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Hydrotrioxides Rather than Cyclic Tetraoxides (Tetraoxolanes) as the Primary Reaction Intermediates in the Low-Temperature Ozonation of Aldehydes. The Case of Benzaldehyde

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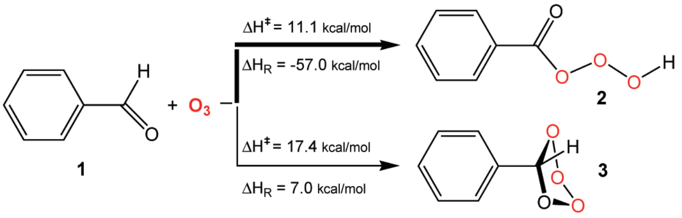

We demonstrate in this work by theory and experiment that benzaldehyde hydrotrioxide (PhC(O)OOOH), the intermediate most likely formed in the low-temperature ozonation of benzaldehyde, is too unstable to be detected by NMR (^{1}H, ^{13}C, and ^{17}O) spectroscopy in various organic solvents at temperatures ≥ -80 °C and that its previous detection must have been erroneous. Several plausible mechanisms for the formation of this polyoxide were explored by using density functional theory. We found that the formation of the hydrotrioxide involves the facile 1,3-dipolar insertion of ozone into the C−H bond ($\Delta H^{\ddagger} = 11.1$ kcal/mol) in a strongly exothermic process ($\Delta H_R = -57.0$ kcal/mol). The hydrotrioxide then quickly decomposes in a second concerted, exothermic reaction involving an intramolecular H transfer to form benzoic acid and singlet oxygen ($O_2(^1\Delta_g)$) (ΔH‡ $=$ 5.6 kcal/mol), $\Delta H_R = -14.0$ kcal/mol). The equilibrium is thus expected to be shifted toward the products; therefore, this intermediate cannot be observed experimentally. Peroxybenzoic acid, still another major reaction product formed in the ozonation reaction, is formed as a result of the surprising instability of the RC(O)O−OOH bond ($\Delta H_R = 23.5$ kcal/mol), generating HOO$^\bullet$ and benzoyloxyl radicals. Both of these radicals can then initiate the chain autoxidation reaction sequence—the abstraction of a H atom from benzaldehyde to form either a benzoyl radical and HOOH or a benzoyl radical and benzoic acid. Because only very small amounts of HOOH were detected in the decomposition mixtures, the recombination of the benzoyl radical with the HOO$^\bullet$ radical ($\Delta H_R = -80.7$ kcal/mol) appears to be the major source of peroxybenzoic acid. A theoretical investigation of the mechanistic possibility of the involvement of still another intermediate, a cyclic tetraoxide (tetraoxolane) formed as a primary product in the 1,3-dipolar cycloaddition of ozone to the carbonyl group of the aldehyde, revealed that the tetraoxide is a "real" molecular entity with the five-membered ring adopting an envelope conformation. The tetraoxide is destabilized by 7.0 kcal/mol relative to the reactant complex, and the transition state for its formation is 17.4 kcal/mol above the reactant complex, which, although accessible under the reaction conditions, is not expected to be competitive with the reaction generating the hydrotrioxide.

Introduction

Ozonation reactions play an important role in the polluted atmosphere, wastewater purification, ozone toxicity studies, and chemical synthesis.[1−3] Although the involvement of hydrotrioxides, ROOOH, in the reaction of C−H bonds in various saturated compounds with ozone has already been documented,[3] the mechanistic details and the potential involvement of hydrotrioxides in the ozonation of aldehydes were much less explored.

Proton NMR spectroscopic evidence for the existence of an unusually stable hydrotrioxide (up to +10 °C) believed to be

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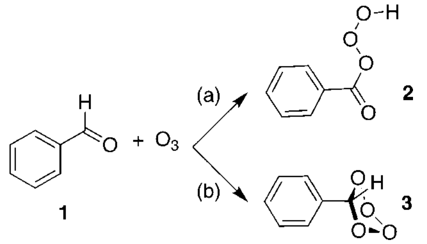
SCHEME 1. Ozonation of Benzaldehyde



benzaldehyde hydrotrioxide was reported.[4,5] We demonstrate in this work by theory and experiment that benzaldehyde hydrotrioxide (**2**, Scheme 1) is too unstable to be detected by NMR spectroscopy in various organic solvents at temperatures above −80 °C and that its previous detection must have been erroneous.

