^{17}O NMR Spectroscopic Characterization and the Mechanism of Formation of Alkyl Hydrotrioxides (ROOOH) and Hydrogen Trioxide (HOOOH) in the Low-Temperature Ozonation of Isopropyl Alcohol and Isopropyl Methyl Ether: Water-Assisted Decomposition

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Abstract: Low-temperature ozonation of isopropyl alcohol (**1a**) and isopropyl methyl ether (**1b**) in [D$_6$]acetone, methyl acetate, and *tert*-butyl methyl ether at $-78\,^{\circ}$C produced the corresponding hydrotrioxides, $Me_2C(OH)(OOOH)$ (**2a**) and $Me_2C(OMe)(OOOH)$ (**2b**), along with hydrogen trioxide (HOOOH). All the polyoxides investigated were characterized for the first time by ^{17}O NMR spectroscopy of highly ^{17}O-enriched species. The assignment was confirmed by GIAO/MP2/6-31++G* calculations of ^{17}O NMR chemical shifts, which were in excellent agreement with the experimental values. Ab initio density functional (DFT) calculations at the B3LYP/6-31G*+ZPE level have clarified the transition structure (**TS1**, $\Delta E^{\neq} = 7.4$ and 10.6 kcal mol^{-1}, relative to isolated reactants and the complex **1a**-ozone, respectively) for the ozonation of **1a**; this, together with the formation of HOOOH and some other products, indicates the involvement of radical intermediates (R$^{\bullet}$, $^{\bullet}$OOOH) in the reaction. The activation parameters for the decomposition of the hydrotrioxides **2a** and **2b** ($E_a = 23.5 \pm 1.5$ kcal mol^{-1}, $\log A = 16 \pm 1.8$) were typical for a homolytic process in which cleavage of the ROOOH molecule occurs to yield a radical pair [RO$^{\bullet}$ $^{\bullet}$OOH] and represents the lowest available energy pathway. Significantly the lower activation parameters for the decomposition of HOOOH ($E_a = 16.5 \pm 2.2$ kcal mol^{-1}, $\log A = 9.5 \pm 2.0$) relative to those expected for the homolytic scission of the HO–OOH bond [bond dissociation energy (BDE) = 29.8 kcal mol^{-1}, CCSD(T)/6-311++G**] are in accord with the proposal that water behaves as a bifunctional catalyst and therefore participates in a "polar" (non-radical) decomposition process of this polyoxide. A relatively large acceleration of the decomposition of the hydrotrioxide **2a** in [D$_6$]acetone, accompanied by a significant lowering of the activation energies, was observed in the presence of a large excess of water. Thus intramolecular 1,3-proton transfer probably also involves the participation of water and is similar to the mechanism proposed for the decomposition of HOOOH. This hypothesis was further substantiated by the B3LYP/6-31++G*+ZPE calculations for the participation of water in the decomposition of CH_3OOOH, which revealed two stationary points on the potential energy surface corresponding to a CH_3OOOH–HOH complex and a six-membered cyclic transition state **TS2**. The energy barriers were comparable with those calculated for HOOOH, that is, $\Delta E^{\neq} = 15.0$ and 21.5 kcal mol^{-1} relative to isolated reactants and the CH_3OOOH–HOH complex, respectively.

Keywords: ab initio calculations • alkyl hydrotrioxides • density functional calculations • hydrogen trioxide • NMR spectroscopy

Introduction

In spite of considerable work carried out on the mechanism of the reaction of ozone with various saturated compounds, a number of fundamental questions still remained unanswered. Several mechanisms (see below) can be envisaged for the oxidation of the C–H bond to form the corresponding hydrotrioxide ROOOH, that is, the key intermediates in these reactions, but an unambiguous substantiation of these proposals is, unfortunately, still lacking.[1]

A concerted 1,3-dipolar insertion of ozone into the C–H bond to form ROOOH has been postulated.[2] A "radical" mechanism involving hydrogen atom abstraction by ozone to form the radical pair [R$^{\bullet}$ $^{\bullet}$OOOH] that collapses to ROOOH has also been suggested.[3] More recently it has been proposed that hydride ion transfer to form a carbenium ion and hydrotrioxide anion pair [R^{+} $^{-}$OOOH] is involved.[4]

In this work we report that the low-temperature ozonation of isopropyl alcohol and isopropyl mether ether yields, in addition to the hydrotrioxides of these compounds, hydrogen trioxide (HOOOH).[5] All the polyoxides were characterized

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unambiguously for the first time by ^{17}O NMR spectroscopy. A reinvestigation of the low-temperature ozonation of benzylic alcohols and ethers[6] by ^{17}O NMR spectroscopy also showed the presence of two polyoxide species among the primary reaction products, that is, the corresponding hydrotrioxide (ROOOH) and HOOOH. All these observations, together with the results of a theoretical density functional investigation of the ozonation of isopropyl alcohol, seem to support the "radical" mechanism for the formation of these polyoxides.

The first unambiguous ^{17}O NMR spectroscopic assignment of the hydrotrioxides (ROOOH) under investigation enabled a detailed study of the decomposition kinetics of these intermediates as well as hydrogen trioxide (HOOOH). A variety of pathways, ranging from predominantly radical ones for ROOOH (in the absence of water) to predominantly nonradical ("polar") contributions for the decomposition of HOOOH and ROOOH in the presence of water, were indicated.

Results and Discussion

NMR spectra: Ozonation of isopropyl alcohol (**1a**; 0.2–0.5 M) with ozone-oxygen or ozone-nitrogen mixtures in [D$_6$]acetone at −78 °C produced the corresponding hydrotrioxide, Me$_2$C(OH)(OOOH) (**2a**), characterized by the OOOH ^1H NMR absorption at $\delta = 12.85$ (δ CH$_3$ = 1.44) and ^{13}C NMR absorptions at $\delta = 25.7$ (CH$_3$) and 104.3 (C) downfield from TMS (−10 °C), in yields of 40–50%. It is interesting to note that the OOOH absorption was split into two components of approximately equal intensity ($\Delta\delta = 0.004$) at all temperatures investigated (−30 to +10 °C). A further OOOH absorption at $\delta = 13.02$, corresponding to another polyoxide species with exchangeable protons (as determined by a relatively fast exchange with CH$_3$OD or DOD at −60 °C), was observed in the ^1H NMR spectra. This absorption was assigned to hydrogen trioxide (HOOOH), on the basis of ^{17}O NMR spectra of polyoxides that were highly enriched with ^{17}O.[7] This assignment was confirmed by GIAO/MP2/6-311++G** calculations of ^{17}O NMR chemical shifts for HOOOH and the hydrotrioxide **2a**, as well as those for CH$_3$OOOH and CH$_3$OOH for purposes of comparison (Figures 1 and 2). The calculated ^{17}O NMR chemical shifts are in excellent agreement with the experimentally observed values (Table 1). In addition, the values for HOOOH were identical with those obtained from the NMR spectra of HOOOH, generated independently by the low-temperature ozonation of hydrazobenzene in various solvents.[7f] This procedure yields solutions of hydrogen trioxide without the interfering presence of other hydrotrioxides.[7f, 8]

Similar observations were also made by studying the low-temperature ozonation of isopropyl methyl ether (**1b**)[9] (0.2–0.5 M) in [D$_6$]acetone at −78 °C. The corresponding hydrotrioxide, Me$_2$C(OMe)(OOOH) (**2b**), characterized by the OOOH ^1H NMR absorption at $\delta = 13.026$ (δ CH$_3$ = 1.38; δ OCH$_3$ = 3.23) and ^{13}C NMR absorptions at $\delta = 23.1$ (CH$_3$), 49.4 (OCH$_3$), and 106.8 (C) (−10 °C), was formed in yields of 30–40%. Again, the presence of HOOOH in this reaction was confirmed by the characteristic OOOH absorption at $\delta = 13.035$ and by the ^{17}O NMR absorptions.

