https://doi.org/10.5194/egusphere-2026-234
Preprint. Discussion started: 26 January 2026
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High Yields of Formic Acid and Acetic Acid during Multi-generational Oxidation of Toluene

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https://doi.org/10.5194/egusphere-2026-234
Preprint. Discussion started: 26 January 2026
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ABSTRACT

Formic acid and acetic acid are the most abundant gas-phase organic acids in the atmosphere, yet their concentrations are substantially underestimated by both global and regional atmospheric models across diverse environments. In this study, we report unexpectedly high yields of formic acid and acetic acid formed during the multi-generational photooxidation of toluene, a canonical anthropogenic volatile organic compound. Their yields show a strong dependence on hydroxyl radical (•OH) exposure ([•OH] × residence time), increasing from 25% and 24% under low exposure (<0.2 equivalent days) to 74% and 40% under elevated exposure (1–3 equivalent days) for formic and acetic acid, respectively. The formation of these organic acids is not significantly affected by NO_x concentrations. A modified box model based on MCM v3.3.1 underestimates the peak concentrations of both acids by approximately a factor of five, indicating substantial gaps in current mechanistic understanding. Although both secondary aerosol formation and organic acid production increase with aging within a certain degree of oxidation, their distinct temporal evolutions indicate that particle photodegradation is not the dominant pathway. The contrasting •OH exposure dependence between organic acids and primary carbonyl compounds further suggests that these acids are predominantly multi-generational oxidation products. These findings demonstrate that multi-generational oxidation of aromatic compounds is an important and previously underappreciated source of atmospheric organic acids. The omission of organic acid formation from aromatic oxidation in current chemical mechanisms likely contributes to their widespread underestimation in models, highlighting the need for detailed laboratory studies and updated chemical mechanisms.

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1 INTRODUCTION

Organic acids are ubiquitous in the troposphere and are important contributors to acidity in precipitation (Stavrakou et al., 2012). Among them, formic acid (HCOOH) and acetic acid (CH_3COOH) are the most abundant gas-phase organic acids in various atmospheric environments, with mixing ratios spanning from a few parts per trillion by volume (pptv) to tens of parts per billion by volume (ppbv) (Chebbi and Carlier, 1996; Veres et al., 2011; Mungall et al., 2018; Ding et al., 2025). Formic acid alone can contribute to more than half of rainwater acidity in many continental regions (Stavrakou et al., 2012). In addition, these organic acids can also affect secondary aerosol formation by modifying aerosol pH and gas-particle partitioning processes (Shen et al., 2018; Tao and Murphy, 2019).

On a global scale, the dominant source for formic acid and acetic acid is considered to be secondary production from the photooxidation of biogenic volatile organic compounds (VOCs), particularly isoprene and its oxidation products (Paulot et al., 2011; Khan et al., 2018; Link et al., 2020). But rapid secondary production and high amounts of formic acid and acetic acid have also been observed in anthropogenic air masses and urban environments (Veres et al., 2011; Yuan et al., 2015; Millet et al., 2015; Liggio et al., 2017), suggesting that anthropogenic VOCs may play a significant role in the formation of formic acid and acetic acid in the polluted areas. However, sources of atmospheric organic acids and their detailed formation pathways are still poorly understood, as evidenced by the fact that current atmospheric chemical models substantially underestimate (up to >10 times) their field-observed concentrations on both global (Paulot et al., 2011; Stavrakou et al., 2012; Chaliyakunnel et al., 2016; Khan et al., 2018) and regional scales (Le Breton et al., 2012; Yuan et al., 2015; Millet et al., 2015; Liggio et al., 2017) in the free troposphere (Paulot et al., 2011; Millet et al., 2015), the forest (Stavrakou et al., 2012; Schobesberger et al., 2016), the urban (Yuan et al., 2015; Bannan et al., 2017; Khan et al., 2018), the polar region (Paulot et al., 2011; Mungall et al., 2018), and the oil sands region (Yuan et al., 2015; Liggio et al., 2017). Such widespread underestimation implies the existence of large and pervasive missing or underestimated sources in current models (Yuan et al., 2015; Liggio et al., 2017). Numerous hypotheses have been proposed to reconcile this model–observation gap, including previously unrecognized contributions from biomass burning (Paulot et al., 2011; Chaliyakunnel et al., 2016), unmeasured anthropogenic intermediate VOCs (Le Breton et al., 2012; Liggio et al., 2017), acetaldehyde tautomerization (Shaw et al., 2018), cloud-mediated methanediol oxidation (Franco et al., 2021), and chemical aging of organic aerosols (Paulot et al., 2011; Malecha and Nizkorodov, 2016, 2017; Bates et al., 2023; Jiang et al., 2023).

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Nevertheless, none of these processes alone can fully account for the high ambient concentrations of formic acid and acetic acid observed in the atmosphere (Yuan et al., 2015; Liggio et al., 2017; Franco et al., 2021).