The mechanistic possibility, already proposed before but never tested, of the involvement of still another intermediate, a cyclic tetraoxide **3** (tetraoxolane)[6−8] formed as a primary product in the cycloaddition of ozone to the carbonyl group of the aldehyde, has also been explored.

It is known that benzaldehydes react with ozone at −70 to +10 °C in inert solvents to form the corresponding benzoic acids as the major products.[9,10] Various amounts of peroxybenzoic acids were also reported to be among the reaction products. Ozone is believed to attack the aldehydes as an electrophilic reagent (Hammett ρ values of −1.1 to −0.6),[9] and the reactions are first-order each in ozone and aldehyde. Studies of the deuterium isotope effect showed relatively low k_H/k_D values of 1.2−2.0 for these reactions when run with ozone−nitrogen mixtures.[9]

Aldehyde hydrotrioxides (ROOOH) were proposed as the initial intermediates in these reactions.[4,5,9−11] These intermediates might be formed by either (a) a concerted 1,3-dipolar insertion of ozone into the C−H bond of the aldehyde or (b) the abstraction of either the H atom or the hydride ion from R−H by ozone to first form the radical (R• •OOOH) or ionic pair (R^+ $^-$OOOH), with subsequent collapse to the hydrotrioxide.[12−14]

Computational Methods

The mechanism for the ozonation of benzaldehyde was investigated using the B3LYP[15−20] level of density functional theory[21,22] (DFT) in combination with the double-ζ-polarized basis set 6-31G(d,p).[23−25] Previous investigations on related ozonation reactions have shown this level of theory to be sufficiently accurate.[3,26−28] All structures were optimized at this level of theory, and second derivatives were calculated to characterize the nature of the obtained stationary points. Intrinsic reaction coordinate (IRC) calculations[29,30] were used to confirm the connectivity between minima and associated transition states. Calculated binding energies have been corrected for basis set superposition error using the counterpoise correction method.[31] The effect of the solvent medium on the systems investigated was included using the conductor-like polarizable continuum model (C-PCM) applying the dielectric constant of acetone ($\epsilon = 20.7$).[32,33]

The decomposition of the hydrotrioxide has been investigated both as a concerted mechanism as well as a radical decomposition. The concerted mechanisms result in the formation of the $O_2(^1\Delta_g)$, which has singlet diradical character. Due to the deficiencies of DFT when describing multireference systems such as $O_2(^1\Delta_g)$, we employed spin projection[34] to provide an accurate description of the complexes involving $O_2(^1\Delta_g)$. At the B3LYP level, this technique has been shown to provide reliable energetic data for complexes involving $O_2(^1\Delta_g)$[35−37] and is able to reasonably reproduce ($\Delta E = 20.9$ kcal/mol) the experimental triplet−singlet splitting of 22.5 kcal/mol.[38]

A recent contribution by Radom et al. assessed the ability of a variety of density functionals to reproduce the bond dissociation energies (BDEs) against experimental and high-level ab initio (W1) data.[39] We have, therefore, investigated the decomposition reaction mechanisms that involve the dissociation into radical pairs against the best-performing functionals identified in their work. These include the restricted open-shell (RO)-BMK,[40] the RO-MPWB1K,[41] and the unrestricted (U)-M05-2X functionals;[42,43] the mean absolute deviation from the W1 (experimental) data across the set of 22 reactions is 0.69 (1.00) kcal/mol, 0.43 (0.74) kcal/mol, and 1.55 (1.33) kcal/mol for the three functionals, respectively.[39] In previous work, the RO-B3LYP functional was also investigated for the same

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set of 22 reactions; the mean absolute deviation from the experimental data for this functional is 1.31 kcal/mol.[44] All structures were optimized at the B3LYP level of theory with the 6-31G(d,p) basis set. Single-point calculations were then carried out using the desired functional in combination with the 6-311+G(3df,2p) basis set,[45] which is consistent with the approach employed by Radom et al.[39] Harmonic vibrational frequencies computed at the B3LYP/6-31G(d,p) level were used to provide zero-point energy and thermal corrections. All calculations were performed in Gaussian 03.[46]

