

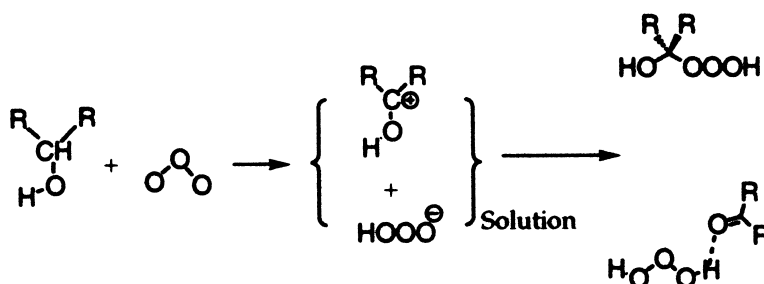
Article

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## The Role of the HOOO<sup>-</sup> Anion in the Ozonation of Alcohols: Large Differences in the Gas-Phase and in the Solution-Phase Mechanism

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**Abstract:** The mechanism of the ozonation of isopropyl alcohol was investigated for the gas and the solution phase using second-order many body perturbation theory and density functional theory (DFT) with the hybrid functional B3LYP and a 6-311++G(3df,3pd) basis set. A careful analysis of calculated energies (considering thermochemical corrections, solvation energies, BSSE corrections, the self-interaction error of DFT, etc.) reveals that the gas-phase mechanism of the reaction is dominated by radical or biradical intermediates while the solution-phase mechanism is characterized by hydride transfer and the formation of an intermediate ion pair that includes the HOOO<sup>-</sup> anion. The product distribution observed for the ozonation in acetone solution can be explained on the basis of the properties of the HOOO<sup>-</sup> anion. General conclusions for the ozonation of alcohols and the toxicity of ozone (inhaled or administered into the blood) can be drawn.

### 1. Introduction

Reactions of ozone with saturated organic materials have been at the focus of organic research for many decades<sup>1</sup> and is experiencing at the moment a renaissance.<sup>2–6</sup> One topic of this research is the ozonation of alcohols and ethers, which is important for chemical synthesis,<sup>1,7,8</sup> soil, groundwater, and wastewater purification,<sup>1,9</sup> bleaching of polysaccharides (starch, cellulose, wood, pulp),<sup>10</sup> drinking water processing, toxicity studies of ozone, and activity studies of medical ozone.<sup>11–15</sup> In the polluted atmosphere, reactions with alcohols and ozone only occur in the absence of OH radicals, which react much faster

with alcohols than with ozone.<sup>16</sup> It is now considered to be a fact that, in the ozonation reaction, hydrogen trioxide, HOOOH,<sup>17–19</sup> its radical HOOO•,<sup>20</sup> and its anion HOOO<sup>-</sup><sup>5,6</sup> are formed as important intermediates and that these species

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also play a role in ozonation reactions of biochemical compounds. A recent paper showed that hydrogen trioxide can also be an intermediate in the  $\text{H}_2\text{O}_2$  production from singlet oxygen and water by antibodies.<sup>21</sup>

Because of the interest in the ozonation of alcohols, various reaction mechanisms have been proposed to rationalize the observed products of the ozonation reaction, peroxides, HOOH, HOOOH, and ROOOH, ketones and aldehydes, as well as acids.<sup>1,2</sup> Bailey<sup>1,22</sup> suggested a 1,3-dipolar insertion of ozone into an activated C–H bond (as in  $\text{R}_2\text{C}(\text{OH})\text{--H}$ ) to yield alkyl hydrotrioxide ROOOH. The second mechanistic possibility included H abstraction by ozone and the formation of the radical pair  $\text{R}\cdot\cdot\text{OOOH}$  that can combine to form again ROOOH.<sup>23</sup> Nangia and Benson<sup>24</sup> suggested that hydride abstraction by ozone could lead to an ion pair, which collapses to give ROOOH. Pryor and co-workers<sup>25</sup> considered H abstraction and hydride abstraction as two extremes between which the real reaction complex could choose according to solvent, temperature, and other reaction factors.

In a recent study, Plesničar and co-workers<sup>2</sup> ozonated isopropyl alcohol at  $-78\text{ }^\circ\text{C}$  in acetone- $d_6$  and identified with the help of  $^{17}\text{O}$  NMR spectroscopy for the first time the hydrotrioxide of isopropyl alcohol,  $\text{Me}_2(\text{HO})\text{COOOH}$ , and hydrogen trioxide, HOOOH (apart from acetone, acetic acid, hydrogen peroxide, and water), in the reaction mixture. In addition, the authors carried out DFT (density functional theory) calculations to analyze the reaction mechanism. Combining experimental and theoretical results, they came to the conclusion that the reaction starts from an ozone–isopropyl alcohol complex, which directs the reaction into a radical channel and a radical pair intermediate. Collapse of the radical pair leads to the observed reaction products.<sup>2</sup> According to their mechanism, the enol rather than the keto form of acetone is first formed, which then rearranges.

