

**FORMIC ACID PRODUCTION FROM PHOTOCHEMICAL
OXIDATION IN CONDENSED AND NON-CONDENSED
MECHANISMS**

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by

Hongyu Chen

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**FORMIC ACID PRODUCTION FROM PHOTOCHEMICAL
OXIDATION IN CONDENSED AND NON-CONDENSED
MECHANISMS**

Approved by:

Dr. Jennifer Kaiser, Advisor
School of Civil and Environmental Engineering
School of Earth and Atmospheric Sciences
Georgia Institute of Technology

Dr. Armistead G. Russell
School of Civil and Environmental Engineering
Georgia Institute of Technology

Dr. Rodney J. Weber
School of Earth and Atmospheric Sciences
Georgia Institute of Technology

Date Approved: Dec 9, 2021

To the students of the Georgia Institute of Technology

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LIST OF SYMBOLS AND ABBREVIATIONS

SOA	Secondary Organic Aerosol
FACD	Formic Acid
VOCs	Volatile Organic Compounds
IEPOX	Isoprene Epoxydiol
RH	Relative humidity
HR-ToF-I-CIMS	High-Resolution Time-of-Flight Iodide-Adduct Chemical Ionization Mass Spectrometer
CIMS	Chemical Ionization Mass Spectrometer
F0AMv4	Framework for 0-D Atmospheric Modeling version4
MCM	Master Chemical Mechanism
GEOS-Chem	Goddard Earth Observing System (GEOS) Chemistry Model
SAPRC-07B	Statewide Air Pollution Research Center Mechanism version 07B
CB6	Carbon Bond 6 mechanism
IPRD	Lumped C ₅ isoprene products
GLYD	Glycolaldehyde
ISOP	Isoprene
RO2	Peroxy radical
RCIM	Reduced Caltech Isoprene Mechanism
ACET	Acetone
ALD2	Acetaldehyde with 3 or more carbons
C2O3	Acetylperoxy radical
CXO3	Acetylperoxy radicals with three or more carbons
FORM	Formaldehyde

GLY	Glyoxal
HO2	Hydroperoxyl radical
MGLY	Methyl glyoxal
PAR	Carbon-carbon single bond
XO2	Peroxy radical generated from NO oxidation to NO ₂
TRPRXN	Counter species for aerosol precursor from monoterpenes
XO2H	NO oxidation to NO ₂ with HO ₂ production from alkoxy radicals
XO2N	Nitrate production from NO reaction with peroxy radicals.
ISOPOOH	Isoprene hydroxy hydroperoxide
HPALDs	Hydroxyl peroxy aldehydes
DHPs	Dihydroperoxy carbonyls
CTM	Chemical Transport Model
NO _x	NO and NO ₂
MVK	Methyl vinyl ketone.
INTR	Nitrates from isoprene oxidation

SUMMARY

Organic acids are secondary components generated from the oxidation of volatile organic compounds in the atmosphere, affecting particulate matter composition, aerosol, and rain acidity. Among them, formic acid is the most abundant gas-phase organic acid, which has been observed over 2.5 ppbV in concentrations in rural areas. However, current atmospheric models' predictions of formic acid are typically biased low, potentially because of the underestimation of direct emissions and chemistry. In our work, we first applied the Framework for 0-D Atmospheric Modeling version4 (F0AMv4) to simulate gas-phase formic acid using four current mechanisms (Master Chemical Mechanism (MCM) v3.3.1, GEOS-Chem Mechanism in version v12-08, SAPRC-07B mechanism and Carbon Bond 6 (CB6) mechanism). The observation data were collected in Yorkville, Georgia, lasted from September to October in 2016 during an intensive campaign. Like earlier studies, the modeled diurnal trend of formic acid was lower than the observation, showing a dissimilar diurnal profile. Then we used the box model combined with the observation data to understand the production of formic acid from isoprene oxidation. Our box model simulations revealed a large difference in formic acid production pathways among four isoprene oxidation mechanisms under different NO_x levels. We discovered that MCM v3.3.1 was likely to underestimate formic acid production from isoprene oxidation because it only considered a small contribution from isoprene epoxydiol (IEPOX) peroxy radicals reacting with HO_2 pathway. However, CB6 mechanism revealed the suppression of formic acid formation under a high NO_x condition as proposed by recent studies, which was not included in all other mechanisms. This mechanism also greatly underestimated the

formic acid production from isoprene reacting with ozone and overlooked the pathway from glycolaldehyde to formic. To better improve the formic acid prediction in the model, additional gas-phase reactions of isoprene and monoterpenes suggested by recent studies were added to our chemical mechanisms. After the modification, we could see a small increase in predicted formic acid concentration. However, these added reactions had little impact on the diel profile of formic acid. According to Gao et al. (2021), the model-measurement discrepancy in formic acid at Yorkville persists, despite modifications to the chemical mechanisms. Our work elaborated the formic acid pathways among each mechanism under different NO_x levels and revealed the role of isoprene and monoterpenes in formic acid production. This shows that the missing monoterpene and isoprene photooxidation reactions discussed in recent studies might not be the only major missing components for formic acid predictions. Models should also consider incorporating other processes like emission.

CHAPTER 1. INTRODUCTION

Organic acids are important species in the total organic mass in the atmosphere. They could be directly emitted from the biogenic and anthropogenic sources and formed through the precursors' secondary reactions. Organic acids can greatly impact secondary organic aerosol (SOA) concentration and rain acidity in remote areas. (Galloway et al. 1982; Jacob 1986; Kavouras, Mihalopoulos, and Stephanou 1998; Keene and Galloway 1984; Keene, Galloway, and Holden 1983; Khare et al. 1999; Le Breton et al. 2012; Millet et al. 2015; Nah, Guo, et al. 2018; Paulot et al. 2011; Sorooshian et al. 2010; Souza 1999; Surratt et al. 2007; Talbot et al. 1990; Yatavelli et al. 2015; Zhang 2004). $PM_{2.5}$ is one air pollutant that can harm air quality and human health. With current emission control over NO_x and SO_2 , SOA's impact on the atmosphere becomes important in the $PM_{2.5}$ composition. Acid rain will cause toxic effects on vegetation, buildings, and human health (Burns et al. 2016). Organic acids have become more significant due to the reduction of SO_2 emissions. Formic Acid ($HCOOH$) is identified as one of the most abundant gas-phase organic acids in the troposphere (Link et al. 2020; Metzger, Mihalopoulos, and Lelieveld 2006; Millet et al. 2015; Stavrakou et al. 2012; Chebbi and Carlier 1996). And since formic acid can be one of the most critical sinks of in-cloud OH radical, it also plays a crucial role in the atmospheric aqueous-phase chemistry by affecting oxidant levels and pH-dependent reaction rates solubilities. (Millet et al. 2015; Jacob 1986).

