Aromatic Photooxidation, A New Source of Atmospheric Acidity

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ABSTRACT Formic acid (HCOOH), one of the most important and ubiquitous organic acids in the Earth’s atmosphere, contributes substantially to atmospheric acidity and affects pH-dependent reactions in the aqueous phase. However, based on the current mechanistic understanding, even the most advanced chemical models significantly underestimate the HCOOH concentrations when compared to ambient observations at both ground-level and high altitude, thus underrating its atmospheric impact. Here we reveal new chemical pathways to HCOOH formation from reactions of both O3 and OH with ketene-enols, which are important and up-to-now undiscovered intermediates produced in the photo-oxidation of aromatics and furans. We highlight that the estimated yields of HCOOH from ketene-enol oxidation are up to 60% in polluted urban areas, and great than 30% even in the continental background. Our theoretical calculations are further supported by the chamber experiment and the modeling study. Considering that aromatic compounds are highly reactive and contribute *ca.* 10 % to global non-methane hydrocarbon emissions and 20 % in the urban areas, the new oxidation pathways presented here might help to narrow the budget gap of HCOOH and other small organic acids, and can be relevant in any environment with high aromatic emissions, including urban areas and biomass burning plumes.

INTRODUCTION

Formic acid (HCOOH) is one of the most abundant and ubiquitous acids in the Earth’s atmosphere, with a significant influence on precipitation acidity, pH-dependent aqueous-phase reactions and in-cloud OH chemistry.1 HCOOH can also play a role in forming cloud condensation nuclei (CCN),2 indirectly influencing radiative forcing and hence climate. Sources of HCOOH include direct emission from terrestrial vegetation and vehicle exhaust, and secondary formation from photochemical oxidation of volatile organic compounds (VOCs), in particular, biogenic species such as isoprene and terpenoids.3 Recent work has also indicated that biomass burning is an important source of HCOOH.4

Both ground-based and airborne/satellite observations of HCOOH concentrations in the atmosphere are substantially under-predicted by current models, at times by a factor of four or more,3, 5 implying that there are large missing sources. A number of potential secondary atmospheric sources have been identified, including OH oxidation of enols 6, OH oxidation of secondary products of isoprene oxidation such as α-hydroxy carbonyls 7 and isoprene nitrates8, and reaction of the Criegee intermediate CH2OO with water vapour9. However, even when all of these sources are incorporated into atmospheric models, a large gap remains in the HCOOH budget, with observations 2 - 3 times larger than model predictions.10 These sources also cannot explain the large and rapid secondary photochemical formation of HCOOH observed in urban areas dominated by anthropogenic activities, in fire plumes or in oil and gas producing areas.4-5, 11-12

Yuan et al. showed that the modeled HCOOH concentration in the wintertime at a site in the Uintah Basin (Utah), an oil and gas producing region with large emissions of aromatic hydrocarbons, high photochemical reactivity and weak biogenic influences, was greatly improved by incorporating a source from aromatics to the model but was little affected by other modified cases.12 HCOOH formation has also been reported in chamber experiments of the oxidation of aromatics, with yields up to 6 - 13% for various aromatic precursors and reaction conditions.13-16 Although it is known that HCOOH can be released from illuminated chamber walls, the observed production cannot be explained solely by this process. Therefore, although both experimental evidence and chemical box model simulations indicate that the oxidation of aromatic species might produce HCOOH, the formation mechanisms and yields are still open questions.

Aromatic hydrocarbons are ubiquitous in the atmosphere, with anthropogenic emissions from vehicle exhaust and solvent evaporations, and natural sources such as biomass burning and vegetation. While the oxidation of aromatics has been examined in a large number of studies15, 17-20, significant uncertainties still exist in the general degradation chemical mechanisms and constraining the carbon balance.