Recent studies have suggested that resolving this discrepancy would require much higher effective molar yields of formic acid from the oxidation of monoterpenes or anthropogenic VOCs than currently assumed (Stavrakou et al., 2012; Liggio et al., 2017). For example, Liggio et al. (2017) estimated that ~50% of formic acid yield would be necessary to reconcile observations and modeling results in an oil sand region (Liggio et al., 2017). In contrast, laboratory-reported yields of formic acid and acetic acid from VOC photooxidation are typically below 15% (Berndt and Böge, 2001; Baltensperger et al., 2005; Paulot et al., 2011; Yuan et al., 2015). Notably, most of these yields were measured under relatively low •OH exposures ([•OH] × residence time), corresponding to less than one equivalent atmospheric photochemical day (Praplan et al., 2014). However, recent studies revealed that molecular fragmentation reactions become increasingly important with oxidative aging (Lambe et al., 2012; Ortega et al., 2013; Isaacman-VanWertz et al., 2018), potentially enhancing the formation of small oxygenated species. Consistent with this hypothesis, substantial increases in gas-phase organic acids have been observed during the aging of biomass-burning emissions (Ortega et al., 2013; Bruns et al., 2017) and diesel exhaust (Friedman et al., 2017). For instance, Bruns et al. (2017) reported that formic acid concentrations increased by factors of ~5–50 with aging. Friedman and Farmer (2018) further demonstrated that the molar yield of organic acid strongly depends on OH radical concentrations during photooxidation of monoterpenes. These findings suggest that the persistent model–observation discrepancy may be owing to an incomplete mechanistic and quantitative understanding of organic acid formation during multi-generational oxidation under atmospherically relevant conditions.

Oxidation flow reactor (OFR) provides a powerful complement to traditional environmental chambers by enabling simulation of oxidation equivalent to multiple days of atmospheric aging within residence times of seconds to minutes through the use of elevated oxidant concentrations (Lambe et al., 2015). A key advantage of OFR is its ability to achieve high photochemical exposure while minimizing wall losses of gases and particles, which can be substantial in Teflon chambers owing to the long residence times typically employed (Zhang et al., 2014; Brune, 2019). The validity of OFR has been demonstrated in numerous studies (Lambe et al., 2015; Peng et al., 2015), and they are increasingly used to investigate the effects of photochemical aging on gas-phase chemistry (Lambe et al., 2015; Friedman and Farmer, 2018), secondary

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organic aerosol (SOA) formation (Bruns et al., 2015), and aerosol optical properties (Lambe et al., 2013). In this study, we employ an OFR to investigate the formation of formic acid and acetic acid during the photooxidation of toluene, a canonical and highly abundant anthropogenic VOC, over a wide range of OH exposure, and examine how these processes affected by relative humidity, initial toluene and NO_x concentration. By the combination of laboratory studies and model simulations, the possible mechanism for the formation of formic acid and acetic acid are also explored.

2 METHODS

2.1 Oxidation Flow Reactor

Toluene photooxidation experiments were conducted in a custom-built quartz oxidation flow reactor (OFR) with a total volume of 2 L (1 m length and 5 cm inner diameter; Figure 1). The reactor temperature was maintained at 298 K by a continuously circulating water jacket. Low-pressure mercury lamps (primary emission at 254 nm) were evenly distributed around the reactor, with up to eight lamps operating simultaneously. The OH radicals in the OFR were generated via the reaction of $O(^1D) + H_2O \rightarrow 2\ \bullet OH$, where $O(^1D)$ was produced by photolysis of externally introduced O_3. O_3 was generated upstream of the OFR using a custom-built O_3 generator in which O_2 was irradiated at 185 nm. Photons at 185 nm were effectively filtered by the quartz sleeves of the lamps, the quartz reactor walls, and the water jacket, thereby minimizing in situ O_3 formation inside the OFR (<10 ppbv). A movable sampling port (6 mm outer diameter) enabled gas and particle sampling at different axial positions along the OFR. The •OH exposure in the OFR was determined using the box model described in Section 2.3, and the results are provided in Table S1 and Figure S1. At 20% RH, the modeled •OH exposures ranged from 2.03×10^{10} to 1.97×10^{12} molecules cm^{-3} s, corresponding to equivalent atmospheric aging of 0.07–6.34 days assuming a 24-h average OH radical concentration of 3.6×10^6 molecules cm^{-3} in urban Beijing (Tan et al., 2018). At 70% RH, the equivalent atmospheric aging times in the experiments were from 0.20 to 15.64 days.

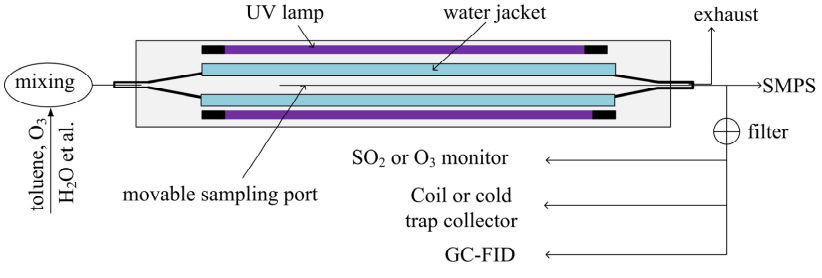

Figure 1. Schematic diagram of the experimental setup.

