



Red-Light-Induced Decomposition of an Organic Peroxy Radical: A New Source of the HO₂ Radical

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Abstract: The gas-phase decomposition of the α -hydroxy methylperoxy radical has been theoretically examined, and the results provide insight into a new source of the hydroperoxy radical (HO₂) in the troposphere. Bimolecular peroxy decomposition is promoted by the red-light or near-IR radiation excitation. The calculations suggest for the first time, an important chemical role for the H₂O·HO₂ radical complex that exist in significant abundance in the troposphere. In particular, the reaction of organic peroxy radicals with the HO₂ radical and the H₂O·HO₂ radical complex represent an autocatalytic source of atmospheric HO₂. This reaction is a new example of red-light-initiated atmospheric chemistry that may help in understanding the discrepancy between the observed and measured levels of the HO_x at sunrise.

A detailed knowledge of peroxy radical chemistry is crucial for understanding the oxidative capacity of atmosphere.^[1] Alkyl peroxy radicals (RO₂) are key components of hydrocarbon oxidation processes.^[2,3] These RO₂ radicals mediate gas-phase reactions depending upon the environment. For example, in polluted conditions where the NO_x concentration is high, the reaction of the RO₂ radical with NO is the major loss channel,^[4] whereas in the low NO_x environments, the reactions of the RO₂ radical with other species become important; the self-reaction or cross-reaction with other peroxy radicals is one of the dominant chemical sinks for the RO₂ radical in these environments.^[2,3,5]

The decomposition of the RO₂ radical is another important degradation pathway in the troposphere. This reaction may provide insight into the source of the hydroperoxy radical (HO₂), which is the most abundant peroxy radical in the atmosphere and plays an important role in ozone cycle and hydrogen peroxide formation.^[4] However, this peroxy loss channel has yet to be considered in models incorporating the RO₂ radicals. The α -hydroxy methylperoxy radical, HOCH₂(O₂) is a prototypical example of the RO₂ radical. This peroxy radical may also serve as a model compound for the hydroxy isoprene peroxy radicals that are produced through the daytime oxidation of isoprene by the OH radical. These hydroxy isoprene peroxy radicals play an important role in determining the tropospheric budget of HO_x, NO_x, HNO₃, and ozone species. Isoprene is the most abundant biogenically emitted non-methane hydrocarbon in the atmos-

phere,^[7] which accounts for about 44% of the total volatile organic compound emission by vegetation.^[8] The HOCH₂(O₂) radical decomposition leads to the HO₂ radical and formaldehyde (HCHO) as shown in Equation (1):



Water vapor is the third most abundant molecule in the Earth's atmosphere. The ability of water to stabilize the radical systems as well as to promote hydrogen-atom transfer (HAT) chemistry in the troposphere by forming a proton wire is well documented in literature.^[9] Water dimers are suggested to be present in noticeable amounts in the atmosphere, that can significantly impact atmospheric reactions.^[10,11] Just like water, the HO₂ radical is also capable of promoting the HAT reactions because of the hydroxy and peroxy functionalities that allow it to form sterically stable H bonds with oxygenates.^[12,13] Since the RO₂ radical decomposition is an HAT reaction, it is mechanistically interesting to examine if water or the HO₂ radical catalysis would make this decomposition an energetically viable event under atmospheric conditions. Since the HO₂ radical is produced in the reaction, the peroxy decomposition could be autocatalytic.

In this letter, we have used electronic structure calculations to investigate the gas-phase decomposition of the HOCH₂(O₂) radical in the presence of H₂O, (H₂O)₂, the HO₂ radical, and the H₂O·HO₂ radical complex that are viable catalysts in the troposphere. For computational details, see the Supporting Information. The uncatalyzed HOCH₂(O₂) decomposition is a concerted HAT reaction that involves the cleavage of carbon-peroxy linkage and the simultaneous 1,4-HAT between the hydroxy oxygen and the terminal peroxy oxygen, and leads to the formation of HCHO and the HO₂ radical (Figure 1). At the CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level of theory, the reaction has a barrier of 14.0 kcal mol⁻¹ and an endothermicity of 15.4 kcal mol⁻¹. The reaction goes through a post-reaction complex, in which the products, HCHO and the HO₂ radical are H-bonded. This complex is 7.4 kcal mol⁻¹ energetically lower than separated products and 8.0 kcal mol⁻¹ higher than the HOCH₂(O₂) radical.