It is well established that the oxidation of aromatic compounds is initiated by reaction with OH radicals via H-abstraction from the alkyl groups or OH-addition to the aromatic ring, followed by further reactions to form peroxide bicyclic peroxy radicals (**BPRs**) (**Figure 1**).21-24 In the presence of NO, **BPR** is mainly transformed into the corresponding peroxide bicyclic alkoxy radical (**BAR**) which undergoes ring-opening that is presumed to lead to equal amounts of α-dicarbonyl and unsaturated 1,4-dicarbonyl co-products.25 However, experimentally determined α-dicarbonyl yields consistently exceed that of unsaturated 1,4-dicarbonyls.20, 26-27 This may be due to difficulties in measuring unsaturated 1,4-dicarbonyl species owing to their high reactivity. Alternatively, it may suggest that our current understanding of the ring opening mechanism, and its subsequent chemistry, is incomplete. In addition to the OH oxidation of the benzene ring aromatics such as benzene, toluene and xylenes, unsaturated 1,4-dicarbonyls are also formed as major ring opening products in the atmospheric oxidation of furans which are emitted in significant amounts in biomass burning events.28-29 The dominant fate of unsaturated 1,4-dicarbonyls in the atmosphere was recently shown in chamber studies to be photoisomerisation to a ketene-enol,30 which might account for the discrepancies in the yield between butenedial and glyoxal. However, the subsequent chemistry of these species is entirely unknown.



**Figure 1.** Schematic potential energy profiles for two different reactions of aliphatic alkoxy radical (AAR) at the level of ROCBS-QB3 (ΔE0K, in kilojoules per mole). Classical deomposition to butenedial is marked in blue, and the new proposed H-shift isomerisation and further decomposition to ketene-enol are in red.

In this work, our theoretical calculations on the benzene system present a new reaction pathway following the ring-opening routes in **BAR** leading to the primary formation of a ketene-enol species and co-product glyoxal. We further investigate subsequent oxidation of the ketene-enol with the major atmospheric oxidants O3 and OH and find significant production of HCOOH from a number of pathways. The predicted mechanisms are further confirmed by the chamber experiment and the modeling study. The results of this study suggest, for the first time, that the formation of HCOOH from the reactions of ketene-enols produced in the photo-oxidation of benzene, alkylbenzenes and furans is an important secondary HCOOH source that is missing in current atmospheric models.

**METHODS**

**Theoretical Methods.** All the molecular structures were optimized at DFT-M06-2X/6-311++G(2df, 2p) level which has been assessed to be suitable for thermokinetic studies.31 The optimized structures were submitted to electronic energies using the complete-basis-set model chemistry (CBS-QB3)32 and the explicitly correlated CCSD(T)-F12a (F12) method with cc-pVDZ-F12 or cc-pVTZ-F12 basis set,33 all using the restricted open-shell wave functions for the radical species. The F12 calculations were performed by using the Molpro 2015 package34 and the rest were carried out using the Gaussian 09 suite of programs.35

The reaction rate coefficients of the unimolecular reactions were calculated using the unimolecular rate theory coupled with the energy-grained master equation for collisional energy transfer (RRKM-ME),36 and the rate coefficients of bimolecular reactions were determined using traditional transition state theory.37 The RRKM-ME calculations were carried out using the Mesmer code.38 A single exponential-down model was used to approximate the collisional energy transfer with <ΔE>down of 250 cm–1. The collisional parameters were estimated using the method of Gilbert and Smith,39 and the asymmetric Eckart model was used for the tunneling correction factors.40

**Chamber experiment and box modeling.**The experiment was performed on July 27, 2009, as part of the Toluene OXidation In a Chamber (TOXIC) campaign (July 2009), with initial mixing ratios of 125 ppbv of (*E*)-butenedial and 520 ppbv of NO. All VOC precursors and products shown, and HONO, were measured by FTIR. NO was measured by chemiluminescence.

Box model runs were performed with the AtChem2 model41 using two different chemical mechanisms: (i) MCMv3.3.1, the butenedial mechanism extracted from the MCMv3.3.1 (mcm.york.ac.uk);42 (ii) BASE, the MCMv3.3.1 mechanism adapted using the photochemistry of butenedial described in Newland et al. (2019) and the chemistry of the ketene-enol described in this work (**Table S1**). The model was constrained to measured *j*(NO2) and a chamber specific auxiliary mechanism is included for the EUPHORE chamber.43

**RESULTS AND DISCUSSION**

**Primary formation of the ketene-enol in the oxidation of benzene.** As shown in **Figure 1**, BAR would decompose through the breaking of the C2-C3 and the -O-O- bridge bonds, forming an aliphatic alkoxy radical (AAR) intermediate. We have identified the transition state of C2-C3 breakage and obtained an energy barrier of 33.4 kJ/mol at the ROCBS-QB3 level. Further breakage of -O-O- bridge bond is barrierless.44-45 Based on the current mechanistic understanding, AAR would exclusively undergo decomposition, eventually forming butenedial accompanied by glyoxal (in blue in **Figure 1**).