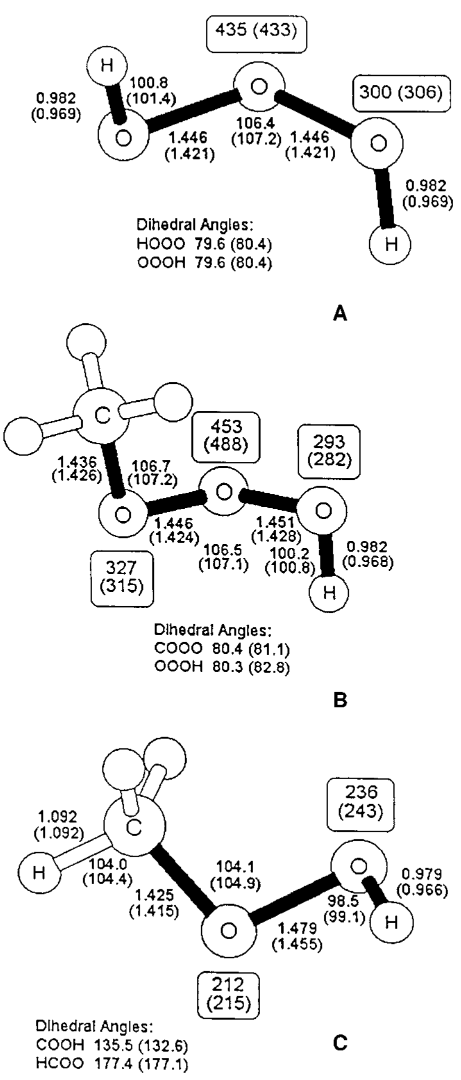


Figure 1. Optimized MP2/6-31++G* and MP2/6-311++G** (in parenthesis) structures (bond lengths in angstroms and angles in degrees) of hydrogen trioxide (**A**), methyl hydrotrioxide (**B**), and methyl hydroperoxide (**C**). The values in the frames are GIAO/MP2/6-31++G* and GIAO/MP2/6-311++G** (in parentheses) ^{17}O NMR chemical shifts downfield from H$_2$^{17}O.

The hydrotrioxide and HOOOH were also formed by the ozonation of **1a** and **1b** in solvents such as methyl acetate and *tert*-butyl methyl ether. In all these cases, a molar ratio ROOOH/HOOOH of approximately 1:0.5–0.7 was observed. Since the rate of decomposition of HOOOH was somewhat different from that of the hydrotrioxide (at least under conditions investigated), unambiguous ^1H and ^{17}O NMR spectroscopic characterization of both polyoxides was possible.

A ^{17}O NMR spectroscopic reinvestigation of the intermediates formed in the low-temperature ozonation of α-methylbenzyl alcohol and methyl α-methylbenzyl ether[6] (see the section on kinetics and Supporting Information) indicated that the two OOOH absorptions in their ^1H NMR spectra at about $\delta = 13$, which was originally interpreted by the existence of two distinct self-associated intermolecularly hydro-

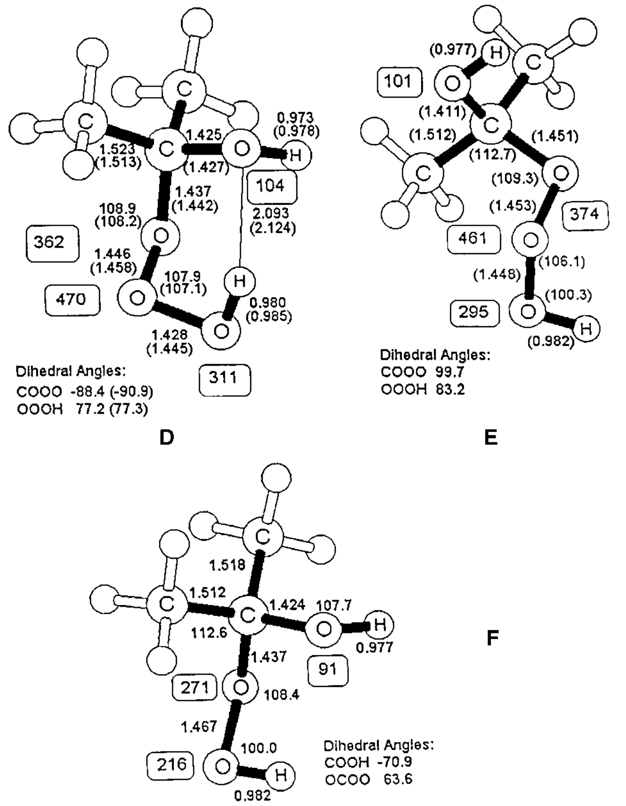


Figure 2. Optimized B3LYP/6-31G* and MP2/6-31++G* (in parenthesis) structures of the intramolecularly hydrogen-bonded form of the hydrotrioxide of **2a** (**D**), the most stable "open" form of **2a** (**E**), and the hydroperoxide of isopropyl alcohol (**F**; MP2/6-31++G*). The values in the frames are GIAO/MP2/6-31++G* ^{17}O NMR chemical shifts ($H_2{}^{17}O$).

Table 1. Experimental and GIAO/MP2/6-31++G** calculated ^{17}O NMR chemical shifts (δ)[b] of the hydrotrioxides of isopropyl alcohol (**2a**), isopropyl methyl ether (**2b**), and hydrogen trioxide (HOOOH) in [D$_6$]acetone at −10 °C.[a]

	δO_1	δO_2	δO_3
$(H_3C)_2C(OH)(O_1\text{-}O_2\text{-}O_3\text{-}H)$	368 (950)[c,d]	445 (2100)[c,d]	305 (350)[c,d]
$(H_3C)_2C(OH)(O_1\text{-}O_2\text{-}H)$	262 (1600)[d]	220 (1600)[d]	
$(H_3C)_2C(OCH_3)(O_1\text{-}O_2\text{-}O_3\text{-}H)$	347 (580)[c,d]	450 (1350)[c,d]	306 (330)[c,d]
$(H_3C)_2C(OCH_3)(O_1\text{-}O_2\text{-}H)$	237 (800)[d]	224 (800)[d]	
$H\text{-}O_1\text{-}O_2\text{-}O_3\text{-}H$	305 (350)[c,d]	421 (1450)[c,d]	305 (350)[c,d]
	306 (calcd)[b]	433 (calcd)[b]	306 (calcd)[b]
$H\text{-}O_1\text{-}O_2\text{-}H$	187 (320)[d]	187 (320)[d]	
	192 (calcd)[b]	192 (calcd)[b]	
$H\text{-}O_1\text{-}H$	307.9[e]		

[a] Values in parts per million downfield from the internal standard $H_2{}^{17}O$. [b] The calculated GIAO/MP2/6-311++G** absolute shielding for H_2O is 343.9 ppm. [c] Area ratio of peaks O_1:O_2:O_3 was 1:1:1 (2:1 for HOOOH). [d] Line widths of the resonances at half-height ($\Delta\nu_{1/2}$) ±5%. [e] Experimental value: H_2O (g), 344 ppm (R. E. Wasylishen, S. Mooibroek, J. B. Macdonald, *J. Chem. Phys.* **1984**, *81*, 1057).

gen-bonded hydrotrioxides, was actually due to the presence of two polyoxide species, that is, the corresponding hydrotrioxide and HOOOH in molar ratio 1:0.35. [Ph(Me)C(OH)-($O_1O_2O_3H$), ^1H NMR ([D$_6$]acetone, −10 °C, TMS): $\delta = 13.07$ (OOOH); ^{17}O NMR ([D$_6$]acetone, −10 °C, $H_2{}^{17}O$): $\delta = 367$ (O_1, $\nu_{1/2} = 2000$ Hz), 451 (O_2, $\nu_{1/2} = 2300$ Hz), 304 (O_3, $\nu_{1/2} = 490$ Hz). HOOOH, ^1H NMR ([D$_6$]acetone, −10 °C, TMS): $\delta = 13.13$ (OOOH); ^{17}O NMR ([D$_6$]acetone, −10 °C, $H_2{}^{17}O$): $\delta = 304$ (O_1, $\nu_{1/2} = 490$ Hz), 420 (O_2, $\nu_{1/2} = 1400$ Hz), 304 (O_3, $\nu_{1/2} = 490$ Hz)].

