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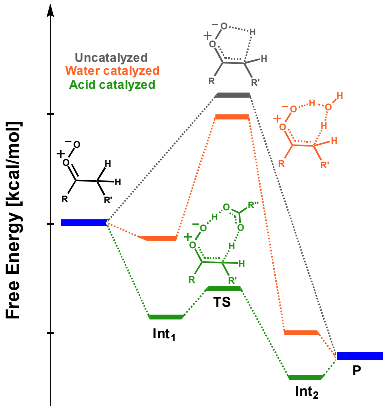

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Barrierless Tautomerization of Criegee Intermediates *via* Acid Catalysis

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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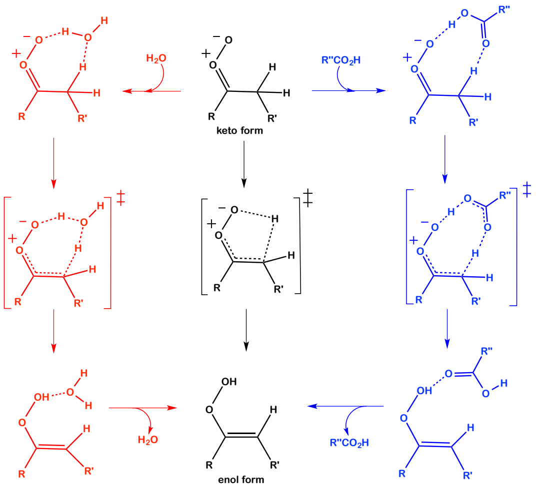
The tautomerization of Criegee intermediates *via* a 1,4 *β*-hydrogen atom transfer to yield a vinyl hydroperoxide has been examined in the absence and presence of carboxylic acids. Electronic structure calculations indicate that the organic acids catalyze the tautomerization reaction to such an extent that it becomes a barrierless process. In contrast, water produces only a nominal catalytic effect. Since organic acids are present in parts-per-billion concentrations in the troposphere, the present results suggest that the acid-catalyzed tautomerization, which can also result in formation of hydroxyl radicals, may be a significant pathway for Criegee intermediates.

The direct generation, detection, and reaction of the Criegee intermediate in the gas-phase by Taatjes and coworkers[1,2] has sparked a renewed interest in Criegee chemistry. The Criegee intermediates are carbonyl oxides that are principally produced in olefin ozonolysis.[3] In the troposphere, they play a significant role in chemistry involving secondary organic aerosols, acids, peroxides, sulfates, and nitrates. At the same time, Criegee chemistry is a key part of ozonolysis-based syntheses that offer safe and scalable routes for preparing pharmaceutical intermediates and other value-added chemicals.[4,5,6] The Criegee intermediates are also implicated in the reaction cycles of flavin-dependent Baeyer−Villiger monooxygenases[7] that provide a green route for synthesizing enantiopure drug compounds.[8]

Recently, Welz *et al.* reported a study of the kinetics for the reactions of Criegee intermediates (CH_2OO, *anti*-CH_3CHOO, and *syn*-CH_3CHOO) with simple carboxylic acids (HCOOH and CH_3COOH).[9] The measured rate coefficients were on the order of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, orders-of-magnitude larger than those previously estimated based on ozonolysis experiments[10] and atmospheric modeling studies.[11] This indicates that the reactions of the Criegee intermediate with organic acids is a substantially more important decay process than has been previously thought. Moreover, it suggests that this pathway could compete with unimolecular decay and reaction with water as key Criegee loss processes, especially in forested[12] and urban environments,[13] where the acid levels are in the parts-per-billion range. In this letter we use electronic structure calculations to examine one possible pathway for the reaction of carboxylic acids with Criegee intermediates: tautomerization *via* a 1,4 *β*-hydrogen atom transfer to form a vinyl hydroperoxide.