However, here we present an unexpected 1,5 H-shift isomerization reaction in **AAR,** transferring an H atom from the carbonyl group -C(3)HO to the alkoxy radical with an energy barrier of 7.7 kJ/mol (as shown in red in **Figure 1**), being highly competitive with decomposition with an energy barrier of 12.2 kJ/mol. The 1,5 H-shift reaction is highly exothermic by 94.6 kJ/mol owing to the formation of a resonance-stabilized intermediate species (**INT** in **Figure 1**) which greatly reduces the energy. Owing to the substantial energy released from **BAR** to **AAR** (194.29 kJ/mol) and from the H-shift in **AAR** (94.6 kJ/mol), the energized ketene-like intermediate species **INT** would undergo unimolecular decomposition rather than reacting with O2, even though the former is endothermic and with an energy barrier of 76.02 kJ/mol. Decomposition would lead to the formation of a ketene-enol accompanied by glyoxal (**Figure 1**).

To obtain the yields of butenedial and ketene-enol from the two different pathways available for **AAR**, we paid special attention to quantify the branching ratio of the 1,5 H-shift influenced by multiple conformers and carried out RRKM-ME calculations. The predicted branching ratios forming butenedial and ketene-enol are 0.634 and 0.364, respectively, with the yield of the O2-adduct being almost negligible (**Figure S1**). Glyoxal is the co-product of both classical and the newly proposed 1,5 H-shift pathways, which might partially account for the discrepancies in the yield between butenedial and glyoxal under dark conditions and without further photolysis of butenedial.19-20, 27

Newland et al. recently showed that butenedial can also undergo rapid photoisomerisation to form a ketene-enol.30 Therefore, the ketene-enol can be formed either directly from primary decomposition of **BAR** as presented here, or from the further photochemistry of butenedial. Thus, the actual yield of ketene-enol from **BAR** should be higher than we predict theoretically (0.364). The ketene-enol is expected to be reactive under atmospheric conditions owing to the presence of the ketene and enol moieties, therefore reactions with the major atmospheric oxidants O3 and OH radicals may be important atmospheric loss processes.

**HCOOH formation from ketene-enol reaction with O3 and OH radicals.** The reaction of the ketene-enol with O3 follows the Criegee mechanism,46 i.e., O3 adds to the unsaturated enol bond and forms two primary ozonides (denoted as POZ\_01 and POZ\_02 in **Figure 2A**), which contain excess energy to break the ring and eventually form four different Criegee intermediates (CIs). It is noted that the ketene double bond is not favored by the electrophilic O3 addition due to the unique cumulene structure of ketene with substantial positive charge on the carbonyl carbon. We have obtained the potential energy surface at the RHF-CCSD(T)-F12a level with the basis set cc-pVTZ-F12. Using the traditional transition state theory, the rate coefficient of O3 additions forming POZ\_01 and POZ\_02 at 298 K is estimated as 1.21 × 1015 and 2.36 × 1016 cm3 molecule1 s1, respectively.



**Figure 2.** (**A**) Reaction scheme of ketene-enol with O3. Two primary ozonides (POZ\_01 and POZ\_02) with differing orientations of the middle O-atom can undergo rapid interconversion. Criegee intermediates (CI) are shown in their zwitterionic forms. The branching ratios of the four different pathways are shown in brackets. (**B**) Reaction scheme of OH additions to C1 and C4 position of ketene-enol. For C4-addition to ketene-enol, the formed peroxy radical (ROO2) would react with NO/HO2/RO2 to form alkoxy radical, which then decomposes to formyl ketene and HCOOH. The peroxy radical ROO1 formed from C1-addition would further undergo unimolecular HO2 elimination to form 4-oxo-butenoic acid (M1), which can undergo secondary reaction with OH to produce HCOOH.