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2.2 Experimental Procedures

Toluene gas with an initial concentration of ~94 ppbv was generated by passing a flow of N_2 (99.999%, Beijing Haipubeifen Gas) over liquid toluene (Merck, ≥ 99.9%) in a temperature-controlled diffusion tube. RH in the OFR was adjusted by introducing water vapor generated using a bubbler. The gas mixture of toluene, O_3, and water vapor were continuously introduced into the OFR at a total flow rate of 2 L min^{-1}, and the initial concentration of O_3 was about 1580 ppbv. Samples were collected at axial positions corresponding to 5%, 25%, 45%, 65%, and 85% of the reactor length using the movable sampling port. Under laminar flow conditions, these positions corresponded to residence times of 3.9, 15.8, 27.5, 39.3, and 51.0 seconds, respectively. Additional experiments were conducted with 2, 4, 6, or 8 lamps to achieve higher •OH exposures. The corresponding •OH exposures under different experimental conditions are summarized in Table S1. The influence of NO_x on organic acid formation was investigated by adding N_2O to the OFR. NO and NO_2 were produced via the reaction $O(^1D) + N_2O \rightarrow 2\ NO$, followed by $NO + O_3 \rightarrow NO_2 + O_2$ (Lambe et al., 2017).

Toluene concentrations were quantified using gas chromatography with a flame ionization detector (GC-FID, Agilent 7890A) (Wu et al., 2017). O_3 and SO_2 were measured using an O_3 analyzer (model 202, 2B Technologies, USA) and an SO_2 analyzer (model 43i-TLE, Thermo), respectively. Particle number size distributions were measured using a scanning mobility particle sizer (SMPS, DMA 3081 connected to CPC 3776, TSI Inc.). Carbonyl compounds were collected using the cold trap method (Huang et al., 2013) and analyzed by high-performance liquid chromatography (HPLC) with ultraviolet detection (Shen et al., 2018, 2024). All experiments were conducted in the absence of seed particles. Gas-phase organic acids were collected using a temperature-controlled scrubbing glass coil maintained at 277 K and extracted with ultrapure water as the stripping solution (Wu et al., 2017; Xing et al., 2018). Gas and stripping solution flow rates were 0.6 L min^{-1} and 0.2 mL min^{-1}, respectively. The efficiency of sample collection was measured as approximately 85% for acetic acid, 95% for formic acid, and 99% for pyruvic acid. The eluent was collected for 15 min, and then the sample was analyzed immediately using ion chromatography (DIONEX ICS–2000) (Shen et al., 2018). The concentration of organic acids was quantified using a mixed liquid standard solution containing formic acid, acetic acid, and pyruvic acid. To evaluate potential artifacts associated with aqueous-phase formation in the stripping solution, five additional gas-phase samples were collected using Horibe tubes with an ethanol cold trap maintained at 183 K. Concentrations measured using the scrubbing coil and Horibe tubes agreed within 10%, indicating that

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aqueous-phase artifacts had a minor influence on measurements. Reported yields of formic acid and acetic acid in this study are apparent yields and were not corrected for their subsequent reactions with OH radicals.

A series of control experiments was conducted to ensure data quality and reproducibility. (1) Before each experiment, high concentrations of O_3 were introduced into the OFR with two lamps illuminated until particle concentrations measured by the SMPS were negligible (< 50 cm^{-3}) and no impurities were detected by GC-FID. (2) O_3 photolysis experiments were performed before each toluene photooxidation experiment to verify consistent irradiation conditions based on comparable O_3 decay rates. (3) Blank experiments were conducted without toluene, with toluene but without O_3, and with both toluene and O_3 but without water vapor. Formic and acetic acid concentrations observed in these blank experiments were low relative to those measured during toluene photooxidation (less than 15%). All reported data were corrected for blank contributions.

2.3 Model Description and Determination of Photon Flux

A zero-dimensional box model based on the Master Chemical Mechanism (MCM) v3.3.1 (http://mcm.leeds.ac.uk/MCM/) and modified following Li et al. (2015) was employed to simulate toluene photooxidation and organic acid formation in the OFR (Li et al., 2015; Jenkin et al., 2015). Rate coefficients for additional reactions were adopted from the latest JPL kinetic evaluation (Li et al., 2015). Photolysis cross sections and quantum yields were taken from Keller-Rudek et al. (2013) (Keller-Rudek et al., 2013). The initial concentrations of toluene, O_3, and water vapor were set according to experimental conditions.

Accurate quantification of photon flux in the OFR is essential for determining photolysis rates in the model. Direct measurement of photon flux is challenging due to attenuation by the water jacket and quartz reactor walls. Therefore, photon flux in the OFR was determined by combining model simulations with direct measurements of O_3 decay in experiments conducted without toluene. The photon flux was iteratively adjusted in the model until the simulated O_3 decay rate matched the observed decay. Using this approach, the photon flux with one lamp illuminated was estimated to be approximately 3.0×10^{15} photons cm^{-3} s^{-1}, consistent with photon fluxes commonly used in OFR studies (Peng et al., 2016). Photon fluxes corresponding to different numbers of illuminated lamps (up to eight) were determined using the same method, and the results are shown in Figure S2. The validity of this approach for photon flux determination, as well as the applicability of the box model to the OFR system, was further evaluated by comparing simulated and measured SO_2 decay rates (Figure S3).