1.1 Sources and Sinks of Formic Acid

Sources of formic acid include direct emissions from anthropogenic activities and biogenic sources as well as secondary production from gas-phase and aqueous photochemical reactions (Chebbi and Carlier 1996; Khare et al. 1999; Glasius 2000). Earlier studies have hypothesized several dominant sources of formic acid for different site locations. (Brütsch et al. 2017; Graedel and Eisner 1988; Khare et al. 1999; Stavrou et al. 2012). On the one hand, for studies conducted in the Mediterranean, emissions from vegetation dominated the formic acid formation because the diurnal trend of formic acid followed leaf transpiration. (Kesselmeier et al. 1998; Kesselmeier et al. 1997; Khare et al. 1999). On the other hand, the photochemical oxidation of isoprene dominates the formic acid productions for studies conducted in temperate forests due to the abundance of isoprene in the forest and a strong correlation between formic acid and other oxidized VOCs (Alwe et al. 2019). In addition, secondary production is considered the most uncertain source of formic acid. And that more than 80% of the secondary sources of formic acid are photooxidation reactions of the non-methane organic compounds (Link et al. 2020; Paulot et al. 2011; Millet et al. 2015; Müller, Stavrou, and Peeters 2019). Recently, the experiment conducted by Link et al. (2020) inferred that up to 70% of the global annual production of formic acid from gas-phase reactions are produced from the oxidation of isoprene.

The atmospheric lifetime of formic acid is estimated to be 2~4 days (Chebbi and Carlier 1996; Millet et al. 2015; Paulot et al. 2011; Stavrou et al. 2012). However, the OH reaction pathway is only responsible for a small portion of its loss since its photochemical reaction rate is slow (τ is around 25 days) (Chebbi and Carlier 1996; Millet

et al. 2015; Paulot et al. 2011). Therefore, the removal of formic acid is mostly through dry and wet deposition. Current studies showed that its deposition rate in current models is dramatically overestimated. Such underestimation might also play an important role in underestimation of modeled formic acid. (Millet et al. 2015)

1.2 Missing Sources of Formic Acid

Organic acids reflect the fate of emitted hydrocarbons in the atmosphere and will impact the formation of SOA (Link et al. 2020). Despite the importance of formic acid, its origins are still poorly understood. Past studies indicated that models were missing significant sources of formic acid, such as chemical reactions and direct emissions. Ito, Sillman, and Penner 2007 pointed out that the estimated formic acid emission levels in current models might be insufficient. Le Breton et al. (2012) and Millet et al. (2010) suggested that such underestimation of formic acid concentration in models might be because of missing anthropogenic origin primary emissions and its precursors' emissions like isoprene from biogenic sources, which was supported by Stavrou et al. (2012). Stavrou et al. (2012)'s satellite evidence showed a significant missing biogenic sources for formic acid. Also, the oxidation of organic compounds was a great contributor to formic acid. Following the call for detailed research on the chemistry of formic acid precursors, recent studies had found that the secondary production from biogenic VOCs was currently underestimated and predominated the formic acid budget. Those studies also revealed that a wide range of different precursors of formic acid remained undefined (Millet et al. 2010; Cady-Pereira et al. 2014; Bannan et al. 2017). Then Link et al. (2020) had identified that 1) the oxidation of methacrolein (MACR), isoprene epoxydiol (IEPOX), and isoprene hydroxy hydroperoxide (ISOPOOH) were formic acid sources 2)

high NO_x concentration would restrain formic acid production from OH oxidation of isoprene pathway. Also, a recent global modeling study found that that oxidation of methanediol might be a possible chemistry source of formic acid (Franco et al. 2021). To validate its role in formic acid production, additional methanediol reactions were added into existing mechanism, which had little impact on formic acid's concentration and diel profile.

1.3 Gaps in Current Mechanisms

Currently, formic acid production is underestimated in all current mechanisms (Stavrakou et al. 2012; Link et al. 2020; Millet et al. 2015). We first applied the Framework for 0-D Atmospheric Modeling version4 (FOAMv4) (Wolfe et al. 2016) to simulate gas-phase formic acid using four current mechanisms (Master Chemical Mechanism (MCM) v3.3.1, GEOS-Chem mechanism in version v12-08, SAPRC-07B mechanism and Carbon Bond 6 (CB6) mechanism) (Bates and Jacob 2019; Carter 2010; Jenkin, Young, and Rickard 2015; Yarwood G. 2010; Wennberg et al. 2018). The observation data were collected in Yorkville, Georgia, lasted from September to October in 2016 during an intensive campaign. Condensed mechanisms GEOS-Chem, SAPRC-07B, and CB6 are mechanisms for chemical transport models (CTMs): SAPRC-07B and CB6 are often used in air quality simulations with CMAQ (Marvin et al. 2017). GEOS-Chem (<http://www.geos-chem.org>) is a chemical transport model using assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office. MCM v3.3.1, an uncondensed and near-explicit mechanism, is usually used in the box model simulation and provides benchmarks for condensed mechanisms performance (Jenkin, Young, and Rickard 2015; Marvin et al.

2017). All mechanisms showed mismatched diel profiles and under-prediction of formic acid.

Nitrogen oxides (NO_x), with high toxicity and reactivity, are a group of gases that has a strong relationship with ozone and function as important precursors of many other secondary air pollutants, which will cause serious health and environmental concerns. (Li et al. 2013; Brimblecombe 1999). With the current control of NO_x anthropogenic emission in rural areas, the resulting atmospheric reactions become important. Current studies start to pay attention to the impact that different NO_x levels have brought to the formic acid productions. According to Link et al. (2020) and Bates and Jacob (2019), isoprene contributes to the formation of formic acid mainly from the “high NO_x ” condition, “low NO_x ” condition, H-shift isomerization, and ozonolysis pathways. Among them, the different NO_x levels will affect isoprene reacting with OH. Moreover, the ozonolysis pathway is isoprene’s reaction with ozone.

Then the formic acid production from isoprene oxidation with four mechanisms is examined. Isoprene is one of the most important precursors of formic acid. Our work filled the missing hole of the lack of detailed pathways contribution of formic acid from isoprene oxidation products such as methyl vinyl ketone among different mechanisms (Link et al. 2020). Also, we highlighted the urgent need for mechanisms to incorporate the suppression of formic acid production from NO termination reactions, which was proposed recently by Link et al. (2020).

