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EDGE ARTICLE

Decomposition of the simplest ketohydroperoxide in the ozonolysis of ethylene

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Hydroperoxides from the ozonolysis of alkenes, in addition to Criegee intermediates, have been proposed as an atmospheric source of OH radical in the absence of sunlight, but have remained largely elusive due to their reactivity. A weak peroxide bond enables facile OH elimination, and subsequent ß-scission can lead to a variety of decomposition products depending on the nature of the peroxide. In this paper we explore this process theoretically for the simplest ketohydroperoxide, hydroperoxyacetaldehyde (HPA), which is believed to be formed in the ozonolysis of ethylene. Despite it being the most stable $C_2H_4O_3$ species in this reaction scheme, lower in energy than the starting materials by around 100 kcal/mol, HPA has only been directly observed once in the ozonolysis of ethylene by photoionization mass spectrometry appearance energy. Here we report predictions of the rotational spectrum of HPA conducted in support of microwave spectroscopy experiments. We suggest a new dissociation path from HPA to glyoxal [$HOOCH_2CHO \rightarrow HCOCH_2O + OH \rightarrow CHOCHO + H$], supported by thermochemical calculations. We encourage the search for glyoxal using complementary experimental methods, and suggest possible future experimental directions. Evidence of glyoxal formation from ethylene ozonolysis might provide evidence of this underappreciated path in an important and long studied reaction system.

Introduction

The ozonolysis of unsaturated hydrocarbons plays a major role in atmospheric chemistry as a primary source of OH radical in the absence of sunlight.[1–5] Hydrocarbon ozonolysis is also likely a major contributor to aerosol formation due to the fact that it can generate heavy, polar, functionalized molecules, which are more facile to condensation than the relatively innocuous hydrocarbon starting materials.[6–12] Aerosols have a large impact on climate models, and gaps in understanding of their formation and evolution hinder further development of such models.[13,14] Although ozonolysis has been studied for over a century, much remains to be understood even in the archetypal case of ethylene ($CH_2{=}CH_2$).[1,12,15–22]

Ozonolysis of ethylene occurs via addition of O_3 to the carbon-carbon double bond to form a cyclic primary ozonide (cyc-CH_2OOOCH_2, POZ), followed by POZ decomposition to a Criegee intermediate (carbonyl oxide) and carbonyl.[16–19,22–25] Alternatively, the POZ could cleave at the O-O bond to form a diradical, which ultimately forms the simplest ketohydroperoxide (KHP), hydroperoxyacetaldehyde (HPA), via internal H-atom abstraction [$CH_2(O)CH_2OO \rightarrow CHOCH_2OOH$].[16,19,26,27] It has been calculated that a considerable fraction of the ozonolysis reaction flux (over 10%) should go through the formation of HPA.[19]

HPA is formed highly energized, lower in energy than the starting materials by roughly 100 kcal/mol,[16,19,27] and so it has previously been suggested that HPA dissociates to formylmethoxy and OH radicals [$HCOCH_2OOH \rightarrow HCOCH_2O + OH$]. This dissociation mechanism is also expected for other KHPs formed in combustion systems.[28] Formylmethoxy radical is proposed to decompose to H, CO and $CH_2{=}O$,[19,27] products, which are not unique to HPA decomposition.

The only direct observation of HPA in an ozonolysis system has been reported by Rousso *et al.*, who identified HPA by appearance energy using photoionization mass spectrometry.[26] Recent investigations by Porterfield *et al.* were able to observe the highly reactive peroxide species hydroperoxymethyl formate ($HOOCH_2OCHO$, HPMF) by high resolution microwave spectroscopy, but saw no clear experimental evidence for HPA in the ozonolysis of ethylene.[1] It is likely that insufficient collisional stabilization under the conditions of Porterfield et al. accounts for the absence of HPA from their observations.

In this paper we describe theoretical efforts to predict HPA's microwave spectrum, work which was completed in tandem with the experiments of Porterfield *et al.* We also consider a new potential decomposition mechanism of HPA, which ultimately leads to formation of glyoxal (HCOHCO), the simplest dione, in order to better understand the difficulty of HPA observation in the ozonolysis of ethylene. Diones were previously reported to be formed in combustion system, presumably through similar decomposition mechanisms of KHPs, however theoretical and experimental studies of such reactions are scarce.[28] As the most stable *trans* conformer of

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glyoxal possesses no permanent dipole moment, it cannot be observed by high resolution microwave spectroscopy. We therefore encourage the search for glyoxal using complementary experimental methods, and suggest possible future experimental directions.