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3 RESULTS AND DISCUSSION

3.1 Production of Organic Acids in Toluene Photooxidation

3.1.1 •OH Exposure Dependence

The major gas-phase organic acids observed during the photooxidation of toluene were formic acid, acetic acid, and pyruvic acid, with minor contributions from lactic acid and oxalic acid under both 20% and 70% RH conditions. Because formic acid and acetic acid together accounted for approximately 90% of the total measured gas-phase organic acids, the following analysis focuses primarily on these two species. Figure 2 illustrates the dependence of the concentrations and molar yields of formic acid and acetic acid on •OH exposure. As •OH exposure increased, their concentrations initially increased and subsequently decreased, reaching maximum at approximately 1–3 equivalent days under both RH conditions. The similar trends observed for formic acid and acetic acid suggest that their formation is governed by closely related chemical pathways during toluene photooxidation. The decrease in organic acid concentrations at higher •OH is primarily attributed to their continued reaction with OH radicals after the complete consumption of toluene. At the highest •OH exposure investigated (15.64 equivalent days), the concentrations of both acids decreased to about 25% of their respective peak values. As shown in Figures 2a and 2c, the change of both formic acid and acetic acid concentration with the increasing •OH exposure at 20% RH is similar to that at 70% RH. However, it is found that organic acid concentrations were consistently higher under low RH (20%) than under high RH (70%) at the identical OH exposures, suggesting that reactions involving water vapor may play a limited role in organic acid formation in this study, in contrast to the substantial contribution of stabilized Criegee intermediate–water reactions commonly observed during alkene ozonolysis (Neeb et al., 1997; Orzechowska and Paulson, 2005; Kang et al., 2025).

Figures 2b and 2d show a strong dependence of the molar yields of formic acid and acetic acid (calculated relative to consumed toluene) on •OH exposure under both 20% and 70% RH conditions. The yields increase from 25% (formic acid) and 24% (acetic acid) at low •OH exposure (<0.2 equivalent days) to maximum values of 74% and 40%, respectively, at intermediate •OH exposures (1–3 equivalent days). Previous studies have shown that molecular fragmentation reactions become increasingly important under conditions of elevated •OH exposure (Lambe et al., 2012; Ortega et al., 2013), which are difficult to achieve in traditional environmental chamber experiments that typically span less than one equivalent day of atmospheric aging. The pronounced increase in organic acid yields with •OH exposure suggests

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that molecular fragmentation processes likely play an important role in formic acid and acetic acid formation.

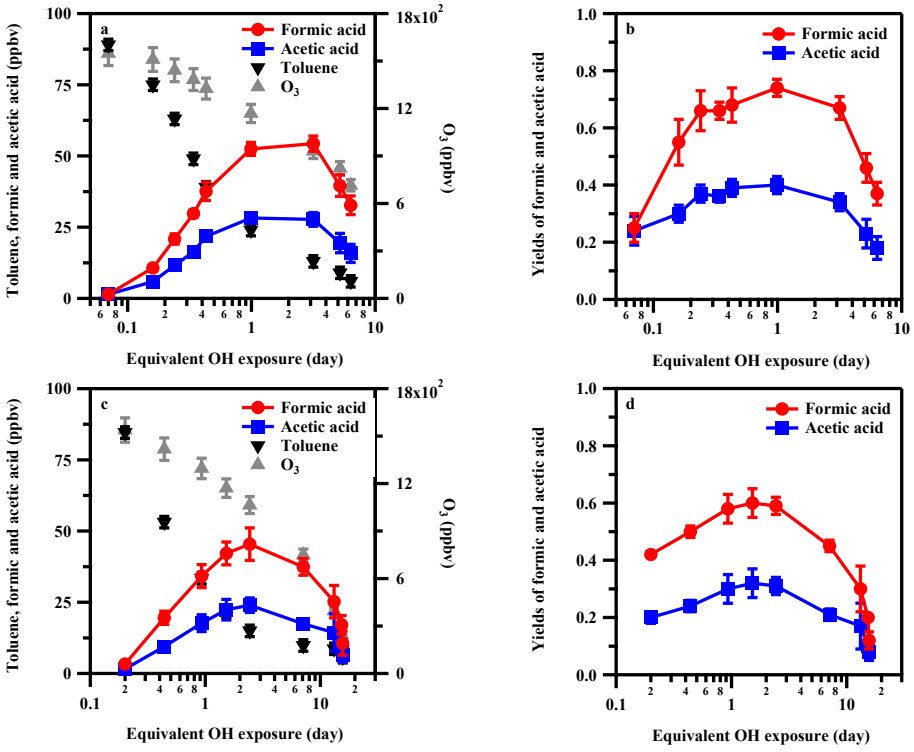

Figure 2. Production of formic acid and acetic acid during the photooxidation of toluene as a function of •OH exposure. Panels (a) and (b) correspond to 20% RH, and panels (c) and (d) correspond to 70% RH. The initial toluene concentration was ~94 ppbv. Error bars represent standard deviations of repeated experiments under identical conditions.