The effect of a single H₂O molecule on the decomposition is analyzed. The potential-energy surface for the bimolecular reaction is significantly modified; the reaction is now mediated by a pre-reaction complex, **Int₁**, in which H₂O forms H bonds with the hydroxy hydrogen and peroxy oxygen atoms of the HOCH₂(O₂) radical (Figure 2 and Table 1). The **Int₁** has a binding energy of 7.2 kcal mol⁻¹. The reaction then proceeds via a seven-membered transition state, **TS** into a post-reaction complex, **Int₂**. Interestingly, the reaction

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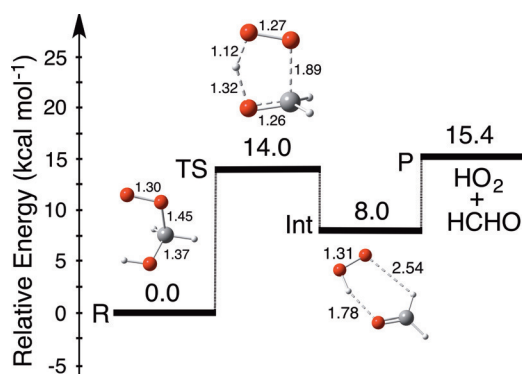


Figure 1. Zero-point-corrected potential-energy surface for the uncatalyzed decomposition of the α -hydroxy methylperoxy radical. The optimized structures of key species along with certain bond distances (in Å) are also shown.

barrier, which is measured relative to the **Int**₁, is raised from 14.0 to 22.6 kcal mol⁻¹. The cleavage of a strong C–O bond in addition to the 1,4-HAT explains the H₂O anticatalysis.

However, the **Int**₂, in which H₂O is H-bonded with both products, HCHO and the HO₂ radical, is 13.6 kcal mol⁻¹ more stable than the separated products. For the water-dimer-mediated reaction, the barrier is even further increased to 24.8 kcal mol⁻¹ (Figure 2). The **Int**₁ and **Int**₂ are 11.0 and 17.9 kcal mol⁻¹ more stable than the separated reactants and products, respectively.

We next examined the prospect of the peroxy decomposition being autocatalytic by analyzing the triplet potential-energy surface for the HO₂ radical-mediated decomposition of the HOCH₂(O₂) radical. Though the calculated barrier of 17.2 kcal mol⁻¹ is lower than that of the water or water dimer reaction, it is still 3.2 kcal mol⁻¹ higher than that for the uncatalyzed one. The **Int**₁ and **Int**₂ are about 2.0 kcal mol⁻¹ energetically lower than those involved in the water-mediated reaction, but are about 5–6 kcal mol⁻¹ less stable than those participating in the water dimer reaction. Since a significant fraction of the HO₂ radical (ca. 20–30 %) exists in a complexed form with water in the troposphere,^[14] the effect of H₂O–HO₂ radical complex on the decomposition is also examined. The reaction has a barrier of 19.5 kcal mol⁻¹ relative to the **Int**₁,

