

Peroxone chemistry: Formation of H₂O₃ and ring-(HO₂)(HO₃) from O₃/H₂O₂

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The recent observation [Wentworth, P., Jones, L. H., Wentworth, A. D., Zhu, X. Y., Larsen, N. A., Wilson, I. A., Xu, X., Goddard, W. A., Janda, K. D., Eschenmoser, A. & Lerner, R. A. (2001) *Science* 293, 1806–1811] that antibodies form H₂O₂ from ¹O₂ plus H₂O was explained in terms of the formation of the H₂O₃ species that in the antibody reacts with a second H₂O₂ to form H₂O₂. There have been few reports of the chemistry for forming H₂O₃, but recently Engdahl and Nelander [Engdahl, A. & Nelander, B. (2002) *Science* 295, 482–483] reported that photolysis of the ozone–hydrogen peroxide complex in argon matrices leads to significant concentrations of H₂O₃. We report here the chemical mechanism for this process, determined by using first-principles quantum mechanics. We show that in an argon matrix it is favorable (3.5 kcal/mol barrier) for H₂O₂ and O₃ to form a [(HO₂)(HO₃)] hydrogen-bonded complex [head-to-tail seven-membered ring (7r)]. In this complex, the barrier for forming H₂O₃ plus ³O₂ is only 4.8 kcal/mol, which should be observable by means of thermal processes (not yet reported). Irradiation of the [(HO₂)(HO₃)-7r] complex should break the HO–OO bond of the HO₃ moiety, eliminating ³O₂ and leading to [(HO₂)(HO)]. This [(HO₂)(HO)] confined in the matrix cage is expected to rearrange to also form H₂O₃ (observed experimentally). We show that these two processes can be distinguished isotopically. These results (including the predicted vibrational frequencies) suggest strategies for synthesizing H₂O₃ and characterizing its chemistry. We suggest that the [(HO₂)(HO₃)-7r] complex and H₂O₃ are involved in biological, atmospheric, and environmental oxidative processes.

Peroxone (the combination of ozone and hydrogen peroxide) is used to treat soil, groundwater, and wastewater contaminated with volatile organic compounds, polycyclic aromatic hydrocarbons, petroleum hydrocarbons, chlorinated solvents, metals, munitions, diesel fuel, methyl *tert*-butyl ether (MTBE), BTEX (benzene, toluene, ethylbenzene, and xylene), trinitrotoluene (TNT), and other waste constituents (1). This mixture of ozone with hydrogen peroxide is far more reactive than either alone (1), but no mechanistic studies have been reported to explain why.

A recent paper (2) showed that mixing O₃ and H₂O₂ in an argon matrix leads to a complex that when photolyzed produces significant concentrations of H₂O₃, indicating that complex intermediates might be involved in the peroxone process.

Another recent paper (3) showed the surprising result that H₂O₃ is apparently involved in the formation of H₂O₂ from ¹O₂ plus H₂O by antibodies. Here a H₂O₃ species reacts with a second H₂O₂ to form [(HOO)(HO₂)-7r] (a head-to-tail seven-member ring complex), which subsequently leads to H₂O₂ (4, 5).

These studies suggest that other poorly understood but important oxidative processes involved in biological, atmospheric, and aqueous systems may involve H₂O₃, [(HOO)(HO₂)-7r], and related unknown or poorly characterized intermediates. Consequently we have been studying the chemistry of some of these possibly important species.

This report presents a detailed mechanistic study of the formation of H₂O₃ from H₂O₂ + O₃. Our results show that a complex of H₂O₂ and O₃ rearranges first to form the [(HOO)(HO₂)-7r] complex claimed in ref. 4 to be involved in

the antibody-catalyzed process. Under irradiation, the HO–OO bond should break, leading to ³O₂ plus [(HO₂)(HO)] confined in the matrix cage, which is expected to rearrange to form H₂O₃, which has been observed in ref. 2. In addition, the same cyclic intermediate complex can form H₂O₃ by a thermal unimolecular rearrangement process. We show that these two processes can be distinguished isotopically.

The computational details are given in the next section, followed by a presentation of the results, a discussion of the implications, and finally a presentation of some conclusions.