Results and Discussion

Ozonation of Benzaldehyde (Experimental Results). Ozonation of benzaldehyde with an ozone−nitrogen mixture, either neat at −30 °C or in various solvents (0.1−1.0 M; acetone-d_6, methyl acetate, *tert*-butyl methyl ether, or methylene chloride-d_2) at −80 °C, produced the corresponding acid and peroxyacid in a molar ratio of 1:4 ± 2 as the reaction products. The peroxybenzoic acid was characterized by OOH ^{1}H NMR absorption at δ 13.2 ± 0.5 ppm, by C═O ^{13}C NMR absorption at 169 ppm, and by ^{17}O NMR at 317 and 275 ppm.[47] The OOH ^{1}H NMR signal, previously attributed to PhC(O)OOOH, exactly matched the OOH ^{1}H NMR signal of peroxybenzoic acid (as well as the ^{13}C and ^{17}O NMR chemical shifts) under the conditions we investigated. The corresponding acid was identified by OH ^{1}H NMR absorption at δ 12.0 ± 0.5 ppm, by C═O ^{13}C NMR absorption at 167 ppm, and by ^{17}O NMR at 252 ppm.[48] It is interesting to mention that the ^{1}H NMR chemical shifts for the OOH absorption of the peroxyacid and those for the OH absorption of the acid remained unchanged during the warming-up (from −80 to +30 °C) and cooling-down procedures. Very small amounts of HOOH were also detected in the decomposition mixtures. However, no other absorptions that could be attributed to either the benzaldehyde hydrotrioxide **2** or the cyclic tetraoxide **3** could be detected by NMR ($\geq$ 2 mol %; ^{1}H, ^{13}C, and ^{17}O NMR) in solutions after the ozonation of benzaldehyde **1** at temperatures $\geq$ −80 °C.[49]

The OOH ^{1}H NMR absorption for peroxybenzoic acid disappeared in the temperature range of −20 to +20 °C, producing benzoic acid. The observed pseudo-first-order kinetics and the activation parameters for the disappearance of peroxybenzoic acid in neat benzaldehyde (Baeyer−Villiger reaction) were comparable to those for the decomposition of the purported benzaldehyde hydrotrioxide[4,5] at approximately the same concentration and temperature range interval (see Table S1 in Supporting Information).

Ozonation of Benzaldehyde (Theoretical Results). The 1,3-dipolar insertions of ozone into either the C−H or C═O bond of the aldehyde were investigated as the primary mechanistic modes (Scheme 1). Additionally, the possibility of an initial H• or H$^-$ abstraction by ozone[12−14] with the the subsequent collapse of the radical (R• •OOOH) or the ionic pair (R$^+$ $^-$OOOH) to form the hydrotrioxide **2** (Scheme 1) was investigated. However, all attempts to locate the TS for an independent abstraction process were unsuccessful.

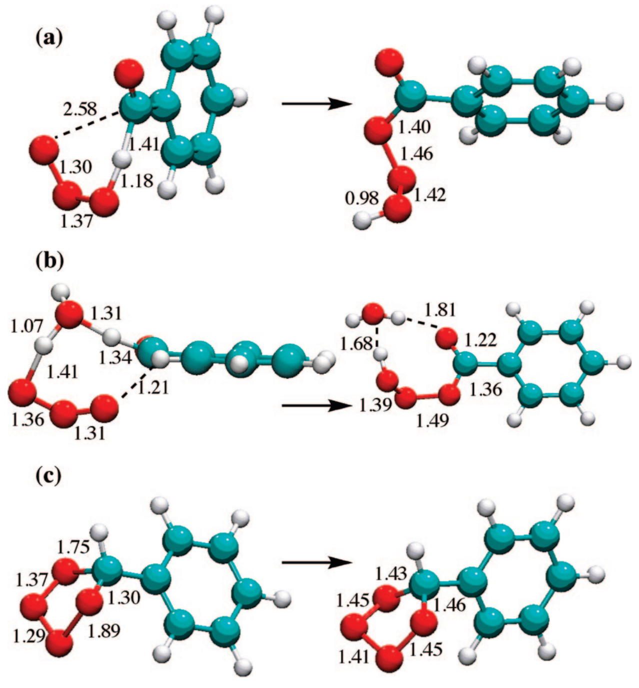

FIGURE 1. Transition state structures and products of the optimized ozonation mechanisms: (a) **TS(1a-2)** → **2**, (b) **TS(1b-2b)** → **2b**, (c) **TS(1c-3)** → **3**.