A study of the temperature and concentration dependence of the OOOH absorptions of the hydrotrioxides **2a** and **2b** (Figure 3, see also Supporting Information) revealed that these polyoxides most likely exist in solution, in accord with our previous proposal, as intramolecularly hydrogen-bonded forms which are in equilibrium with the intermolecularly hydrogen-bonded associates solvated with the oxygen base (B)[6] (Scheme 1). This was indicated by a small but definitive upfield shift of the OOOH absorption of **2a** in [D$_6$]acetone that was observed with increasing temperature and upon dilution of the hydrotrioxide, which corresponds to the

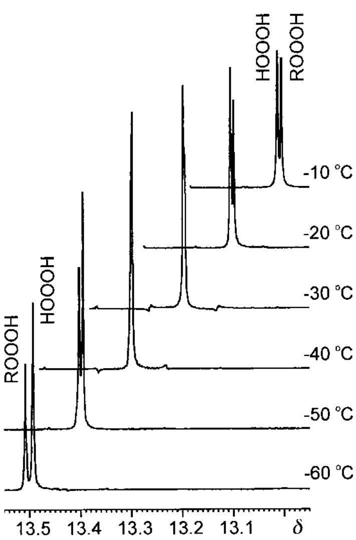
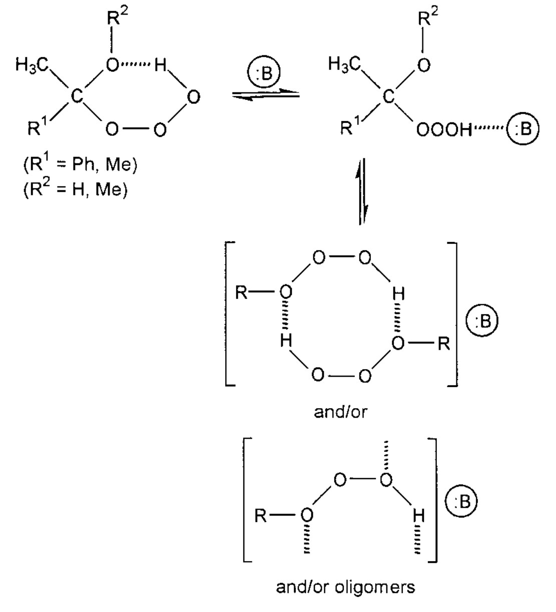


Figure 3. The temperature dependence of the OOOH ^1H NMR absorptions of the hydrotrioxide of **2a** and HOOOH, formed in the low-temperature ozonation of **1a** in [D$_6$]acetone.



Scheme 1. The equilibrium between the various forms of alkyl hydrotrioxides, solvated with oxygen base as solvent (:B).

appearance of larger hydrotrioxide clusters both at low temperatures and at higher hydrotrioxide concentrations. Similar observations were also made by examining the ^{1}H NMR spectrum of HOOOH, thus confirming our previous theoretical prediction[7d] that self-association (dimerization/oligomerization) is also a structural feature of this species.

We believe that the solvated forms of the hydrotrioxides are predominant in solution when oxygen bases are used as solvents (acetone, methyl acetate, *tert*-butyl methyl ether), since the calculated energy of intramolecular hydrogen bonding in the hydrotrioxide **2a**, that is, the energy difference from the hydrogen-bonded conformation **D** to the most stable "open" form **E** (Figure 2),[10a] was 2.1 kcal mol^{-1} (B3LYP/6-31G*) or 1.9 kcal mol^{-1} (MP2/6-31++G*).[10b] This is considerably lower than the expected total binding energies in the intermolecularly hydrogen-bonded systems, that is, ROOOH–B and cyclic dimeric and/or polymeric forms solvated with the oxygen base.[11] For example, the binding energy in the adduct $CH_3OOOH{-}O(CH_3)_2$ was calculated to be 8.2 kcal mol^{-1} at the B3LYP/6-31++G* level (see Supporting Information).

Interchange between all these forms, which contributes to narrow time-averaged features, must be fast since no exchange broadening of the OOOH absorption was observed even at the lowest temperatures investigated (−100 °C, dimethyl ether). The observed OOOH chemical shifts thus reflect both the hydrogen-bond strength and extent in these entities.

The spectrum of each of the alkyl hydrotrioxide investigated showed three well-resolved absorptions for magnetically non-equivalent oxygens with the area ratio of peaks approximately 1:1:1. As expected, a significant deshielding of the $\delta^{17}O$ chemical shifts was observed in going from peroxides ROOH and HOOH to the corresponding alkyl hydrotrioxides ROOOH and HOOOH.[12]

In view of the fact that ^{17}O chemical shifts are more sensitive to solvent effects than $^{14}N/^{15}N$ or ^{13}C shifts[13], it was surprising to observe an excellent agreement of the calculated chemical shifts with the experimentally obtained values for HOOOH and HOOH. Changes of ^{17}O NMR chemical shifts due to changes in conformation of the hydrotrioxide **2a** were clearly evident from calculations of the chemical shifts for the intramolecularly hydrogen-bonded form **D** and the most stable "open" form of **E** (Figure 2).

When the C–D deuterated form of the alcohol **1a** was ozonized in [D$_6$]acetone (in the presence of small amounts of water that are always to be found in the system), the resulting solutions contained the hydrotrioxide in the deuterated as well as non-deuterated form (OOOD/OOOH) in an approximate ratio 30:70 (the ratio is dependent on the amount of HOH present and is apparently crucial in the exchange mechanism), as determined by $^{1}H/^{2}H$ NMR spectroscopy. This observation additionally seems to support the proposal that dimeric/oligomeric cyclic and/or acyclic aggregates are present in solutions of **2a**. Furthermore, it has been recently reported that entropic effects considerably reduce the preference of D versus H bonds when these atoms occupy bridging as opposed to terminal positions.[14]

The mechanism for the formation of the hydrotrioxides and hydrogen trioxide (HOOOH): To gain mechanistic insight into the first step of the reaction, that is, the formation of ROOOH and HOOOH, ab initio density functional calculations at the B3LYP/6-31G* + ZPE level were used to fully optimize the stationary points on the singlet potential energy surface of the title reaction.[5, 15] Some stationary points were also recalculated at the MP2/6-31G* level.

In going from the reactants to the product ROOOH, two stationary points were calculated that were found to be an intermediate complex (**G**) of the van der Waals type and a transition state **TS1** (Figure 4). The intermediate complex **G** was found to be held together by a stabilization energy of 3.1 kcal mol^{-1} (4.3 kcal mol^{-1} at the MP2/6-31G* + ZPE level[16]). The transition state **TS1** was calculated to be 7.4 kcal mol^{-1} less stable than the isolated reactants and 10.6 kcal mol^{-1} less stable than **G**. A highly asymmetric transition state with considerable O–H bond formation and no C–O bond formation was indicated. The activation parameters, that is, $\Delta H^{\neq} = 9.6$ kcal mol^{-1} and $\Delta S^{\neq} = -13.1$ cal mol^{-1} K^{-1}, are in excellent agreement with those reported for the ozonation of diisopropyl ether in CCl_4 ($E_a = 10.0$ kcal mol^{-1}, $\log A = 7.9$).[17]

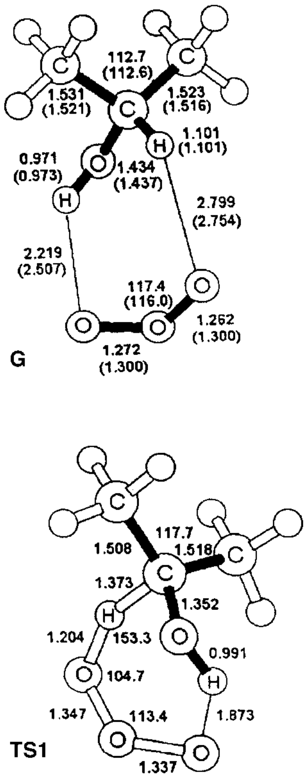


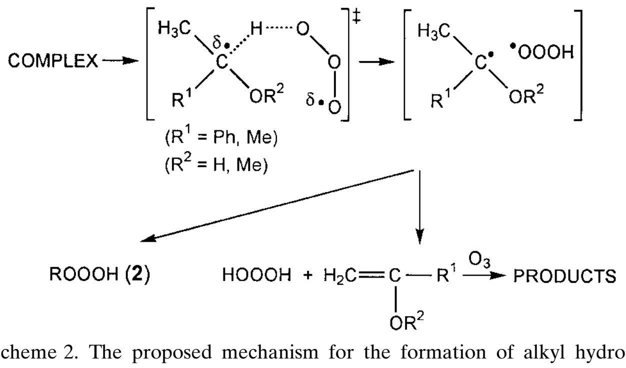
Figure 4. Optimized B3LYP/6-31G* structures of the isopropyl alcohol-ozone complex **G** (MP2/6-31G* values in parenthesis), and the transition state **TS1** for the ozonation of **1a**.