The uncatalyzed tautomerization of *syn*-CH_3CHOO oxide is predicted to have an activation barrier of ~14.9 – 21.2 kcal/mol depending on the level of theory.[14] However, the present calculations find that this barrier is significantly lowered or even completely removed in the presence of organic acids. In the troposphere, monocarboxylic acids and low molecular weight dicarboxylic acids, such as oxalic acid, are present in appreciable amounts (parts per billion, ppb)[15-18] and their tendency to enhance gas-phase hydrogen-transfer reactions is increasingly being recognized;[19-26] recent satellite measurements reveal that the formic acid (HCOOH) levels in urban air are much higher than previously estimated.[27] It has even been suggested that sulfuric acid (H_2SO_4), an inorganic acid and a key precursor in aerosol formation, can catalyze such hydrogen transfers.[20,22,26] In addition, the role of aromatic acids to catalyze particulate formation has been verified through laboratory experiments.[28] Organic acids are also produced during the various unimolecular and bimolecular Criegee processes and thus can play a role in ozonolysis-based syntheses.[3]



Scheme 1. General mechanistic pathways for the unassisted (*black*), water-assisted (*red*), and acid-assisted (*blue*) tautomerization of a Criegee intermediate through 1,4 *β*-hydrogen transfer.

Hydroxyl radical (•OH) plays a central role in the oxidation chemistry of the troposphere.[29] Its sulfuric acid-forming reaction with sulfur dioxide[1] deeply impacts aerosol formation and the earth's climate.[30] While ozone photolysis is the primary source of hydroxyl radical, a growing body of experimental[31-37] and theoretical evidence[37-43] indicates that Criegee chemistry also serves as an important source of tropospheric •OH. Specifically, the tautomerization of the Criegee intermediate to form the hydroperoxide olefins constitutes the main mechanism for •OH generation via ozonolysis.[34,38,39,41] As shown in Scheme 1, this reaction involves a 1,4 β-hydrogen atom transfer (H-transfer) between the β-carbon of the Criegee intermediate and its terminal oxygen, and the subsequent homolytic O-O bond cleavage to form •OH. The possibility of secondary •OH-forming Criegee channels has also been discussed in the literature.[40,44-45] The impacts outlined above for facile tautomerization of Criegee intermediates, including the potential formation of •OH, provides a strong impetus to study the role of acid catalysis in Criegee chemistry.

In this letter, the results of electronic structure calculations on the unassisted and organic acid-assisted intramolecular 1,4 hydrogen-transfer in Criegee intermediates with β-hydrogens are presented. Free energy calculations predict that an acid-assisted reaction to form a vinyl hydroperoxide is a barrierless process irrespective of the Criegee intermediate considered. By comparison, water has only a weak catalytic effect on the free-energy barrier, in part due to entropic factors, suggesting that the 1,4 hydrogen-transfer may be relatively insensitive to humidity.

While there are ample examples of a single molecule or a molecular cluster reducing the activation energy of an atmospherically or industrially important reaction, to our knowledge the catalytic effect of acids on the tautomerization of a Criegee intermediate has not been previously examined. To explore the reaction, we examined the uncatalyzed and catalyzed hydrogen-transfer in C_2- and C_3-based Criegee intermediates as well as in those produced during the ozonolysis of isoprene and α-pinene (Scheme S1, ESI). Note that such a reaction mechanism cannot occur with the simplest Criegee intermediate, CH_2OO, because it lacks β-hydrogens. Isoprene, the most common biogenic hydrocarbon in the troposphere, is emitted by terrestrial vegetation.[46] It dominates the global total emission of biogenic volatile organic compounds with its annual emission strength varying between 200 and 600 teragrams of carbon. Among the monoterpenes that account for 10-50% of the total emitted mass of non-methane biogenic volatile organic compounds, α-pinene has the highest emission rate into the atmosphere and is believed to be the largest contributor to the formation of secondary organic aerosols.[47,48,49,50]

Electronic structure calculations (the details of which are provided in the ESI) are performed at the CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level of theory (298.15 K, 1 atm) that has been previously found to describe hydrogen-transfer processes,[19,20] including Criegee chemistry,[51] well. The accuracy of the M06-2X/aug-cc-pVTZ theoretical method chosen for geometry optimization is confirmed by comparing the thermochemistry of the uncatalyzed reaction calculated using various DFT and wavefunction based methods including CCSD, CCSD(T), and LPNO-CEPA/1 (Tables S1-S3, ESI).