In view of the controversial mechanistic suggestions<sup>1,2,22–25</sup> and in view of the importance of the ozonation of alcohols, we report in this work a more complete mechanistic study of the ozonation of isopropyl alcohol. We will show that the quantum chemical description of the reaction mechanism faces various problems reaching from the dangers of small basis set descriptions for peroxide reactions to the necessity of basis set superposition error (BSSE) corrections for van der Waals complexes, the importance of thermochemical corrections to get energy quantities relevant for the experimental situation, the testing of the stability of the DFT solutions, the problems of broken-spin descriptions, the complications brought about by the self-interaction error (SIE) of DFT, or the decisive role of solvation effects. Most of these problems were not considered in previous investigations on ozonation reactions and polyoxide descriptions.

Our calculations will show that there is an important difference between the mechanism for the gas phase and that for the solution phase. Furthermore, we will show that neither

ozonation in the gas phase nor ozonation in the solution phase generates the ozone–isopropyl alcohol complex in the way that it can be experimentally detected or become decisive for the reaction. The important intermediate for the reaction in solution is the  $\text{HOOO}^-$  anion,<sup>5,6</sup> which strongly influences the product variety observed experimentally. We will show that our results are relevant for a better understanding of the ozonation of organic substrates in general and that of alcohols with activated C–H bond in specific. The mechanistic role of intermediate trioxides will be described, in particular, their meaning for the toxicity of ozone when inhaled or administered as medical ozone.

## 2. Computational Methods

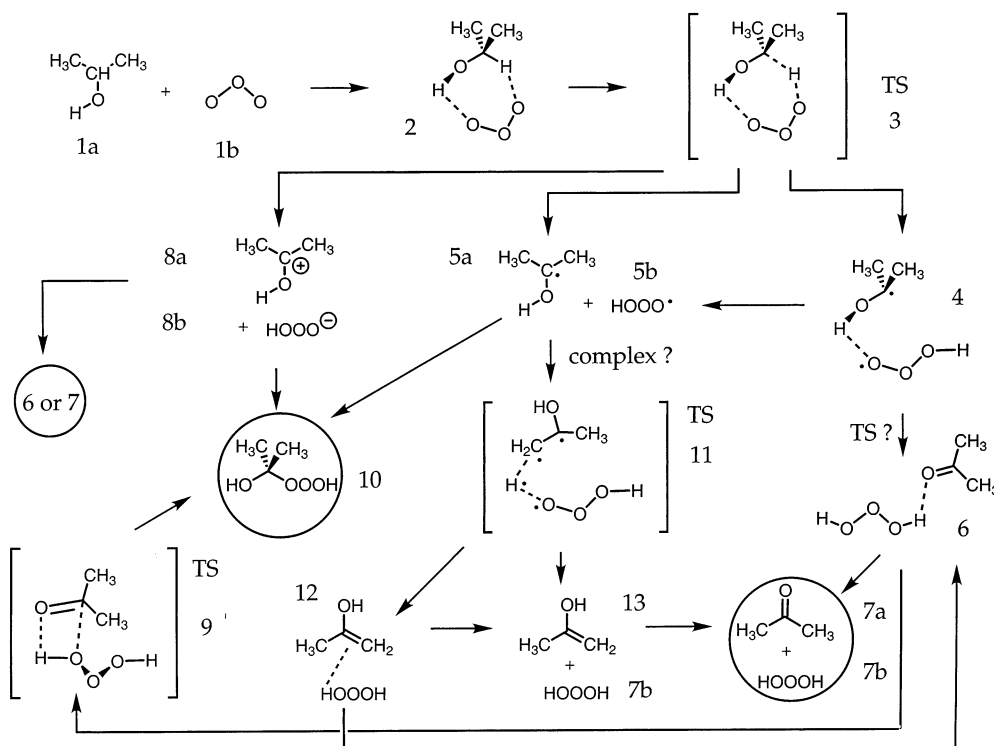
In this work, second-order many body perturbation theory with the Møller–Plesset perturbation operator (MBPT)<sup>26</sup> and density functional theory (DFT)<sup>27</sup> were used with Pople's 6-31G(d,p) basis set<sup>28a</sup> to explore the potential energy surface (PES) of the reaction system. Peroxides require an extended basis set of at least triple- $\zeta$  quality to obtain reliable descriptions of their properties. Diffuse functions are necessary to describe the interactions of the oxygen lone-pairs, while f-type polarization functions are needed for a correct assessment of the strength of the O–O bond.<sup>29</sup> For this reason, the 6-311++G(3df,3pd) basis set<sup>28b</sup> was employed, which is known to lead to reasonable results in the case of polyoxides.<sup>29</sup>

