CHEMICAL STRUCTURE OF ATMOSPHERIC PRESSURE PREMIXED LAMINAR FORMIC ACID/HYDROGEN FLAMES

K.N. Osipova1,2, S. Mani Sarathy3, O.P. Korobeinichev1, A.G. Shmakov1,2

1Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk 630090, Russia,
2Novosibirsk State University, Novosibirsk 630090, Russia
3King Abdullah University of Science and Technology, Clean Combustion Research Center, Physical Sciences and Engineering Division, Thuwal, Kingdom of Saudi Arabia

* Corresponding author:
Andrey Shmakov
Voevodsky Institute of Chemical Kinetics and Combustion
Institutskaya str. 3, Novosibirsk 630090, Russia
Tel: +7 383 333 33 46
Fax: +7 383 330 73 50
E-mail: shmakov@kinetics.nsc.ru

Abstract

The work presents an experimental and kinetic modeling study of laminar premixed formic acid [HC(O)OH]/H2/O2/Ar flames at different equivalence ratios (φ=0.85, 1.1 and 1.3) stabilized on a flat burner at atmospheric pressure, as well as laminar flame speed of HC(O)OH/O2/Ar flames (φ=0.5-1.5) at 1 atm. Flame structure as well as laminar flame speed were simulated using three different detailed chemical kinetic mechanisms proposed for formic acid oxidation. The components in the fuel blends show different consumption profiles, namely, hydrogen is consumed slower than formic acid. According to kinetic analysis, the reason of the observed phenomenon is that the studied flames have hydrogen as a fuel but also as an intermediate product formed from HC(O)OH decomposition. Comparison of the measured and simulated flame structure shows that all the mechanisms satisfactorily predict the mole fraction profiles of the reactants, main products, and intermediates. It is noteworthy that the mechanisms proposed by Glarborg et.al, Konnov et.al and the updated AramcoMech2.0 adequately predict the spatial variations in the mole fractions of free radicals, such as H, OH O and HO2. However, some drawbacks of the mechanisms used were identified; in
particular, they predict different concentrations of CH₂O. As for laminar flame speed simulations, the Konnov et.al mechanism predicts around two times higher values than in experiment, while the Glarborg et.al and updated AramcoMech2.0 show good agreement with the experimental data.

**Keywords**
formic acid, hydrogen, flame structure, molecular-beam mass spectrometry, laminar flame speed

**Introduction**
Carboxylic acids are intermediate species of oxidation of alcohols, esters, hydrocarbons, biomass etc. Thus, the mechanisms and kinetics of their oxidation are of crucial importance and deserve extensive study. Formic acid (HC(O)OH) is the simplest and lightest carboxylic acid. Recently formic acid was proposed as prospective hydrogen carrier to be used in hydrogen based energy systems [1-3]. However, blends of formic acid with oxygen have low burning velocity [4], so, the addition of high reactivity hydrogen to formic acid can help to increase and control flame speed of H₂/HC(O)OH fuel blends by changing components ratio.

Despite the above studies, gas-phase chemistry of formic acid is still poorly understood. The thermal decomposition of HC(O)OH was studied in experiments in a batch reactor [5-6] and a flow reactor [6] at intermediate temperatures, and in shock tubes [7-10] at high temperatures.

Bone and Gardner [11] performed static reactor experiments of formic acid oxidation in the temperature range of 613 - 743 K, but reported no quantitative results. Gaydon and Wolfhard [12] studied formic acid/oxygen burner stabilized flames at a pressure of 9 torr by spectroscopic analysis. They observed only CO and OH in emission spectrum but CH, C₂, and HCO species were not detected.

De Wilde and van Tiggelen [4] did a comparative experimental study of premixed flame propagation for methanol/O₂, formaldehyde/O₂ and formic acid/O₂ blends. The flame speed of HC(O)OH was significantly lower than those of methanol or formaldehyde; however, a direct comparison was not
possible because the latter system had higher dilution ratio. Formic acid has a low heat of combustion, thus, flames propagate only in \(\text{HC(O)OH/O}_2/N_2\) blends where the amount of \(N_2\) is lower than in air mixtures.