Overall the ozonation of **1a** to form the intramolecularly hydrogen-bonded ROOOH (**2a**) is exothermic by 55.8 kcal mol^{-1}, while the adduct 2-hydroxypropene-HOOOH lies 33.3 kcal mol^{-1} below the energy of the isolated reactants. The energies of the radical and ion pair at infinite separation are 3.3 and 127.3 kcal mol^{-1}, respectively, above the energy of the isolated reactants.[5]

It is evident that the calculated **TS1** cannot accommodate the formation of HOOOH in terms of a concerted 1,3-dipolar insertion mechanism. However, the geometry of **TS1** resembles that of the forming HOOO radical[18, 19] much more than that of the "hydrotrioxide anion".[20] Furthermore, a detailed theoretical investigation of the latter species at various levels of sophistication revealed an extraordinarily long HO–OO "bond", which indicates a non-covalent interaction between HO anion and O_2.[21, 22] It is interesting to note, that similar observation was also made in the case of the "CH_3OOO anion". Therefore, it appears unlikely that such an entity could survive as a discrete molecule ($HOOO^-$) in solutions of organic solvents containing water.[23]

The mechanism of the ozonation of the C–H bond therefore most likely involves the formation of the radical pair at a sufficiently large separation after the transition state of the rate-determining step, and thus allows both the collapse with less than unit efficiency of the pair to ROOOH and the abstraction of the hydrogen atom from the 2-hydroxy-2-propyl radical with the subsequent formation of the enol, that is, 2-hydroxypropene and HOOOH.[24] It should be pointed out that ozonation of $(CD_3)_2CH(OH)$ yielded the deuterated hydrogen trioxide, HOOOD ($^1H/^2H$ NMR spectroscopy) in acetone.

The activation energy for the recombination of the radicals in the cage to form ROOOH is most probably very low or zero. At the same time, the BDEs (bond dissociation energies) of the C–H bonds adjacent to the radical center in 2-hydroxy-2-propyl radical are expected to be even lower than those of the C–H bonds adjacent to the radical centers derived from the saturated hydrocarbons (33.5 ± 3 kcal mol^{-1}).[25] Therefore, hydrogen atom abstraction from the beta position of the 2-hydroxy-2-propyl radical by HOOO radicals is most probably fast enough (an exothermic process by ≥56 kcal mol^{-1}) to compete with diffusion out of the solvent cage (Scheme 2).



Scheme 2. The proposed mechanism for the formation of alkyl hydrotrioxides and hydrogen trioxide (HOOOH) in the ozonation of alcohols and ethers.

It is well known that radicals are much less solvated than their corresponding anions. However, MP2/6-31++G* calculations of the solvation of the HOOO radical with dimethyl ether as a model aprotic oxygen base revealed a binding energy (BE) of 10.0 kcal mol^{-1} between both components (Figure 5). For comparison, a somewhat higher BE of 12.1 kcal mol^{-1} between the HOO radical and dimethyl ether was calculated (HO radical, BE = 8.9 kcal mol^{-1}; see Supporting Information). This observation seems to support the hypothesis that the solvated HOOO radical might survive for a brief period of time even after diffusion from the cage. This is also consistent with the standard enthalpy of formation, ($\Delta_f H^\circ_{298}$), of the HOOO radical of -1 ± 5 kcal mol^{-1} measured recently by the FTICR-MS technique; this implies that this species is a relatively stable intermediate, which should be observable even at room temperature.[7i, 26, 27]

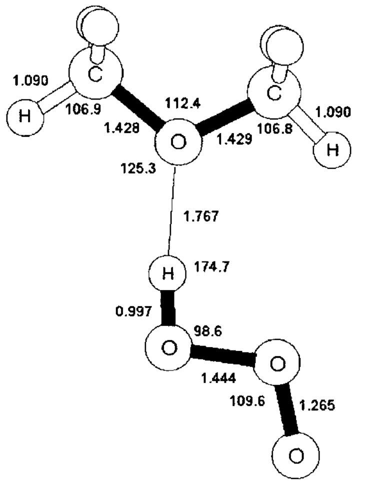


Figure 5. The optimized MP2/6-31++G* structure of the dimethyl ether-hydrotrioxyl radical complex ($E = -380.00058$ au). All the labeled atoms are coplanar [$(CH_3)_2O$, -154.51535 au, $d(C-O) = 1.420$ Å, $\sphericalangle$ OCO = 111.3°; $HOOO^{\bullet}$, -225.46932 au, $d(H-O) = 0.988$ Å, $d(O_1-O_2) = 1.443$ Å, $d(O_2-O_3) = 1.262$ Å, $\sphericalangle$ H-O_1-O_2 = 99.8°, $\sphericalangle$ O_1-O_2-O_3 = 111.5°, $\sphericalangle$ H-O_1-O_2-O_3 = 0°).

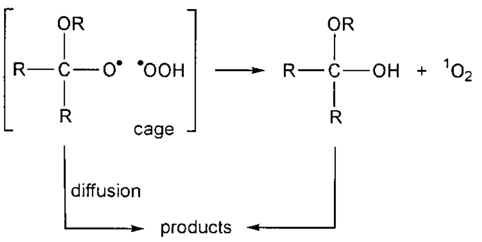
The origin of the experimentally observed rate acceleration of the formation of ROOOH and HOOOH in polar aprotic ("basic") solvents, could be attributed to the enhanced polarization of **TS1** relative to the reactants. We believe that hydrogen bonding between the forming OOOH radical and the OH group plays a crucial role in the increased reactivity of the alcohol compared with that of simple hydrocarbons. The additional stabilization of **TS1** by the complexation of the OOOH with oxygen base, as discussed above (Figure 5), might also be important, particularly in the ozonation of saturated systems without an OH group, that is, the hydrogen-bond donor.

Mechanisms for the decomposition of the hydrotrioxides (ROOOH) and hydrogen trioxide (HOOOH): A detailed investigation of the products in the decomposition mixture, after warming the ozonized solutions of **1a** in *tert*-butyl methyl ether, by GC/MS and NMR spectroscopy indicated the presence of acetone (37 ± 5 %), peroxyacetic acid (11 ± 2 %), acetic acid (39 ± 5 %), formic acid (7 ± 2 %), hydrogen peroxide (11 ± 3 %), water, isopropoxymethanol ($H_2C(OH)OCH(CH_3)_2$) (5 ± 1 %), and oxygen (Σ^3O_2/Δ^1O_2). It should be noted that peroxyacetic acid, formic acid, and isopropoxymethanol were already present in the ozonized solutions of **1a**

at −78 °C, and that their concentrations did not change significantly during the decomposition of **2a**/HOOOH.[28] Product analysis of the decomposition mixture after warming the ozonized solutions of **1b** in [D$_6$]acetone revealed acetone (32 ± 5%), methyl acetate (23 ± 4%), methanol (29 ± 5%), formic acid (8 ± 2%), 2-hydroperoxy-2-methoxypropane (3 ± 1%), hydrogen peroxide (5 ± 1%), water, and oxygen (Σ^3O_2/Δ^1O_2). Methyl acetate and formic acid were already present in the ozonized solutions of **1b** at −78 °C, and, once again, their concentrations did not change significantly during the decomposition of **2b**/HOOOH.

Kinetic studies: The kinetics of decomposition of **2a** and **2b** were measured by following the decay of the OOOH, CH$_3$, and OH/OCH$_3$ absorptions, and in all cases they were found to obey cleanly first-order kinetics over at least 3–4 half-lives in all solvents investigated. All absorptions disappeared at practically the same rate. Selected kinetic and activation parameters for the decomposition of **2a** and **2b**, as well as HOOOH, in [D$_6$]acetone, methyl acetate, and *tert*-butyl methyl ether are collected in Table 2 (for complete kinetic data, see Supporting Information).

The activation parameters for the decomposition of the hydrotrioxides **2a** and **2b** ($E_a = 23.5 \pm 1.5$ kcal mol^{-1}, $\log A = 16 \pm 1.8$) are typical of homolytic processes. The splitting of ROOOH into a radical pair, RO$^•$ and $^•$OOH, is the lowest energy path available. The BDE for the RO–OOH bond in the alcohol hydrotrioxide **2a** was calculated to be 25.2 kcal mol^{-1} at the B3LYP/6-31G* level. Subsequent abstraction of the hydrogen atom in the cage leads to the corresponding tetrahedral intermediate[29] and singlet oxygen (Δ^1O_2), as previously suggested by Benson[4a] (Scheme 3). The radicals may also diffuse out of the cage to abstract hydrogen or cleave exothermically to form other products. The addition of a radical inhibitor, that is, 2,6-di-*tert*-butyl-4-methylphenol, has a relatively small effect on the rates and the activation parameters for the decomposition of the hydrotrioxides **2a** and **2b** and, therefore, appears to favor the "in cage" reaction pathway.[30] This is in contrast with the observation that alkoxyl radicals participate significantly in the induced decomposition of cumyl hydrotrioxide in [D$_6$]acetone.[31]



Scheme 3. Radical decomposition of the alkyl hydrotrioxides.