The intramolecular 1,4 hydrogen-transfer in a Criegee intermediate with β-hydrogens is a modified version of keto-enol tautomerism in which a β-hydrogen shifts to the terminal Criegee oxygen leading to the formation of vinyl hydroperoxide, indicated as the enol form in Scheme 1. In the absence of any catalyst, the reaction follows a concerted mechanism through a 5-membered cyclic transition state. At the CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level, the tautomerization of *syn*-CH_3CHOO has a calculated free-energy barrier of $\Delta G^{\ddagger}$ = 16.7 kcal/mol (Fig. S1, ESI), in agreement with previous theoretical estimates of 14.9 – 21.2 kcal/mol.[14] Moreover, the rearrangement is 17.8 kcal/mol exoergic, which is also consistent with prior projections of $\Delta E \approx -20.0$ kcal/mol. Interestingly, the tautomerization is more favorable than conventional keto-enol processes, where $\Delta E^{\ddagger}\sim 55$ kcal/mol.[21,52] Moreover, the enol-like form (vinyl hydroperoxide) is significantly lower in energy than the keto-like form (Criegee intermediate), whereas, the conventional enols tend to be 10-15 kcal/mol less stable than the keto forms. This distinct feature of Criegee chemistry can be attributed to the zwitterionic nature of the Criegee intermediate's electronic structure that increases the nucleophilicity of the hydrogen-accepting terminal oxygen, thereby activating the cleavage of the C-H bond and favoring the formation of the enol-like form.

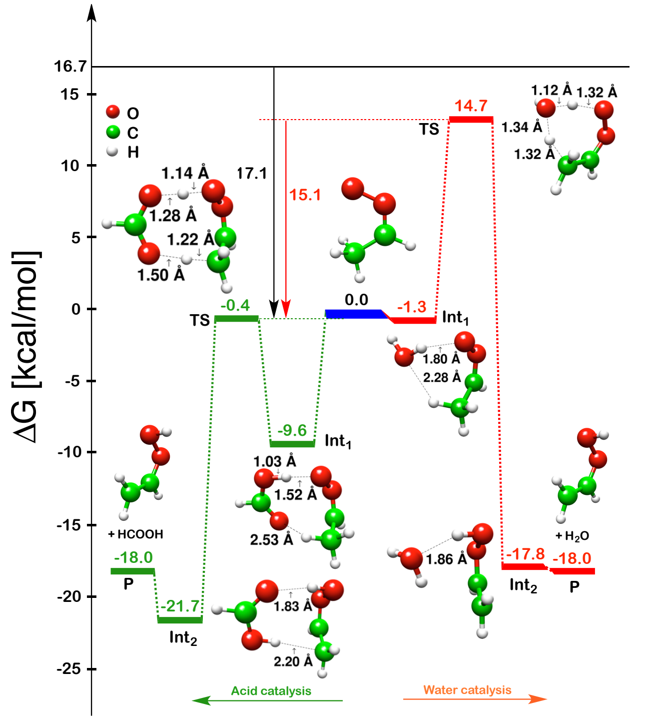


Fig. 1 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ-calculated free-energy profiles of HCOOH-catalyzed (*green lines*) and water-catalyzed (*red lines*) tautomerization of *syn*-CH_3CHOO (298.15 K, 1 atm, kcal/mol). The free-energy barrier of an uncatalyzed reaction is also shown (horizontal black line). All Energies are reported with respect to the separated reactants. See Fig. S2 (ESI) for enthalpy profiles.

Because water is the dominant trace component in the troposphere, its potential catalytic influence on the bimolecular Criegee chemistry has been repeatedly examined.[14,40,41] Indeed, Anglada *et al.* have previously studied the water-catalyzed tautomerization of C_2- and C_3-based Criegee intermediates as well as of those resulting from the isoprene ozonolysis.[40] According to their calculations, although water lowers the enthalpic barrier, the incorporation of entropic contributions raises the free-energy barrier to a nearly equivalent extent, drastically reducing the effect of this reaction. They estimated that only 5.2-13.5% of the total bimolecular Criegee intermediate + H_2O chemistry occurs via the tautomerization channel.