The initial complex formed between ozone and the benzaldehyde is not strongly bound. At the B3LYP level, the binding energy is −0.3 kcal/mol; however, this is most likely an underestimation of the true binding energy of the two species. DFT is unable to accurately describe dispersion-bound complexes, and this type of interaction is expected to exist in the benzaldehyde−ozone complex. Nonetheless, the complex, though relatively weakly bound, provides a reliable representation of the starting structure for the ozonation reaction. In the water-catalyzed version of the reaction to form **2** (vida infra), the increase in the binding energy is consistent with the formation of H-bonds between the complex and H_2O since DFT is able to accurately represent such interactions.

The insertion of ozone into the C−H bond (path a, Scheme 1) results in the formation of the hydrotrioxide of benzaldehyde (**2**, Figure 1). This reaction occurs with a low barrier ($\Delta H^\ddagger$ = 11.1 kcal/mol, Table 1) and is strongly exothermic (ΔH_R = −57.0 kcal/mol, Table 1). These results are consistent with a relatively low kinetic isotope effect observed in the ozonation of benzaldehyde.[9] The inclusion of solvent effects, via the continuum model, does not have a substantive effect on the calculated reaction energetics—the activation energy is slightly increased, and the reaction becomes slightly more exothermic (Table 1). This indicates that the polarizing nature of the solvent has little effect on the energetics of the reaction; however, water may play an additional explicit role in catalyzing the reaction. We, therefore, considered the possible role of a water molecule in the ozonation of benzaldehyde **1**.

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TABLE 1. Energetics of Ozonation Reactions[a]

	ΔE	ΔH	ΔG	ΔG_{solv}	BE
1a	0	0	0	0	−0.3
TS(1a-2)	14.6	11.1	15.1	13.2	
2	−58.0	−57.0	−52.6	−61.0	
1b	0	0	0	0	−5.1
TS(1b-2b)	23.6	18.8	23.0	21.0	
2b	−71.0	−69.7	−66.0	−73.3	−13.8
1c	0	0	0	0	−1.7
TS(1c-3)	18.2	17.4	22.1	17.7	
3	6.4	7.0	11.5	6.0	

[a] Relative energies, enthalpies, and free enthalpies in kcal/mol. ΔG_{solv} values are the relative free energies from the solvent phase single-point calculations of the gas phase optimized structures. Binding energies (BE) are BSSE-corrected using the counterpoise correction.

In Table 1, the compounds listed as **1b**, **TS(1b-2b)**, and **2b** represent the same reaction as indicated by path a in Scheme 1, but with an additional water molecule (see Figure 1b). The inclusion of the water molecule did not have a favorable effect on the activation enthalpy, which was increased by 7.7 kcal/mol ($\Delta H^{\ddagger} = 18.8$ kcal/mol, Table 1). However, the reaction is slightly more exothermic due in part to the more favorable H-bond complex formed in the product, as evidenced by the increased binding energy of **2b** relative to **1b**.

The possibility of inserting the ozone molecule into the C=O bond (path b, Scheme 1), where the final product is the cyclic tetraoxide (tetraoxolane **3**, Scheme 1), was also considered. The calculated product for this pathway indicates that **3** is a stable system, with the five-membered ring adopting an envelope conformation (Figure 1c). This is the most stable conformation; however, the reaction is destabilized by 7.0 kcal/mol (ΔH, Table 1) relative to the reactant complex. The transition state in forming **3** is 17.4 kcal/mol[51] above the reactant complex, which, although accessible under the reaction conditions, is not expected to be competitive with the reaction generating **2**[52] (for the calculated IR spectra for **2** and **3**, see Supporting Information). Furthermore, the inclusion of solvent effects via the C-PCM calculation is unable to lower the barrier to cyclization. The activation energy in forming **3** is slightly increased to 17.7 kcal/mol (ΔG_{solv}, Table 1) when the effect of the polar solvent (acetone) is included.

Formation of Benzoic Acid. The concerted decomposition of the hydrotrioxide results in the formation of benzoic acid and singlet oxygen ($O_2(^1\Delta_g)$). The H transfer can occur intramolecularly (Figure 2) or in a water-assisted, concerted mechanism (see Supporting Information). However, in analogy with the formation of **2**, the calculated activation enthalpy ($\Delta H^{\ddagger} = 8.9$ kcal/mol) for the decomposition reaction indicates that the presence of a water molecule is unfavorable (Figure S1 in Supporting Information). Nonetheless, in both cases (with and without H_2O), the reaction is facile.