Computational Details

All quantum mechanical (QM) calculations used the B3LYP flavor of density functional theory (DFT) (6–10), which includes a generalized gradient approximation (GGA) and some exact exchange (hybrid method). The 6-31G** basis set (11, 12) was used on all atoms, and a full geometry optimization was carried out for all stable complexes and saddle points. Vibrational frequencies (from the analytic Hessian) were calculated to ensure that each minimum is a true local minimum (containing only positive frequencies) and that each transition state has only a single imaginary frequency (one negative eigenvalue of the Hessian). The Pulay modified scaled quantum mechanical (SQM) method was used to predict the vibrational frequencies (13). Scale factors for O–O stretching, O–H stretching, O–O–O bending, O–O–H bending, and O–O–O–H torsion are 0.917, 0.905, 0.920, 0.939, and 0.855, respectively. All QM calculations were carried out with JAGUAR (14).

To obtain more accurate energetics, we also carried out calculations with the cc-pVTZ basis set (15), using the optimized geometries from the 6-31G** basis. It was reported that calculations with B3LYP/6-311+G (3df,2p) lead to a mean absolute error of 3.11 kcal/mol for a collection of 148 simple inorganic/organic molecules (16).

For molecules such as ¹O₂ and O₃, which have significant open-shell character, standard density functional theory methods often lead to much larger errors. Thus with B3LYP the singlet and triplet gap for O₂ is $\Delta E (^1\Delta_g - ^3\Sigma_g^-) = 10.4$ kcal/mol, in poor agreement with the experimental value of 22.5 kcal/mol (17). Consequently, we used spin-projection techniques (18) to ensure a proper description of the complexes involving ¹O₂. This procedure leads to $\Delta E (^1\Delta_g - ^3\Sigma_g^-) = 20.5$ kcal/mol, in reasonable agreement with experiment.

Fig. 1 summarizes the whole reaction profile from H₂O₂ + O₃ to H₂O₃ + O₂, where LM stands for “local minimum” and TS stands for “transition state.” All energetics are reported for ΔH (298 K), in kcal/mol, where the calculated vibrational frequencies were used with standard quantum statistical formulas to obtain the entropy and enthalpy as a function of temperature.

Abbreviation: LM, local minimum.

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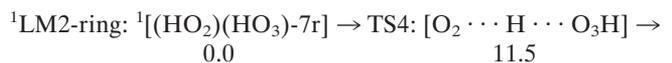
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Table 1. Predicted fundamentals for the [(HO₂)(HO₃)-7r] complex, in wavenumbers, based on the scaled quantum mechanical analysis of the Hessian from B3LYP/6-31G calculations**

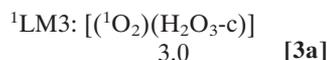
Mode	Character	Wavenumber, cm ⁻¹		
		(HO ₂)(HO ₃)	(HO ₂)(H ¹⁸ O ₃)	(DO ₂)(DO ₃)
ν_1	Antisymmetric OH stretch	3,190.3 (737.3)	3,188.8	2,331.8
ν_2	Symmetric OH stretch	3,030.1 (260.9)	3,020.6	2,220.2
ν_3	HOO bend of HO ₃	1,511.6 (64.7)	1,506.1	1,216.9
ν_4	HOO bend of HO ₂	1,466.9 (65.4)	1,460.1	1,180.5
ν_5	OO stretch of HO ₂	1,173.8 (9.1)	1,173.7	1,096.3
ν_6	Symmetric OO stretch of HO ₃	1,167.2 (29.7)	1,102.7	1,074.7
ν_7	Antisymmetric OO stretch of HO ₃	956.8 (72.1)	956.3	780.5
ν_8	HOOO-oop	787.9 (100.6)	743.6	690.8
ν_9	HO ₂ -HO ₃ -slide	588.5 (161.4)	588.1	512.0
ν_{10}	O-O-O bend in HO ₃	533.2 (5.6)	505.0	432.3
ν_{11}	Antisymmetric hydrogen-bond stretch	273.2 (49.9)	271.4	261.8
ν_{12}	Ring torsion-twist	219.6 (3.2)	210.2	216.8
ν_{13}	Symmetric hydrogen-bond stretch	175.1 (1.9)	171.1	170.4
ν_{14}	Ring torsion-chair	116.3 (0.5)	110.3	116.0
ν_{15}	Ring torsion-boat	65.3 (0.8)	64.7	64.2

The calculated infrared intensities for [(HO₂)(HO₃)-7r] are listed in parentheses.

