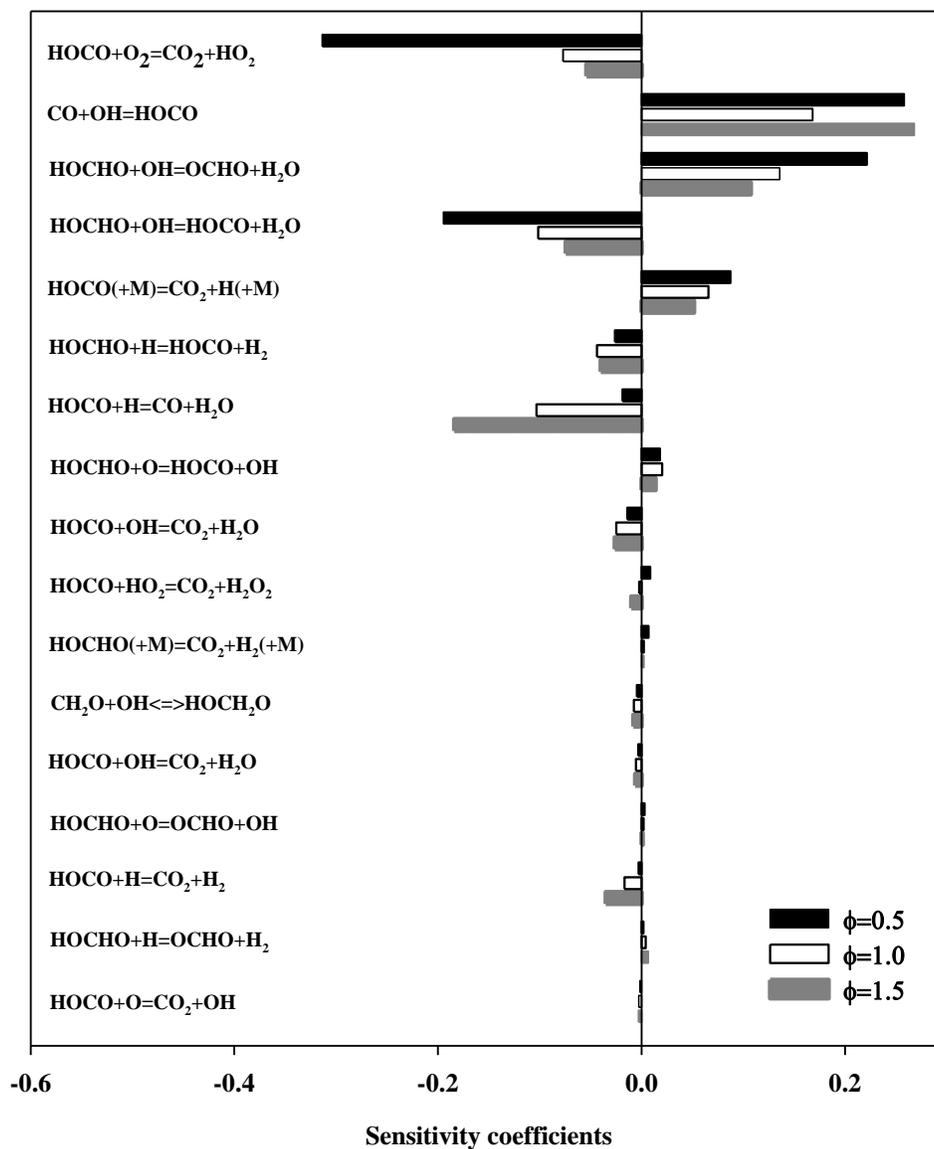
SENSITIVITY ANALYSIS

Figure 5. Sensitivity coefficients for flame speed towards reaction of formic acid consumption and formation for $HOCHO/O_2/N_2$, T_0=373K. (Model 2)

Figure 5 shows the sensitivity coefficients of formic acid and its radicals' reactions to laminar flame speed of $HOCHO/O_2/N_2$ at 373K obtained with Model 2. As previously mentioned, the temperature increase of 50K caused no change in sensitivity coefficients values, therefore, sensitivity coefficients obtained for the case of 423K are not given.