The ozonation reaction (path a, Scheme 1) results in an open-chain structure (i.e., the *trans* form of ROOOH, see Figure 1a); however, the intramolecular H transfer requires the *cis* form of the OOOH chain. The rotation of the *trans* to *cis* isomer of **2** proceeds over two moderate barriers, with the final *cis* product 8.2 kcal/mol lower in energy than **2** (Figure 2). The intramolecular H transfer has a low activation enthalpy ($\Delta H^{\ddagger} = 5.6$ kcal/mol), and the resulting formation of benzoic acid is exothermic ($\Delta H_R = -14.0$ kcal/mol). As outlined in the Computational Methods, spin projection was used in the calculation of the activation and reaction enthalpies for the final step in this reaction, where $O_2(^1\Delta_g)$ is formed. There is a small fraction of spin contamination (f_{sc}) in the TS ($f_{sc} = 0.17$), whereas the product complex has a much larger contamination ($f_{sc} = 0.97$, see Supporting Information for details on the calculation of f_{sc} and spin-projected energies).

All subsequent barriers for the decomposition of **2** are less than those required for the initial ozonation reaction, and, therefore, the peak contribution of the hydrotrioxide is expected to be small due to the rapid decomposition process. This is also true for the water-catalyzed decomposition reaction when compared with the activation enthalpy required to form **2b** (see Supporting Information). Given that the benzoic acid complex is favored from both a kinetic and thermodynamic perspective and that the reaction from **1** can occur spontaneously, it is not surprising that we are not able to detect intermediate **2**. The final complex of benzoic acid and $O_2(^1\Delta_g)$ dissociates in a barrierless process ($\Delta H = -1.7$ kcal/mol) to further stabilize the singlet diradical character of O_2.

Formation of Peroxybenzoic Acid. Another major product resulting from the ozonation reaction is peroxybenzoic acid, which is formed as a result of the surprising instability of the RC(O)O−OOH bond in **2**. As a result of this instability, **2** decomposes into hydroperoxyl and benzoyloxyl radicals (Scheme 2a) rather than into benzoylperoxyl and hydroxyl radicals (as suggested previously).[10,53] Both of these radicals can then initiate the chain autoxidation reaction—the abstraction of a H atom from benzaldehyde to form either a benzoyl radical and HOOH (Scheme 2b) or a benzoyl radical and benzoic acid (Scheme 2c). However, because only very small amounts of hydrogen peroxide were detected in the decomposition mixtures, it appears that an alternative reaction involving the hydroperoxyl radical (Scheme 2d) must be an important one. This reaction leads to one of the major observed products of the ozonation reaction, peroxybenzoic acid. The peroxyacid may also be formed by an additional radical reaction (Scheme 2e); benzoyl radicals could also react with triplet oxygen (formed from singlet oxygen and, much less likely, present as an impurity in the ozone−nitrogen stream) to form benzoylperoxyl radicals. The abstraction of a hydrogen atom from benzaldehyde by the benzoylperoxyl radical is then able to produce the observed peroxybenzoic acid (Scheme 2f).

We have also considered the addition of ozone to the benzoyl radical formed in the reactions outlined in Scheme 2b,c,f. However, we were unable to optimize the RC(O)OOO• intermediate as a stable molecular entity. Such a radical most likely immediately dissociates into RC(O)O• + O_2. It is, therefore, unlikely that the reaction is a two-step process, but rather, a direct O abstraction from ozone may take place to yield the benzoyloxyl radical that is shown as one of the products in Scheme 2a.

To assess the equilibrium of the competing reaction mechanisms in Scheme 2, we have calculated the relative stabilities

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(50) For ether hydrotrioxides, see: Plesničar, B.; Cerkovnik, J.; Tekavec, T.; Koller, J. *Chem.—Eur. J.* **2000**, *6*, 809.

(51) Benson et al. (see ref 7) estimated a minimum activation energy of 10.6 kcal/mol for the formation of the cyclic tetraoxide of acetaldehyde.

(52) Klopman et al. (see ref 6) reported relatively fast exchange between ^{18}O-enriched isobutyraldehyde and ozone in a reversible equilibrium (via cyclic tetraoxide). Our preliminary experiments showed no exchange between benzaldehyde and ^{18}O-labeled ozone at−70 ± 10 °C.

(53) The bond dissociation enthalpy for the RC(O)OO−OH bond was calculated in the same manner and has a value of 37.4 kcal/mol. For comparison, the bond dissociation enthalpy for the HO−OOH bond was calculated to be 31.1 kcal/mol (31.7 ± 1.4 kcal/mol; Shum, L. G. S.; Benson, S. W. *J. Phys. Chem.* **1983**, *87*, 3479).

