Atmospheric Chemistry Hot Paper

International Edition: DOI: 10.1002/anie.201509311
German Edition: DOI: 10.1002/ange.201509311

Red-Light-Induced Decomposition of an Organic Peroxy Radical: A New Source of the HO_2 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 (HO_2) 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 $H_2O{\cdot}HO_2$ radical complex that exist in significant abundance in the troposphere. In particular, the reaction of organic peroxy radicals with the HO_2 radical and the $H_2O{\cdot}HO_2$ radical complex represent an autocatalytic source of atmospheric HO_2. 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 (RO_2) are key components of hydrocarbon oxidation processes.[2,3] These RO_2 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 RO_2 radical with NO is the major loss channel,[4] whereas in the low NO_x environments, the reactions of the RO_2 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 RO_2 radical in these environments.[2,3,5]

The decomposition of the RO_2 radical is another important degradation pathway in the troposphere. This reaction may provide insight into the source of the hydroperoxy radical (HO_2), 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 RO_2 radicals. The α-hydroxy methylperoxy radical, $HOCH_2(O_2)$ is a prototypical example of the RO_2 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, HNO_3, and ozone species. Isoprene is the most abundant biogenically emitted non-methane hydrocarbon in the atmosphere,[7] which accounts for about 44 % of the total volatile organic compound emission by vegetation.[8] The $HOCH_2(O_2)$ radical decomposition leads to the HO_2 radical and formaldehyde (HCHO) as shown in Equation (1):

$$HOCH_2(O_2) \rightarrow HCHO + HO_2 \qquad (1)$$

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 HO_2 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 RO_2 radical decomposition is an HAT reaction, it is mechanistically interesting to examine if water or the HO_2 radical catalysis would make this decomposition an energetically viable event under atmospheric conditions. Since the HO_2 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 $HOCH_2(O_2)$ radical in the presence of H_2O, $(H_2O)_2$, the HO_2 radical, and the $H_2O{\cdot}HO_2$ radical complex that are viable catalysts in the troposphere. For computational details, see the Supporting Information. The uncatalyzed $HOCH_2(O_2)$ 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 HO_2 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 HO_2 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 $HOCH_2(O_2)$ radical.

The effect of a single H_2O 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, **Int_1**, in which H_2O forms H bonds with the hydroxy hydrogen and peroxy oxygen atoms of the $HOCH_2(O_2)$ radical (Figure 2 and Table 1). The **Int_1** 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, **Int_2**. Interestingly, the reaction

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201509311.

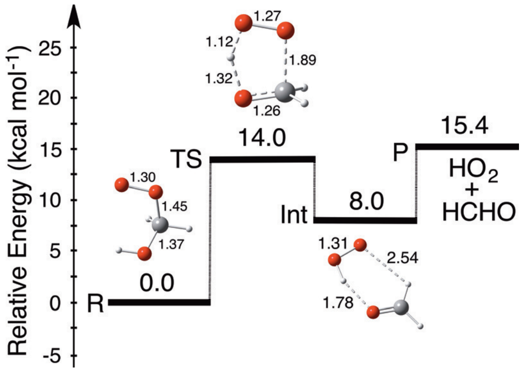

Figure 1. Zero-point-corrected potential-energy surface for the uncatalyzed decomposition of the α-hydroxy methylperoxy radical. The optimized structures of key species along with certain bond distances (in Å) are also shown.

barrier, which is measured relative to the $\mathbf{Int_1}$, 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 H_2O anticatalysis. However, the $\mathbf{Int_2}$, in which H_2O is H-bonded with both products, HCHO and the HO_2 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 $\mathbf{Int_1}$ and $\mathbf{Int_2}$ 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 HO_2 radical-mediated decomposition of the $HOCH_2(O_2)$ 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 $\mathbf{Int_1}$ and $\mathbf{Int_2}$ 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 HO_2 radical (ca. 20–30 %) exists in a complexed form with water in the troposphere,[14] the effect of $H_2O{\cdot}HO_2$ radical complex on the decomposition is also examined. The reaction has a barrier of 19.5 kcal mol^{-1} relative to the $\mathbf{Int_1}$,

