# *Ab initio* and kinetic modeling studies of formic acid oxidation

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## Abstract

A detailed chemical kinetic model for oxidation of formic acid (HOCHO) in flames has been developed, based on theoretical work and data from literature. Ab initio calculations were used to obtain rate coefficients for reactions of HOCHO with H, O, and $HO_2$. Modeling predictions with the mechanism have been compared to the experimental results of de Wilde and van Tiggelen (1968) who measured the laminar burning velocities for HOCHO flames over a range of stoichiometries and dilution ratios. The modeling predictions are generally satisfactory. The governing reaction mechanisms are outlined based on calculations with the kinetic model. Formic acid is consumed mainly by reaction with OH, yielding OCHO, which dissociates rapidly to $CO_2$ + H, and HOCO, which may dissociate to CO + OH or $CO_2$ + H, or react with H, OH, or $O_2$ to form more stable products. The branching fraction of the HOCHO + OH reaction, as well as the fate of HOCO, determines the oxidation rate of formic acid. At lower temperatures $HO_2$, formed from HOCO + $O_2$, is an important chain carrier and modeling predictions become sensitive to the HOCHO + $HO_2$ reaction.
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## 1. Introduction

Organic acids are among the pollutants of urban and rural atmospheres and contribute to acid rain formation [1,2]. Emissions of monocarboxylic acids have been detected from IC engines [3,4] and they are known to form in biomass pyrolysis [5]. The simplest of these acids is formic acid (HC(O)OH, or here HOCHO), which has been identified as an intermediate in oxidation of oxygenated hydrocarbons such as methanol [6] and DME [7]. The detection of carboxylic acid emissions from engines has prompted interest in the combustion chemistry of these components and their formation in laminar premixed hydrocarbon flames has been investigated both experimentally [8] and in terms of chemical kinetic modeling [9].

Detailed reaction subsets for HOCHO formation and oxidation have been proposed by Marinov [10], Fischer et al. [7] and, more recently, by

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Battin-Leclerc et al. [9]. Battin-Leclerc et al. conclude that formic acid in hydrocarbon flames is mostly formed from the addition of OH radicals to formaldehyde, followed by the elimination of a hydrogen atom [9], $CH_2O + OH \ (+M) \rightleftharpoons HOCH_2O \ (+M)$, $HOCH_2O \ (+M) \rightleftharpoons HOCHO + H \ (+M)$. This mechanism is similar to what has been proposed earlier for acetaldehyde [11]. Addition of OH to acetylene may also prove to be a source of formic acid. Alzueta et al. [12] identified the chain-propagating sequence $C_2H_2 \xrightarrow{+OH} C_2H_2OH \xrightarrow{+O_2} OCHCHO + OH$ as important for onset of reaction for $C_2H_2$ at atmospheric pressure and temperatures above 700 K. Interest in this oxidation pathway for atmospheric chemistry has motivated experimental and theoretical work on the $C_2H_2 + OH + O_2$ reaction at low temperature. Hatakeyama et al. [13] showed in smog-chamber experiments that the reaction generates formic acid (+HCO), as well as glyoxal (+OH). The yield of formic acid in the $C_2H_2OH + O_2$ reaction at lower temperatures has been determined to be in the range 30–50% [13–15]. Since the branching fraction for the reaction is not expected to be strongly temperature dependent, it is possibly a source of formic acid also at combustion conditions, particularly at increased pressure.

Despite the interest in formic acid as the simplest monocarboxylic acid and as an intermediate in and possible pollutant from combustion, work on its gas-phase chemistry at elevated temperatures is scarce. The thermal decomposition of HOCHO has been characterized in batch reactor [16,17] and flow reactor [17] experiments at intermediate temperatures, and in shock tubes [18–21] at high temperatures. However, the oxidation of formic acid is poorly characterized experimentally. Bone and Gardner [22] conducted static reactor experiments on formic acid oxidation at temperatures between 613 and 743 K, but reported no quantitative results. At higher temperatures, data on the gas-phase oxidation of formic acid have been obtained from premixed flames. Gaydon and Wolfhard [23] conducted a spectroscopic study of low-pressure formic acid/oxygen flames. They found that these flames could be stabilized at pressures as low as 9 torr. The emission spectrum showed the presence of CO and OH in the flames, while CH, $C_2$, and HCO were not detected. Later, de Wilde and van Tiggelen [24] measured the laminar burning velocity for a wide range of $HOCHO/O_2/N_2$ flames. These data constitute to our knowledge the only quantitative results on the oxidation of formic acid.

The objective of the present study is to develop a detailed chemical kinetic model for oxidation of HOCHO at elevated temperatures, based on ab initio calculations for key consumption reactions of HOCHO, together with the best available thermodynamic data and rate constants from the literature. The resulting model is evaluated by comparing predictions with the available experimental results and used to analyze HOCHO oxidation pathways and rate limiting steps at high temperatures.

## 2. Detailed kinetic model

In the present study, the starting mechanism and corresponding thermodynamic properties were drawn from recent work by the authors on oxidation of $H_2$, CO and $C_1/C_2$ hydrocarbons [25–28]. Both the thermochemistry and the HOCHO oxidation subset of the mechanism were carefully updated. The thermodynamic properties for selected species are shown in Table 1. The data for HOCHO are well established [29], while the properties for HOCO and OCHO have been in question. For HOCO, we rely on the present on-line recommendation of Goos, Ruscic, and Burcat, obtained using the Active Thermochemical Tables (ATcT) approach [31,32], while for OCHO properties were drawn from the theoretical study by Fabian and Janoschek [30]. Compared to the values used by Battin-Leclerc et al. [9], the heats of formation of HOCO and OCHO are smaller by 3 and 23 kJ mol$^{-1}$, respectively.

Table 2 lists the key reactions in the HOCHO oxidation scheme with the rate coefficients used in the present work. The full mechanism is available as supplemental material. Our subset for HOCHO oxidation is quite different from those proposed by Marinov [10], Fischer et al. [7] and Battin-Leclerc et al. [9]. Marinov estimated rate constants for reactions of formic acid with O/H radicals by analogy to reactions of $CH_3CHO$ and $CH_3OH$. He assumed that HOCO and OCHO dissociated instantaneously to form $CO + OH$ and $CO_2 + H$, respectively. Fischer et al. adopted the HOCHO subset of Marinov, adding a few further reactions with estimated rates. Battin-Leclerc et al. introduced HOCO and OCHO as intermediates in HOCHO oxidation, but employed a reduced reaction subset including only thermal dissociation of HOCHO and HOCHO + OH. In the present work, we characterize the key reactions of HOCHO by ab initio calculations and supplement them with theoretical work from the literature on reactions of HOCO.

### 2.1. Ab initio calculations

Most reactions of HOCHO with the radical pool have not previously been characterized experimentally or theoretically. In this work we have conducted ab initio calculations for reaction of HOCHO with H, O and $HO_2$. Energies of molecules and transition states were computed at the W1Usc level of theory [43], implemented in the