To close the gap between observed and modeled formic acid production, we have added additional gas-phase reactions of isoprene and monoterpenes suggested by recent

studies into existing chemical mechanisms (Aschmann, Arey, and Atkinson 1996; Butkovskaya et al. 2006; Carter 2010; Millet et al. 2015; Paulot et al. 2011). As stated in Gao et al. (2021), Our modified mechanism showed a small increase in acid concentrations and little impact on the diel profile. These results indicated that the missing monoterpene and isoprene photooxidation reactions discussed in recent studies (Millet et al. 2015; Paulot et al. 2011) might not be the only major missing components for formic acid predictions. Models should also consider about incorporating other processes like emission.

CHAPTER 2. BOX MODEL SIMULATION

This chapter is reproduced from Gao et al. (2021); sections 2 and 3.

2.1 Observational Data

Ambient data was collected from August 15th to October 13th in Yorkville, Georgia (Chen et al. 2020; Nah, Guo, et al. 2018; Nah, Ji, et al. 2018). This rural site is surrounded primarily by forests and agriculture fields, with some nearby cattle and poultry operations. There are no major roadways, and a few small, rural roads in the vicinity of the site, so near-by anthropogenic emissions can be considered negligible. The major local precursors of organic acids in this area are most likely isoprene, monoterpenes, and other biogenically-derived organics. Long range transport can also be significant given that the lifetime of formic acid is about two to four days, depending on major sinks, which include photooxidation, wet and dry deposition and some other sinks like uptake by dust particles (Chebbi and Carlier 1996; Hatch, Gough, and Tolbert 2007; Millet et al. 2015; Paulot et al. 2011; Stavrou et al. 2012).

Observations included temperature, RH, solar radiation, wind speed and wind direction; ozone, ammonia, sulfur dioxide, inorganic acids, and trace organics including gaseous and condensed phase organic acids and their precursors (Chen et al. 2020; Nah, Ji, et al. 2018). Gas phase functionalized oxygenated organic species (IEPOX, IEPOX+OH products: C₅H₈O₃, C₄H₈O₃, and C₄H₆O₃ and methanediol) were characterized by High-Resolution Time-of-Flight Iodide-Adduct Chemical Ionization Mass Spectrometer (HR-ToF-I-CIMS) (Chen et al. 2020). The gas phase formic acid concentration was

characterized by sulfur hexafluoride CIMS (SF6-CIMS) (Nah, Guo, et al. 2018; Nah, Ji, et al. 2018). Additional gas phase species characterized were acetic acid, oxalic acid, etc., and observations of condensed phase species, including formate ion. As expected, due to its high volatility, formic acid concentrations were much higher than condensed phase formate ion (Nah, Guo, et al. 2018).

The observed diel trend of the observed formic acid showed a rapid and early rise in the morning, broadly peak from about 10 am to 4 pm (similar to temperature: Figure 1), then has a sharp decrease in the evening. The rapid rise in the morning was more consistent with either a temperature or sunlight-driven emissions source as the increase was found to begin relatively earlier and more rapidly than the observed isoprene, IEPOX, ozone and methanediol (Figure 1, Figure 2). Furthermore, the trends of the observed relative humidity and formic acid are opposite. Given the long chemical lifetime of formic acid in the atmosphere that is about 25 days, the rapid decrease in the evening was consistent with deposition. Therefore, the rapid increase and decrease of the formic acid may be due to a bidirectional process that a reservoir like dew formed at night and absorbed the formic acid. And when the temperature rises, the formic acid reemits into the atmosphere.

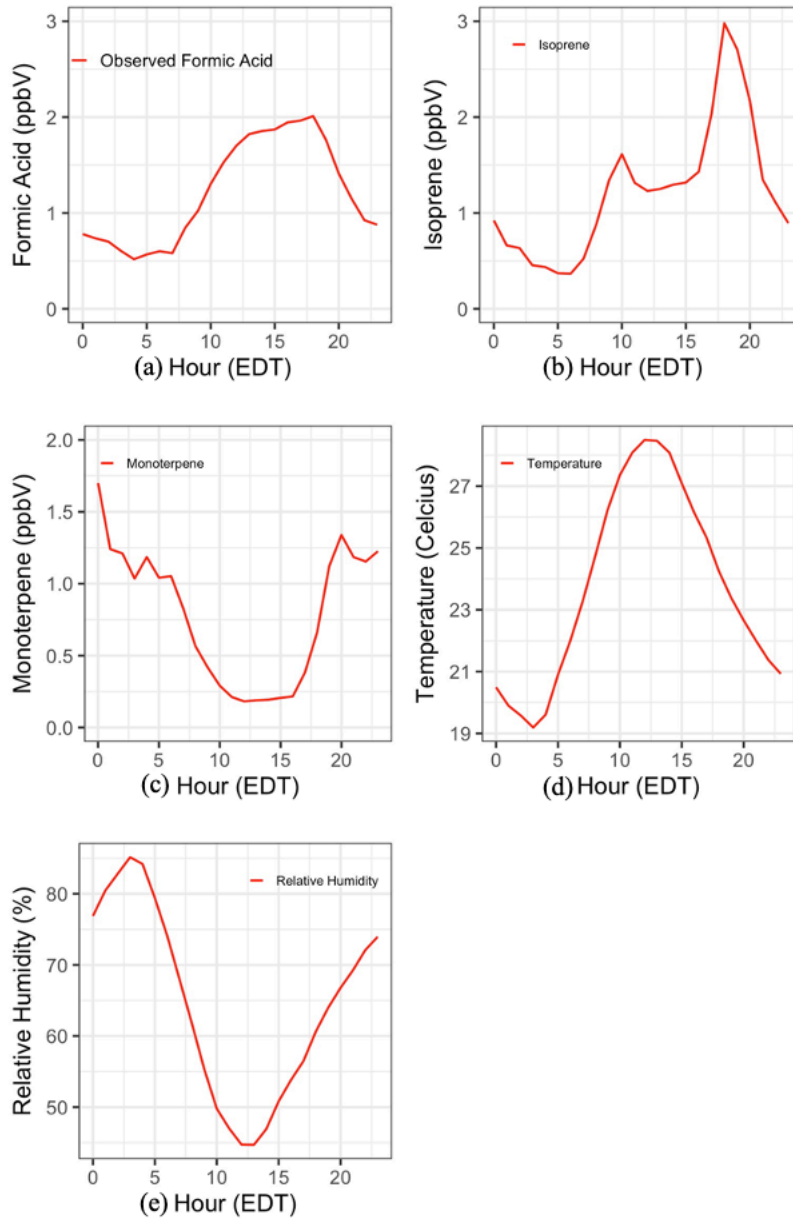


Figure 1– The diurnal trend of the observed formic acid data collected from August 15th to October 13th in Yorkville, Georgia. The Observed data are hourly recorded. (a) formic acid, (b) isoprene, (c) monoterpene, (d) Temperature, (e) Relative Humidity (%)