Each POZ undergoes two different ring scissions to form four Criegee intermediates, CI\_01\_a/b and CI\_02\_a/b, as shown in **Figure 2A**. Detailed energies are available in **Table S1**. Formyl ketene is formed as the co-product of both CI\_01\_a and CI\_02\_a, and HCOOH is the co-product of both CI\_01\_b and CI\_02\_b. Note that two POZs with differing orientations of the middle O-atom can undergo rapid interconversion with a low barrier of ˂ 15 kJ/mol. We have modelled the prompt formation of the four CIs using RRKM-ME calculations and set the formation processes of CIs as irreversible because of the substantial energy released. The calculation results show that the branching ratios of the formation of CI\_01\_a, CI\_01\_b, CI\_02\_a and CI\_02\_b are 0.13, 0.69, 0.03 and 0.15, respectively. Thus, the total primary yield of HCOOH from O3 reactions with ketene-enol is 0.84.

Subsequent reactions of the four different CIs were also investigated. CI\_01\_a would cyclize to dioxirane and CI\_02\_a would isomerize to performic acid, which has been well studied in previous work.47 CI\_01\_b would cyclize to a 3-membered dioxirane over a barrier of 40.3 kJ/mol while CI\_02\_b would go through a barrierless 1,5-cyclization to a 5-membered dioxolene. Both cyclic compounds are expected to be highly unstable and break into fragments. Detailed energies and reaction pathways are available in **Table S1** and **Figure S2**.

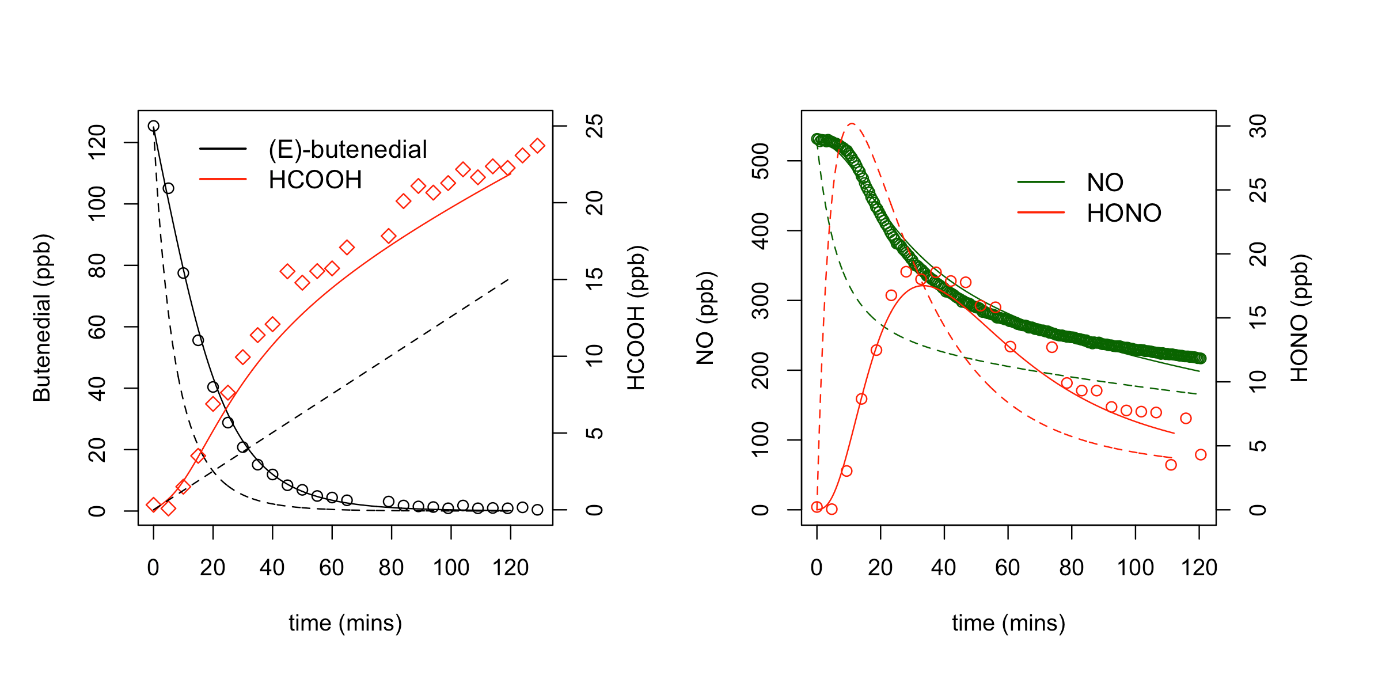
As for site-specific OH addition to dienes such as isoprene, the reaction of ketene-enol with OH radicals proceeds mainly as OH additions to the two terminal carbons of C1 and C4 as shown in **Figure 2B**. Reaction energies are obtained at the RHF-UCCSD(T)-F12a level with the basis set cc-pVTZ-F12, and the rate coefficient of OH additions to C1- and C4- positions at 298 K are estimated as 7.52 × 1011 and 4.27 × 1011cm3 molecule1 s1, respectively. The transition states for both C1 and C4 additions are submerged under the reactants by 15.79 kJ/mol and 16.04 kJ/mol, respectively. The rate constant of OH addition to ketene-enol at C1 position is 2~5 times faster than the reported OH reaction with ketene (CH2CO) under various temperatures and pressures.48-49 Compared with previous studies on the OH addition to vinyl alcohol (ethenol, CH2CHOH) at the α-carbon, the relative energy of the transition state of C4-addition predicted here is 2.6 kJ/mol lower than that reported by So et al.6 and 3.1 kJ/mol lower than recently reported by Lei et al.50 The slightly lower energy of the transition states and faster reaction rates we obtained here might be explained by the resonance stabilization of the radical formed after addition of OH to ketene-enol, similar to that of conjugated dienes.51