Furthermore，we also compare the yields of formic acid and acetic acid measured from the photooxidation of toluene with literature results. Seuwen and Warneck (1996) quantified the yield of formic acid during the oxidation of toluene (Seuwen and Warneck, 1996), its yield (approximately 13%) was more than five times lower than the peak value observed in our study. In addition to toluene, the yields of formic and acetic acid produced from other aromatic compounds reported by previous studies were also lower than our results (Gery et al., 1985; Bandow and Washida, 1985; Bandow et al., 1985; Berndt et al., 1999; Wyche et al., 2009; Müller et al., 2012). For example, Berndt et al. (1999) reported a formic acid yield of ~13% from benzene oxidation, and Wyche et al. (2009) observed a formic acid yield of 14% from 1,3,5-trimethylbenzene under high-NO_x conditions (Berndt et al., 1999; Wyche et al., 2009).

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This discrepancy is likely due to differences in experimental conditions. Previous chamber studies were typically conducted under relatively low •OH radical exposures, where primary oxidation products dominate. In contrast, formic and acetic acids likely form as secondary or later-generation products, which require higher •OH exposures (Lambe et al., 2012; Isaacman-VanWertz et al., 2018; Drozd et al., 2019). Evidence supporting the role of higher •OH exposures in organic acid formation comes from two previous studies. Wyche et al. (2009) observed formic acid and acetic acid yields of 49% and 33%, respectively, during the photooxidation of 1,3,5-trimethylbenzene under low-NOx conditions, where the aromatic precursor was nearly fully consumed (Wyche et al., 2009). Similarly, Murschell et al. (2018) reported formic acid yields as high as 43% during the oxidation of the chlorinated aromatic herbicide 2-methyl-4-chlorophenoxyacetic acid under very high •OH exposure (Murschell and Farmer, 2018). Consistent with these findings, combustion studies, which effectively accelerate atmospheric oxidation, also reported enhanced formation of formic and acetic acids from toluene relative to non-aromatic compounds such as propane and isooctane (Zervas, 2005; Battin-Leclerc et al., 2007). Additionally, previous experiments often used very high concentrations of aromatic compounds (hundreds of ppb to ppm levels), which likely suppressed •OH radical concentrations and limited effective oxidative aging. Our experiments similarly show that increasing toluene concentrations inhibit the formation of organic acids. At 20% RH, the yield of formic acid decreased from 74% to 48% as the initial toluene concentration increased from 94 to 381 ppbv. Together, these results highlight the critical role of •OH exposure in controlling organic acid formation during aromatic oxidation. Further discussion of these yield discrepancies is provided in Sections 3.2 and 3.3.

3.1.2 NO_x Dependence

Small organic acids, such as formic and acetic acid, are commonly thought to form via reactions of peroxyacyl radicals with HO_2/RO_2 radicals. The presence of NO_x is expected to suppress this pathway by preferentially reacting with peroxy radicals, diverting them toward NO reaction channels that favor nitrate and carbonyl formation over organic acid production. To investigate the influence of NO_x on organic acid formation, N_2O was introduced into the OFR to generate NO_x resulting in 0–29 ppbv of NO concentrations. As shown in Figure 3, molar yields of formic acid and acetic acid were not significantly affected by NO concentration under both 20% and 70% RH conditions. Even at the highest NO levels (~29 ppbv), which the ratio of NO concentration to HO_2 radicals (simulated by model) exceeded 1000, substantial production of organic acids (~40% for formic acid and ~20% for acetic acid at 20% RH) were also observed.

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If organic acid formation were dominated by the peroxy radical pathway, such high NO: $•HO_2$ ratios would be expected to strongly suppress their yields. However, at 70% RH, organic acid yields even increased slightly with increasing NO concentrations. The observed lack of suppression therefore provides strong evidence that a NOx-insensitive pathway dominates organic acid production during toluene photooxidation. This result is consistent with field observations of rapid organic acid formation in polluted environments, where NO_x levels are typically elevated (Veres et al., 2011; Yuan et al., 2015; Millet et al., 2015; Liggio et al., 2017), and offers a plausible explanation for the persistent underestimation of organic acid concentrations in atmospheric models under both pristine and polluted conditions (Stavrakou et al., 2012; Yuan et al., 2015; Bannan et al., 2017; Khan et al., 2018).

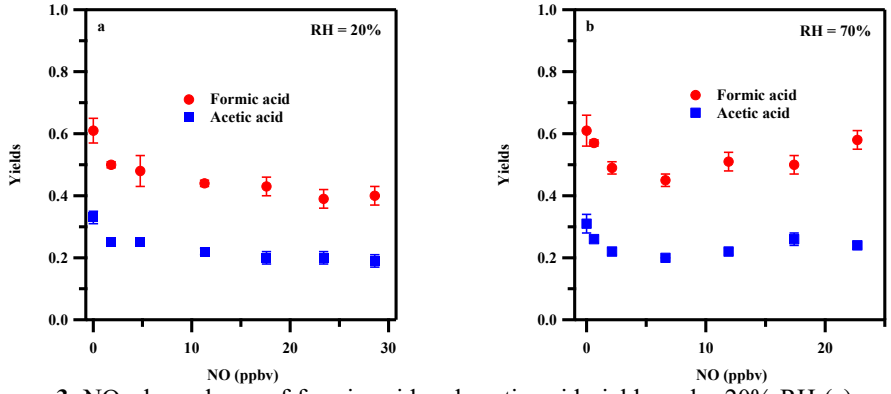

Figure 3. NO_x dependence of formic acid and acetic acid yields under 20% RH (a) and 70% RH (b) conditions. Error bars represent standard deviations from repeated experiments under identical conditions.