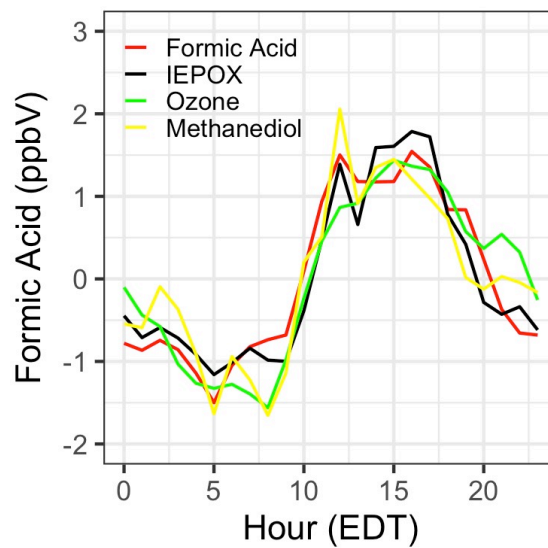


Figure 2– Diurnal trend of the observed formic acid (red line), IEPOX (black line), ozone (green line) and methanediol (yellow line) concentrations (Concentrations are all normalized. The normalized value = (concentration value – mean of the dataset) / standard deviation of dataset).

2.2 Box Model and Mechanisms Overview

We used the Framework for 0-D Atmospheric Modeling version4 (F0AMv4) (Wolfe et al. 2016) equipped with four existing chemical mechanisms: Master Chemical Mechanism (MCM) v3.3.1, GEOS-Chem Mechanism in version v12-08, SAPRC-07B mechanism and Carbon Bond 6 (CB6) mechanism (Bates and Jacob 2019; Carter 2010; Jenkin, Young, and Rickard 2015; Yarwood G. 2010; Wennberg et al. 2018).

MCM is a near-explicit mechanism. It's highly detailed and commonly used in photochemical box models for tropospheric chemistry while providing a benchmark for condensed mechanisms evaluation (Jenkin, Young, and Rickard 2015). The total number of species is 610 and the total number of reactions is 1974 in MCM mechanism. Besides, MCM groups all RO₂ as a single species when representing peroxy radical self-termination pathways. This single RO₂ species reacts indiscriminately with other unique RO₂ (Link et al. 2020).

GEOS-Chem v12-08 adopted their isoprene oxidation pathway from the reduced Caltech isoprene mechanism (RCIM) (Bates and Jacob 2019), which is version 4.1 of the “Reduced-plus” mechanism. This mechanism condenses the ensuing oxidation cascade for the practical range in the atmosphere adopted from Wennberg et al. (2018)'s mechanisms repository and includes the complete oxidation reactions of isoprene from multiple pathways like OH, ozone, and NO₃ (Bates 2017). There are 148 species and 412 reactions in GEOS-Chem v12-08 mechanism. In the latest update, RCIM was compiled with the full explicit mechanisms to keep product yields of known compounds the same, which allows it closely to track early-generation compound yields and mixing ratios as

those in the full explicit mechanism. Also, RCIM brings a novel treatment for the isoprene-hydroxy-peroxy radical system. Bates and Jacob (2019) has the detailed description.

The SAPRC-07B mechanism led to the highest formic acid levels (Figure 3), which was still biased low by a factor of ~ 4 during the daytime compared to the observations. None of the mechanisms caught the rapid increase and sharp decrease in the observed FACD trend. Due to the low simulation of the FACD using CB6, we added the additional gas-phase reactions found in the literature into the mechanism.

The CB mechanism condenses the tropospheric chemistry in a concise magnitude. The version of CB6 used was equipped with 159 species and 329 reactions but did not include all the potential FACD chemical formation routes, such as photooxidation reactions of precursors and potential heterogeneous pathways (Link et al. 2020; Millet et al. 2015; Nguyen et al. 2015; Paulot et al. 2011; Yarwood G. 2010).

2.3 Box Model Simulation

2.3.1 Box Model Setup

While the box model cannot capture the full dynamics that other Chemical Transport Models (CTM) will, it can provide insights as to the potential impacts of changing chemical mechanisms and adding reactions on the FACD formation, and show which reactions are significantly affect the levels and diel profile of the simulated FACD.

We first used primary VOCs and inorganic trace gases measured at the Yorkville site to constrain the species for all mechanisms following Kaiser et al. (2016) and Link et

al. (2020). The simulations incorporated the dry deposition as described in Nguyen et al. (2015) and chose the representative species based on Kaiser et al. (2016) to scale the variation of the diurnal deposition rate. The dilution rate used in all the simulations was 4 day^{-1} (Kaiser et al. 2016). The observed solar radiation at each time step normalized to the maximum solar radiation were used to scale the photolysis rates. The simulation ran six days with two days for model spin-up.

2.3.2 *Base Case Simulation*

The main pathway to form FACD in the MCM v3.3.1 mechanism is CH_2OO Criegee intermediate reaction, and most of the CH_2OO is formed from the photochemical reactions between isoprene and ozone. The isoprene-OH oxidation pathways lead to a greater fraction of the FACD formation in GEOS-Chem mechanism than those in the MCM, though the formation of FACD is still mainly from the isoprene-ozone pathways. This result was similar to Bates and Jacob (2019) and Link et al. (2020). SAPRC-07B includes all the formic acid precursors ozonolysis pathways. However, the formic acid concentrations may be overestimated because this mechanism lumps C_5 isoprene products into one species (IPRD), which can include species that are not precursors to formic acid formation. In addition, SAPRC-07B has more pathways to form FACD than CB6 mechanism, including the ozonolysis of monoterpenes, isoprene, and isoprene products.

The SAPRC-07B mechanism led to the highest formic acid levels (Figure 3), which was still biased low by a factor of ~ 4 during the daytime compared to the observations. None of the mechanisms caught the rapid increase and sharp decrease in the observed

FACD trend. Due to the low simulation of the FACD using CB6, we added the additional gas-phase reactions found in the literature into the mechanism.