As evident from Table 2, HOOOH decomposes somewhat faster than hydrotrioxide **2a** under the conditions investigated. The significantly lower E_a (16.5 ± 2.2 kcal mol^{-1}) and $\log A$ (9.5 ± 2.0) values, compared with the expected values for the homolytic scission of the HO–OOH bond [BDE = 29.8 kcal mol^{-1}, CCSD(T)/6-311++G**;[32] 31.8 kcal mol^{-1}, CBS-QCI/APNO; 34.8 kcal mol^{-1},[18e] G2M(RCC,MP2); 31.6 kcal mol^{-1},[18d] Q6311(T)//QCISD/6-31G**; 33.9 kcal mol^{-1}, G2(MP2)] are in accord with our previous proposal that water behaves as a bifunctional catalyst and thus participates in a "polar" (non-radical) decomposition process of HOOOH.[7g,k] Thus, the calculated energy barriers for a water-catalyzed decomposition of this polyoxide are in good agreement with the experimentally observed values.[5,7f,g,k] It should be noted, however, that sufficient water was present after the ozonation of alcohol **1a** and ether **1b** in all the solvents investigated (−78 °C) to complex, at least theoretically, all the HOOOH

Table 2. Kinetic and activation parameters for the decomposition of the hydrotrioxides of isopropyl alcohol (**2a**), isopropyl methyl ether (**2b**), and hydrogen trioxide (HOOOH) formed in the low-temperature ozonation of isopropyl alcohol (**1a**), and isopropyl methyl ether (**1b**) in various solvents.[a]

			ROOOH						HOOOH			
	Solvent	T [°C]	δ ROOOH	δ CH$_3$	$k \times 10^4$ [s^{-1}] OOOH[b]	$k \times 10^4$ [s^{-1}] CH$_3$[c]	E_a [kcal mol^{-1}]	$\log A$	δ	$k \times 10^4$ [s^{-1}]	E_a [kcal mol^{-1}]	$\log A$
2a	*tert*-butyl	−10	12.663	1.45	1.2		25.3[b]	17.3[b]	12.653	5.6	16.7	10.5
	methyl ether	−5	12.648		(2.0)[d]		(25.8)[b,d]	(17.4)[b,d]				
	methyl acetate	−10	12.57	1.41	1.8	1.7	21.3[b]	14.1[b]	12.66	13.6	17.2	11.5
							21.6[c]	14.3[c]				
	[D$_6$]acetone	−10	12.85		1.3	1.4	24.2[b]	16.2[b]	13.04	1.6	18.8	11.9
			(12.86)[d]		(0.68)[d]		(26.2)[b,d]	(17.6)[b,d]	(13.05)[d]	(0.8)[d]	(21.7)[d]	(14.0)[d]
							23.8[c]	15.9[c]				
2b	*tert*-butyl	−10	12.673	1.39	4.0		24.6[b]	17.1[b]	12.597	0.33	16.8	9.5
	methyl ether		(12.695)[d]		(4.2)[d]		(25.5)[b,d]	(17.9)[b,d]	(12.610)[d]	(0.30)[d]	(17.0)[d]	(9.4)[d]
	neat	−10	12.734	1.36	6.4		22.9[b]	15.9[b]	12.572	1.26	16.0	9.5
			(12.636)[d]		(6.0)[d]		(23.3)[b,d]	(16.2)[b,d]	(12.524)[d]	(1.1)[d]	(15.5)[d]	(9.0)[d]
	methyl acetate	−10	12.419	1.38	2.9	1.9	25.0[b]	17.4[b]				
			(12.421)[d]		(3.5)[d]		(23.6)[b,d]	(16.2)[b,d]				
		0					24.4[c]	16.7[c]	12.408	1.9	13.8	7.3
									(12.388)[d]	(0.78)[d]	(14.0)[d]	(7.2)[d]
	[D$_6$]acetone	−10	13.026		4.0	5.0	22.8[b]	15.7[b]				
			(13.018)[d]		(5.0)[d]		(23.4)[b,d]	(16.2)[b,d]				
		−5					22.4[c]	15.4[c]	12.984	1.0	16.4	9.4
									(12.986)[d]	(1.0)[d]	(19.3)[d]	(11.9)[d]

[a] Temperature range (−30 °C to +20 °C). c(ROOOH) = 0.005–0.1 M. Standard deviations ±10%. [b] By following the decay of the ROOOH absorption. [c] By following the decay of the CH$_3$ absorption of the hydrotrioxide (ROOOH). [d] Runs in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BMP) (molar ratio, BMP/hydrotrioxide = 5:1).

present. The somewhat smaller rates and higher activation energies for the decomposition of HOOOH in *tert*-butyl methyl ether (B see Scheme 1; of comparable concentrations), compared to the values in other solvents, may reflect the lower solubility of water in this solvent and/or the formation of complexes of the type B ⋯ HOOOH ⋯ B, which presumably diminish the catalytic effect of water. A relatively strong complexation, that is, $BE = 16.5\,kcal\,mol^{-1}$, of HOOOH with dimethyl ether (B) as a model oxygen base, was calculated by using B3LYP/6-31++G* (see Supporting Information). In such cases, homolytic contributions to the decomposition pathways for HOOOH, particularly at higher temperatures, cannot be completely excluded.

Since water plays such a crucial role in the decomposition of HOOOH, we also decided to study the effect of water on the rate of the decomposition of the hydrotrioxide **2a**.[33] It is evident from Figure 6 (see also Supporting Information) that the presence of a relatively large excess of water in ozonized solutions of **1a** in [D$_6$]acetone has a relatively small effect on the rate of the decomposition of HOOOH. This is in accord with the above postulate that almost all the HOOOH was already complexed with water prior to the addition of more water.[34] In addition, somewhat smaller activation energies were obtained (after repeated measurements) in comparison with the values obtained for the samples without added water. On the other hand, a relatively large acceleration of the decomposition of the hydrotrioxide **2a** accompanied by a significant lowering of the activation energies (Figure 7) was observed in the presence of a large excess of water. In this case, the observed rates (and activation parameters) most probably reflect the fact that the decomposition is proceeding by several simultaneous first-order processes, which presumably involve both radical and non-radical pathways. Among the latter, water assisted decomposition, similar to that already proposed for the decomposition of HOOOH (Scheme 4), appears to be important. This type of decomposition of ROOOH seems to be more general, since faster decomposition with lower activation parameters were also observed for the decomposition of **2a** in the presence of a relatively large excess of methanol (see Supporting Information).

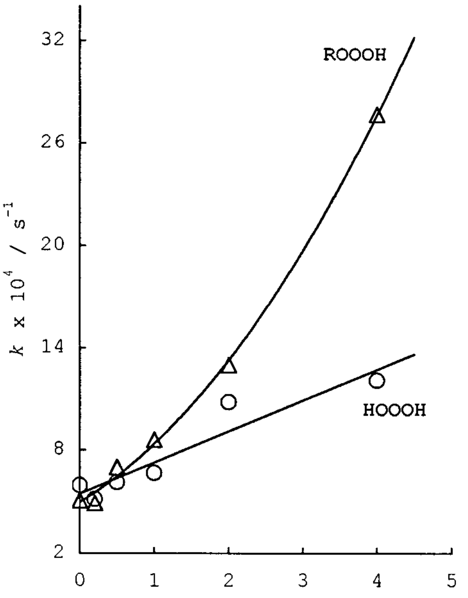


Figure 6. The dependence of the rate-constants for the decomposition of the hydrotrioxide of **2a** (ROOOH) and HOOOH on the amount of added water in [D$_6$]acetone at 0 °C.