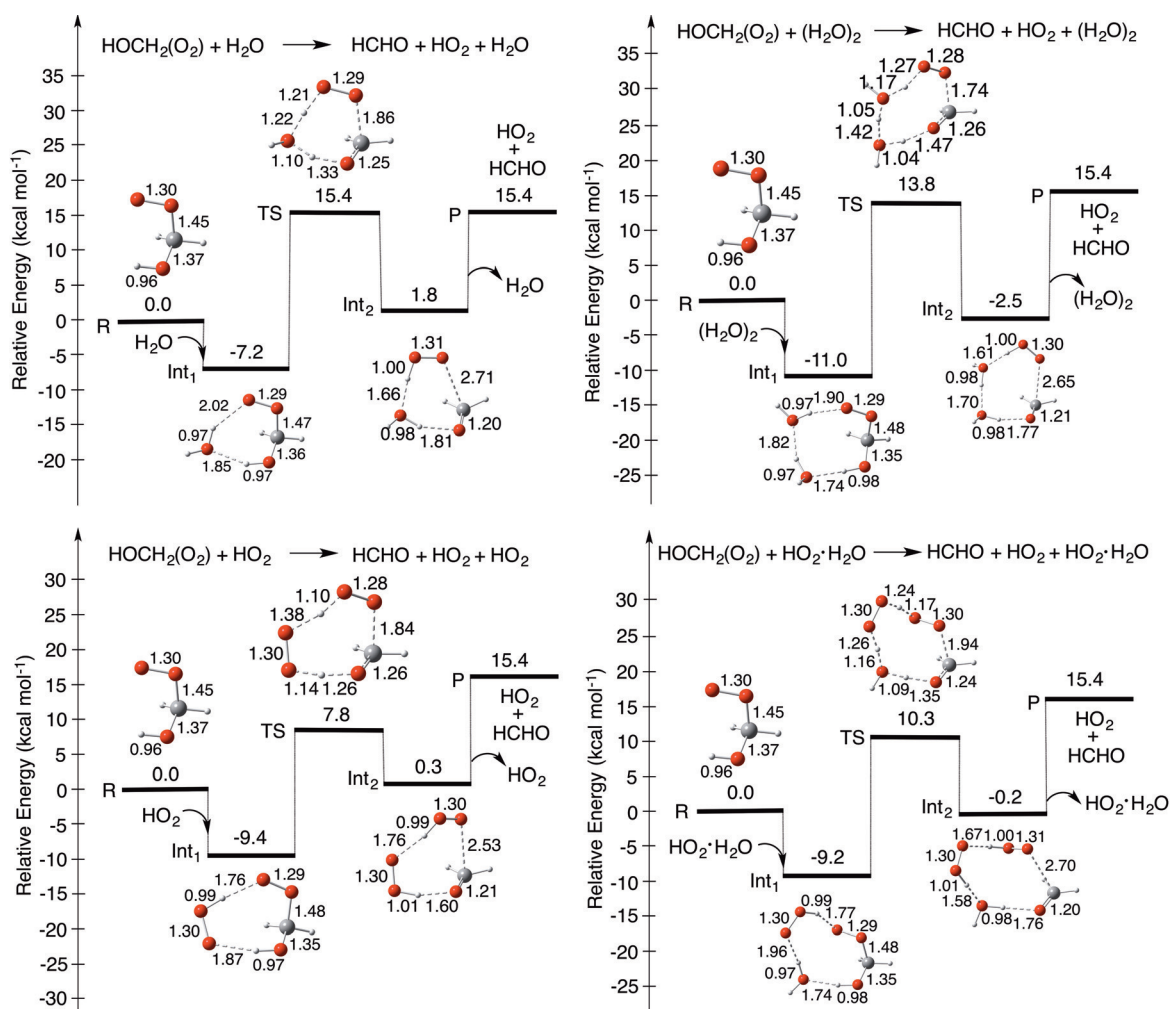


Figure 2. Zero point-corrected potential energy surfaces for the decomposition of the α -hydroxy methylperoxy radical in the presence of water, water dimer, hydroperoxy radical, and water-hydroperoxy radical complex. The optimized structures of key species along with certain bond distances (in Å) are also shown.

Table 1: Calculated first electronic excitation, first O–H overtone excitation, and binding energies of the pre-reaction and the post-reaction complexes involved in the unimolecular/bimolecular decomposition of the α -hydroxy methylperoxy radical. Details of the calculations are given in the Supporting Information.