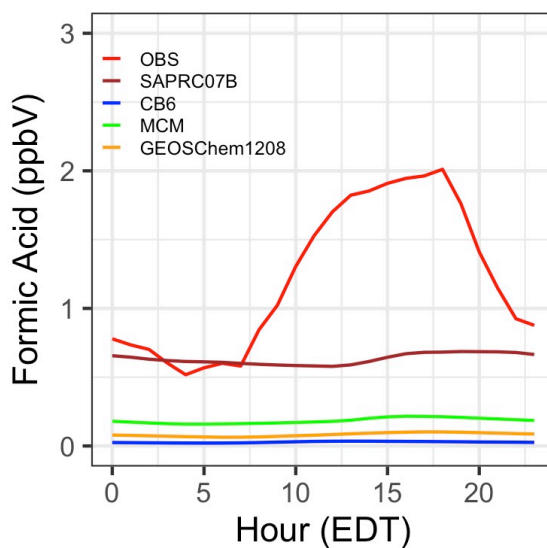


Figure 3 – The diurnal trend of the observed and base box-model simulated formic acid concentration using different chemical mechanisms at the Yorkville, GA site. The red line is the observed formic acid. The brown line is the simulation using the original SAPRC07B chemical mechanism. The blue line is the simulations using the original CB6 chemical mechanism. The green line is the simulation using MCM v3.3.1 and the orange line is the simulations using GEOS-Chem v12-08.

CHAPTER 3. FORMIC ACID PRODUCTION FROM ISOPRENE UNDER DIFFERENT NO_x LEVELS

3.1 Mechanism Pathways

To better understand the reasons why all mechanisms are under predicting the formic acid concentration, we investigated the pathways of formic acid formation from isoprene in four existing chemical mechanisms: Master Chemical Mechanism (MCM) v3.3.1, GEOS-Chem Mechanism in version v12-08, SAPRC-07B mechanism, and Carbon Bond 6 (CB6) mechanism (Bates and Jacob 2019; Carter 2010; Jenkin, Young, and Rickard 2015; Yarwood G. 2010; Wennberg et al. 2018).

The MCM v3.3.1 mechanism only considered two intermediate pathways to form formic acid: 1) the reaction of CH₂OO, 2) from hydroxymethyl-methyl- α -lactone (HMML). Particularly, CH₂OO contributed the majority of the formic acid production, while HMML's contribution is negligible. Most of the CH₂OO was generated directly from isoprene reacting with ozone. In addition, there was a reasonable amount of CH₂OO generated from the reaction with methyl vinyl ketone (MVK), which was mainly formed from 1-2-ISOPOOH. Meanwhile, the contribution of 4-3-ISOPOOH to MVK concentrations was negligible in MCM v3.3.1, which corresponded to Link et al. (2020)'s experiment results. Link et al. (2020) also proposed that methacrolein (MACR) may contribute a certain amount of formic acid. However, its pathway from the reaction of isoprene epoxydiol (IEPOX) peroxy radicals with HO₂ was trivial, which was considered as an important source of formic acid according to Link et al. (2020)'s experiment.

GEOS-Chem v12-08 incorporated much more detailed reactions to form formic acid. Most of the formic acid is generated from the isoprene reacting with OH and NO₃. Unlike MCM v3.3.1, the reaction of isoprene with ozone only produced a small amount of formic acid in GEOS-Chem v12-08. Also, the HMML pathway generated more formic acid than the CH₂OO, which was the main pathway in MCM v3.3.1. In addition to reacting with ozone to go through the CH₂OO pathway as in MCM v3.3.1, MACR would also react with OH to be a source of HMML. Also, GEOS-Chem v12-08 considered the formic acid pathways from trans-Beta isoprene epoxydiol, cis-Beta isoprene epoxydiol, and Delta isoprene epoxydiol, which was trivial in MCM v3.3.1. In general, isoprene reacts with OH is the major contributor of formic acid, consistent with the finding in Link et al. (2020) and Bates and Jacob (2019).

SAPRC-07B only considered the formic acid formation directly from the ozonolysis of isoprene, MVK, MACR, and other lumped C5 isoprene products. Therefore, we expect the formic acid using this mechanism has a similar trend with the one using MCM v3.3.1.

As for Carbon Bond 6 (CB6), it lumped the MACR and MVK into one specie named isoprene products (ISPD). In this mechanism, nitrates from isoprene oxidation (INTR) can react with OH to form formic acid. Moreover, it contains the pathway from isoprene epoxydiol (IEPOX) to form formic acids. Specifically, IEPOX is generated from the products of isoprene peroxy radical reacting with HO₂ while INTR is generated from isoprene peroxy radical reacting with NO. These two reactions is competitive based on NO_x level (Link et al. 2020).

Current studies started to pay attention to the impact that different NO_x levels have brought to the formic acid productions. According to Link et al. (2020) and Bates and Jacob (2019), isoprene contributes to the formation of formic acid mainly from “high NO_x concentration”, “low NO_x concentration”, H-shift isomerization, and ozonolysis pathways. Among them, the different NO_x affects the reactions of isoprene with OH, while ozonolysis originates from isoprene reacting with O₃.

3.2 Methods

We conducted box model simulations to quantify the concentration of formic acids from isoprene oxidation under “high NO_x” and “low NO_x” conditions, using the Framework for 0-D Atmospheric Modeling version4 (F0AMv4) (Wolfe et al. 2016) with the four mechanisms mentioned above.

We used observed isoprene and other inorganic trace gases: O₃, CO, NO, NO₂ measured at the Yorkville site to constrain the species. The H₂ concentration was set to 550 ppbv all the time. The simulations incorporated the dry deposition as described in Nguyen et al. (2015) and chose the representative species based on Kaiser et al. (2016) to scale the variation of the diurnal deposition rate. The dilution rate used in all the simulations was 4 day⁻¹ (Kaiser et al. 2016). The ratio of the observed solar radiation at each time step and the maximum observed solar radiation were used to scale the photolysis rates. The simulation ran six days with two days for model spin-up.

To explore the pathways under different NO_x levels, we multiplied the observed NO and NO₂ with a coefficient. According to Link et al. (2020), the coefficient was set to 1 to represent the “high NO_x” condition and 0.001 for the “low NO_x”. (The NO_x level

at 12:00 pm for “low NO_x” condition will be 0.001314 ppb and 1.314 ppb for “high NO_x” condition)

We only focused on the main oxidation products of isoprene and pathways that form formic acid in each mechanism. For all mechanisms, we will track the production of formic acid from MACR, MVK and isoprene reacting with ozone based on Link et al. (2020). Since MCM v3.3.1 does not treat IEPOX as the major contribution to the formic acid, we only investigate the IEPOX production in other mechanisms. As discussed above, we also would like to evaluate the contribution from isoprene reacting with OH and NO₃ to formic acid concentrations in GEOS-Chem v12-08 as well as the contribution of INTR and IEPOX inside the CB6.