Detailed reaction subsets for \(\text{HC(O)OH}\) oxidation have been proposed by Marinov [13], Fischer et al. [14], and Battin-Leclerc et al. [15].

Marshall and Glarborg [16] used an \textit{ab initio} quantum chemistry approach to calculate rate constants for reactions of formic acid with \(O, H\) and \(\text{HO}_2\) radicals, and proposed an updated mechanism for formic acid oxidation at intermediate and high temperatures. The mechanism satisfactorily reproduced laminar flame speed of \(\text{HC(O)OH/O}_2/N_2\) blends obtained in the work of de Wilde and van Tiggelen [4].

A. Elwardany et.al measured rate constants of monomolecular decomposition of formic acid and acetic acid in a shock tube at temperatures from 1230 to 1821 K and at pressures from 1 to 6.5 atm. [17].

The submechanism of formic acid oxidation is present in the mechanism of acetic acid oxidation, developed based on data on laminar burning velocity of acetic acid flames [18], as well as in mechanism of butanoic and pentanoic acids oxidation, the base of which was experimental data on the acids oxidation in a jet-stirred reactor [19].

At the moment, there is no available data on species concentration profiles in laminar premixed flames of formic acid and formic acid/hydrogen fuel blends at atmospheric pressure. Such data is needed for verification and further improvement of combustion models of formic acid oxidation.

The aim of the work is the experimental measurement of chemical and thermal structure of laminar premixed flames of \(\text{HC(O)OH/H}_2/O_2/\text{Ar}\) blends with different equivalence ratios, stabilized on a flat burner at atmospheric pressure, and numerical simulation of structure of these flames with available mechanisms as well as experimental and numerical study of laminar flame speed of \(\text{HC(O)OH/O}_2/\text{Ar}\) blends.
Experimental

The chemical structure of HC(O)OH/H2/O2/Ar flames at 1 atm was studied using a quadrupole mass spectrometer with a molecular-beam sampling system and electron ionization. The detailed description of the experimental setup and data processing procedure is given in our previous papers [20-21]. A brief description is provided below.

Laminar premixed flames of HC(O)OH/H2/O2/Ar blends were stabilized on Botha-Spalding flat burner [22]. The burner is a perforated brass disc of 16 mm in diameter. The burner thickness was 3 mm and the holes diameter - 0.5 mm. The distance between the holes centers was 0.7 mm. In the experiment, the burner was moved in the vertical direction. The distance between the burner surface and the probe tip was measured with a cathetometer, the accuracy was up to ±0.01 mm. The composition of the fresh gas mixture and the flame stabilization conditions are in the Table 1. These specific mixture compositions were chosen to ascertain the effects of the HC(O)OH:H2 ratio on flame structure, as well as to stabilize these flames under similar conditions (width of the combustion zone, temperature in the zone of final combustion products, gas velocity at the surface of the burner).

Table 1. Molar composition of fresh gas mixtures and the flame stabilization conditions

<table>
<thead>
<tr>
<th>φ</th>
<th>Reactant mole fraction</th>
<th>Gas mixture velocity at the burner surface (cm/s)</th>
<th>HCOOH/H2 ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HC(O)OH</td>
<td>H2</td>
<td>O2</td>
</tr>
<tr>
<td>≈ 0.85</td>
<td>0.171</td>
<td>0.067</td>
<td>0.140</td>
</tr>
<tr>
<td>≈ 1.1</td>
<td>0.161</td>
<td>0.063</td>
<td>0.10</td>
</tr>
<tr>
<td>≈ 1.3</td>
<td>0.212</td>
<td>0.083</td>
<td>0.116</td>
</tr>
</tbody>
</table>