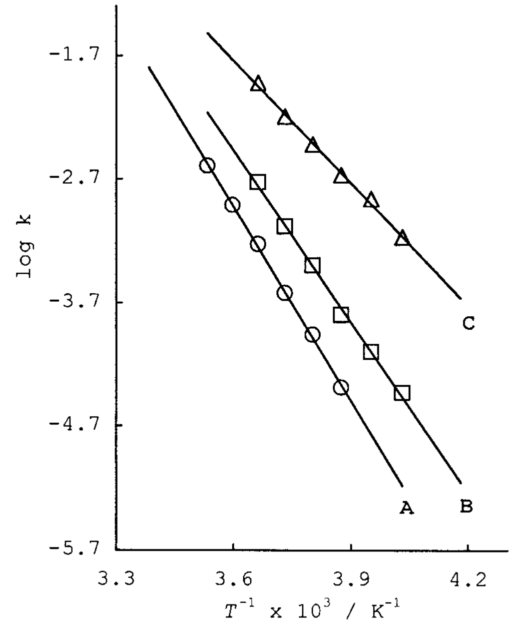
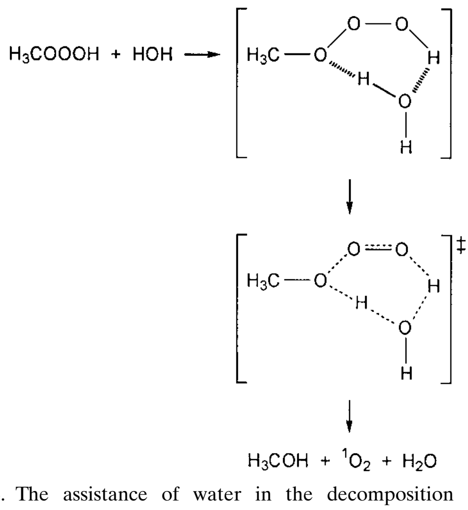


Figure 7. Arrhenius plots for the decomposition of the hydrotrioxide of **2a** in [D$_6$]acetone with various amounts of water added. A) Without added water ($E_a = 23.8\,kcal\,mol^{-1}$, $\log A = 15.9$); B) 2.8 vol.% of water ($E_a = 21.0\,kcal\,mol^{-1}$, $\log A = 14.2$); C) 25 vol.% of water ($E_a = 15.1\,kcal\,mol^{-1}$, $\log A = 10.2$).



Scheme 4. The assistance of water in the decomposition of methyl hydrotrioxide.

A further experimental observation deserves a mention. A systematic study of the effect of concentration on the rate of the decomposition of **2a** and HOOOH revealed (see Figure 8, and Supporting Information) that the rate of decomposition of hydrotrioxide **2a** was slightly dependent on its concentration, whilst considerably increased rates of decomposition

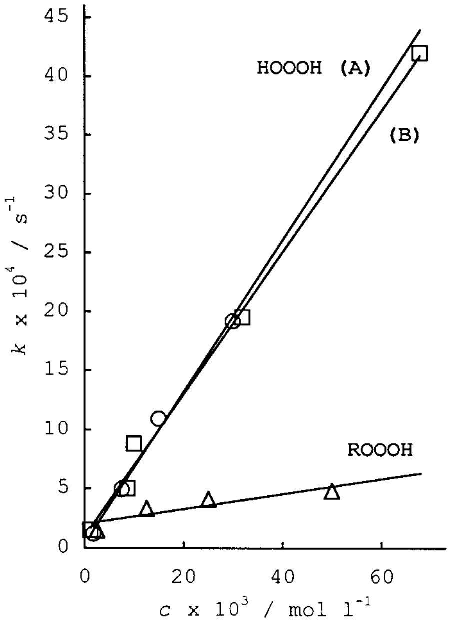


Figure 8. The concentration dependence of the rate constants for the decomposition of the hydrotrioxide of **2a** (ROOOH) and HOOOH (A) formed in the low-temperature ozonation of **1a**, and HOOOH (B) generated by the low-temperature ozonation of hydrazobenzene in methyl acetate at 0 °C.

were observed at higher HOOOH concentrations. The observed "pseudo first-order" rate constants therefore most probably reflect the participation of increasingly more complex aggregates, that is, dimeric and/or oligomeric (polimeric) clusters of HOOOH, complexed with water (and presumably also with "basic" solvent), in the decomposition of this polyoxide as its concentration progressively increases.

In order to test the hypothesis depicted in Scheme 4, we performed B3LYP/6-31++G*+ZPE calculations for the participation of water in the intramolecular 1,3-proton transfer in methyl hydrotrioxide (CH_3OOOH) as a model compound. As in the case of HOOOH,[7g] two stationary points were calculated, that is, a $CH_3OOOH{-}HOH$ complex (**H**) and a six-membered cyclic transition state **TS2** (Figure 9). The calculated energy barriers were comparable with those found in the case of HOOOH,[7g,k] that is, $\Delta E^{\neq} = 15.0$ and 21.5 kcal mol^{-1}, relative to isolated reactants and $CH_3OOOH{-}HOH$ complex, respectively (Table 3). Again, water was found to act as a bifunctional catalyst in this reaction by accepting H from CH_3OOOH to a greater extent rather than transferring its own H to the hydrotrioxide and thus causing considerable polarization of the $CH_3O{-}OOH$ bond. The Mulliken population analysis showed that the migrating hydrogen behaves as a proton in this reaction. The calculated energy barrier for the 1,3-proton transfer in the heterolytic fragmentation of CH_3OOOH was in good agreement with our experimental results and considerably lower than the values calculated for the homolytic cleavage of the $CH_3O{-}OOH$ bond (for example, BDE = 31 kcal mol^{-1}[18e]).

Although water, as well as alcohols (and silanols), play an important role in the decomposition of silyl hydrotrioxides ($R_3SiOOOH$) to form the corresponding silanols and/or disiloxanes and HOOOH,[7d] no such processes with the formation of hydrogen trioxide could be detected in the decomposition of hydrotrioxides **2a** and **2b**. Neither was the hydrotrioxide **2a** formed in the reaction of HOOOH with acetone. However, analogous reactions, for example, the decomposition of the hydroxy-hydroperoxide $Me_2C(OH)(OOH)$ into acetone and HOOH (shown by ^1H and ^{17}O NMR spectroscopy to be assisted by the presence of water), which is an important step in the Shell process for the production of HOOH,[35a] and the reverse reaction,[35b] are well known in the peroxide chemistry.

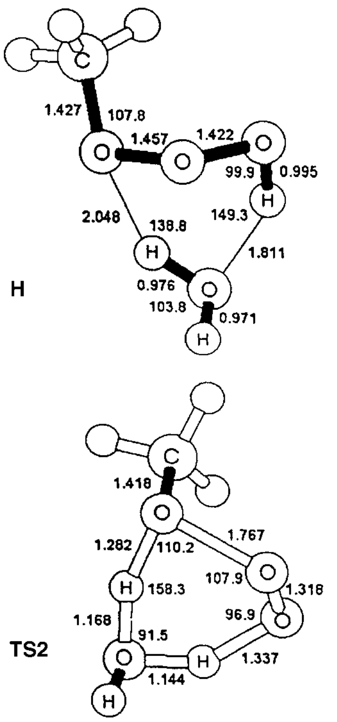


Figure 9. Optimized B3LYP/6-31++G* structures of the methyl hydrotrioxide/water complex **H** and the transition state **TS2** for the reaction $CH_3OOOH + HOH \rightarrow CH_3OH + {}^1O_2 + HOH$.

Table 3. Energies [au] of reactants, complex (**H**), transition structure (**TS2**), and products for the intramolecular proton transfer in the methyl hydrotrioxide/water system at the B3LYP/6-31++G*+ZPE level of theory.[a,b]

	B3LYP/6-31++G*	B3LYP/6-31++G*+ZPE
$CH_3OOOH + HOH$	−342.430051 (0.0)	−342.350606 (0.0)
$CH_3OOOH{-}HOH$ (**H**)	−342.444883 (−9.3)	−342.361226 (−6.5)
TS2	−342.404706 (15.9)	−342.326603 (15.0)
$CH_3OH + {}^1O_2 + HOH$	−342.414033 (10.0)	−342.337985 (7.9)

[a] Relative energies [kcal mol^{-1}] are given in parentheses. [b] B3LYP/6-31++G*+ZPE: HOH, $E = -76.401603$ au; CH_3OOOH, $E = -265.949003$ au; $^1O_2$, $E = -150.262339$ au; CH_3OH, $E = -115.674043$ au.

Experimental Section

Instrumentation: Low-temperature ^1H, ^2H, ^{13}C, and ^{17}O NMR spectra were recorded on a Bruker Avance 300 DPX (^1H NMR, 300.13 MHz; ^2H NMR, 46.07 MHz; ^{13}C NMR, 75.48 MHz; ^{17}O NMR, 40.70 MHz) and on Varian Unity Inova-600 spectrometers (^1H NMR, 600.09 MHz; ^{17}O NMR, 81.37 MHz) with TMS (^1H and ^{13}C NMR), [D$_6$]acetone (^2H NMR), and

$H_2{}^{17}O$ (^{17}O NMR) as internal standards. GC/MS was performed on a Hewlett Packard 6890 chromatograph (HP-5MS column).