For the DFT calculations, the hybrid functional B3LYP<sup>30</sup> (B, Becke exchange functional;<sup>31</sup> LYP, Lee–Young–Parr correlation functional<sup>32</sup>) was employed. Results of the MBPT2 calculations turned out to be less reliable in general, although they were needed as an independent test of the structure and stability of the van der Waals complexes investigated. DFT descriptions of dispersion-bounded van der Waals complexes are notoriously bad,<sup>33</sup> and deficiencies of DFT have also been found when H-bonded complexes are described with basis sets of double- $\zeta$  quality.<sup>34</sup>

The geometries of all structures shown in Figure 1 were optimized both at the MBPT2 and at the B3LYP levels of theory. The DFT description was always tested for internal or external stability.<sup>35</sup> In the case of instability (for example, the restricted DFT (RDFT) solution of transition state (TS) **3** turns out to be unstable, which was not observed in the previous investigation), a broken-symmetry (BS)-unrestricted DFT (UDFT)<sup>36</sup> solution of the problem in question was considered. DFT as a density theory is not as sensitive to spin

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**Figure 1.** Proposed reaction mechanism for the ozonation of isopropyl alcohol. Encircled compounds are experimentally observed. Structures in brackets correspond to transition states (TS).

contamination as MBPT2. In previous work, it was shown that a BS-UDFT solution, despite a relatively large deviation of the calculated  $\langle \hat{S}^2 \rangle$  from its ideal value, yields reliable information in the case of biradicals or structures with biradical character, provided the singlet–triplet excitation of the structure investigated is not larger than 3–5 kcal/mol.<sup>36</sup> For UMBPT2, the spin projection method was applied to obtain a PMBPT2 (projected MBPT2) description with the correct  $\langle \hat{S}^2 \rangle$  value.<sup>26,37</sup>

Another problem encountered in connection with the DFT calculations is the SIE of the Becke exchange functional in B3LYP (the LYP correlation functional is SIE-free).<sup>38</sup> The SIE becomes significant for odd-electron problems.<sup>39</sup> The H-transfer from a closed-shell system to a radical, which involves the breaking of a  $\sigma$ -bond and the formation of a new  $\sigma$ -bond involving the single electron of the radical, is as a three-electron problem and, accordingly, has a strong SIE leading, for example, to an underestimation of the reaction barrier.<sup>40</sup> Therefore, we

recalculated the energy with self-interaction corrected DFT as described by Gräfenstein and co-workers.<sup>41</sup>

The topology of the PES was determined by following the reaction path from a TS to reactants and products using the intrinsic reaction coordinate (IRC calculations).<sup>42</sup> The stationary points found on the PES were characterized by vibrational frequencies, which were then also used to determine thermochemical corrections and entropies needed to obtain enthalpy differences  $\Delta H(298)$  and free enthalpy differences  $\Delta G(298)$ . For this purpose, B3LYP/6-31G(d,p) was used.

Binding energies of the van der Waals complexes investigated in this work were corrected for BSSEs using the counterpoise method of Boys and Bernardi.<sup>43</sup> The BSSE corrections for the 6-31G(p,p) basis are substantial (2, 2.85 kcal/mol; 6, 2.24 kcal/mol; 12, 1.97 kcal/mol), while they are relatively small for the 6-311++G(3df,3pd) basis set (2, 0.35 kcal/mol; 6, 0.27 kcal/mol; 12, 0.08 kcal/mol).

The influence of a solvent on the energetics of the ozonation was investigated by using a reaction field with the self-consistent isodensity polarized continuum (SCIPCM) approach,<sup>44</sup> which provides an estimate of electrostatic solvent effects. In this approach, an isodensity surface is calculated at the level of theory employed. Such an isodensity surface has been found to define rather accurately the volume of a molecule,<sup>45</sup> and, therefore, it should also define a reasonable cavity for the dissolved molecule within the polarizable continuum where the cavity can iteratively be adjusted when improving wave function and electron density distribution during a self-consistent field (SCF) calculation at the DFT level, as was done in this work. DFT/SCIPCM energies for the dielectric constant  $\epsilon$  of acetone (20.7<sup>46</sup>) were determined by utilizing MBPT2 or DFT geometries obtained for the gas phase.