Owing to the presence of an allyllic group after C1-addition, a pair of peroxy radicals would be formed from O2 additions to C2 and C4 positions. However, O2 addition to C2 is fast reversible with a reverse rate of 5.0 × 108 s1 and therefore was not considered.The peroxy radical **ROO1** formed from O2 addition to C4 would undergo unimolecular HO2 elimination to form 4-oxo-butenoic acid (**M1**) which is denoted as MALDALCO2H in the MCM and assigned to be formed from butenedial oxidation. **M1** could further react rapidly with OH and form HCOOH, as shown in **Figure 2B**. For C4-addition to ketene-enol, further O2 addition can only take place at C3 position. The formed peroxy radical (**ROO2**) could react with NO/HO2/RO2 to form alkoxy radical, which then would decompose to formyl ketene and HCOOH. Detailed reaction energies are available in **Table S1**.

**Table 1** Calculated effective rate coefficients (k, in cm3 molecule1 s1)

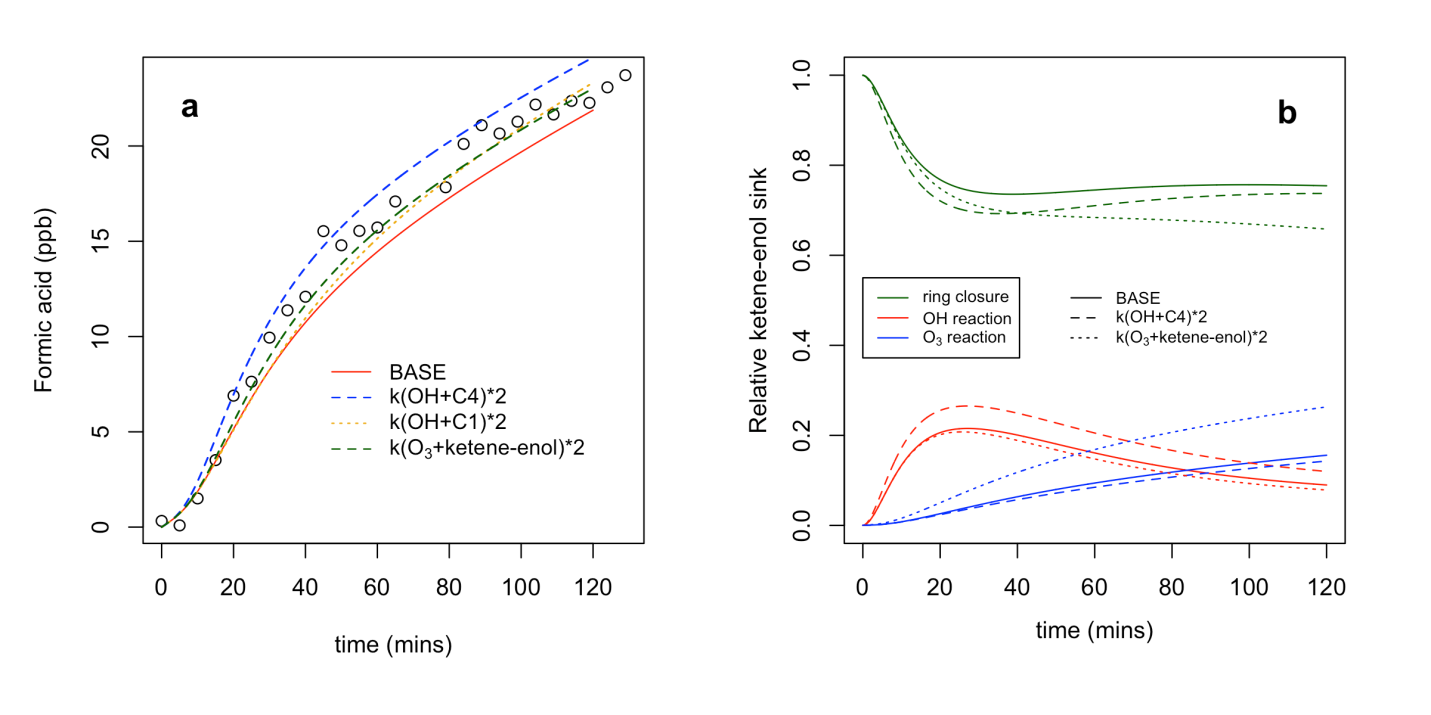
|  |  |
| --- | --- |
| **Reaction** | **K** |
| *Ketene-enol* + O3 → CI\_01\_a + formyl ketene | 2.34 × 10-16 |
| *Ketene-enol* + O3 → CI\_01\_b + HCOOH | 1.24 × 10-15 |
| *Ketene-enol* + O3 → CI\_02\_a + HCOOH | 2.70 × 10-16 |
| *Ketene-enol* + O3 → CI\_02\_b + formyl ketene | 5.40 × 10-17 |
| *Ketene-enol* + OH (C1-add) → M1 + HO2 | 7.52 × 10-11 |
| *Ketene-enol* + OH (C4-add) → HCOOH + formyl ketene + OH | 4.27 × 10-11 |

**Chamber Experiment and Mechanism Simulations.** In order to assess the theoretical calculations presented, model simulations were carried out with the proposed ketene-enol chemistry (**Table 1**) and compared to observations from an (*E*)-butenedial photo-oxidation experiment performed in the large outdoor environmental simulation chamber, EUPHORE.52 The overall measured chemical production of HCOOH during the experiment was 10 ppbv (corrected for auxiliary chamber chemistry – see SI), which gives a HCOOH yield of roughly 8 % from (*E*)-butenedial under the conditions of the experiment.



**Figure 3.