3.3 Results

Under the “low NO_x” condition (Figure 4), the formic acids in MCM v3.3.1 and SAPRC-07B were generated mainly from isoprene reacting with ozone. However, in GEOS-Chem v12-08, the reaction of isoprene with OH and NO₃ was the main contributor. Also, the part of formic acid generated from IEPOX was different between GEOS-Chem v12-08 and CB06. However, in all mechanisms, formic acid produced from MACR and MVK were low, which matched the experiment results from Link et al. (2020). When the NO_x level is low, MCM v3.3.1 produced the highest formic acids level because there was many HO₂ reactions and negligible NO pathways. This was also why formic acid levels was similar to using MCM v3.3.1 in the low and high NO_x condition.

Under the “high NO_x” condition (Figure 5), there was a significant amount of formic acid from OH oxidation of isoprene oxidation nitrates (INTR) in CB6 mechanism. To be

noticed, the IEPOX oxidation in all the mechanisms only contributed negligibly to the formic acid predictions. The SAPRC-07B mechanism had the highest levels of formic acids because it had the most condense mechanisms. The increase of formic acids under the “high NO_x” condition in SAPRC-07B was due to the rising of ozone concentrations and the predominant pathways to form formic acid in SAPRC-07B mechanism are through ozonolysis of isoprene and isoprene products. As in the CB6 mechanism, we found that compared with the formic acid formation under low NO_x condition, INTR and OH reaction formed more formic acid in high NO_x condition (Fig. 5 and 6). This was because INTR was formed through the reaction between isoprene oxidation products and NO, which was competitive with the IEPOX formation pathway.

Except for CB6 mechanisms, all other three mechanism showed an increased formic acid level as the NO_x level increased (Figure 4, Figure 5). This might be because the ozone levels were increased due to the growth of NO_x levels. So, more formic acid was formed through isoprene and its products photooxidation reactions. However, according to Link et al. (2020), more formic acid should be generated under the “low NO_x” condition since 1) NO termination reactions can suppress formation of organic acids and 2) HO₂ and NO pathways are competitive reactions. We could see a clear competition between INTR and IEPOX in CB6 mechanisms. This was because the formation of these two species was related to the variability of the NO_x level. Also, the contribution from the isoprene reacting with ozone pathway increased when the NO_x level is high.

Such NO_x-dependent productions of formic acid from box model results will be helpful for finding out their major production pathways at different NO_x levels. With aerial

observations, our study can be used to evaluate 3-D Chemistry Transport Model performance from different pathways.

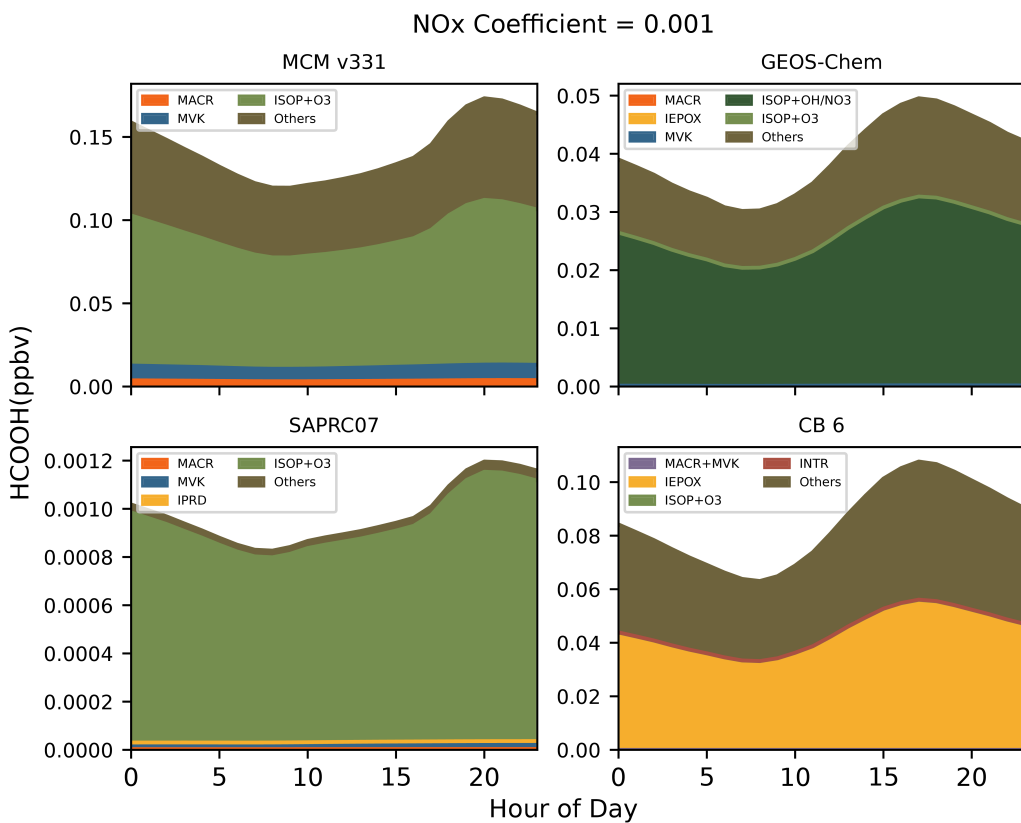


Figure 4 – The contribution of main pathways in each mechanism in the last model day when the NO_x level is low (coefficient = 0.001) NO_x level at 12:00 pm is 0.001314 ppbv.