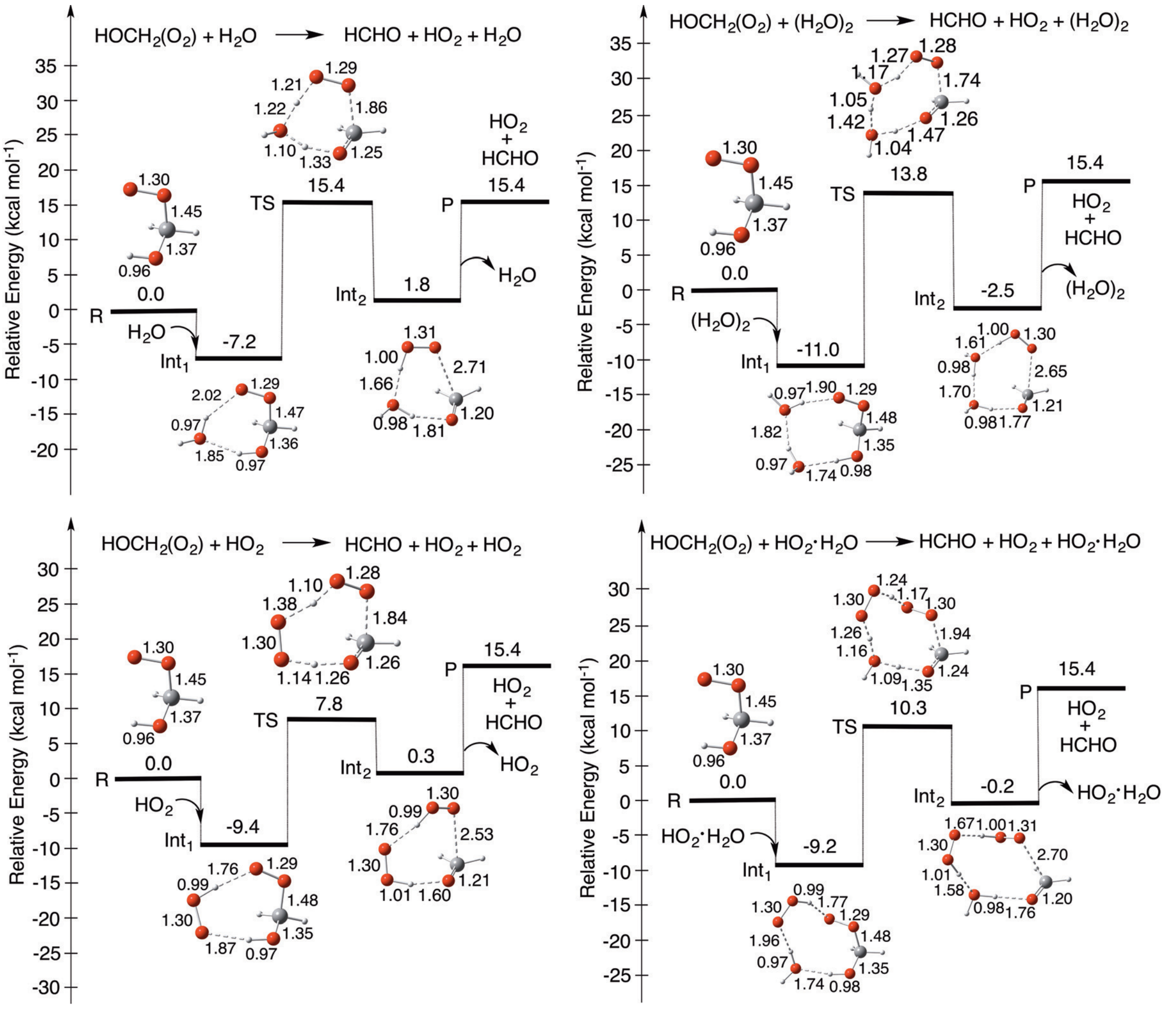

Figure 2. Zero point-corrected potential energy surfaces for the decomposition of the α-hydroxy methylperoxy radical in the presence of water, water dimer, hydroperoxy radical, and water·hydroperoxy radical complex. The optimized structures of key species along with certain bond distances (in Å) are 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$_1$ ($HOCH_2(O_2)+H_2O$)	27.2	21.7	18.2	7.2	22.6
Int$_1$ ($HOCH_2(O_2)+H_2O{\cdot}H_2O$)	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$_1$ ($HOCH_2(O_2)+HO_2{\cdot}H_2O$)	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$_2$ ($HOCH_2(O_2)+H_2O$)	24.4	16.6	12.2	13.6	
Int$_2$ ($HOCH_2(O_2)+H_2O{\cdot}H_2O$)	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$_2$ ($HOCH_2(O_2)+HO_2{\cdot}H_2O$)	24.7	19.4[c]	11.5	15.6	
	24.7	7.8[e]	11.5	15.6	