The flow rates of unburned gas blends were set with mass flow controllers (MKS Instruments Inc.). The temperature of the burner was kept at 368 K with the help of water supplied to the burner cooling jacket. For flame sampling we used a quartz sonic probe (internal opening angle of 40
degrees and a orifice diameter of 0.08 mm). To minimize flame perturbations caused by the probe, the thickness of walls near to the probe’s tip was also 0.08 mm. The gas jet in the probe expanded freely and was skimmed into a molecular beam, which passed through a modulator and a collimator and entered to the electron ionization region. Soft ionization was used to minimize contributions of fragment ions to the measured peaks. The range of ionizing electron energies was 10.9-16.65 eV (electron scattering energy of ±0.25 eV). To obtain high signal-to-noise ratio, the electrons energy was chosen individually for each species. The list of measured species, their ionization energies, and the calibration method applied are given in the Supplementary Material (Table S1). The statistical and relative uncertainties of MBMS signals are below 20% because the standard deviation for poor signal-to-noise ratios is around 20%. The resultant accuracy of determining the mole fraction of the reactants and major stable products (O2, H2, CO2, H2O, CO, HC(O)OH) was, as a rule, ± 20% of the maximum value of their mole fractions in flame. So, the accuracy of reactants and major products (O2, H2, CO2, H2O, CO, HC(O)OH) concentration measurement was ± 20% of the maximum value of their mole fractions in flame. The mole fraction of other species was determined with the accuracy of ± 50%. The mentioned uncertainties appear mostly because of calibration errors and inaccuracies of ionization cross-section values.

The temperature profiles of flames were measured with a S-type thermocouple (Pt/Pt + 10 % Rh) placed at 0.2 mm from the probe tip. The detailed description of thermocouple chart and temperature measurement procedure is provided in [23].

To consider gas dynamic perturbations caused by the probe, we shifted experimental profiles of species upstream to the burner by several probe orifice diameters. We used the same method as in our previous studies [20-21]. In each flame, mole fraction profiles were shifted by the same distance. The shift value was equal to the distance at which water and temperature profiles become constant at the same place. Specifically, our flames were shifted by around ~0.3-0.4 mm.

Laminar flame speed for HCOOH/O2/Ar blends were also obtained with the method described in [24]. We used Mache-Hebra nozzle burner to measure laminar flame speed, which generates a flame
with a regular conical shape. The values of cone base and height were obtained from digitized images of the flame cone in shadow photographs. In this method, the flame is close to adiabatic, so, it is assumed that there are almost no heat losses to the burner. The estimated confidence interval for the burning velocity was ±10–15%. In estimating the accuracy of our speed measurements, we took into account, first, the error in measuring the volumetric flow rate of unburnt gases (up to ±2%) and, second, the error in measuring the surface of the flame cone (±10%).

**Modeling**

The PREMIX module in CHEMKIN PRO software was used to simulate flames structure and laminar flame speed. Windward differencing was used and the grid was refined according to adaptive mesh parameters \( \text{GRAD} = 0.05 \) and \( \text{CURV} = 0.05 \); multi-component and thermal diffusion options were used in the calculations. To consider effects caused by the probe presence, calculations were performed using the measured temperature profiles as input data. For simulations, we used available mechanisms of formic acid oxidation, which include Glarborg et al. [16] and Konnov et al. [18] mechanisms as well as an updated version of AramcoMech2.0 mechanism. The base chemistry of Aramco 2.0 mechanism [25] has been widely tested, so, \( \text{C}_0\text{-C}_3 \) hydrocarbons chemistry was taken from it and merged with the sub-mechanism of formic acid oxidation [16]. Table 2. has summary information of these mechanisms, including the number of reactions and species.