Methods

The HPA conformer space including rotamers was evaluated at the MP2/ANO0 level of theory.[29,30] Its equilibrium structures were then optimized at the all electron (AE)-CCSD(T)/cc-pCVQZ level of theory, and anharmonic effects relevant to rotational constants, dipole moments, and thermochemistry were incorporated through second order vibrational perturbation theory (VPT2) calculations using the frozen core (FC)-CCSD(T)/ANO0 level of theory. Previous work with similar levels of theory proved sufficient for accurate predictions of rotational spectra of a variety of molecules, including cases with relevant peroxide and hydrogen-bonding features.[31–39] Thermochemical calculations were performed following the mHEAT protocol, with a UHF reference for the open-shell intermediates.[40–43] Excited electronic states were found to be too high in energy to participate in the processes investigated here. The CFOUR quantum chemistry program was used for all of the calculations, except for the open-shell CCSDT(Q) calculations which were performed using the MRCC code as interfaced with CFOUR.[44,45]

Results and Discussion

The rotational constants and dipole moments calculated for HPA are given in Table 1, and its lowest lying conformer geometries are shown in Figure 1. The lowest lying geometry lies more than 350 cm^{-1} (1 kcal/mol) lower than the second lowest lying conformer, making it the expected dominant conformer in the rotational spectrum. This stabilization is due to the internal hydrogen bond between the peroxy hydrogen and the carbonyl oxygen, whereas the higher conformer has the peroxy group *trans* to the carbonyl oxygen. We have thus far neglected hindered rotations. The calculated ground state geometry possesses relatively strong dipole components of roughly 1-2 Debye (Table 1), making its detection through microwave spectroscopy reasonably favorable. The predicted rotational spectrum of *cis*- and *trans*-HPA, along with the unidentified lines from Porterfield *et al.*'s measured spectrum, is shown in Figure 2.[1] The two spectra could not be matched, indicating the absence of HPA in this experimental study.

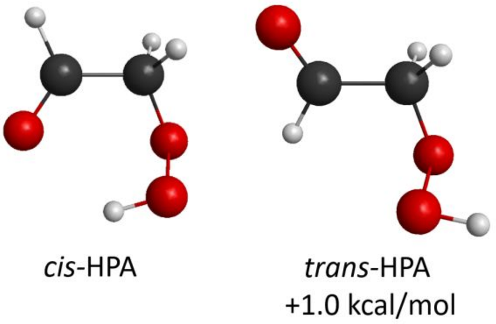


Figure 1. The calculated lowest-lying conformers of HPA. The next rotamer lies at almost +4 kcal/mol.