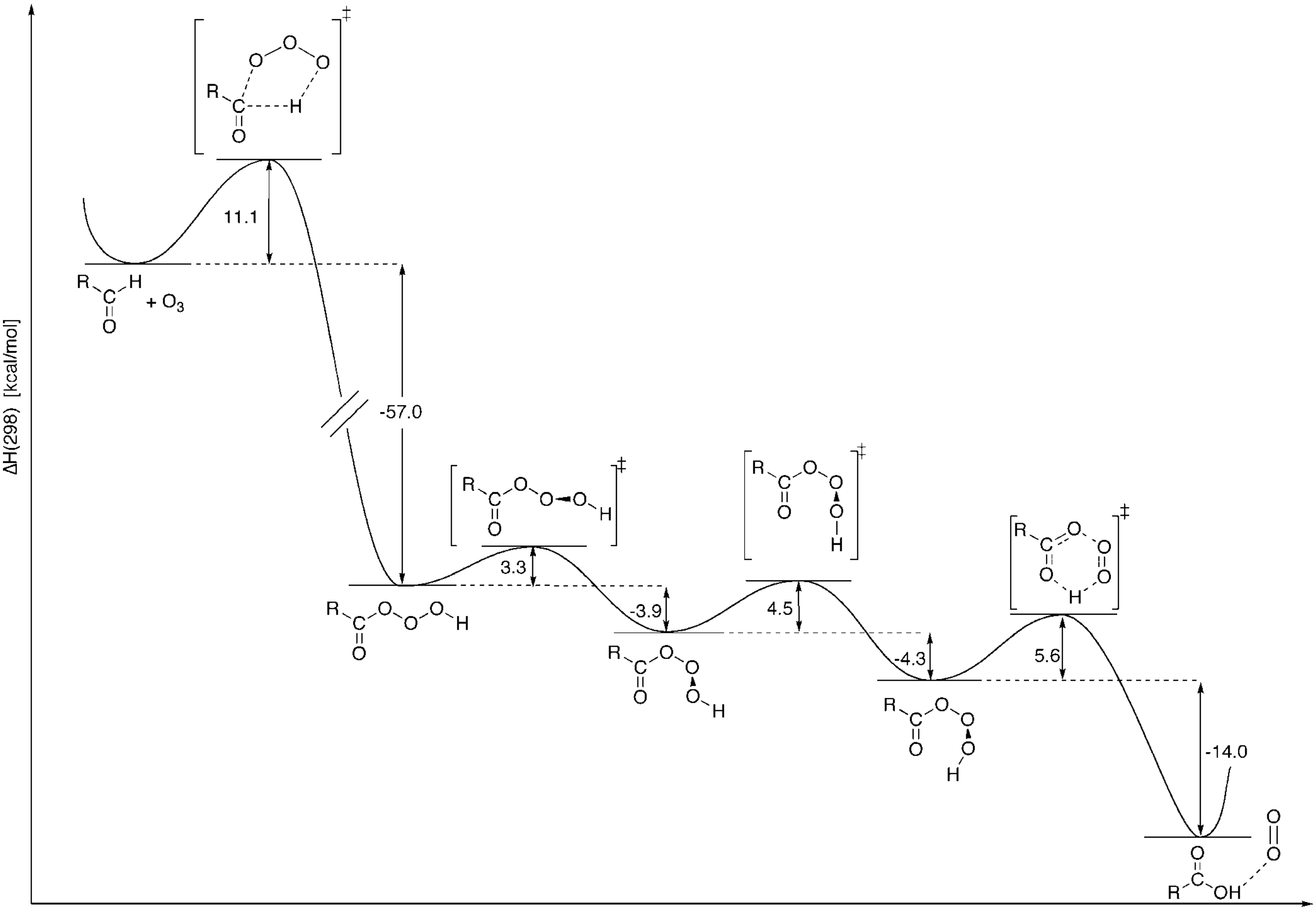
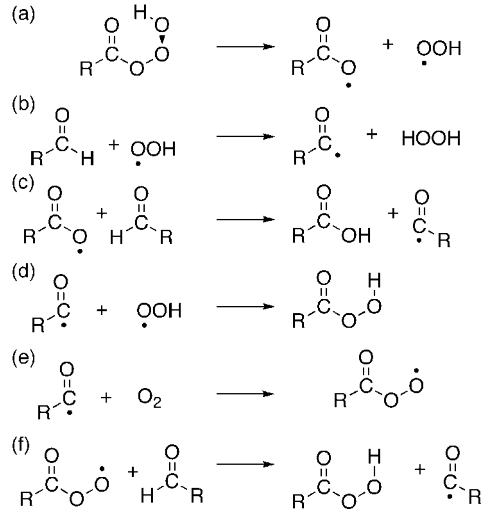


FIGURE 2. Energy profile for the concerted reaction of ozone and benzaldehyde to form benzoic acid and singlet oxygen ($O_2(^1\Delta_g)$).