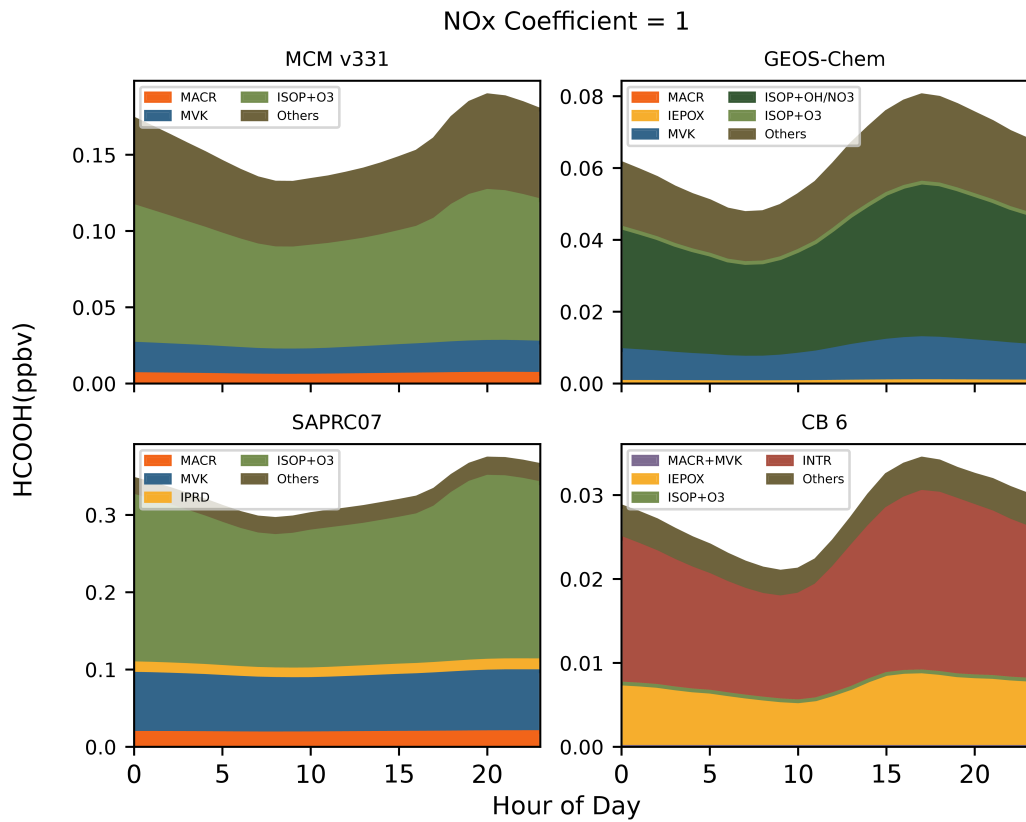


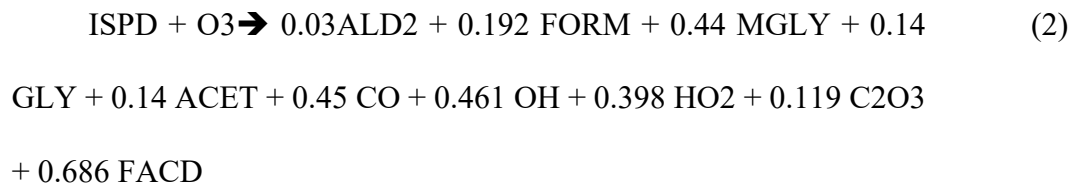
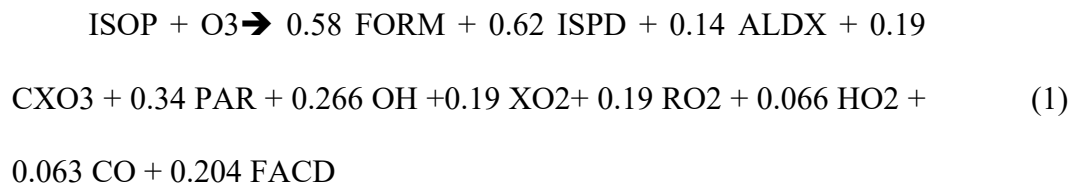
Figure 5 – The contribution of main pathways in each mechanism in the last model day when the NO_x level is high (coefficient = 1). NO_x level at 12:00 pm is 1.1314 ppbv.

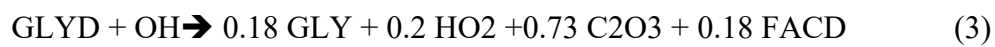
CHAPTER 4. MECHANISMS MODIFICATIONS

This chapter is reproduced in Gao et al. (2021), section 3.

Through the literature review, isoprene (ISOP) can react with ozone and produce formic acid with a 20.4% molar yield (Carter 2010), while products from the isoprene and OH reaction can react with ozone with an estimated yield of formic acid of 68.6% (Aschmann, Arey, and Atkinson 1996; Carter 2010). Glycolaldehyde (GLYD) is also a formic acid precursor. Based on the average temperature in this study, the formation yield of formic acid was about 18% from the glycolaldehyde and OH reaction (Butkovskaya et al. 2006). In the original CB6 chemical mechanism, isoprene products (ISPD: methacrolein, methyl vinyl ketone, etc.) could have an ~15% molar yield of formic acid from the reaction with ozone.

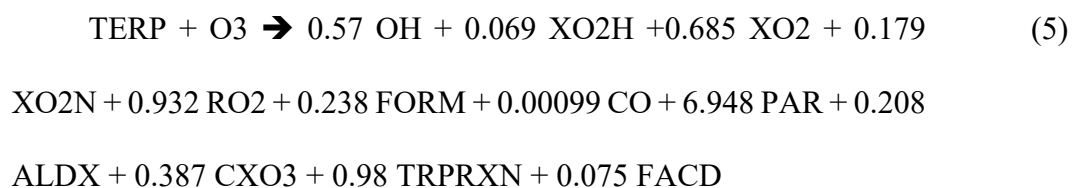
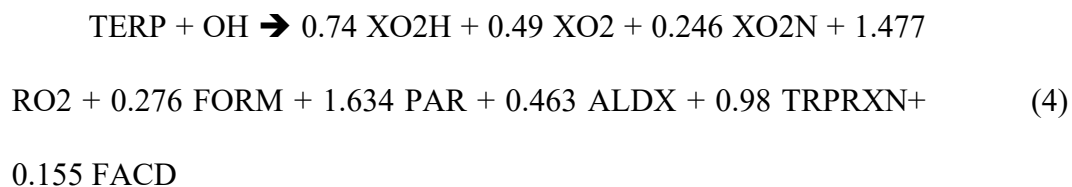
After accounting for conservation of carbon, the modified reactions are:





where the chemical species are ACET: acetone, ALD2: acetaldehyde, ALDX: aldehydes with 3 or more carbons, C2O3: acetylperoxy radical, CXO3: acetylperoxy radicals with 3 or more carbons, FACD: formic acid, FORM: formaldehyde, GLY: glyoxal, HO2: hydroperoxyl radical, MGLY: methyl glyoxal, PAR: carbon-carbon single bond, RO2: total peroxy radical concentration, XO2: NO oxidation to NO₂ via peroxy radical.