** Chamber model vs measurement comparison of the EUPHORE (E)-butenedial photo-oxidation experiment (27/07/2009; chamber open at 15:13 local time). Butenedial (black circles), formic acid (red diamonds), NO (green circles), HONO (red circles). Dashed lines are output from MCMv3.3.1 model run (HCOOH wall source only), solid lines are from BASE model runs, using the chemistry presented here and in Newland et al. (2019). The chamber is opened at time t=0.

A box model was used to compare the mechanisms presented herein (BASE, solid line) to the experimental measurement, and to the Master Chemical Mechanism (MCMv3.3.1, dashed line).42 More details and further model measurement comparisons are shown in SI. As shown in **Figure 3**, the measured HCOOH (red diamonds) is well predicted by the BASE model run. The major HCOOH production channels in the experiment are shown in **Figure S3**. It should be noted that no chemical HCOOH production is present in the MCMv3.3.1 mechanism, and the production (dashed line in **Figure 3**) is exclusively from illumination of the chamber walls (**Figure S4**). **Figure 4** shows the sensitivity of the modelled HCOOH production in the BASE run to the theoretically calculated rates of reaction of OH and O3 with the ketene-enol. All rate constant adjustments are only a factor of 2, corresponding to the adjustment to the barrier of <2 kJ/mol at the room temperature, and thus within the expected uncertainties of the calculations at the RHF-CCSD(T)-F12a level with the basis set cc-pVTZ-F12. Doubling the rate of OH addition to C1 (yellow dotted line) does not greatly increase HCOOH production, particularly early in the experiment because HCOOH is being formed as a second-generation product of the ketene-enol + OH reaction. Doubling the rate of OH addition to C4 (blue dashed line), to 8.54 × 1011 cm3 s1, gives a good fit to the measured HCOOH. For the O3 + ketene-enol reaction, doubling the calculated reaction rate (green dashed line) gives a good fit to the measurement.