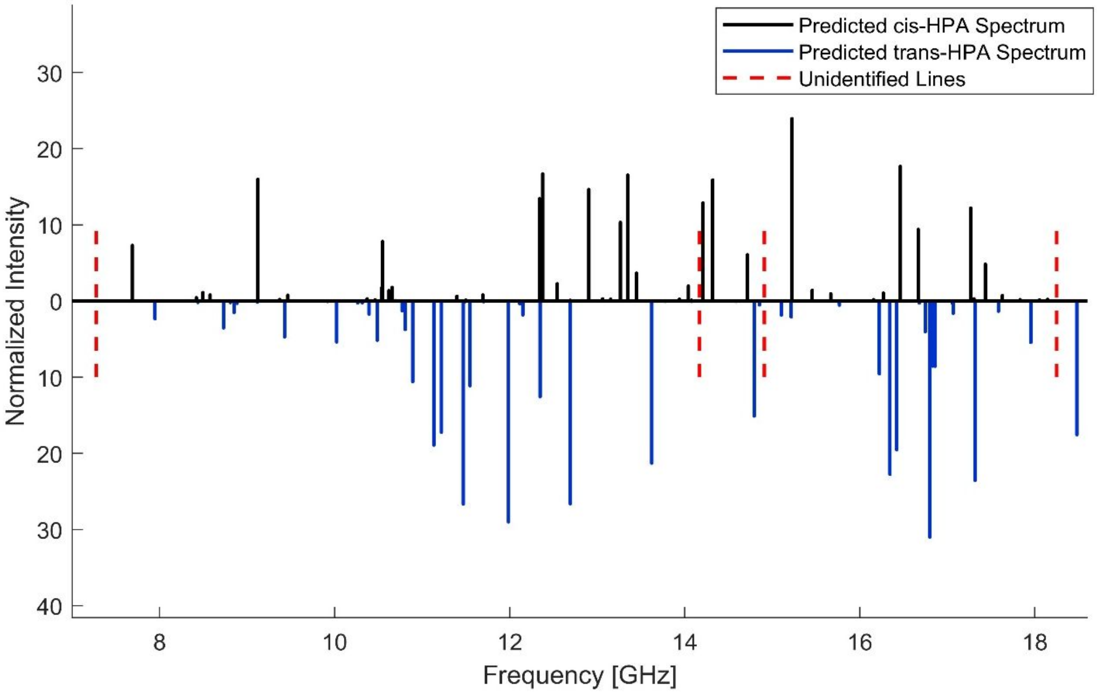


Figure 2. The predicted rotational spectra of *cis*-HPA (positive axis directions, black) and *trans*-HPA (negative axis direction, blue) as calculated at the (AE)-CCSD(T)/cc-pCVQZ level of theory with anharmonic corrections incorporated through (FC)-CCSD(T)/ANO0 VPT2 calculations. Simulated using PGOPHER for a temperature of 3K.[55] The unidentified lines in the measured spectrum are given as red-dashed lines.[1]

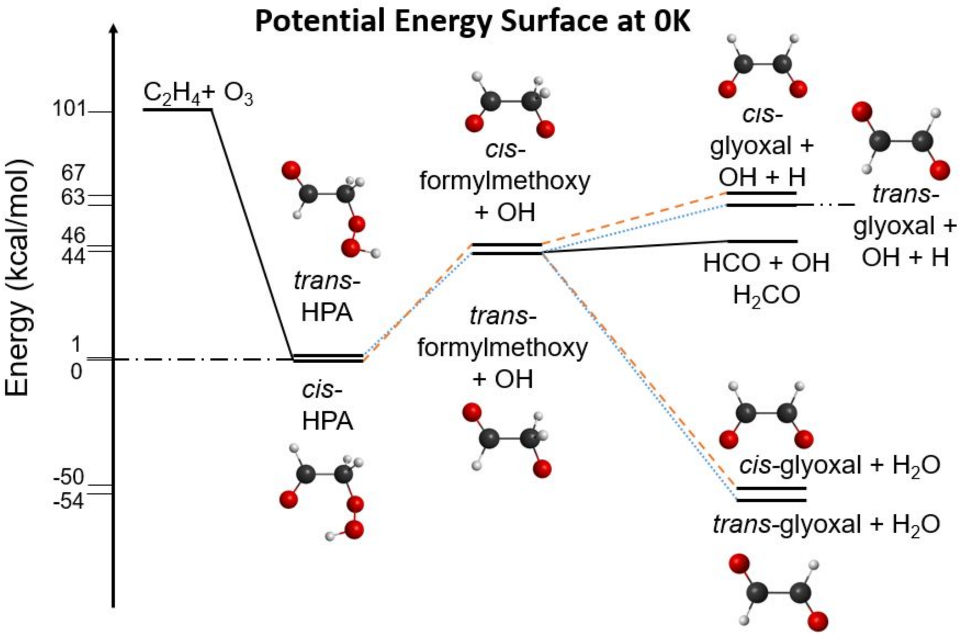
Table 1. The calculated rotational constants (A,B,C), and dipole moments for HPA's conformers.