3.2 Underestimated Organic Acid Yields in Chemical Models

To further assess the ability of current chemical mechanisms to reproduce observed organic acid formation, we compared our experimental results with simulations using the MCM v3.3.1 model. For acetic acid, two formation pathways are included in MCM v3.3.1 (reactions R1 and R2):

$$CH_3CO_3• + HO_2• \rightarrow CH_3COOH + \text{other products} \quad \text{R1}$$

$$CH_3CO_3• + RO_2• \rightarrow CH_3COOH + \text{other products} \quad \text{R2}$$

Model simulations indicate that reaction R2 ($CH_3CO_3•$ + $RO_2•$) dominates acetic acid production (>90%). While the model can reproduce the general trend of acetic acid concentrations, initially increasing and then decreasing with •OH exposure, it substantially underestimates the observed values. The maximum modeled yield (~7% at ~3 equivalent days)

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is roughly five times lower than measured yields under both RH conditions (Figure 4a–b). This discrepancy suggests that additional formation pathways, not included in the current model, may significantly contribute to acetic acid production during toluene photooxidation.

It is noted that formic acid is not considered as the product of •OH oxidation of aromatic compounds including toluene in the current model. Therefore, we implemented four candidate pathways based on previous studies prior to model simulation (Yetter et al., 1989; Archibald et al., 2007; Fittschen et al., 2014; Yuan et al., 2015; Shaw et al., 2018). (1). $HOCH_2OO$•chemistry: Analogous to the acetic acid mechanism, formic acid can also be formed from either the reaction of $HOCH_2OO$• with HO_2• or the bimolecular reaction of $HOCH_2OO$• (Jenkin et al., 2008; Yuan et al., 2015). 2. Vinyl alcohol (CH_2=CHOH) oxidation: Formic acid formation via the OH radical initiated oxidation of vinyl alcohol, which is generated through acetaldehyde tautomerization. Both photo-induced and organic-acid-catalyzed tautomerization processes were included (Archibald et al., 2007; Yuan et al., 2015; Shaw et al., 2018). 3. HCHO + •OH reaction: Direct formation through HCHO + •OH → HCOOH + H, with a rate coefficient of 2.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1} (Yetter et al., 1989). 4. CH_3O_2• + •OH reaction: Formic acid formation via CH_3O_2• + •OH → HCOOH + H_2O, with a very high rate coefficient of 2.8×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Fittschen et al., 2014). Model evaluation indicates that pathways 1–3 contributed minimally (<1%). Pathway 1 ($HOCH_2OO$• chemistry) exhibits much lower yields than the analogous acetic acid mechanism due to the low stability and consequently low concentration of $HOCH_2OO$ radicals relative to CH_3CO_3 radicals. Pathways 2 and 3 involve aldehydes as precursors, which also limit formic acid production. Only pathway 4 (CH_3O_2• + •OH) produced a substantial amount of formic acid, with a maximum modeled yield of ~13% at ~3 equivalent days. However, the modeled concentrations of formic acid are still approximately five times lower than the experimental measurements (Figure 4c–d). Pathway 4 is highly sensitive to NO_x, and our experimental results, which show that organic acid formation is insensitive to NO_x levels, suggest that this pathway is unlikely to be the dominant mechanism for organic acid production. Overall, these results indicate that the known pathways account for only a small fraction of the observed formic and acetic acid production, implying the existence of additional, yet unidentified, formation pathways for organic acids.

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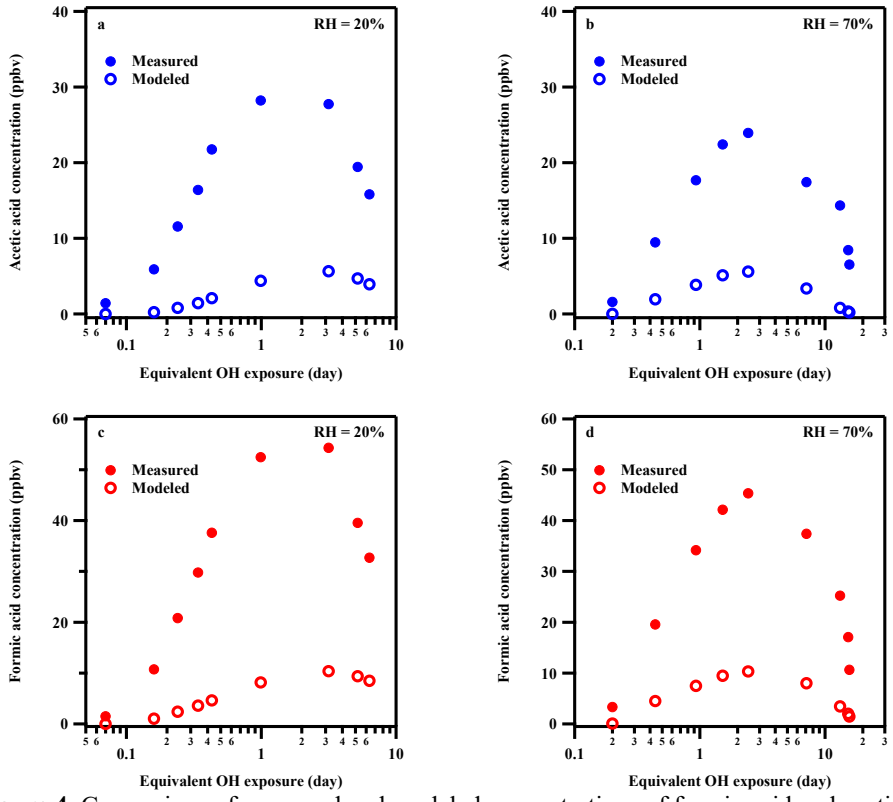