**Figure 4.** **a**. Sensitivity of modelled HCOOH in BASE model run to the reaction rates of the ketene-enol with OH and O3. **b**. Relative sink of ketene-enol to ring closure, OH and O3 reactions during experiment for three of the scenarios shown in a.

The BASE run also fits the concentration-time profiles of most of the measured species better than the MCMv3.3.1 mechanism (**Figure S5**). Much of the improvement is driven by getting the timing and magnitude of the formation of the radicals OH and HO2 right. In the MCMv3.3.1 run, NO is removed too quickly due to the production of large amounts of HO2 in the mechanism. This reaction produces large amounts of OH which removes (*E*)-butenedial too fast and leads to the earlier formation of secondary products (**Figure S5**). However, Newland et al.30 recently showed that photolysis of butenedial has low initial radical yields and the major channel is photoisomerisation to the ketene-enol. It is also clear from comparison to the measured HONO (formed from OH + NO) and NO time-series that the MCMv3.3.1 run produces radicals too early, while the BASE run is in good agreement with the measurement.



**Figure 5.** Direct formation pathways for formic (HCOOH) and acetic acid (CH3COOH) from selected BAR isomers formed in the oxidation of toluene. BARs are denoted as Rn-ijOO-s-kO-a, in which n is the site of OH addition, i and j are the sites connecting the −OO− unit, k is the site of the second O2 addition, and a/s is the anti/syn conformer, representing the direction of –OO− or –O relative to –OH group. Two ketene-enol species formed directly from BARs or from photoisomerisation of unsaturated dicarbonyls are shown in the dash boxes. Further oxidation of ketene-enols with OH/O3 can form HCOOH and CH3COOH.

**Predicted HCOOH production from the photo-oxidation of aromatics.** Aromatic hydrocarbons including **BTEX** (benzene, toluene, ethylbenzene and xylenes) are present at high concentrations in urban areas.53-54 This work shows that OH oxidation of benzene will lead to the ketene-enol both directly via decomposition of the **BAR** following a 1,5 H-shift,and from photoisomerisation of the butenedial formed from classical decomposition of the **BAR** (under typical mid-day conditions (*j*(NO2) = 8 × 10-3 s-1; [OH] = 5 × 106 cm-3), > 75 % of butenedial will photoisomerise to the ketene-enol). Ketene-enol species are also expected to be formed via both pathways in the photo-oxidation of more reactive monoaromatics, such as toluene, xylenes and tri-methylbenzenes. In the case of toluene, initiated OH addition and further O2 additions would lead to multiple isomers of **BAR**. Subsequent reactions of selected **BAR** isomers are shown in **Figure 5**. We further calculated the branching ratio for classical decompositions and new proposed 1,5 H-shift reactions of different **BAR** isomers from toluene oxidation (**Table S1**). Combining with the proportion of different **BAR** isomers, we obtained the yield of dicarbonyls and ketene-enols as 0.38 and 0.13, respectively (**Table S2**). With the presence of a methyl group, ketene-enol oxidation can form both formic and acetic acid(**Figure 5**). Owing to the diversity of **BAR**s formed in the photooxidation of alkyl substituted aromatic compounds, and the ambiguous photolysis rate of specific alkyl substituted unsaturated dicarbonyls to the corresponding ketene-enol, the yields of HCOOH and other small organic acids such as CH3COOH need to be studied carefully in the future. Using the calculated rate coefficients for reactions of ketene-enol with O3 and OH (**Table 1**) and the ring-closure rate coefficient of 3.2 × 103 s1 reported recently,30 we estimate the loss of ketene-enol to reactions with OH, O3 and to ring closure for a range of atmospherically relevant scenarios (**Table 2**). Recent studies from field observations and satellite retrievals have indicated severe ozone pollution in China where hourly maximum ozone concentrations frequently exceeded 150 ppbv.55 For these high ozone scenarios, ketene-enol removal is dominated by reaction with O3, and even under ‘background’ conditions ozonolysis still accounts for ≥ 30% of the sink.