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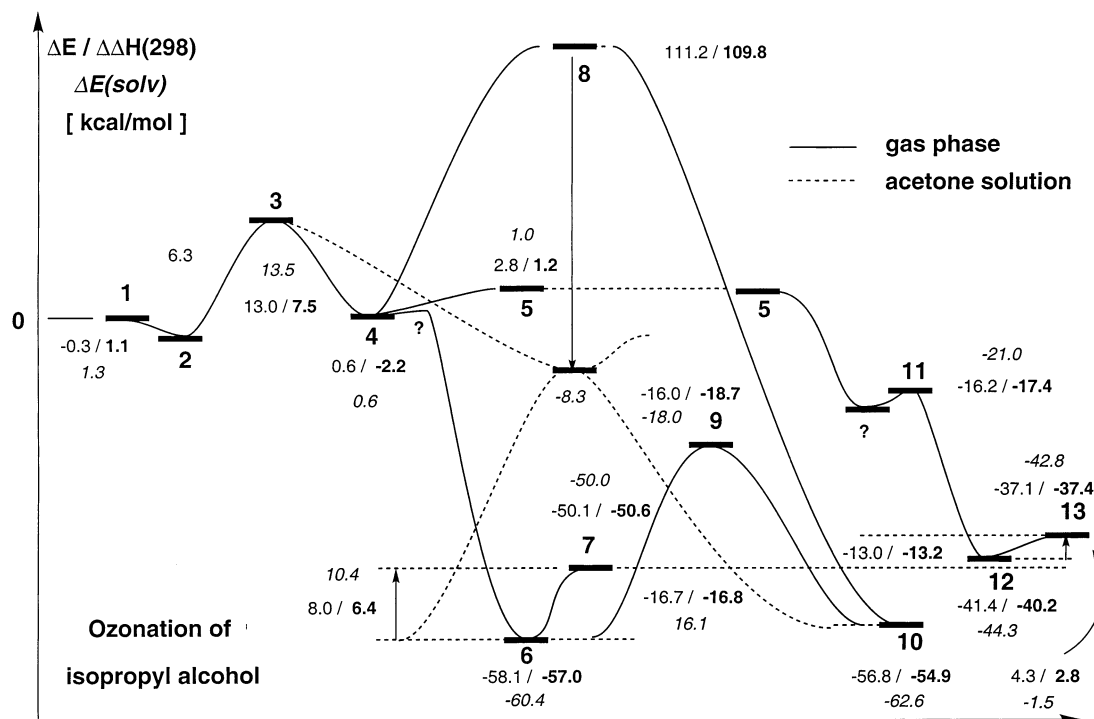
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**Figure 2.** Energy diagram for the ozonation of isopropyl alcohol in the gas phase. As a reference, the energy/enthalpy of the reactants isopropyl alcohol **1a** and ozone **1b** is used. Numbers in normal print correspond to energy differences  $\Delta E$  in the gas phase, in bold print to enthalpy differences  $\Delta\Delta H(298)$  at 298 K in the gas phase, and in italics to energy differences in acetone solution. Dashed lines indicate the change in the reaction mechanism caused by solvation of ion-pair **8** in acetone solution. Stationary points indicated by question marks could not be found. B3LYP/6-311++G(3df,3pd) calculations (solvation effects at B3LYP/6-31G(d,p)).

The electronic structure of the molecules studied was investigated by (a) determining atomic charges with the natural bond orbital (NBO) analysis of Weinhold<sup>47</sup> and (b) analyzing the electron density distribution with the help of bond critical points<sup>48</sup> and difference density distributions. All calculations were carried out with the program packages COLOGNE 2002<sup>49</sup> and Gaussian 98.<sup>50</sup>

### 3. Results and Discussion

The mechanistic scheme shown in Figure 1 was explored using MBPT2 and DFT/B3LYP theory. In Table 1, calculated relative energies, enthalpies, solvation energies, and free energies are listed using the energy (enthalpy) of the reactants isopropyl alcohol (**1a**) and ozone (**1b**) as a reference (heats of formation  $\Delta H_f^\circ(298)$ : 34.1 and  $-76.02$  kcal/mol).<sup>51</sup> Reaction energies and reaction enthalpies obtained at the B3LYP/

**Table 1.** Energetics of the Ozonation of Isopropyl Alcohol As Calculated at the B3LYP Level of Theory<sup>a</sup>

type	molecule	6-31G(d,p)		6-311++G(3df,3pd)		$\Delta\Delta H^\circ(298)$	$\Delta G(298)$
		$\Delta E(\text{gas})$	$\Delta(\text{sol})$	$\Delta E(\text{gas})$	$\Delta E(\text{sol})$		
reactants	<b>1a + 1b</b>	0.00	-3.80	0.00	0.00	0.00	0.00
complex	<b>2</b>	-1.19	-2.18	-1.02	0.60	0.31	8.26
TS	<b>3</b> , RDFT	12.08	-3.92	12.86	12.74	9.97	21.48
	<b>3</b> , BS-UDFT	4.92	-3.09	5.74	6.45	2.73	13.49
complex <sup>b</sup>	<b>4</b>	2.39	-3.75	0.59	0.64	-2.19	9.62
radical pair	<b>5a + 5b</b>	5.25	-5.60	2.77	0.98	1.21	-1.36
complex	<b>6</b>	-55.80	-6.12	-58.10	-60.42	-57.02	-49.54
product	<b>7a + 7b</b>	-47.74	-9.05	-50.09	-49.76	-50.59	-52.49
ion pair	<b>8a + 8b</b>	129.80	-123.30	111.22	-8.27	109.80	107.18
TS	<b>9</b>	-15.19	-5.78	-16.03	-18.01	-18.70	-8.52
product	<b>10</b>	-57.83	-5.73	-56.83	-62.08	-54.92	-42.46
TS	<b>11</b>	-13.81	-8.60	-16.21	-21.00	-17.39	-5.84
complex	<b>12</b>	-35.87	-6.68	-41.38	-44.26	-40.24	-32.49
product	<b>13a + 7b</b>	-31.05	-9.50	-37.13	-42.82	-37.39	-38.24