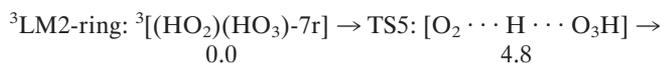
directly to the formation of HOOOH, as indicated in Eq. 3 (see Fig. 1). Because the LM2-ring is expected to have nearly degenerate singlet and triplet spin states, we considered both spin states.



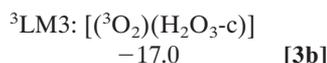
0.0 11.5



3.0 [3a]



0.0 4.8



-17.0 [3b]

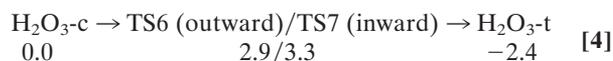
For the triplet case, the net reaction is 17.0 kcal/mol exothermic (because of formation of the ground state triplet molecule, ³O₂), leading to a barrier of only 4.8 kcal/mol. Forming ¹O₂ is endothermic by 3.0 kcal/mol with a barrier of 11.5 kcal/mol. Thus at low temperatures the triplet process is expected to dominate. Because of the rapid singlet-triplet conversion in

[(HO₂)(HO₃)-7r], it is likely to produce H₂O₃ even at low temperature.

The H₂O₃ formed in Eqs. 3a and 3b is in the *cis* form, with both O-H groups pointing toward the same side of the O-O-O plane of H₂O₃ (See Fig. 1). The O₂ and H₂O₃ complexes (LM3) formed are very weakly bound (binding energy = 0.2 kcal/mol), so that they are likely to dissociate even in the matrix.

The *cis* H₂O₃ can rotate its OH bond (either inward or outward) to convert to the *trans* global minimum of H₂O₃ with a low barrier as in Eq. 4 (refs. 4 and 19; ref. 19 reported detailed theoretical studies of H₂O₃).

Starting with ¹⁸O₃ + H₂O₂, the thermal process would lead to the formation of H¹⁸O¹⁸O¹⁸OH. Table 2 gives the predicted vibrational frequencies, which should be useful for experimental validation of these results.



0.0 2.9/3.3 -2.4 [4]

Formation of H₂O₃ by Photolysis. We find that free HOOO radical has a planar *cis* configuration. It is bound by only 3 kcal/mol with respect to HO and ³O₂, with a barrier to decomposition of only 4 kcal/mol.

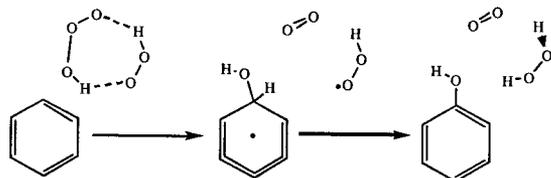
Table 2. Predicted fundamentals of *cis* HOOOH and *trans* HOOOH, H¹⁸O¹⁸O¹⁸OH, HOOOD, and DOOOD, in wavenumbers, based on the scaled quantum mechanical analysis of the Hessian from B3LYP/6-31G calculations**

Molecule	Wavenumber, cm ⁻¹								
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
H ₂ O ₃ -c	3,522.0	3,518.7	1,359.9	1,329.5	900.7	768.0	485.5	418.4	190.4
H ₂ O ₃ -t	3,533.1 (3,529.6)	3,528.4 (3,529.6)	1,353.6 (1,359.1)	1,349.6 (1,347.4)	899.5 (821.0)	770.2 (776.3)	506.5 (509.1)	410.4 (387.0)	346.9 (346.4)
H ¹⁸ O ¹⁸ O ¹⁸ H-t	3,531.2 (3,529.6)	3,518.3 (3,520.3)	1,352.4 (1,357.0)	1,347.0 (1,344.3)	887.6 (NR)	759.9 (768.0)	495.1 (NR)	408.9 (386.6)	346.3 (346.0)
HO ¹⁸ O ¹⁸ OH-t	3,528.4	3,533.1	1,348.7	1,347.0	874.8	745.6	502.9	408.4	346.1
H ₂ ¹⁸ O ₃ -t	3,521.1	3,516.4	1,344.8	1,343.8	848.3	726.1	480.3	405.6	344.8
HO ₃ D-t	3,530.7 (3,529.6)	2,580.5 (2,610.4)	1,351.4 (1,349.9)	1,009.2 (NR)	896.3 (814.6)	770.0 (772.0)	499.5 (NR)	387.1 (369.2)	276.6 (NR)
D ₂ O ₃ -t	2,582.2 (2,610.4)	2,579.0 (2,610.4)	1,013.6 (1,007.3)	1,004.2 (NR)	892.8 (NR)	769.8 (762.6)	492.6 (NR)	317.1 (301.6)	252.8 (273.5)