Figure 4. Comparison of measured and modeled concentrations of formic acid and acetic acid at different OH exposures. (a) Acetic acid at 20% RH; (b) Acetic acid at 70% RH; (c) Formic acid at 20% RH; (d) Formic acid at 70% RH.

3.3 Organic Acids Formed from the Multi-generation oxidation

Previous modeling studies have suggested that the aging of SOA could significantly contribute to the atmospheric budgets of organic acids (Paulot et al., 2011), and laboratory experiments have confirmed the production of organic acids during SOA photodegradation (Malecha and Nizkorodov, 2016, 2017; Jiang et al., 2023). In this study, we analyzed the relationship between SOA particle mass and organic acid production to evaluate this potential pathway. However, the distinctly different temporal profiles of gas-phase organic acid production and SOA formation (Figure 5) imply that SOA photodegradation is not the primary source of the observed high organic acid yields. First, SOA formation exhibits a delay relative to the rapid production of organic acids, consistent with the "incubation period" for aromatic SOA formation (Ng et al., 2007; Wyche et al., 2009). Substantial organic acid yields are observed even mass concentration of SOA is negligible (Figure 5a), effectively ruling out SOA photodegradation as the primary

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source. Second, when gas-phase organic acid concentrations begin to decline, SOA mass continues to increase (Figure 5), indicating decoupled formation and removal pathways for SOA and organic acids. At very high •OH exposures (Figure 5b), while organic acid concentrations decrease, SOA mass remains nearly unchanged. This suggests that gas-phase organic acids are more reactive toward gas-phase oxidants than the more persistent SOA, consistent with the generally longer lifetimes of aerosol-phase organics against oxidation (Isaacman-VanWertz et al., 2018). Although SOA photodegradation can produce small oxygenated VOCs (including formic and acetic acids), previous studies showed that aromatic-derived SOA generates much lower yields of such products compared to biogenic SOA (e.g., from isoprene or α-pinene) (Malecha and Nizkorodov, 2016). These evidence support the inference that SOA photodegradation may be not the main driver of the exceptionally high formic and acetic acid yields observed during toluene photooxidation.

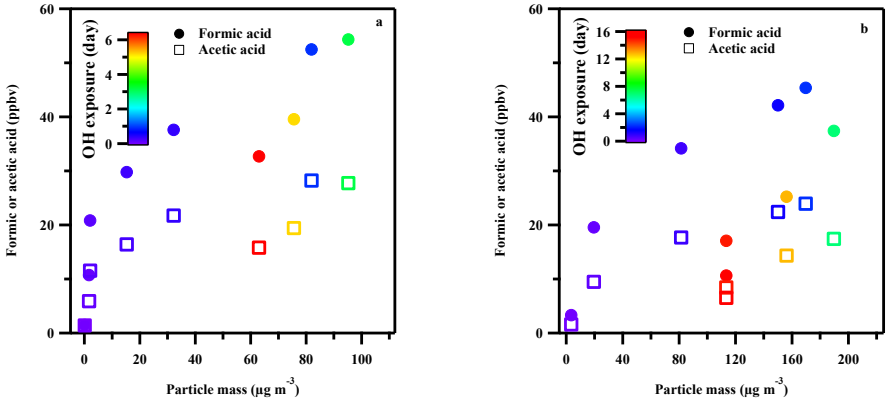

Figure 5. Correlations of particle mass concentration with gas-phase formic acid and acetic acid during the photooxidation of toluene at different •OH exposure. a: 20% RH; b: 70% RH. Color of marker represents different •OH exposure levels.

To further investigate the origin of the high organic acid yields observed during toluene photooxidation, we first examined key first-generation ring-opened products, namely glyoxal and methylglyoxal, which are well-known primary products in aromatic photooxidation (Volkamer et al., 2001). In our experiments, the molar yields of these carbonyl compounds at low •OH exposure are 11% and 10%, respectively, aligning with results reported in previous studies (Gery et al., 1985; Bandow et al., 1985). Figure 6 displays that the yields of glyoxal and methylglyoxal decreased rapidly with increasing •OH exposure, dropping to approximately 1% at higher exposures. In contrast, the yields of formic and acetic acids showed a distinct maximum at intermediate •OH exposures (1–3 equivalent days). Previous studies have