We have recalculated the reaction path for the water-catalyzed tautomerization to make comparisons with the acid-catalyzed reaction using the same theoretical description. The calculations are consistent with those of Anglada *et al.* in that a water molecule produces a significant change in the calculated potential energy surface (Fig. S2), but the effect nearly disappears upon inclusion of entropic effects, as shown in Fig. 1.[40] Indeed, the calculated free-energy barrier of the water-catalyzed reaction is only 2.0 kcal/mol lower than for the uncatalyzed reaction.

On the other hand, in the presence of organic acids the tautomerization is not only enhanced, it becomes a barrierless process. The HCOOH-catalyzed reaction proceeds through a strongly bound prereaction complex, **Int$_1$** (ΔG = -9.6 kcal/mol), which involves two hydrogen bonds between HCOOH and the Criegee intermediate. Note that, as shown in Fig. 1, the O-H bond of HCOOH in **Int$_1$** is noticeably elongated due to the high nucleophilicity of the terminal Criegee oxygen. Then, **Int$_1$** converts into **Int$_2$**, a hydrogen-bonded complex between HCOOH and vinyl hydroperoxide, *via* a transition state that represents a submerged barrier (relative to the separated reactants). The **Int$_2$** postreaction complex is 21.7 kcal/mol lower in free energy than the reactants and, due to two intermolecular hydrogen bonds, 3.7 kcal/mol more stable than the separated products.

Clearly, HCOOH causes a dramatic lowering of the barrier relative to the unassisted and water-assisted tautomerizations. The calculated transition state for the HCOOH-catalyzed reaction lies 0.4 kcal/mol in free energy below the separated reactants indicating a facile tautomerization of the Criegee intermediate. The catalytic superiority of a single HCOOH molecule is mainly attributed to the pair of carbonyl and hydroxyl functionalities that facilitate an efficient hydrogen transfer through a double hydrogen-shift reaction. As a result, the distance across which the β-hydrogen migrates is considerably reduced and the reaction occurs *via* a 9-membered cyclic transition state that is less sterically strained than the transition states for the uncatalyzed and water-catalyzed reactions.

The cleavage of the O-OH bond in the vinyl hydroperoxide leads to the formation of •OH and vinyloxy radical. Contrary to earlier reports,[41,45] recent multi-reference *ab initio* calculations indicate that this bond breaking process involves a free-energy barrier of 18.8 kcal/mol and an endergonicity of 11.6 kcal/mol.[53] Since the vinyl hydroperoxide is formed with an excess free energy of 18.0 kcal/mol, the overall •OH forming reaction involving the acid-catalyzed Criegee tautomerization might be expected to be a nearly barrierless reaction. However, the presence of the organic acid stabilizes the vinyl hydroperoxide through two hydrogen bonds and might delay or inhibit the •OH formation by accepting excess energy. Additional study will be required to elucidate the role of the acid-catalyzed tautomerization on •OH formation, including in understanding the time or pressure-dependences seen in ozonolysis experiments.[54,55]

The calculated free-energy profiles indicate that the HCOOH-catalyzed tautomerization may be an important decay channel for Criegee intermediates in the troposphere. Given the substantially submerged barrier, it could be a competitive pathway with the better-studied, and also barrierless, addition reaction of HCOOH with Criegee intermediates to form hydroperoxy alkyl esters.[56,57] However, the recent experiments of Welz *et al.* on Criegee intermediate reactions with formic acid do not show obvious indications of the tautomerization reaction, as the measured rate constants are not strongly dependent on the presence of a β-hydrogen in the Criegee intermediate, *i.e.,* the rate constants are the same within error bars for *anti*-CH_3CHOO + HCOOH and *syn*-CH_3CHOO + HCOOH.[9] However, the ionization energy of the tautomerization product of the latter reaction, vinyl hydroperoxide, has been calculated to be 9.18 eV,[2] sufficiently low that it would presumably be detected in the experiments of Welz *et al.* (before it decays to form •OH). Thus, additional experimental and theoretical work will likely be required to definitively determine the role of the tautomerization reaction in Criegee intermediate reactions with carboxylic acids. The selective isotope labeling on the methyl group of the *syn*-CH_3CHOO (CD_3CHOO) could be an interesting experiment to test the proposed mechanism. Such an isotopic substitution should exclusively lead to the formation of CD_2CHOOH, rather than CD_2CHOOD, and thus, the •OH, but not the •OD should appear as the final product in the experiment.