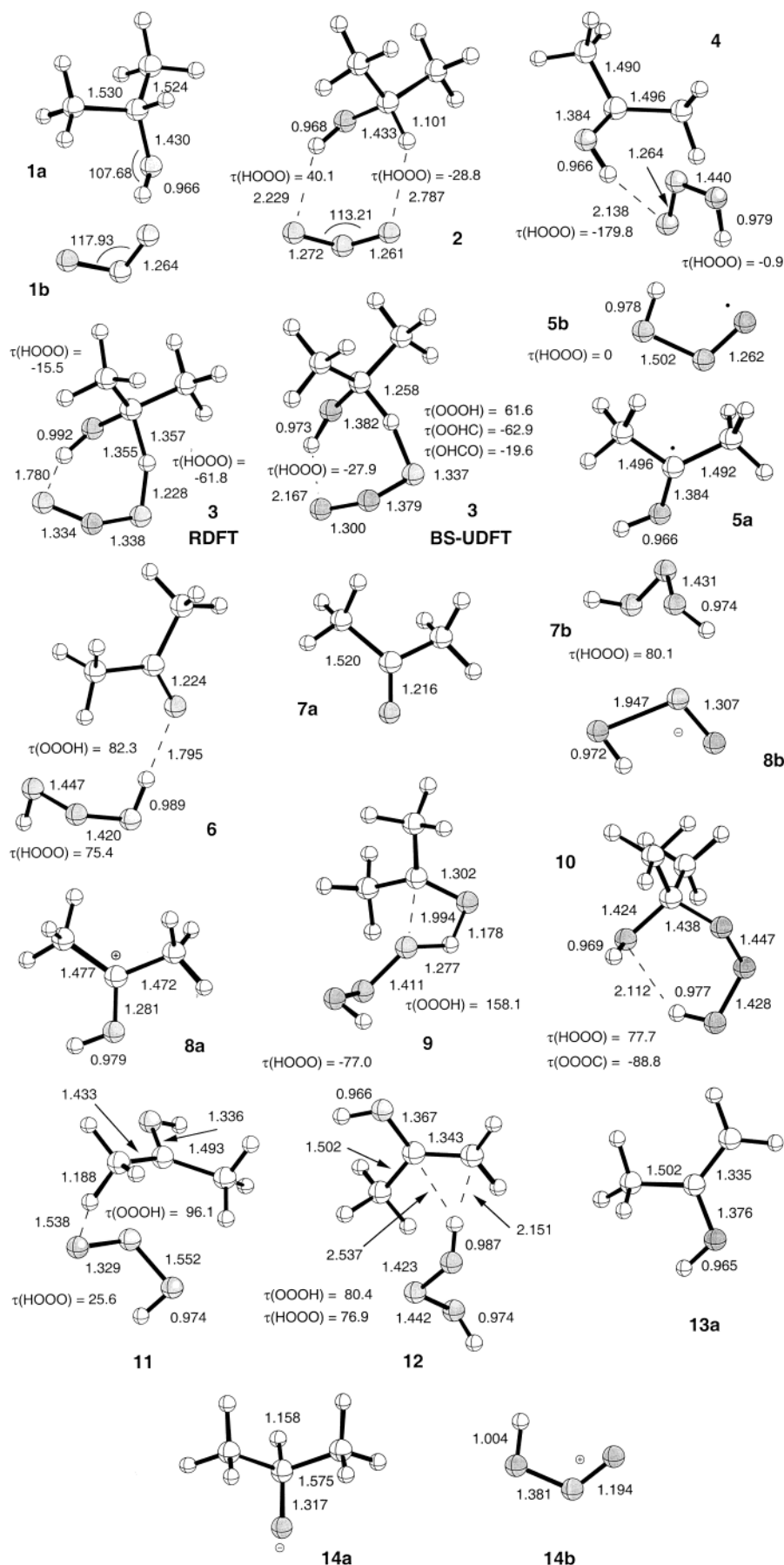
<sup>a</sup> All energies are in kcal/mol. B3LYP/6-311++(3df,3pd) energies were obtained at B3LYP/6-31G(d,p) geometries. Complex energies are given with BSSE corrections.  $\Delta(\text{sol})$  denotes the electrostatic part of the solvation energies calculated at SCIPCM/B3LYP/6-31G(d,p). For acetone, a dielectric constant of 20.7 was used. <sup>b</sup> The MBPT2/6-31G(d,p) geometry was used.