		Rotational Constant (B_0) [MHz]	**Dipole Moment (μ_0) [Debye]**
cis	A	9149	1.57
	B	4407	2.12
	C	3335	0.93
trans	A	13777	2.18
	B	2969	0.98
	C	2643	0.73

Our thermochemical calculations on HPA, together with Active Thermochemical Tables (ATcT) data, show that HPA is lower in energy than the starting materials by 101.3 kcal/mol, in fair agreement with Anglada *et al.* and Nguyen *et al.* (approx. 2.5 kcal/mol difference) and in good agreement with Pfeifle *et al.* (0.1 kcal/mol).[1,16,19,27,41,46–48] A major contribution to the difference between the high accuracy calculations performed by us and Pfeifle *et al.* and the calculations performed by Anglada *et al.* and Nguyen *et al.* was the inclusion of CCSDT(Q) calculations, which contributed around -1.85 kcal/mol to HPA's final calculated energy and -0.94 kcal/mol to its enthalpy of formation. This large contribution is attributed to lone pair-lone pair interactions of the two adjacent peroxy oxygen atoms.[31–33,43] As mentioned earlier, this low energy of HPA suggests that HPA is formed hot, and is therefore prone to further dissociation. In agreement with Anglada *et al.*, Nguyen *et al.* and Pfeifle *et al.* we find that the dissociation takes place through OH removal and formation of formylmethoxy.[16,19,27] We find that the energy needed for that dissociation process is 44.3 kcal/mol, in good agreement with Anglada *et al.* and Pfeifle *et al*, making OH and formylmethoxy lower in energy than the starting materials by 57.1 kcal/mol, and consequently predicting this process to be highly favorable.[16,19]

Previous experimental studies of similar reaction schemes and similar reaction conditions suggest the lack of observation of HPA under the conditions of Porterfield *et al*. was due to insufficient collisional stabilization of the products. For example, although the microwave spectrum of the POZ is well known, it was not observed by Porterfield *et al*., or Womack *et al*. under similar experimental conditions.[21] This case is comparable to HPA, in that formation of the POZ is highly exothermic (roughly 50 kcal/mol)[49], and the POZ possesses relatively weak O-O bonds.[19,50] POZ fragmentation happens rapidly as the O-O bond gets vibrationally excited with excess internal energy, a process we expect to be even more rapid in HPA given that its formation is roughly 50 kcal/mol more exothermic than POZ formation.

While Nguyen *et al.* and Pfeifle *et al.* suggested that the formed formylmethoxy radical subsequently dissociates to produce HCO and H_2CO (a process endothermic by 1.6 kcal/mol from formylmethoxy + OH and exothermic by 55.5 kcal/mol from the starting materials),[19,27] we submit that formation of glyoxal should be considered as well. Formylmethoxy can undergo a C-H β scission to form glyoxal + H + OH. Although production of H + OH makes this process endothermic from HPA by 63.4 kcal/mol (19.1 kcal/mol from formylmethoxy + OH) and exothermic from the starting materials by 38 kcal/mol, subsequent reactions of H and OH will make this process exothermic; for example, formation of a water molecule will lead to exothermicity with respect to HPA by 54.3 kcal/mol, and by 155.6 kcal/mol with respect to the starting materials.[48] We could not locate a transition state leading to the concerted loss



Scheme 1. The conformer-dependent glyoxal formation paths. The *trans* path is given as the blue-dotted lines and the *cis* path is given as the orange-dashed lines.

of a water molecule, however, but a roaming or bimolecular process is conceivable.

Comparison with Porterfield *et al.*'s suggested mechanism for formation of HPMF followed by dissociation to formic anhydride supports our suggested glyoxal mechanism.[1] HMPF has a similar structure to HPA, with only an additional oxygen atom between the carbon atoms, and a similar ring structure stabilized by the internal hydrogen bond. Formic anhydride is also similar to glyoxal, with the addition of an oxygen atom between the carbon atoms. Porterfield *et al.* found a correlation between formation of HPMF and formic anhydride, and suggested a theoretical mechanism of the loss of OH followed by an H loss towards the formation of formic anhydride, resembling our suggested mechanism here. This path is endothermic with respect to HPMF by 52.8 kcal/mol, which is less by 11.5 kcal/mol than calculated for the equivalent HPA dissociation process; however HPMF is formed in the reported experimental system with an excess energy of only 40 kcal/mol (full Criegee and formic acid thermalization) to around 90 kcal/mol (no thermalization), with the secondary chemistry involved in its formation favoring the probability for thermalization. This makes the HPMF process energetically comparable to glyoxal formation from HPA, i.e. exothermic in total by 13-63 kcal/mol. Formation of a water molecule as opposed to H + OH induces the exact same energy shift, increasing the exothermicity by 117.6 kcal/mol.[48]