Materials: All solvents were the purest commercially available products and were (except for [D_6]acetone) rigorously dried and distilled according to the literature methods. The purity was checked by GC/MS. Isopropyl alcohol and its deuterated forms (99%, Aldrich) were used as received, while isopropyl methyl ether was prepared by reduction of 2,2-dimethoxypropane with lithium aluminium hydride/aluminium chloride by the literature procedure.[36] An authentic sample of isopropoxymethanol was prepared by bubbling gaseous HCHO into isopropyl alcohol.[37] All these compounds were checked by NMR and GC/MS and were found to be >99% pure.

2-Hydroperoxy-2-hydroxypropane (3a): Compound **3a** was synthesized by the ozonolysis of 2,3-dimethyl-2-butene (99+%, Aldrich) in *tert*-butyl methyl ether saturated with water at $-40\,^{\circ}C$. This hydroperoxide is unstable at room temperature and decomposes to hydrogen peroxide and acetone. ^1H NMR (300 MHz, *tert*-butyl methyl ether, $-10\,^{\circ}C$, TMS): $\delta =$ 10.0 (s, 1H; OOH), 5.0 (s, 1H; OH), 1.33 (s, 6H; CH_3); ^{13}C NMR (75.5 MHz, *tert*-butyl methyl ether, $-10\,^{\circ}C$, TMS): $\delta = 101.3$ (C), 25.4 (CH_3).

2-Hydroperoxy-2-methoxypropane (3b): Compound **3b** was synthesized by the ozonolysis of 2,3-dimethyl-2-butene in methanol at $-60\,^{\circ}C$ by the literature procedure.[38] Samples with ^{17}O labels were prepared with ^{17}O-enriched ozone. ^1H NMR (300 MHz, [D_6]acetone, $25\,^{\circ}C$, TMS): $\delta = 10.1$ (s, 1H; OOH), 3.20 (s, 3H; OCH_3), 1.30 (s, 6H; CH_3); ^{13}C NMR (75.5 MHz, [D_6]acetone, $25\,^{\circ}C$, TMS): $\delta = 104.9$ (C), 48.9 (OCH_3), 22.7 (CH_3).

Ozonation procedure: Ozone-oxygen mixtures were produced by the passage of oxygen through a Welsbach T-816 ozonator. Ozone-nitrogen mixtures were obtained as already reported. The concentration of ozone in the gas stream was measured by the literature procedure. The generation of ^{17}O-enriched ozone was accomplished by the passage of ^{17}O-enriched oxygen (58% $^{17}O_2$, ISOTEC) through a semimicro ozonator.[39] The efficiency of ozone generation was considerably increased by pumping unreacted ^{17}O-enriched oxygen back to the ozonator (Cole-Parmer Masterflex L/S variable-speed tubing pump).

Product analysis: Decomposition products of **2a** and **2b** were determined by a combination of techniques. All products, except hydrogen peroxide, were determined by GC/MS with calibrated internal standards and known reference materials. All products were also collected and identified by NMR spectroscopy. Hydrogen peroxide was determined by ^1H NMR and ^{17}O NMR spectroscopy, and by other analytical methods already described previously.[6]

Kinetic studies: Kinetic measurements for the decomposition of the hydrotrioxides and HOOOH were made by monitoring the decay of the OOOH, CH_3, and OH/OCH_3 (for ROOOH) absorptions by ^1H NMR spectroscopy, with TMS as internal standard. Kinetic and activation parameters were obtained by standard procedures.

Methods of calculation: Various levels of theory were employed. GIAO/MP2/6-31++G* and GIAO/MP2/6-311++G** ^{17}O NMR chemical shifts were calculated by using ACES II package of programs.[40] Ab initio density functional calculations were performed using the B3LYP hybrid functional[41] as implemented in GAUSSIAN98 with various Pople's basis sets to fully optimize the molecules and transition states under investigation.[42, 43] The nature of each critical point was characterized by computing the harmonic vibrational frequencies. Zero-point energy (ZPE) corrections, calculated without scaling of the harmonic frequencies, were used to calculate the activation parameters. MP2 and MP4 perturbation theory, and CCSD(T)[45, 46] theory were also used for the geometry optimization of some molecular entities.

Acknowledgements

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[8] Low-temperature ozonation of hydrazobenzene in [D_6]acetone produced azobenzene (35 ± 5%), azoxybenzene (19 ± 3%), HOOOH (27 ± 4%), and hydrogen peroxide (19 ± 3%). Hydrogen trioxide, generated in this way, decomposed in the temperature range -20 to $+20\,^{\circ}C$ to produce oxygen (Σ^3O_2/Δ^1O_2) and water.

[9] Murray et al. have already studied the low-temperature ozonation of isopropyl methyl ether (neat). However, due to the state of the art of the NMR equipment at that time, and/or too high a concentration of the polyoxides formed in the reaction, they were unable to observe two OOOH absorptions in the ^1H NMR spectra of the ozonized solutions of **1b**. (F. E. Stary, D. E. Emge, R. W. Murray, *J. Am. Chem. Soc.* **1976**, *98*, 1880.)

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[19] HOOO$^\bullet$: B3LYP/6-31G*, $d(\mathrm{H{-}O_1}) = 0.981$ Å, $d(\mathrm{O_1{-}O_2}) = 1.503$ Å, $d(\mathrm{O_2{-}O_3}) = 1.262$ Å, $\sphericalangle$ H-O$_1$-O$_2$ = 98.8°, $\sphericalangle$ O$_1$-O$_2$-O$_3$ = 112.2°, $\sphericalangle$ H-O-O-O = 0°, $E = -226.05297$ au. For comparison, CCSD(T)/6-311++G**: (*cis*) $d(\mathrm{H{-}O_1}) = 0.974$ Å, $d(\mathrm{O_1{-}O_2}) = 1.497$ Å, $d(\mathrm{O_2{-}O_3}) = 1.261$ Å, $\sphericalangle$ H-O$_1$-O$_2$ = 99.2°, $\sphericalangle$ O$_1$-O$_2$-O$_3$ = 111.8°, $\sphericalangle$ H-O-O-O = −9.9°, $E = -225.63311$ au; (*trans*) $d(\mathrm{H{-}O_1}) = 0.970$ Å, $d(\mathrm{O_1{-}O_2}) = 1.535$ Å, $d(\mathrm{O_2{-}O_3}) = 1.244$ Å, $\sphericalangle$ H-O$_1$-O$_2$ = 109.6°, $\sphericalangle$ H-O-O-O = 180°, $E = -225.63351$ au. For a complete list of B3LYP, MP, and CCSD(T) calculations (various basis sets) on HOOO$^\bullet$, see Supporting Information.

[20] It is also indicative that the geometry of **TS1** resembles that of the forming 2-hydroxy-2-propyl radical ($d(\mathrm{C{-}O}) = 1.385$ Å) more than that of 2-hydroxy-2-propyl cation (1.281 Å) (see Supporting Information).

[21] For previous calculations on HOOO$^-$, see: a) K. B. Mathisen, O. Gropen, P. N. Skancke, U. Wahlgren, *Acta Chem. Scand. A*, **1983**, *37*, 817; b) see ref. [7g].

[22] HOOO$^-$: B3LYP/6-31G* (CCSD(T)/6-311++G**): $d(\mathrm{H{-}O_1}) = 0.972$ Å (0.966), $d(\mathrm{O_1{-}O_2}) = 1.734$ Å (1.882), $d(\mathrm{O_2{-}O_3}) = 1.336$ Å (1.315), $\sphericalangle$ H-O$_1$-O$_2$ = 87.6° (85.1), $\sphericalangle$ O$_1$-O$_2$-O$_3$ = 108.5° (110.1), $\sphericalangle$ H-O-O-O = 0° (−43.7), $E = -226.05817$ au (−225.68255). It is interesting to note that there is practically no difference in the endothermicity for the decomposition of HOOO$^-$ into HO$^-$ and Δ^1O$_2$ ($\Delta E = 25.0$ kcal mol^{-1}) and the decomposition into HO$^\bullet$ and superoxide anion O$_2^{\,-}$ ($\Delta E = 25.1$ kcal mol^{-1}) at the CCSD(T)/6-311++G** level of theory (HO$^-$, $E = -75.64605$ au; HO$^\bullet$, $E = -75.59647$ au; O$_2^{\,-}$, $d(\mathrm{O{-}O}) = 1.354$ Å, $E = -150.04603$au; Δ^1O$_2$, $d(\mathrm{O{-}O}) = 1.224$ Å, $E = -149.99662$ au). For a complete list of B3LYP, MP, and CCSD(T) calculations (various basis sets) on HOOO$^-$ and CCSD(T)/6-31++G* calculations on CH$_3$OOO$^-$, see Supporting Information.