SCHEME 2. Radical Decomposition Reactions of 2



and activation barriers (where applicable) for these mechanisms. The results from the single-point calculations using the density functionals outlined in the Computational Methods are reported in Table 2. The RO-BMK and RO-MPWB1K methods are generally found to slightly overestimate the BDE relative to the W1 results, whereas RO-B3LYP and U-M05-2X generally underestimate the BDE relative to the W1 results.[39,44] Therefore, we have taken a simple average of the four results for each reaction, and it is these average values that are discussed below.

TABLE 2. Relative Enthalpies of Radical Reactions Described in Scheme 2[a]

	RO-B3LYP	RO-BMK	RO-MPWB1K	U-M05-2X	average
ΔH_R (Scheme 2a)	18.8	24.7	23.9	26.6	24
ΔH‡ (Scheme 2b)	7.4	11.8	9.6	10.2	10
ΔH_R (Scheme 2b)	5.3	5.4	6.0	5.7	6
ΔH_R (Scheme 2c)	−16.3	−21.6	−19.4	−24.1	−20
ΔH_R (Scheme 2d)	−76.2	−81.8	−82.4	−82.6	−81
ΔH_R (Scheme 2e)	−32.7	−37.9	−36.3	−35.2	−36
ΔH‡ (Scheme 2f)	3.7	7.6	5.4	6.0	6
ΔH_R (Scheme 2f)	−4.6	−5.1	−5.3	−4.9	−5

[a] Results are reported for each functional as relative enthalpies (ΔH(298)) in kcal/mol.

The initial dissociation reaction of **2** to form the benzoyloxyl radical and the hydroperoxyl radical (Scheme 2a) requires an enthalpy of ca. 24 kcal/mol, which is the lowest BDE (RO−OOH) value reported of any hydrotrioxide studied until now.[53] The dissociation enthalpies predicted by the four methods span a range of ca. 8 kcal/mol, with the two less-reliable functionals (RO-B3LYP and U-M05-2X) predicting the highest and lowest values. The average value obtained is slightly less than the RO-BMK and RO-MPWB1K results, which were found by Radom et al. to be the most accurate functionals and generally to slightly overestimated the BDEs.[39] Although the dissociation enthalpy is relatively high, the formation of **2** is a strongly exothermic process, and as such, there is sufficient energy in the system to allow the dissociation to occur. Moreover, the entropic gain from the dissociation is also a driving force behind this reaction. Thus, based on the low BDE and the favorable entropic effects, the RC(O)O−OOH bond should dissociate spontaneously under the reaction conditions.[53]

The formation of hydrogen peroxide via Scheme 2b is limited due to the endothermicity of the reaction. The barrier to the abstraction of the H atom from benzaldehyde by the hydroperoxyl radical is moderate ($\Delta H^{\ddagger} \approx 10$ kcal/mol), however, the endothermicity of the reaction implies that the reverse reaction has a relatively low barrier of ca. 4 kcal/mol. Thus, the equilibrium for such an abstraction reaction would be shifted toward the reactants. On the other hand, the benzoyloxyl radical resulting from the initial dissociation is able to easily abstract a H atom from benzaldehyde (Scheme 2c) in a strongly exothermic reaction ($\Delta H_R \approx -20$ kcal/mol),[54] generating benzoic acid and the benzoyl radical.

The unreacted hydroperoxyl radical from the initial dissociation is able to react with the benzoyl radical formed in Scheme 2c in a barrierless, strongly exothermic reaction ($\Delta H_R \approx -80$ kcal/mol), resulting in the observed peroxybenzoic acid. The unfavorable equilibrium in the reaction outlined in Scheme 2b and the strong exothermicity of the recombination reaction of Scheme 2d are consistent with the observation that only very small amounts of hydrogen peroxide were detected in the decomposition mixtures.