https://doi.org/10.5194/egusphere-2026-234
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proposed that oxidation of glyoxal and methylglyoxal contributes to formic and acetic acid formation (Paulot et al., 2011). But these pathways are excluded in this study given the substantially lower yields of glyoxal and methylglyoxal observed. Moreover, the poor linear correlation between the yields of formic acid and acetic acid and the first-generation ring-opened products suggests that these acids are secondary or later-generation products formed through multistep oxidation processes instead of the primary oxidation products. Previous study elucidated that the fragmentation and further oxidation of five-membered oxygen-containing heterocyclic compounds, which were important intermediates in the oxidation of aromatic compounds, can yield acetic acid (Forstner et al., 1997; Bahreini et al., 2005; Walavalkar et al., 2017). However, this pathway is still controversial due to the lack of robust evidence. The major precursors and detailed mechanisms for the multigenerational oxidation resulting in the high yield of formic acid and acetic acid during the photooxidation of toluene warrants further investigations.

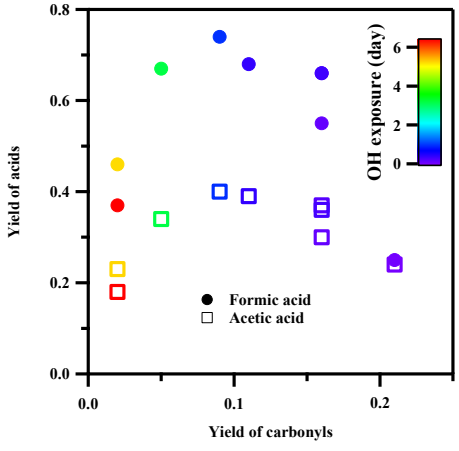

Figure 6. Correlations of yields of carbonyl compounds (sum of glyoxal and methylglyoxal) with yields of gas-phase formic acid and acetic acid during the photooxidation of toluene at different •OH exposure (20% RH). Markers are color-coded to represent different •OH exposure levels.

4 ATMOSPHERIC IMPLICATIONS

This study reveals unexpectedly high yields of formic acid (up to 74%) and acetic acid (up to 40%) during the multi-generational photooxidation of toluene, achieved over equivalent atmospheric aging times of 1–3 days in our oxidation flow reactor experiments. The formation of these organic acids showed minimal sensitivity to NO_x concentrations and relative humidity. The up-to-date MCM v3.3.1 model substantially underestimates the observed organic acid

https://doi.org/10.5194/egusphere-2026-234
Preprint. Discussion started: 26 January 2026
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concentrations in the OFR. While both small gas-phase organic acids and low-volatility particulate matter increase with atmospheric aging (within a certain degree of oxidation), their differing production timescales suggest that photodegradation of SOA particles may not be the dominant formation pathway for organic acids. Combined with the measurement of carbonyl compounds, we proposed that the observed organic acids are predominantly from the multi-generational oxidation of toluene. A mechanistic understanding of the multi-generation oxidation of toluene, particularly the photooxidation of intermediate products such as maleic anhydride, requires further exploration (Lu et al., 2024; Wang et al., 2024).

Our findings also provide new insight into understanding organic acid budgets in urban atmospheres. Previous studies have observed rapid secondary production of organic acids in urban air masses (Veres et al., 2011), but model simulations have significantly underestimated their concentrations (Le Breton et al., 2012; Yuan et al., 2015). The high yields of formic and acetic acids at elevated •OH exposures may help explain these discrepancies. Liggio et al. (2017) found that the underestimation of organic acids increased with reaction time, while Yuan et al. (2015) reported that the peak concentrations of formic acid occurred 4–6 days after the peak benzene levels (Yuan et al., 2015; Liggio et al., 2017). In their studies, they evaluated the contributions of aromatics to formic acid, assuming a yield of 15%, and concluded that aromatics contribute about 11%–12% of the total formic acid production. If a yield of 74% is adopted, the contributions of aromatics would be as high as 55%–60%. This outcome may explain the remaining 50% of missing sources in the model after considering the known sources (Yuan et al., 2015; Liggio et al., 2017). The large amounts of small gas-phase organic acids produced from the photooxidation of aromatics in urban areas could further affect the aerosol pH and the formation of particles. Additionally, while small organic acids such as formic and acetic acid have long been recognized as useful tracers for atmospheric VOC oxidation and SOA aging (Munger et al., 1986; Hansen et al., 2014), our results suggest that their utility as reliable tracers for SOA production is limited to a relatively narrow •OH exposure window (approximately 0.2–3 equivalent days). Beyond this range, their concentrations decouple from SOA mass due to differences in reactivity and removal pathways (Isaacman-VanWertz et al., 2018).

Acknowledgements

The authors gratefully thank the National Key Research and Development Program of China (2022YFC3701102) for financial support.

https://doi.org/10.5194/egusphere-2026-234
Preprint. Discussion started: 26 January 2026
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Author contributions

ZC, LH, and HS designed the research. HS performed research, analyzed the data, and drafted the initial manuscript. LH and ZC revised the manuscript. MZ and YY assisted with the model simulation. YZ, HL, and HW provided valuable comments and suggestions for the manuscript.

Competing interests

All authors declare they have no competing interests.

Data availability

The data used in this study is available upon request from the corresponding author.

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https://doi.org/10.5194/egusphere-2026-234
Preprint. Discussion started: 26 January 2026
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