Stationary point	Electronic excitation	First O–H stretching overtone excitation		Binding energy ^[a] [kcal mol ^{−1}]	Effective barrier [kcal mol ^{−1}]
	1st excited state [kcal mol ^{−1}]	catalyst anharmonic [kcal mol ^{−1}]	peroxy species ^[b] anharmonic [kcal mol ^{−1}]		
HOCH ₂ (O ₂)	25.8	—	18.7	—	14.0
Int ₁ (HOCH ₂ (O ₂) + H ₂ O)	27.2	21.7	18.2	7.2	22.6
Int ₁ (HOCH ₂ (O ₂) + H ₂ O·H ₂ O)	27.4	20.5 ^[c]	20.3	11.0	24.8
	27.4	18.7 ^[d]	20.3	11.0	
Int ₁ (HOCH ₂ (O ₂) + HO ₂)	27.4	16.8	19.4	9.4	17.2
Int ₁ (HOCH ₂ (O ₂) + HO ₂ ·H ₂ O)	27.0	19.1 ^[c]	19.1	9.2	19.5
	27.0	16.8 ^[d]	19.1	9.2	
Int (HOCH ₂ (O ₂))	24.2	—	17.5	7.4	
Int ₂ (HOCH ₂ (O ₂) + H ₂ O)	24.4	16.6	12.2	13.6	
Int ₂ (HOCH ₂ (O ₂) + H ₂ O·H ₂ O)	24.2	20.3 ^[c]	12.5	17.9	
	24.2	15.7 ^[e]	12.5	17.9	
Int ₂ (HOCH ₂ (O ₂) + HO ₂)	25.4	12.5	16.6	15.1	
Int ₂ (HOCH ₂ (O ₂) + HO ₂ ·H ₂ O)	24.7	19.4 ^[c]	11.5	15.6	
	24.7	7.8 ^[e]	11.5	15.6	

[a] The binding energies of the **Int₁**s and **Int₂**s are calculated relative to separated reactants and products, respectively. [b] Peroxy species in the **Int₁**s and **Int₂**s correspond to the HOCH₂(O₂) and the HO₂ radicals, respectively. [c] These values correspond to the overtone excitation of the O–H stretching vibration in the catalyst that interacts with the hydroxy or carbonyl end of formaldehyde. [d] These values correspond to the overtone excitation of the O–H stretching vibration in the catalyst that interacts with the peroxy end of the HOCH₂(O₂) radical. [e] These values correspond to the overtone excitation of the O–H stretching vibration in the catalyst that interacts with the HO₂ radical product.

which is 2.3 kcal mol^{−1} higher than that of the HO₂ radical-mediated reaction. The **Int₁** is 0.2 kcal mol^{−1} less stable than that in the HO₂ radical reaction, whereas the **Int₂** is 0.5 kcal mol^{−1} more stable than that in the HO₂ radical reaction.

Though the bimolecular decompositions involve relatively larger barriers than the uncatalyzed one, these reactions are mediated by the **Int₁**s that are more stable than separated reactants. In the **Int₁**s, the peroxy radical and catalyst are stabilized via H bonds. The key H bonds are O–H H bonds, which result in the binding energies of 7.2–11.0 kcal mol^{−1} for these **Int₁**s. The overtone excitation of the O–H stretching vibration in the **Int₁** may provide sufficient energy to overcome the decomposition barrier. The potential importance of vibrationally excited reagents in atmospheric reactions has started to receive considerable interest.^[15] Vibrational overtone excitation of the X–H (X = O, N, S, and C) bond of any reagent can give rise to an increase in the rate coefficient of many orders of magnitude.^[16–18] Our calculations indicate that the overtone excitation of $\nu_{\text{OH}} \geq 1$ would be suffice to make the bimolecular reaction happen except the water dimer reaction, for which the effective barrier is 4.4 kcal mol^{−1} higher than the first O–H overtone (Table 1). However, the overtone-driven decomposition of the **Int₁**s would compete with their reversion back into the reactants. The latter photochannel might be dominant for the water and the water dimer-mediated decomposition because of the high energy transition states, whereas for the HO₂ radical and the H₂O·HO₂ radical complex reaction, the photodecomposition might be feasible because the transition states are only 7.8 and 10.3 kcal mol^{−1} above the separated reactants. Thus, under atmospheric conditions, only the HO₂ radical and the