[a] The binding energies of the **Int$_1$**s and **Int$_2$**s are calculated relative to separated reactants and products, respectively. [b] Peroxy species in the **Int$_1$**s and **Int$_2$**s correspond to the $HOCH_2(O_2)$ and the HO_2 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 $HOCH_2(O_2)$ radical. [e] These values correspond to the overtone excitation of the O—H stretching vibration in the catalyst that interacts with the HO_2 radical product.

which is 2.3 kcal mol^{-1} higher than that of the HO_2 radical-mediated reaction. The **Int$_1$** is 0.2 kcal mol^{-1} less stable than that in the HO_2 radical reaction, whereas the **Int$_2$** is 0.5 kcal mol^{-1} more stable than that in the HO_2 radical reaction.

Though the bimolecular decompositions involve relatively larger barriers than the uncatalyzed one, these reactions are mediated by the **Int$_1$**s that are more stable than separated reactants. In the **Int$_1$**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 **Int$_1$**s. The overtone excitation of the O—H stretching vibration in the **Int$_1$** 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 $\nu_{OH} \geq 1$ 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 **Int$_1$**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 HO_2 radical and the $H_2O{\cdot}HO_2$ 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 HO_2 radical and the $H_2O{\cdot}HO_2$ radical complex-mediated decompositions of the $HOCH_2(O_2)$ radical are expected to yield the HO_2 radical product. The probablity of such a photoreaction is also enhanced by the fact that a significant fraction (20–30%) of the HO_2 radical exists as the $H_2O{\cdot}HO_2$ radical complex in the troposphere.[14]

Alternatively, electronic excitation of the organic peroxy species in the **Int$_1$** 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 **Int$_1$**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 HO_2 either with or without H_2O. However, these products are generated in the post-reaction complexed state, **Int$_2$**. The **Int$_2$**s are stabilized relative to separated products from 13.6 to 17.9 kcal mol^{-1}, suggesting that the HO_2 radical from the reaction is tied up in the complex. Thus, any direct observation of the HO_2 radical resulting from this reaction mandates its dissociation from the **Int$_2$**, which requires breaking of the O—H H bonds in the complex. The energetics indicate that O—H overtone excitation at vibrational levels $\nu_{OH} \geq 1$ in the **Int$_2$**s is capable of promoting the dissociation at energies in excess of the reaction endothermicity (Table 1). We also note that because the **Int$_2$**s involve the stablized HO_2 radical; exciting the lowest electronic transition in the peroxy moiety might also provide another excitation source to photodissociate the **Int$_2$**. The EOM-CCSD/aug-cc-pVTZ calculated lowest electronic excited state for the **Int$_2$**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 $HOCH_2(O_2)$ moiety in the **Int$_1$**s, and the HO_2 moiety in the **Int$_2$**s or through overtone excitation of the O−H bond in these complexes constitute an important photomechanism, by which the HO_2 product is released. Any missing photolytic source that can account for the HO_2 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 photoexcitation must occur between $650\,nm < \lambda < 1250\,nm$.[19] Results from Table 1 and Figure 1 suggest that the $HOCH_2(O_2)$ 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 $HOCH_2(O_2)$ satisfies all the requirements to be a missing photolytic source of the HO_2 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, $\lambda > 650\,nm$; and is strongly dependent on solar zenith angle and could be a significant source of the HO_2 radical, which may play a crucial role in resolving the discrepancy between the observations and the predictions of the HO_2 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 $H_2O{\cdot}HO_2$ radical complex that exist in significant abundance in the troposphere. In particular, the reaction of organic peroxy radicals with the HO_2 radical and the $H_2O{\cdot}HO_2$ radical complex represent an autocatalytic source of the HO_2 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

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 15711–15714
Angew. Chem. **2015**, *127*, 15937–15940

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Received: October 6, 2015