Because dicarboxylic acids have an appreciable presence in the troposphere,[16,17] we next investigated their catalytic effect on Criegee intermediate tautomerization. We first examined the simplest dicarboxylic acid, oxalic acid. The catalyzed tautomerization follows the same route as that involving HCOOH shown in Fig. 1 with only small differences in the relative free energies (Table S3, ESI). The reaction catalyzed by malonic acid, the next larger dicarboxylic acid, has a higher barrier than for oxalic acid by 1.6 kcal/mol. This effect is attributable to the presence of a relatively weaker intramolecular hydrogen bond in the latter case;[19] $R_{O\text{-}H}$ = 1.98 Å for oxalic acid compared to $R_{O\text{-}H}$ = 1.74 Å for malonic acid (Fig. S3, ESI).

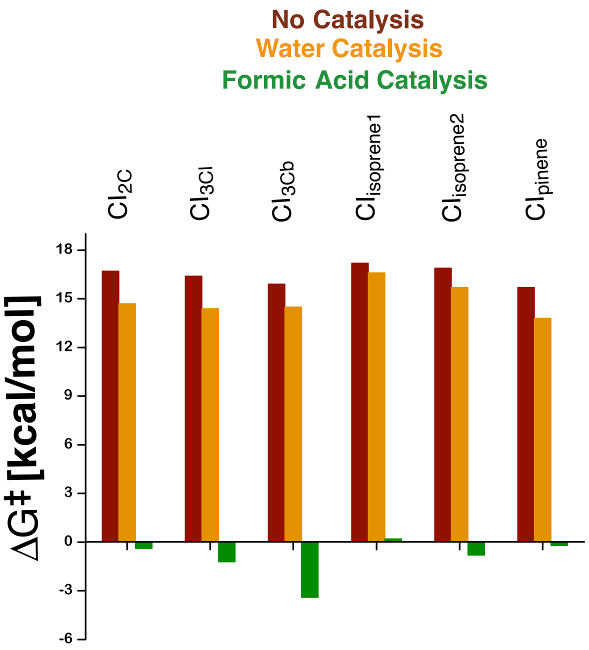


Fig. 2 Calculated free-energy barriers for the uncatalyzed and catalyzed Criegee intermediate tautomerization studied in the present work (298.15 K, 1 atm, kcal/mol). Here CI_{2C}, CI_{3Cl} and CI_{3Cb} refer to *syn*-CH_3CHOO, *syn*-CH_3CH_2CHOO and $(CH_3)_2COO$, respectively.

It is also interesting to examine the role of the Criegee intermediate structure by comparing the tautomerization of the *syn*-CH_3CH_2CHOO and $(CH_3)_2COO$ isomers. As indicated in Fig. 2, the calculated free-energy barriers of the unassisted tautomerizations of *syn*-CH_3CH_2CHOO and $(CH_3)_2COO$ (see also Fig. S4 and Fig. S6, ESI) are similar to that of the *syn*-CH_3CHOO reaction. This is consistent with a recent study by Liu *et al.*, in which the ZPE-CCSDT/6-311+G(2d,p) calculated barrier heights for the uncatalyzed tautomerization of the C_2 and C_3 Criegee intermediates were found to be similar.[58] The current calculations, presented in Fig. 2, find free-energy barriers of -1.2 and -3.4 kcal/mol for the HCOOH-catalyzed tautomerization of *syn*-CH_3CH_2CHOO and

$(CH_3)_2COO$, respectively (see Fig. S5 and Fig. S7, ESI). This indicates there is a small, but non-negligible, dependence of the acid-catalyzed barrier on the Criegee intermediate structure. Interestingly, the free-energy barriers of the water-catalyzed tautomerizations (which are just 1.4-2.0 kcal/mol lower than the uncatalyzed reaction) differ by only 0.5 kcal/mol and those for the uncatalyzed reactions are only 0.1 kcal/mol apart.