Figure 6 presents the dependence of the U_{exp}/U_{mod} value on the equivalence ratio: U_{exp} is the experimental value of laminar burning velocity and U_{mod} is the corresponding value obtained with a numerical simulation using Model 2.
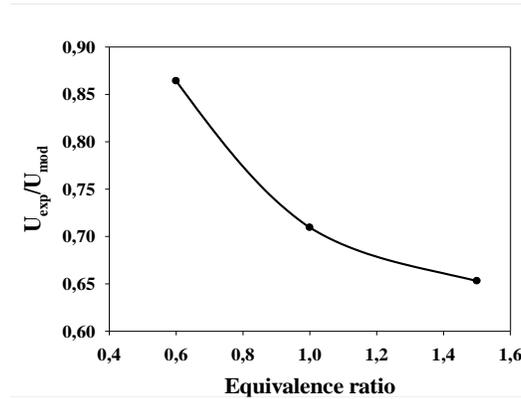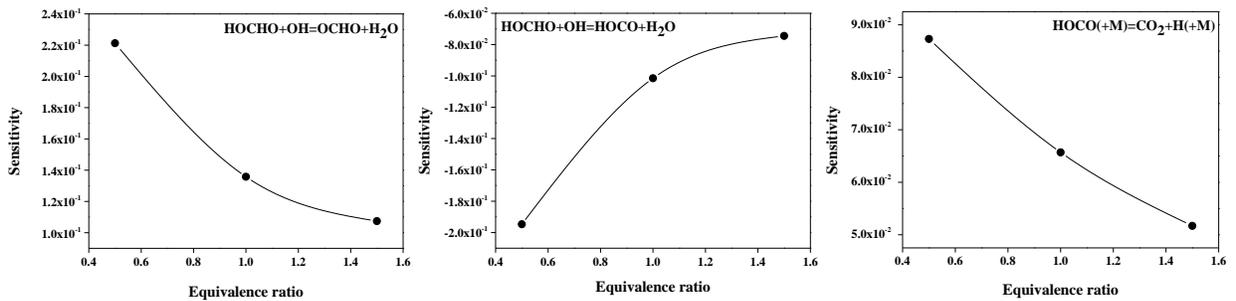

Figure 6. U_{exp}/U_{mod} vs. equivalence ratio (Model 2).

It can be seen that the trend of U_{exp}/U_{mod} vs. the equivalence ratio is repetitive. Therefore it can be assumed that, to improve the mechanism, it is necessary to find reactions for which the value of the sensitivity coefficient is similarly dependent on φ. Also, the curve of the sensitivity coefficient vs. the equivalence ratio should not intersect the horizontal axis. The dependence of the sensitivity coefficient to laminar flame speed for these reactions is shown in Figure 7.
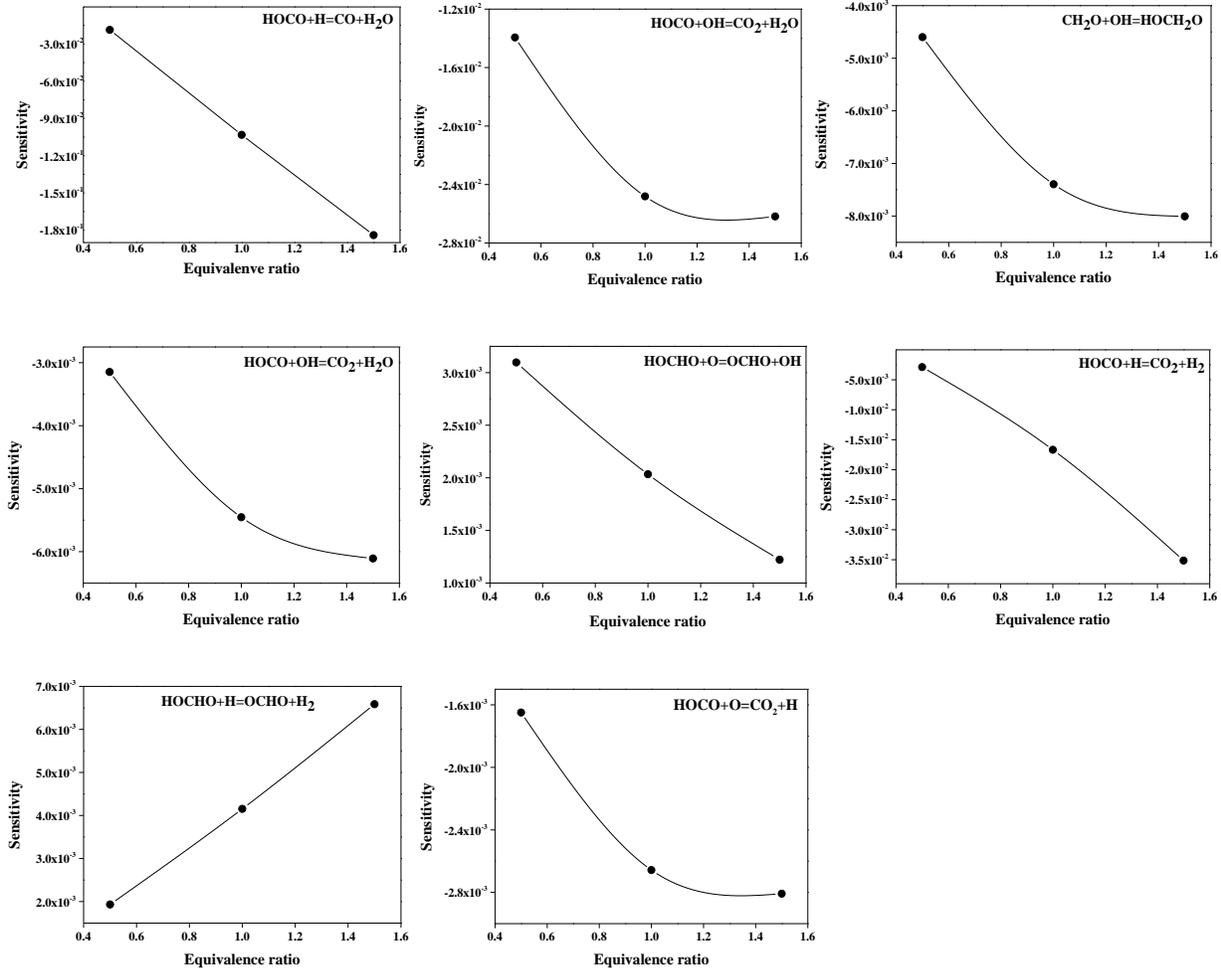