Calculations were also performed to explore the conformer space of the suggested mechanism (Scheme 1). While for HPA the second lowest lying conformer is only 1.0 kcal/mol higher than the lowest lying conformer, for formylmethoxy the difference is 1.9 kcal/mol and for glyoxal the difference is 4.4 kcal/mol. For HPA, the second conformer has the carbonyl oxygen *trans* to the peroxy oxygens, while for formylmethoxy and for glyoxal the *trans* conformers are the lowest lying ones. This suggests the possibility of two different paths, a *trans* and a *cis* path leading to *trans* and *cis* glyoxal respectively. Due to the low energy difference between HPA's conformers relative to its excess energy, a substantial amount of HPA is likely to form in the *trans* conformer. This conformer should be able to react through the *trans* path with a barrier lower by 1.0 kcal/mol than the one considered for the lowest lying conformer. However, the *cis* path originating from the lowest HPA conformer has a barrier larger by 2.9 kcal/mol than the *trans* path towards formylmethoxy, and a total energy difference to glyoxal larger by 5.4 kcal/mol than the *trans* path, making it less favourable both kinetically and thermochemically. This energy difference is small enough relative to the initial HPA activation to make the formation of *cis*-glyoxal and its detection in this reaction system at least possible.

We suggest a number of experiments to potentially test this suggested mechanism. First, glyoxal is one of the only proposed $C_2H_2O_2$ species in this system[19] and has a well-studied photoionization energy[38]; thus a mass spectrometry study can assist in its identification. In addition, we suggest that under proper thermalization conditions *cis*-glyoxal should be formed. In contrast to *trans*-glyoxal, *cis*-glyoxal has a non-zero dipole moment, making its microwave spectroscopy detection possible. Reacting deuterated ethylene, CD_2CH_2, with ozone should produce mono-deuterated glyoxal, CDOCHO, with a small but in principle detectable dipole even in the *trans* conformation.[51] Another way to create a microwave detectable product is to use a substituted ethylene as a precursor, such as propylene, to yield methyl glyoxal (or its differently substituted equivalent), but further studies would be necessary to demonstrate the equivalence of these reaction mechanisms. Other spectroscopic methods, such as fluorescence and phosphorescence, can be used to detect glyoxal as well.[52–54] It should be noted that other paths might lead to the formation of glyoxal from ethylene ozonolysis, such as recombination of two HCO radicals, but HCO is formed in very low concentrations and dissociates rapidly, making the formation of glyoxal by this path unlikely.

Conclusions

In this study, we suggested a new possible product, glyoxal, in the ethylene ozonolysis system. This suggestion arose from the unexpected absence of detected HPA in this system in a search using high resolution microwave spectroscopy, aided by high accuracy *ab-initio* calculations to predict its rotational spectrum.

This suggested path passes through formylmethoxy after the removal of OH, in a good agreement with the calculated paths by Anglada *et al.*, Nguyen *et al.* and Pfeifle *et al.*; however unlike the products emphasized by Nguyen *et al.* and Pfeifle *et al.* we submit that a full dissociation toward OH, HCO and H_2CO is not the only possible outcome, with OH + H + glyoxal newly suggested.[16,19,27] We have shown that a comparison with the mechanisms of formation of HPMF and its dissociation toward formic anhydride, as suggested by Porterfield *et al.*, supports our mechanism due to the chemical and thermochemical resemblance of these reactions.[1] In addition, two conformer-dependent paths were suggested, with the one resulting in *trans* glyoxal being kinetically and thermodynamically favored.

Finally, we encourage the experimental search for glyoxal in the ozonolysis of ethylene and related systems to prove this path. Mass spectrometry experiments with deuterated ethylene and further computational and experimental work about the ozonolysis of substituted ethylene derivatives (such as propylene) could all provide potential support for this underappreciated path in an important and long studied reaction system.

Conflicts of interest

There are no conflicts to declare.

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