The tautomerizations of two of the possible biogenic Criegee intermediate conformers produced during the isoprene ozonolysis ($CI_{isoprene1}$ and $CI_{isoprene2}$) is quite similar to that of *syn*-CH_3CHOO. In particular, as indicated in Fig. 2, the two isoprene derived Criegee intermediates have similar uncatalyzed free-energy barriers, 17.2 and 16.9 kcal/mol for $CI_{isoprene1}$ and $CI_{isoprene2}$, respectively, compared to 16.7 kcal/mol for *syn*-CH_3CHOO. The participation of a water molecule also has a small effect on this barrier, reducing it by 1.6, 1.2, and 2.0 kcal/mol for $CI_{isoprene1}$, $CI_{isoprene2}$, and *syn*-CH_3CHOO, respectively. In a recent study,[40b] Anglada *et al.* have also stressed the importance of entropy effects in the water-catalyzed tautomerization of $CI_{isoprene1}$ and $CI_{isoprene2}$, *i.e.*, according to their calculations, the catalytic effect of a water molecule on the tautomerization reaction is significantly reduced by entropic contributions. However, the results in Fig. 2 clearly show that formic acid has a dramatic catalytic effect, reducing the free-energy barrier to 0.2 and -0.8 kcal/mol for $CI_{isoprene1}$ and $CI_{isoprene2}$ (see also Fig. S8–S11, ESI), quite similar to the $\Delta G^{\ddagger}$ = -0.4 kcal/mol barrier for *syn*-CH_3CHOO.

Finally, we consider the tautomerization of one of the Criegee intermediates formed during *α*-pinene ozonolysis (CI_{pinene}). (Fig. S12–S13, ESI). As indicated in Fig. 2, the calculated free-energy barriers for the uncatalyzed, water-catalyzed, and HCOOH-catalyzed tautomerization of the *α*-pinene Criegee intermediate, CI_{pinene}, are within 1.0 kcal/mol of the barriers estimated for the *syn*-CH_3CHOO. Combined with the results for the isoprene-derived intermediates, this indicates that the Criegee intermediate structure does not have a major impact on the tautomerization reaction energetics.

Conclusions

In summary, electronic structure calculations indicate that the formic acid-catalyzed tautomerization occurs with a submerged free-energy barrier for all the Criegee intermediates we have examined, including those derived from biogenic sources. This behaviour is in stark contrast to the case of water, which exhibits only a minor catalytic effect on the reaction. The high catalytic activity of monocarboxylic acids is due to the presence of two oxygen functionalities that facilitate the hydrogen atom transfer by converting it to a double hydrogen-shift reaction. Like monocarboxylic acids, the dicarboxylic acids catalyze the reaction to the extent that it becomes barrierless, but the catalytic effect is somewhat smaller due to the presence of an intramolecular hydrogen bond that inhibits the hydrogen shift. These calculations suggest the possibility of a facile bimolecular channel in the presence of carboxylic acids for the decay of Criegee intermediates to vinyl hydroperoxides and, potentially, hydroxyl radical, which may have significant implications for ozonolysis including in the context of tropospheric chemistry.

Notes and references

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Electronic Supplementary Information (ESI) available: Computational details, structures of Criegee intermediates considered, calculated free-energy reaction profiles, and Tables containing detailed energetic information. See DOI: 10.1039/c000000x/

This work is funded by NIFA/USDA grant no. 2011-10006-30362. We thank Dr. Michael Lundin and Dr. Andrew Danby for many useful discussions.

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