6-311++G(3df,3pd) level of theory are shown in the energy diagram of Figure 2. Calculated geometries are summarized in Figure 3.

B3LYP/6-311++G(3df,3pd) calculations suggest that isopropyl alcohol forms with ozone a van der Waals complex **2**, the stability of which is just 1.4 kcal/mol, which is reduced to 1.0 kcal/mol when BSSE corrections are included. If thermo-

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**Figure 3.** Geometries of the structures encountered in the ozonation of isopropyl alcohol. Bond lengths are in Å, and angles are in deg. B3LYP/6-31G(d,p) calculations. For 4, the UMBPT/6-31G(d,p) geometry is given (see text).

chemical corrections are added, **2** is no longer stable (destabilized by 0.3 kcal/mol relative to **1**, Table 1), so that an experimental detection of **2** can be excluded. Entropy is also more favorable for the separated reaction partners rather than **2** ( $\Delta G(298) = 8.3$  kcal/mol, see Table 1). In an acetone solution, a complex of the reaction partners does not exist, as was clearly revealed by the solvation corrections (Table 1) and the fact that in acetone solution more stable acetone–2-propanol complexes are formed. Hence, the previous claim (based on calculations with a small basis set not including BSSE corrections) that there is an ozone–isopropyl alcohol complex in the entry channel of the reaction<sup>2</sup> has to be rejected. An ozone–water complex was observed both experimentally and theoretically;<sup>52</sup> however, in this complex, one water H atom interacts with both terminal O atoms, and the dipole moments of water and ozone are arranged in an antiparallel fashion to lead to maximal dipole–dipole attraction. Such a complex configuration in the case of **2** would not be the starting point for a H-transfer reaction, and therefore an ozone–isopropyl alcohol complex should not play any role in the gas-phase mechanism. In acetone solution, **2** or any other ozone–alcohol complex can be excluded anyway.

Although **2** has no experimental relevance, it indicates on the PES the starting point for the migration of the activated (C–)H atom from isopropyl alcohol to ozone. At RDFT, the transition state geometry for this reaction (TS **3**) was found to describe a double H-transfer leading directly to **6** (Figures 1 and 3). However, this description is flawed by the fact that RDFT enforces an incorrect pairing of electrons. A stability test reveals that the RDFT solution for TS **3** is internally unstable (not observed in previous investigations), which simply has to do with the large biradical character of TS **3** (see Figures 1 and 3). The BS-UDFT description of TS **3** leads to an unreasonably small activation enthalpy of just 2.7 kcal/mol (Table 1), although the calculated geometry of the TS (Figure 3), suggesting a single H-transfer supported by some weak H-bonding between the OH group and the other terminal O atom of ozone, seems to be reasonable. Obviously, the reaction barrier is underestimated at the BS-UB3LYP level of theory, which has to do with the fact that H-migration from **1a** to **1b** represents a three-electron problem; that is, one of the  $\pi$ -electrons of ozone and the two bonding electrons of the C–H bond to be broken are involved. Odd-electron problems are known to lead to a notorious failure of DFT.<sup>39–41</sup> The self-interaction error (SIE) of the B-exchange functional (LYP does not possess a SIE error) leads to an underestimation of the TS energy as is amply discussed in the literature.<sup>38–41</sup> Applying the SIE-corrected theory,<sup>36,41</sup> an activation enthalpy  $\Delta H(298)$  of 9.7 kcal/mol is found.

IRC calculations at the BS-UB3LYP level of theory reveal that H-migration leads to a H-bonded complex **4** between the two radicals formed in the H-migration process (as was already indicated in the BS-UDFT geometry of TS **3**; see Figure 3). H-bonding involving radicals was observed before,<sup>53</sup> and it was found that DFT/B3LYP fails to describe these complexes in an appropriate way. Hence, the BS-UB3LYP structure of **4** was reoptimized at the UMBPT2 level of theory, which led to the geometry shown in Figure 3. These calculations reveal that for **4** the H-migration process is finished and that H-bonding

between the HOOO and the alcohol radical is more pronounced than that in TS **3**, but still weak. Single point BS-UB3LYP calculations at the UMBPT2 geometry suggest that **4** is 3.4 kcal/mol more stable than the separated radicals **5a** and **5b**. In the gas phase, **4** is an important intermediate, which by dissociation leads to the separated radicals **5** or, alternatively, reacts via internal H-migration to yield the H-bonded HOOO–ozone complex **6**.