Table 2. The reaction mechanisms used for the HC(O)OH/H\(_2\)/O\(_2\)/Ar flame structure modeling.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Number of species</th>
<th>Number of reactions</th>
<th>Year</th>
<th>Reference</th>
<th>Model №</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glarborg et al</td>
<td>27</td>
<td>75</td>
<td>2015</td>
<td>[16]</td>
<td>Model 1</td>
</tr>
<tr>
<td>Konnov et al</td>
<td>100</td>
<td>1140</td>
<td>2016</td>
<td>[18]</td>
<td>Model 2</td>
</tr>
<tr>
<td>Updated AramcoMech2.0</td>
<td>305</td>
<td>1761</td>
<td>2019</td>
<td>This study</td>
<td>Model 3</td>
</tr>
</tbody>
</table>
Results and discussion

Figure 1 presents experimentally measured temperature and concentration profiles of stable species in lean, near stoichiometric, and rich flames of HC(O)OH/H2/O2/Ar blend. In addition, this figure has concentration profiles of O2, H2O, CO, CO2, simulated with the three available mechanisms of formic acid oxidation. The reaction zone in these flames is around 0.5 mm. All the mechanisms satisfactorily reproduce experimental data. CO concentration profile is better described by Model 1 and by Model 3. CO2 concentration profile is better described by Model 2. At a distance of 3 mm from the burner surface, the measured and simulated concentrations of O2, H2O, CO, CO2 are close to values calculated by thermodynamic equilibrium.

Fig. 1. Measured and simulated mole fraction profiles of oxygen and of the major products and measured temperature profiles in the flame of the HC(O)OH/H2 fuel blends

Figure 2 shows experimental and simulated concentration profiles of H2 and HC(O)OH. Model 1 and Model 3 better describe the experimental H2 data. Model 2 gives slightly higher concentration of H2 in the reaction zone. HC(O)OH concentration profile obtained with Model 1 and Model 2 agree with experimental results, while Model 3 predicts a slightly higher concentration at the burner exit. H2 has larger consumption zone than HC(O)OH. The reason is that H2 has additional pathways of its formation from formic acid. A similar trend of H2 formation from heavier fuels was observed in [26-27].
Fig. 2. Measured and simulated mole fraction profiles of the hydrogen and formic acid in the flames of the HC(O)OH/H₂:

All the mechanisms correctly predict peak position of H, OH and O radical concentrations and agree with each other (Fig. S1, Supplemental Materials).

The peak position of H₂O₂ and HO₂ (Fig. 3.) is correctly described by all the mechanisms, but maximum concentration of these species observed in the experiment is 2-2.5 times lower than simulated values.

Fig. 3. The measured and simulated mole fraction profiles of H₂O₂ and HO₂ in the flames of the HC(O)OH/H₂ fuel blend

The main primary products of HC(O)OH consumption are C(O)OH and HC(O)O radicals. These species were not detected experimentally because their low ionization energy and gas-phase
concentrations render them beyond the detection limit of our mass-spectrometer. However, all the models agree with each other (Fig. S2, Supplemental Materials).

It is worthy to note that Model 2 and Model 3 predict formation of formaldehyde from HC(O)OH in much higher concentration than Model 1 (Fig. 4). Additional experiments on stoichiometric flame of HC(O)OH/O\textsubscript{2}/Ar (Ar fraction was 0.55) showed that maximum concentration of CH\textsubscript{2}O equals to 2.5*10\textsuperscript{-4} when modeling with Model 2 predicts a value around 2.5*10\textsuperscript{-5}, with Model 3 – around 1.0*10\textsuperscript{-4}, and according to Model 1 it is only around 4*10\textsuperscript{-9} (Fig. S3, Supplemental Materials). Simulated mole fraction profiles of formaldehyde are on the Figure 4.

![Simulated profiles of CH\textsubscript{2}O mole fraction in the flames of the HC(O)OH/H\textsubscript{2} fuel blend](image)

Fig. 4. The simulated profiles of CH\textsubscript{2}O mole fraction in the flames of the HC(O)OH/H\textsubscript{2} fuel blend

Since Model 1 and Model 3 have the same reaction subsets for formic acid oxidation, the analysis of oxidation reactions of HC(O)OH/H\textsubscript{2} fuel blends was compared between Model 3 and Model 2.