The experimental data (2) are listed in parentheses for comparison (NR, not reported). The modes are as follows: ν_1 , symmetric OH stretch; ν_2 , antisymmetric OH stretch; ν_3 , antisymmetric HOO bend; ν_4 , symmetric HOOO bend; ν_5 , symmetric OO stretch; ν_6 , antisymmetric OO stretch; ν_7 , OOO bend; ν_8 , antisymmetric torsion; and ν_9 , symmetric torsion.

than those in which the H_2O_3 is formed photolytically (because this would also form H_2O).

We suggest that $[(\text{HO}_2)(\text{HO}_3)\text{-}7\text{r}]$ and H_2O_3 may both play roles in oxidative processes ranging from the peroxone environmental cleanup process to the antibody conversion of $^1\text{O}_2$ and H_2O to H_2O_2 . Free OH is often postulated to be the reactive intermediate in such systems, despite the short lifetime. $[(\text{HO}_2)(\text{HO}_3)\text{-}7\text{r}]$ is essentially a capped OH radical, giving it a much longer lifetime than free OH. Thus the chemistry of $[(\text{HO}_2)(\text{HO}_3)\text{-}7\text{r}]$ would resemble that of free OH. For example, attack on an aromatic ring might proceed as



where the HO_2 in the complex can extract the H from the ring after attack by the OH.

It has long been recognized that hydrogen peroxide is an efficient catalyst for the decomposition of ozone (33) but that peroxone ($\text{O}_3 + \text{H}_2\text{O}_2$) is effective at destroying organic contaminants in water chemistry (1). We believe that the spectacular effectiveness of the peroxone process results from a variety of reactive intermediates (H_2O_3 , $[(\text{HO}_2)(\text{HO}_3)\text{-}7\text{r}]$) and their products (HO_3 , HO_2 , OH). Knowledge of the mechanistic details connecting these species should help to understand and improve the peroxone processes for environmental applications and should help establish the role of these intermediates in a variety of biological and environmental oxidations.

These same reactive intermediates (H_2O_3 , $[(\text{HO}_2)(\text{HO}_3)\text{-}7\text{r}]$) and their products (HO_3 , HO_2 , OH) might also be formed in the atmosphere, where conditions of low temperature and low H_2O concentrations might lead to modest concentrations of such intermediates. It is hoped that the mechanistic analysts and vibrational frequencies for the various intermediates provided

here might help identify these species in atmospheric or laboratory experiments.

Conclusions

Detailed mechanisms for the formation of H_2O_3 from $\text{H}_2\text{O}_2 + \text{O}_3$ are explored in this report. We predict that the codepositing of O_3 and H_2O_2 in an argon matrix leads to formation of the $[(\text{HO}_2)(\text{HO}_3)\text{-}7\text{r}]$ head-to-tail cyclic complex. We have predicted the vibrational frequencies of this complex to aid experimental validation.

We predict that thermal decomposition of $[(\text{HO}_2)(\text{HO}_3)\text{-}7\text{r}]$ (by means of hydrogen transfer from the HO_2 moiety to the HO_3 moiety) will lead directly to H_2O_3 (with all 3 O atoms arising from the O_3), whereas H_2O will decompose this species to form $^1\text{O}_2$ plus H_2O . These predictions should help to define optimal experimental conditions for making H_2O_3 .

On the other hand, UV irradiation of the $[(\text{HO}_2)(\text{HO}_3)\text{-}7\text{r}]$ complex will break the HO-OO bond of the HO_3 moiety, eliminating $^3\text{O}_2$ and forming a $[(\text{HO}_2)(\text{HO})]$ complex. We expect that this $[(\text{HO}_2)(\text{HO})]$ confined in the matrix cage will rearrange to form H_2O_3 . In this case just one of the terminal O atoms comes from O_3 . This formation of only H^{18}OOH from $^{18}\text{O}_3$ has been observed experimentally.

We suggest that $[(\text{HO}_2)(\text{HO}_3)\text{-}7\text{r}]$ and H_2O_3 are involved in biological, atmospheric, and environmental oxidative processes.

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