[23] It is interesting to note that this non-covalently bound aggregate forms a 1:1 hydrogen-bonded adduct with water (HOOO$^-$–HOH) with the binding energy between both components (two intermolecular hydrogen bonds) of 21.0 kcal mol^{-1} at the B3LYP/6-31++G* level of theory (see Supporting Information). The characteristic feature of this adduct was an even longer HO–OO "bond" and a somewhat shortened HOO–O bond relative to the non-solvated HOOO "anion". The mechanism of the fragmentation of this assembly is currently under investigation in our laboratory.

[24] Our preliminary studies of the topology of the potential energy surface descending from the transition state **TS1** by using IRC calculations (C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.* **1989**, *90*, 2154; *J. Phys. Chem.* **1990**, *94*, 5523) have confirmed the intermolecularly hydrogen-bonded radical pair, that is, hydrotrioxyl radical 2-hydroxy-2-propyl radical complex (O–H$\cdots$OOOH) as the first intermediate product. The IRC calculations of further reactions of this radical pair to form the end products of the title reaction (currently under invesitigation but computationally very time consuming) are beyond the scope of the present study. We thank one of the reviewers for suggesting these studies.

[25] X.-M. Zhang, *J. Org. Chem.* **1998**, *63*, 1872.

[26] a) M. Speranza, *J. Phys. Chem. A* **1998**, *102*, 7535; b) for the first direct experimental evidence for HOOO radical, see: F. Cacace, G. de Petris, F. Pepi, A. Troiani, *Science* **1999**, *285*, 81.

[27] Our calculations revealed that the reaction HOOO$^\bullet$ → HO$^\bullet$ + ^{3}O$_2$ was endothermic by 5.1 and 4.9 kcal mol^{-1} for the trans and cis form, respectively, at the CCSD(T)/6-311++G** level (Σ^3O$_2$, $d(\mathrm{O{-}O}) = 1.211$ Å, $E = -150.04486$ au).

[28] Peroxyacetic and formic acid are presumably formed by the ozonolysis of the enol.[1a, 3b] The initially formed formaldehyde is oxidized further (O$_3$/O$_2$), and also reacts with isopropyl alcohol to form isopropoxymethanol.

[29] Tetrahedral intermediates were actually detected in the decomposition mixture at low temperatures. For example, 2-hydroxy-2-methoxypropane was detected as unstable intermediate during the decomposition of the hydrotrioxide **2b**. This intermediate decomposed faster than **2b** at temperatures above −50°C. [^{1}H NMR (300 MHz, [D$_6$]acetone, −70°C, TMS): $\delta = 5.32$ (s, 1H; OH), 3.19 (s, 3H; OCH$_3$), 1.31 (s, 6H; CH$_3$); ^{13}C NMR (75.5 MHz, [D$_6$]acetone, −70°C, TMS): $\delta = 97.3$ (C), 48.0 (OCH$_3$), 27.0 (CH$_3$)].

[30] Selected kinetic and activation parameters for the decomposition of the hydrotrioxides of α-methylbenzyl alcohol and methyl α-methylbenzyl ether, and HOOOH generated by the low-temperature ozonation of the alcohol and ether are as follows: Ph(Me)C(OH)(OOOH), [D$_6$]acetone, $k(-10\,°\mathrm{C})$, $3.7 \times 10^{-4}\,\mathrm{s}^{-1}$, $E_a = 21.3$ kcal mol^{-1}, $\log A = 14.3$; HOOOH, $k(-10\,°\mathrm{C})$, $11.9 \times 10^{-4}\,\mathrm{s}^{-1}$, $E_a = 17.6$ kcal mol^{-1}, $\log A = 11.\,7$; Ph(Me)C(OMe)(OOOH), [D$_6$]acetone, $k(-10\,°\mathrm{C})$, $12.5 \times 10^{-4}\,\mathrm{s}^{-1}$, $E_a = 23.2$ kcal mol^{-1}, $\log A = 16.3$; HOOOH, $k(-10\,°\mathrm{C})$, $3.3 \times 10^{-4}\,\mathrm{s}^{-1}$, $E_a = 13.7$ kcal mol^{-1}, $\log A = 7.8$. (For a complete list of kinetic data, see Supporting Information.)

[31] a) W. A. Pryor, N. Ohto, D. F. Church, *J. Am. Chem. Soc.* **1983**, *105*, 3614; b) Our preliminary study on the low-temperature ozonation of cumene at lower concentrations (0.1–0.4 M) than originally investigated (ca. 3.6 M),[31a] in [D$_6$]acetone, revealed the appearance of two polyoxides, that is, cumyl hydrotrioxide [^{1}H NMR (300 MHz, [D$_6$]acetone, −10°C, TMS): $\delta = 13.38$ (s, 1H; OOOH)], and HOOOH [$\delta = 13.22$ (s, 2H; OOOH)] in molar ratio 1.00:0.35 in the reaction mixture. The kinetic and activation parameters for the decomposition of cumyl hydrotrioxide and HOOOH are: k (−10°C), $1.0 \times 10^{-4}\,\mathrm{s}^{-1}$, $E_a = 23.0 \pm 1.0$ kcal mol^{-1}, $\log A = 15.5 \pm 1.0$; HOOOH: $k(-10\,°\mathrm{C})$, $0.60 \times 10^{-4}\,\mathrm{s}^{-1}$, $E_a = 17.0 \pm 1.0$ kcal mol^{-1}, $\log A = 10.0 \pm 1.0$ (without inhibition). The activation parameters for the decomposition of cumyl hydrotrioxide are in excellent agreement with those obtained by Pryor et al. in [D$_6$]acetone in the presence of 2,6-di-*tert*-butyl-4-methylphenol as an inhibitor. It therefore appears that a higher polarity and/or greater hydrogen bond acceptor capability of the medium ([D$_6$]acetone, :B, see Scheme 2) affects the outcome of the reaction.

[32] CCSD(T)/6-311++G**, HOOOH: $d(\mathrm{H{-}O}) = 0.978$ Å, $d(\mathrm{O{-}O}) = 1.432$ Å, $\sphericalangle$ H-O-O = 101.9°, $\sphericalangle$ O-O-O = 107.6°, $\sphericalangle$ H-O-O-O = 82.0°, $E = -226.267699$ au.

[33] See also: C. von Sonntag, H.-P. Schuchmann, in *Peroxyl Radicals* (Ed.: Z. Alfassi), Wiley, New York, **1997**, pp. 173–234.

[34] All attempts to obtain anhydrous solutions of ROOOH/HOOOH with molecular sieves as drying agent (dry box) failed, since water was formed as a result of the induced decomposition of HOOOH by ozone as well as in the spontaneous decomposition of this polyoxide. Molar ratio HOOOH:HOH was in all cases approximately 1:2–3.

[35] a) G. Goor, W. Kunkel, O. Weiberg, in *Ullmann's Encyclopedia of Industrial Chemistry Vol. A13*, 5th ed., p. 443; b) A. Rieche, *Angew. Chem.* **1958**, *70*, 251.

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[43] Density functional calculations (DFT), performed with B3LYP functional, have been shown to be comparable in accuracy with those of CCSD(T) in cases with some multireference character such as

ozone,[44a, 44b] and in some other "difficult" peroxide species (FOOF).[44b, 44c] In addition, the transition state structures for alkene epoxidation by peroxyformic acid,[44d, 44e] for example, obtained at the B3LYP level, are remarkably close to those calculated at CCSD, CCSD(T), and QICD levels of theory.

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[45] a) K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479; b) R. J. Bartlett, J. D. Watts, S. A. Kucharski, J. Noga, *Chem. Phys. Lett.* **1990**, *165*, 513 (CCSD(T)).

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[47] See, for example: a) D. Cremer, *J. Chem. Phys.* **1978**, *69*, 4440; b) For a comprehensive discussion of the early use of ab initio methods (including MP calculations) for the study of peroxides and polyoxides, see: D. Cremer, in *The Chemistry of Peroxides* (Ed.: S. Patai), Wiley, Chichester, **1983**, pp. 1–84; c) J. E. Carpenter, F. Weinhold, *J. Phys. Chem.* **1988**, *92*, 4306, and references cited therein; d) J. A. Dobado, J. M. Molina, *J. Phys. Chem.* **1993**, *97*, 7499; e) O. Mo, M. Yanez, I. Rozas, J. Elguero, *J. Chem. Phys.* **1994**, *100*, 2871; f) Y. -Y. Chuang, D. G. Truhlar, *J. Phys. Chem. A* **1999**, *103*, 651.

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