There was no formic acid formation pathway from monoterpene oxidation in the base CB6 chemical mechanism, but (Paulot et al. 2011) and Millet et al. (2015) suggested that monoterpenes could have a molar yield of formic acid of ~15% from reactions with OH and about 7.5% from reactions with ozone. To capture this, additional formic acid formation from monoterpene (TERP) reactions were added as well:



where TRPRXN: counter species for aerosol precursor from monoterpenes, XO2H: NO oxidation to NO₂ with HO₂ production from alkoxy radicals, XO2N: nitrate production from NO reaction with peroxy radicals.

Using this result, Gao et al. (2021) showed that After adding the gas phase isoprene and monoterpene photooxidation reactions into the CB6 mechanisms, the simulated formic acid increased about 0.2 ppbV, which is in the middle of the range of the simulated FACD using other mechanisms, closely matching the MCM results (Figure 6). Also, after adding the FACD formation pathway through monoterpene and OH reaction in SAPRC07B, the simulated formic acid increased about 0.06 ppbV. However, the diurnal trend of the simulated formic acid increased about 0.06 ppbV. However, the diurnal trend of the simulated FACD still could not capture the peak of the observations during the daytime.

In addition, Gao et al. (2021) also incorporated the modifications into the CMAQ model and it had a similar results to the box model result.

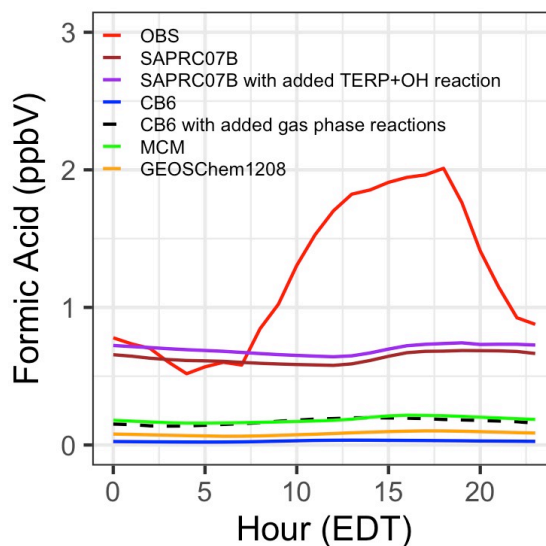


Figure 6 – The diurnal trend of the observed and box-model simulated formic acid concentration using different chemical mechanisms at the Yorkville, GA site. The red line is the observed formic acid. The brown and purple lines are the simulations using the original and revised SAPRC07B chemical mechanism. The blue and dashed black lines are the simulations using the original and revised CB6 chemical mechanism. The green line is the simulations using MCM v3.3.1 and the orange line is the simulations using GEOS-Chem v12-08.

CHAPTER 5. CONCLUSION AND FUTURE WORK

5.1 Conclusion

Based on the comparison between the observed and simulated formic acid concentrations, some potential reactions or other processes were missing from the model to capture the dynamics of formic acid.

We have investigated four mechanisms' main formic acid formation pathways from isoprene. The direct formic acid production from isoprene, either with OH or ozone, significantly contributes to all the mechanisms. Only GEOS-Chem v12-08 and CB6 had the NO pathways to form isoprene nitrates, which produced more formic acid under high NO_x condition. Isoprene and NO reaction in GEOS-Chem v12-08 generated a considerable formic acid, and CB6 had a pathway to produce formic acid from INTR. These two pathways significantly affected the viability of formic acid concentrations under different NO_x levels. According to Link et al. (2020) and Bates and Jacob (2019), the “high NO_x ” and “low NO_x ” had a great influence on the reactions of isoprene with OH. Consequently, the different NO_x conditions could significantly affect the formic acid levels. Since NO termination reactions can suppress formation of organic acids (Link et al. 2020), formic acid concentration should decrease as the NO_x level increases. Furthermore, this trend was only captured by the CB6 mechanism. The reason might be that the NO_x concentration in this project was not high enough to suppress the ozone concentration, which correlated with OH concentration. Also, MCM v3.3.1 and GEOS-Chem v12-08 merely considered the formic acid generated from IEPOX. The IEPOX pathway in CB6 shows a great

contribution under the low NO_x level because of the rise of IEPOX concentration from more HO_2 and RO_2 (from isoprene oxidation) reactions. Our work filled the missing hole of the lack of detailed production of formic acid from isoprene oxidation products such as MVK and IEPOX among different mechanisms (Link et al. 2020). Also, we highlighted the urgent need for mechanisms to incorporate the suppression of formic acid production from NO termination reactions, which was proposed recently by Link et al. (2020).

Several additional gas phase isoprene and monoterpene photooxidation reactions were added to the CB6 mechanism and the SAPRAC07 mechanism in the box model. Although these reactions could explain a small part of the low formic acid's simulation during the daytime, the simulated formic acid was still biased low with the addition of those gas-phase chemical reactions. Also, the diel profile of the updated simulations still could not capture the rapid rise and sharp decrease of the observed formic acid. As stated in Gao et al. (2021), Our modified mechanisms indicated the missing monoterpene and isoprene photooxidation reactions discussed in recent studies (Millet et al. 2015; Paulot et al. 2011) might not be the only major missing components for formic acid predictions.

5.2 Future Work

Although current studies cannot quantify the contribution of isoprene oxidation from other correlated formic acid sources, it was hypothesized to be the most possible candidate of the principal sources of formic acid from gas-phase reactions in the global atmosphere. The gap in current models could be explained by a missing source of formic acid from isoprene combined with a widespread chemical source from various precursor types (Millet et al. 2015; Link et al. 2020).

As for the sole isoprene-oriented pathways among the current mechanisms we have investigated, only the CB6 mechanism had captured the decrease of formic acid when the NO_x level increased as described in Link et al. (2020). The ability of models to capture formic acid variation under different NO_x levels would affect global estimates of formic acid, especially in regions where NO_x level was not high. More detailed pathways of isoprene reacting with OH under different NO_x level should be incorporated in the other three mechanisms. Also, the contribution of IEPOX pathways varies a lot in different mechanisms. Therefore, future experiments and studies are required to quantify IEPOX's contribution to formic acid formation. Similarly, the contribution from MVK also showed a great discrepancy between mechanisms, and no literature values were available for the production of acids from these isoprene oxidation products (Link et al. 2020). Future laboratory work for the formation of formic acid at different NO_x levels are urgently needed since this may change the way we view formic acid-related atmospheric reactions.

To better capture the formic acid concentration and its diel profile, more sources, like emission processes, should be considered to fill the missing formic acid production gap.

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