**Table 2** Loss rates of ketene-enol to reaction with OH, O3 and ring closure, and HCOOH yields (assuming all RO2 reacts with NO), under a set of atmospherically relevant scenarios. HCOOH / CH3COOH production rate (ppt hr-1) from a range of aromatic compounds in each scenario; summer and winter time *j*(NO2) = 8 *×* 10-3 s-1 and 6 *×* 10-3 s-1 respectively; *k*(unsaturated 1,4 dicarbonyl + OH) = 5 × 10-11 molecules cm-3 s-1

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Scenario b** | **[OH] / cm-3** | **[O3] / ppbv** | **Relative fractional losses of ketene-enol a** | | | **HCOOH yield from ketene-enol** | **HCOOH / CH3COOH**  **production ppt hr-1** c | | | |
| ***L*OH** | ***L*O3** | ***L*RC** | *Benzene* | *Toluene* | *Furan* |
| ***Polluted urban (summer)*** | 1 × 107 | 150 | 0.11 | 0.61 | 0.29 | 0.59 | 7 | 70 | 372 |
| ***Polluted urban (winter)*** | 5 × 106 | 100 | 0.07 | 0.54 | 0.39 | 0.51 | 3 | 31 | 179 |
| ***Continental Background (summer)*** | 4 × 106 | 50 | 0.08 | 0.38 | 0.54 | 0.38 | 2 | 19 | 118 |
| ***Continental Background (winter)*** | 2 × 106 | 35 | 0.05 | 0.31 | 0.64 | 0.30 | 1 | 7 | 49 |

a *L*OH = loss of ketene-enol to reaction with OH, *L*O3 = loss to reaction with ozone, *L*RC = loss to ring closure;

b see e.g. Stone et al. (2012) for example OH concentrations, Parrish et al. (2012) for continental background ozone mixing ratios 56-57

c Assuming an aromatic mixing ratio of 1 ppbv; BAR from benzene behaves as reported here i.e. 0.364 decompose directly to the ketene-enol and 0.634 to the unsaturated 1,4 dicarbonyl; branching ratios of ketene-enols and unsaturated 1,4-dicarbonyls from different BAR isomers from toluene are shown in **Table S2**

Oxidation of the ketene-enol then produces HCOOH, with the yield strongly dependent on the concentrations of O3 and OH. The predicted HCOOH yield from ketene-enol reactions is ≥ 30% for all scenarios shown in **Table 2**, and > 50% for polluted scenarios. The HCOOH / CH3COOH production rates (ppt hr1) for OH-initiated oxidation of benzene, toluene, and furan for each scenario are calculated in **Table 2**, assuming a mixing ratio of the aromatic of 1 ppbv. On a per molecule basis the species with faster OH reaction rates have higher acid production rates. Toluene, as the dominant aromatic compound in urban environments, has a predicted production rate of HCOOH and CH3COOH about ten times faster than predicted for benzene. Furthermore, as furan has a predicted production rate of HCOOH even higher than toluene (**Table 2**), although mixing ratios of furans are low in the ambient atmosphere, they have been measured to be up to tens of ppb in biomass burning plumes,58 and hence have the potential to make a significant contribution to substantial secondary organic acid production in fire plumes.4

**Atmospheric Implication**. The mechanistic work presented here highlights a new and important role of ketene-enols, formed from the OH-initiated oxidation of aromatic hydrocarbons and furans, in contributing to a significant missing source of atmospheric acidity through the formation of HCOOH and other small organic acids via bimolecular reaction with O3 and OH radicals, and in narrowing the gap between observed and modelled HCOOH concentrations in urban areas and in biomass burning plumes. Nonetheless, further detailed experimental and theoretical work is required on the atmospheric chemistry of ketene-enols, to confirm the mechanistic details of these pathways in the oxidation of other alkyl substituted and oxygenated aromatic hydrocarbons, and to consider the influence of atmospheric conditions such as temperature and actinic flux.

ASSOCIATED CONTENT

**Supporting Information**. Chamber experiment and box modeling; the calculated reaction energies and the kinetics results; additional chemical mechanism used in BASE model run; EUPHORE auxiliary mechanism; major HCOOH production channels; formic acid and ozone wall production rates; model-measurement comparison of other species. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no conflict of interest.

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SYNOPSIS