It was not possible to find the TS leading from **4** to **6** at either the DFT or the MBPT2 level of theory. This could mean that the corresponding barrier is rather small (as is typical of a strongly exothermic reaction;  $-54.8$  kcal/mol, see Figure 2) or that it is elusive to the theoretical methods applied in this work. For example, the TS leading from **4** to **6** represents another odd-electron problem (again, three electrons are involved in the second H-transfer), which implies a SIE and a serious underestimation of the reaction barrier. An early TS would also possess large biradical character, which UMBPT2 is unable to describe. We refrained from searching for the TS because of the fact that the reaction observed by Plesničar and co-workers<sup>2</sup> actually takes place in acetone solution and that in this medium electrostatic interactions with the medium reduce the energy difference between the separated radicals **5** and the radical complex **4** to just 0.3 kcal/mol (Table 1). Considering, in addition, the entropy factor, which is in favor of the radical pair, then **5** is characterized by a free energy  $\Delta G(298)$ , which is 11 kcal/mol lower than that of **4**.

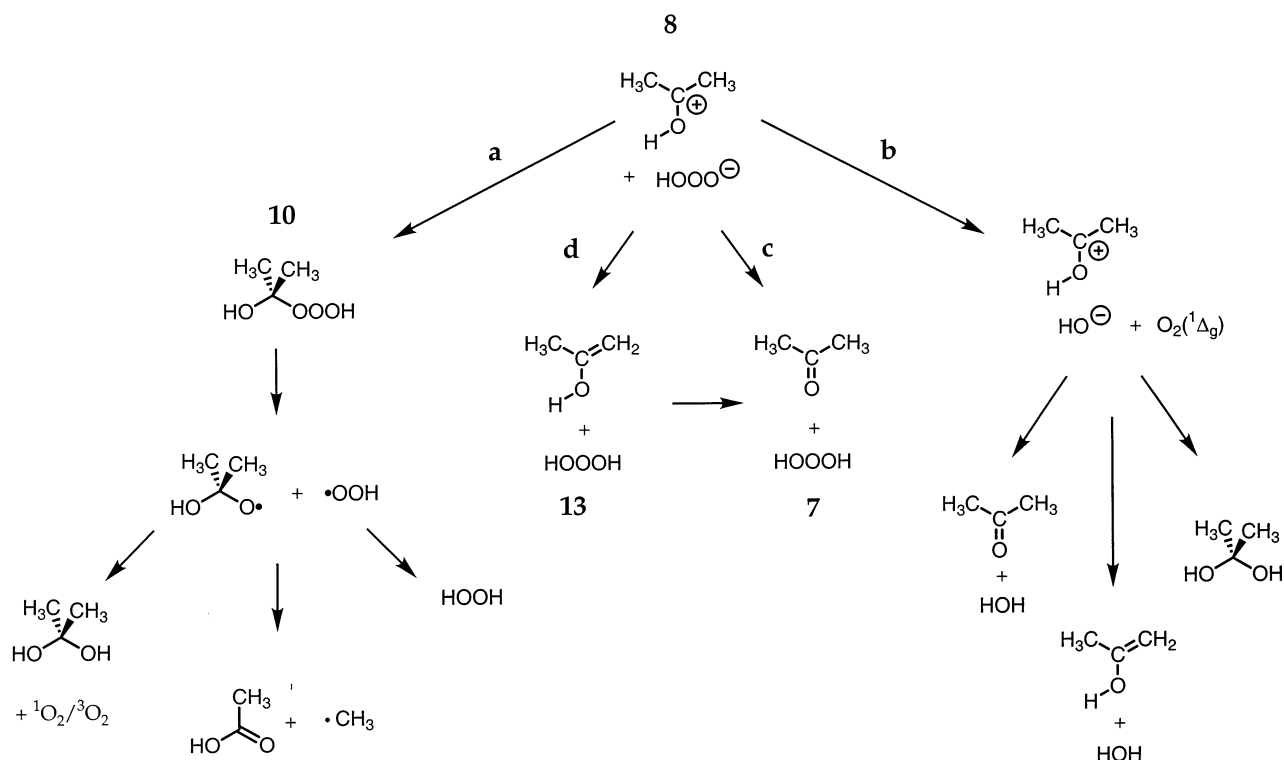
These results indicate that **4** no longer plays a role in the solution phase and that **5** may be directly formed from **1** via TS **3**. Furthermore, the polarity of the solvent acetone is sufficient to support an electron transfer from radical **5a** to radical **5b** or alternatively a heteropolar C–H bond cleavage in TS **3** so that the ion-pair **8** is formed. In the gas phase, this ion pair would have a relative energy of 111.2 kcal/mol ( $\Delta\Delta H(298)$ : 109.8 kcal/mol, Table 1), while in acetone, solution solvation reduces this energy by 123.3 kcal/mol to  $-8.3$  kcal/mol; that is, in acetone solution, the ion-pair **8** (in a solvent separated form) is 8.3 kcal/mol more stable than the reactants **1** and 9.3 kcal/mol more stable than radicals **5**.