18

Figure 7. Sensitivity coefficients to laminar flame speed for key reactions of formic acid decomposition vs. equivalence ratio. (Model 2).

The highest values (in modulus) in the sensitivity coefficients were obtained for the following reactions: $HOCHO+OH=OCHO+H_2O$, $HOCHO+OH=HOCO+H_2O$, $HOCO(+M)=CO_2+H(+M)$, $HOCO+H=CO+H_2O$, $HOCO+OH=CO_2+H_2O$. Therefore, one possible way to improve agreement between experimental and numerical data may include the refinement of rate constants of these reactions.

So, it can be concluded that, for better agreement between the experimental and numerical data regarding the laminar flame speed of $HOCHO/H_2$ flames, it is necessary to refine the rate

constants of reactions involving formic acid, since there appears to be no significant reason for revising the submechanism of hydrogen oxidation reactions.

CONCLUSIONS

1) This work presents experimental data on the laminar flame speed of $HOCHO/O_2/N_2$ vs. the equivalence ratio ($\varphi=0.5-1.5$) at the initial temperature of unburned gas of 373K and 423K, as well as data on laminar burning velocity of $HOCHO/H_2/O_2/N_2$ blends vs. φ at 368K.

2) It was revealed that the modeling data of the laminar burning velocity of $HOCHO/O_2/N_2$ flames, obtained using three different chemical-kinetic mechanisms of formic acid oxidation, satisfactorily reproduced experimental results for only lean flames, but as the equivalence ratio increased, agreement between simulation values and experiments decreased.

3) An increase of 50K in the initial temperature of the $HOCHO/O_2/N_2$ blend did not significantly affect the nature of the dependence of the laminar flame speed on the equivalence ratio, in both experimental data and in the results from numerical simulation.

4) The addition of 20% hydrogen to the $HOCHO/O_2/N_2$ blend led to a noticeable increase (~1.5 times for a stoichiometric flame) in the burning velocity of formic acid flames over the entire range of the equivalence ratio.

5) For $HOCHO/H_2/O_2/N_2$ flames, the sub mechanism of hydrogen oxidation had a greater effect on the agreement with experimental data than for $HOCHO/O_2/N_2$ blends.

6) The comparison of experimental and modeling results for the formic acid flames studied showed that further study and refinement of the rate constants of elementary chemical reactions involving formic acid is absolutely necessary.

ASSOCIATED CONTENT

Supporting Information

Available data on laminar flame speed (DOC)

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Notes

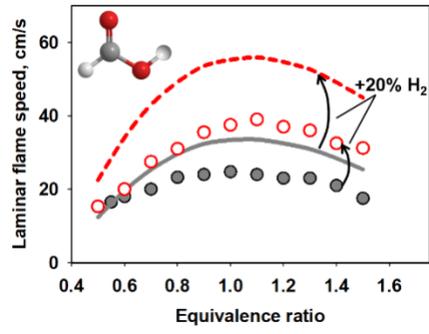The authors declare no competing financial interest.

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