Figure 5 shows calculated reaction fluxes contributing to consumption and production processes of HC(O)OH and H\textsubscript{2} (HC(O)OH ROP and H\textsubscript{2} ROP). Results for the near stoichiometric (equivalence ratio 1.1) are presented here; similar results were seen for the lean and rich flames, as shown in the Supplemental Material (Fig. S4a and Fig. S4b). The maximum of HC(O)OH ROP is closer to the burner surface where as the maximum of H\textsubscript{2} ROP is further downstream. This means formic acid starts to react at lower temperatures than H\textsubscript{2}. On the other hand, H\textsubscript{2} forms from HC(O)OH in reactions HC(O)OH+H=HC(O)O+H\textsubscript{2} and HC(O)OH+H=C(O)OH+H\textsubscript{2}; only the latter contributes significantly.

Figure 5 shows that according to Model 2, the contribution of the reaction HC(O)OH+H=C(O)OH+H\textsubscript{2} is higher than in Model 3. At the temperature of 1350K, when HC(O)OH
ROP reaches its peak, this rate constant Model 2 is ~8.8 times higher. This difference in the rate constant value results in less monotonous decrease of H2 concentration in Model 2. This effect is more pronounced in the rich flame (Fig. 2). Thus, to provide better agreement of experimental and numerical data on H2 concentration profile, the rate constants of HC(O)OH+H=C(O)OH+H2 reaction should be refined, especially in Model 2.

It should be noted, that comparison of our experimental and simulation data on flame speed of HC(O)OH/O2/Ar (mole fraction of Ar is 0.55, T0=368°C) at \( \phi=0.5-1.5 \) showed that Model 2 predicts 2 times higher flame speed than in experiments (Fig. 6).
Fig. 6. Dependence of laminar flame burning velocity from equivalence ratio for HC(O)OH/O₂/Ar, mole fraction of Ar is 0.55, T₀=368°C

Model 1 reproduces our experimental data for lean blends within the experimental error, and slightly overpredicts the flame speed values for rich blends. In the work of Glarborg et al [16], the same trend was observed for HC(O)OH/O₂/N₂ blended flames: experimental data from the work of de Wilde and van Tiggelen [4] and modeling results agreed better for lean mixtures. Therefore, the key reactions of HC(O)OH should be refined in both mechanisms. Model 3 shows better agreement with experimental data in rich conditions.

To evaluate the contribution of each reaction to the total consumption rate of formic acid, we calculated the integrated rates of all the reactions, which involve HC(O)OH, as was done previously [21]. These values (in percent) are given in Figure 7.

Figure 7 shows that formic acid is mainly consumed in reactions HC(O)OH+OH=C(O)OH+H₂O, HC(O)OH+OH=HC(O)O+H₂O and HC(O)OH+H=C(O)OH+H₂. Depending on equivalence ratio, contribution of these reactions changes 1.5-2 times – the increase of equivalence ratio results in the decrease of contribution of reactions with OH and O radicals and in the increase of contribution of reactions with H. The reason is that the change of fuel blend composition causes a change of peak concentration of these active species. Moreover, the most predominant intermediate radical species in Figure 7, (C(O)OH and HC(O)O, are less active than other radicals (H, OH, O). This means that in presence of formic acid, H₂ has lower flame speed because the rate of chain branching processes.
decreases. This could enable controlling the combustion regime of HC(O)OH/H₂ fuel blend with changing of components ratio. Figure 7 also shows that increasing equivalence ratio causes an increase in the contribution of HC(O)OH+H=CH₂O+OH by 2 times, according to Model 2. In Model 1 this direct channel is absent. Model 3 has HC(O)OH+H=OHCH₂O channel, which subsequently leads to formaldehyde formation.