We also considered a second competitive mechanism that may also contribute to the formation of peroxybenzoic acid—the benzoyl radicals reacting with triplet oxygen in a strongly exothermic reaction ($\Delta H_R \approx -36$ kcal/mol) to form benzoylperoxyl radicals (Scheme 2e). The abstraction of a hydrogen atom from benzaldehyde by the benzoylperoxyl radical to generate peroxybenzoic acid occurs with only a moderate barrier ($\Delta H^{\ddagger} \approx 6$ kcal/mol) in a slightly exothermic reaction ($\Delta H_R \approx -5$ kcal/mol, Scheme 2f).

Conclusions

The formation of the hydrotrioxide of benzaldehyde through ozonation was found to occur in a facile mechanism involving the 1,3-dipolar insertion of ozone into the C−H bond. The inclusion of solvent effects via a continuum solvent model had a minor destabilizing effect on the reaction enthalpies, and the presence of an explicit water molecule was also found to be mildly destabilizing. The hydrotrioxide is formed in an exothermic reaction; however, this intermediate can then decompose in a second concerted, exothermic mechanism to form benzoic acid and singlet oxygen ($O_2(^1\Delta_g)$). Given the low barrier and the exothermicity of the latter phase of the reaction, the equilibrium is expected to be shifted strongly toward the products of the reaction, and the intermediate is not observed experimentally under conditions investigated in this work.

Peroxybenzoic acid was formed from the ozonation reaction as a result of the instability of the RC(O)O−OOH bond and subsequent autoxidation reaction sequence. The decomposition of the hydrotrioxide to form a benzoyloxyl radical and a hydroperoxyl radical is accessible as a result of the exothermicity of the ozonation reaction and is driven by the entropic gain resulting from dissociation. The resulting benzoyloxyl radical is able to react with benzaldehyde in an exothermic reaction to generate the benzoyl radical that, in turn, reacts in a strongly exothermic reaction with the hydroperoxyl radical to form the observed peroxybenzoic acid. The formation of peroxybenzoic acid through the reaction of O_2 with benzoyl radicals to generate benzoylperoxyl radicals and the subsequent abstraction of a H atom from benzaldehyde was also investigated and found to be a viable additional mechanism by which peroxybenzoic acid is produced. Both radical mechanisms will be operative and essentially diffusion-controlled; that is, the reaction with O_2 or hydroperoxyl radicals requires diffusion out of the solvent cage after the initial decomposition and hydrogen abstraction from benzaldehyde. Thus, although the reaction between the benzoyl and hydroperoxyl radicals is more exothermic, we expect both radical mechanisms to be competitive and irreversible.

Although the cyclic tetraoxide **3** is a stable molecular entity, the transition state for its formation is too high to compete with the reaction generating the hydrotrioxide **2**. However, both intermediates, the hydrotrioxide **2** and the cyclic tetraoxide **3**, should, at least potentially, be detected by IR matrix spectroscopic techniques.

Experimental Section

Ozonations were performed by using ozone−nitrogen mixtures that were prepared by ozone absorption on silica gel at −78 °C and blowing with nitrogen gas. Ozone was released from silica gel by raising the temperature of the bath[3,11] and delivered either into the neat benzaldehyde or into a solution of the aldehyde in the appropriate solvent (for details, see Supporting Information).

Reaction products (i.e., benzoic, peroxybenzoic acids, and hydrogen peroxide) formed in the ozonation of benzaldehyde were determined by ^{1}H, ^{13}C, and ^{17}O NMR spectroscopy using reference materials. Reaction products were also methylated using a diazomethane−diethyl ether solution and analyzed by GC/MS. In this way, benzoic acid was detected as the methyl ester.

The kinetics of the disappearance of peroxybenzoic acid was measured by following the decay of the OOH signal by ^{1}H NMR using TMS as the internal standard. Kinetic and activation parameters for the first-order reaction were obtained by standard procedures.[3]

WARNING. On several occasions, we encountered violent (explosive) decompositions of mixtures obtained during the low-temperature ozonation (−80 °C) of either neat benzaldehyde or solutions of benzaldehyde with an ozone−nitrogen mixture.

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Supporting Information Available: General experimental methods, experimental kinetic data, calculations of spin-projected energies, the effect of explicit water molecule in the ozonation of **1**, the calculated IR spectra for **2** and **3**, and the calculated geometries and energies of all structures (in xyz format). This material is available free of charge via the Internet at http://pubs.acs.org.

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(54) Attempts to locate a TS for this reaction were unsuccessful because the H abstraction occurs in a barrierless process.