H₂O·HO₂ radical complex-mediated decompositions of the HOCH₂(O₂) radical are expected to yield the HO₂ radical product. The probability of such a photoreaction is also enhanced by the fact that a significant fraction (20–30 %) of the HO₂ radical exists as the H₂O·HO₂ radical complex in the troposphere.^[14]

Alternatively, electronic excitation of the organic peroxy species in the **Int₁** might also provide sufficient energy to surmount the decomposition barrier. The calculated equation-of-motion coupled-cluster singles and doubles (EOM-CCSD)/aug-cc-pVTZ data indicate that the lowest electronic excitation in the **Int₁**s occurs in the range of 25.8 to 27.4 kcal mol^{−1}, which is noticeably higher in energy than the effective decomposition barrier, implying that these peroxy decompositions might become feasible via absorption of near-IR or visible radiation. Since the absorption intensities of overtone excitations are usually weak, the electronic excitation-initiated chemistry would play a bigger role in the peroxy decomposition.

As can be seen from Figure 1 and Figure 2, the products of these reactions are HCHO and HO₂ either with or without H₂O. However, these products are generated in the post-reaction complexed state, **Int₂**. The **Int₂**s are stabilized relative to separated products from 13.6 to 17.9 kcal mol^{−1}, suggesting that the HO₂ radical from the reaction is tied up in the complex. Thus, any direct observation of the HO₂ radical resulting from this reaction mandates its dissociation from the **Int₂**, which requires breaking of the O–H H bonds in the complex. The energetics indicate that O–H overtone excitation at vibrational levels $\nu_{\text{OH}} \geq 1$ in the **Int₂**s is capable of promoting the dissociation at energies in excess of the reaction endothermicity (Table 1). We also note that because

the **Int₂**s involve the stabilized HO₂ radical; exciting the lowest electronic transition in the peroxy moiety might also provide another excitation source to photodissociate the **Int₂**. The EOM-CCSD/aug-cc-pVTZ calculated lowest electronic excited state for the **Int₂**s lies in the range of 24.2–25.4 kcal mol^{−1}, which is at least 6.3 kcal mol^{−1} higher than the energy required to break up these complexes. Thus, absorption of red light or near-IR radiation through the HOCH₂(O₂) moiety in the **Int₁**s, and the HO₂ moiety in the **Int₂**s or through overtone excitation of the O–H bond in these complexes constitute an important photomechanism, by which the HO₂ product is released. Any missing photolytic source that can account for the HO₂ budget has been described as having the general features of being: 1) involved in a single photon excitation to promote decomposition, 2) the strength of the bonds being broken must be less than 45 kcal mol^{−1}, and 3) the photo-excitation must occur between 650 nm < λ < 1250 nm.^[19] Results from Table 1 and Figure 1 suggest that the HOCH₂-(O₂) radical can photodissociate upon single photon absorption either through the overtone of the O–H stretching vibration in the radical or through the low-lying excited state of the O–O peroxy moiety. Thus, the direct dissociation of the HOCH₂(O₂) satisfies all the requirements to be a missing photolytic source of the HO₂ radical in the atmosphere. Moreover, results from this study also suggest that the bimolecular photodecomposition of the organic peroxy radical, in all cases occur at a wavelengths, λ > 650 nm; and is strongly dependent on solar zenith angle and could be a significant source of the HO₂ radical, which may play a crucial role in resolving the discrepancy between the observations and the predictions of the HO₂ levels at high solar zenith angles corresponding to the photochemistry at dawn or dusk.^[20]

The present theoretical calculations suggest, for the first time, an important chemical role of the H₂O·HO₂ radical complex that exist in significant abundance in the troposphere. In particular, the reaction of organic peroxy radicals with the HO₂ radical and the H₂O·HO₂ radical complex represent an autocatalytic source of the HO₂ radical. This reaction also serves as a new example of red-light-initiated atmospheric chemistry that may help in understanding the discrepancy between the observed and measured levels of HO_x at high solar zenith angles.

Keywords: atmospheric chemistry · computational chemistry · potential-energy profiles · radical–molecule reactions · radicals

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