Conclusions

In this study, laminar premixed flames of HC(O)OH/H₂/O₂/Ar blends with different equivalence ratio stabilized on a flat burner at 1 atm were studied. We measured temperature profiles and concentration profiles of reagents (HC(O)OH, H₂, O₂), main combustion products (H₂O, CO, CO₂) and H, O, OH and HO₂ radicals. Formic acid starts to oxidize at lower temperatures than H₂. Three mechanisms of HCO(O)H oxidation were tested against experimental data. In Model 2, the rate constant of the reaction HC(O)OH+H=C(O)OH+H₂ is much higher than in other mechanisms and has to be refined. Model 1 also needs further improvement to provide better agreement with the experimental data on flame speed of rich HC(O)OH/H₂/O₂/Ar blends. Presence of formic acid can effectively decrease the rate of hydrogen oxidation, which makes it possible to control combustion regime of HC(O)OH/H₂ fuel blend with changing of components fraction. The reason is the competition of reactions of H, O and OH radicals with H₂ and HC(O)OH. Comparison of experimental and numerical data on laminar flame speed of HC(O)OH/O₂/Ar blends showed that Model 2 gives two times higher values, Model 1 agrees with experimental results under lean
conditions and gives higher values for rich flames. Model 3 provided even better agreement for rich conditions.

**Acknowledgements**

The research at King Abdullah University of Science and Technology (KAUST) was support by Saudi Aramco.

**References**


[25] Saudi Aramco mechanism release v. 2.0, Combustion Chemistry Centre, National University of Ireland, Galway, 2016

List of figure Captions

Fig. 1. Measured and simulated mole fraction profiles of oxygen and of the major products and measured temperature profiles in the flame of the HC(O)OH/H₂ fuel blends

Fig. 2. Measured and simulated mole fraction profiles of the hydrogen and formic acid in the flames of the HC(O)OH/H₂ fuel blend

Fig. 3. The measured and simulated mole fraction profiles of H₂O₂ and HO₂ in the flames of the HC(O)OH/H₂ fuel blend

Fig. 4. The simulated profiles of CH₂O mole fraction in the flames of the HC(O)OH/H₂ fuel blend

Fig. 5. The profiles of the main reaction rates of formic acid (HC(O)OH ROP) and hydrogen (H₂ ROP) in the HC(O)OH/H₂/O₂/Ar blend flames with equivalence ratio 1.1. The rate profiles for reactions with contribution less than 1% are not shown.

Fig. 6. Dependence of laminar flame burning velocity from equivalence ratio for HC(O)OH/O₂/Ar, mole fraction of Ar is 0.55, T₀=368°C.

Fig. 7. Primary reaction pathways of HC(O)OH consumption in HC(O)OH/H₂/O₂/Ar fuel blend. The arrows length shows the integrated contribution of a particular reaction.
List of Supplemental Materials:

Table S1. The measured species. IE: ionization energy (reference data); E-energy of ionizing electrons; RICS*: relative ionization cross-section method.

Fig. S1. The measured and simulated profiles of H, OH and O in the flames of the HC(O)OH/H$_2$ fuel blend

Fig. S2. The simulated profiles of HOCO+OCHO mole fraction in the flames of the HC(O)OH/H$_2$.

Fig. S3. The measured and simulated mole fraction profiles of the reactants and the major products and measured temperature profiles in the flame of the stoichiometric HC(O)OH/O$_2$/Ar mixture (mole fraction of Ar is 0.55, T$_0$=368°C).

Fig S4a. The profiles of the main reaction rates of formic acid (HC(O)OH ROP) and hydrogen (H$_2$ ROP) in the HC(O)OH/H$_2$/O$_2$/Ar blend flames (updated AramcoMech2.0). The rate profiles for reactions with contribution less than 1% are not shown.

Fig S4b. The profiles of the main reaction rates of formic acid (HC(O)OH ROP) and hydrogen (H$_2$ ROP) in the HC(O)OH/H$_2$/O$_2$/Ar blend flames (Konnov et al mech). The rate profiles for reactions with contribution less than 1% are not shown.