The existence of the HOOO<sup>−</sup> anion was recently confirmed by a combination of experimental and quantum chemical investigations.<sup>5,6</sup> Theory predicts that the anion possesses a triplet ground state of little stability typical of a van der Waals complex between HO<sup>−</sup> and O<sub>2</sub>(<sup>3</sup> $\Sigma_g^-$ ). Chemically more relevant is a singlet state, which is 9.8 kcal/mol above the triplet state<sup>5</sup> and which has a strong O–OOH bond with some double bond character and a weakly covalent OO–OH bond (1.80 Å) according to CCSD(T)/6-311++G(3df,3pd) calculations (the longest O–O bond ever found for a peroxide). In aqueous solution, the singlet adopts a geometry closely related to that of HOOOH (OO(O), 1.388; (O)OO(H), 1.509 Å;  $\tau$ (OOOH), 78.3<sup>o5</sup>), justifying that the singlet state can be considered as the anion of HOOOH. Dissociation into the HO anion and O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) requires 15.4 ( $\Delta H(298)$ : 14.3) kcal/mol,<sup>5</sup> thus giving the ion-pair **8** some finite lifetime in acetone solution.

These results clearly indicate that the mechanism of the reaction in the gas phase differs from that in solution. The gas-phase mechanism involves molecules with radical character and is characterized by the intermediary of **4** from where the reaction bifurcates either to radicals **5**, which can recombine to yield

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**Figure 4.** The central role of ion-pair **8** for the mechanism of the ozonation of isopropyl in acetone solution.

the alkyl hydrotrioxide **10** (Figures 1 and 2), or via a methyl H-bonded intermediate (not found in this work) and TS **11** to the enol–HOOOH complex **12**. If a second HOOOH molecule forms a H-bond to the O atom of the enol, H-migration will yield the HOOOH-complexed acetone **6**. This rearrangement has a lower activation enthalpy<sup>54</sup> than is needed for the direct tautomerization from the uncomplexed enol **13** to the uncomplexed acetone **7** (Figures 1 and 2).

Results are in line with known thermochemical data: The heat of formation of HOOOH was estimated to be between  $-23$  and  $-29$  kcal/mol.<sup>55</sup> Utilizing the heat of formation for acetone ( $-51.9$  kcal/mol<sup>51</sup>), we obtained a reaction enthalpy  $1 \rightarrow 7$  from  $-44$  to  $-50$  kcal/mol, which comes close to the calculated value of  $-50.6$  kcal/mol. The enol of acetone is known to be  $13.9 \pm 2$  kcal/mol less stable in the gas phase than the keto form.<sup>56</sup> The enthalpy difference obtained in this work is 13.2 kcal/mol (Table 1). Hence, the data listed in Table 1 can be considered reliable.

In the gas phase, **6** is formed with an excess energy of more than 60 kcal/mol, which is sufficient to react via TS **9** to alkyl hydrotrioxide **10**. However, in solution, energy dissipation is fast, and a barrier of 38 kcal/mol (the solvent effect on the barrier is small; see Table 1) can no longer be surmounted by the reaction complex. (All attempts to detect by NMR spectroscopic techniques the hydrotrioxide of isopropyl alcohol in solutions of HOOOH in acetone at temperatures below 10 °C failed. Hydrogen trioxide was generated independently for this purpose by the low-temperature ozonation of hydrazobenzene.<sup>18d,e</sup>) Once

the acetone complex **6** is generated, it should be stable enough to be observed experimentally at low temperatures. The complex binding enthalpy (BSSE corrected) is 6.4 kcal/mol, typical of the binding energy of a H-bonded ketone–water complex.<sup>57</sup> Solvation effects reduce the binding energy by 1.6 kcal/mol, while entropy effects destabilize complex **6** relative to the separated molecules **7a** and **7b** (see  $\Delta G(298)$  values in Table 1).

Depending on the structure of the ion-pair **8** in acetone solution (solvent separated ion pair; tight ion pair with the anionic charge opposite to the cationic charge; H-bonded ion-pair  $R^+-OH\cdots^-O_3H$ ), a charge neutralizing reaction to yield **6** is possible, as indicated by the dashed lines in Figure 2. The formation of the enol complex **12**, which would imply a proton migration from the methyl group of cation **8a** to the terminal O of anion **8b**, cannot be excluded. The enol could then rearrange to give acetone via a second path.

#### 4. Chemical Relevance of Results

In a sufficiently polar solvent such as acetone, the ozonation of secondary alcohols (e.g., isopropyl alcohol) leads in a fast hydride abstraction reaction (activation enthalpy of 7.5 kcal/mol, Figure 2) to the ion-pair **8** that is 8 kcal/mol more stable than **1**. Similar results can be expected for less polar solvents such as methyl acetate ( $\epsilon = 6.68^{46}$ ), dimethyl ether ( $\epsilon = 5.02^{46}$ ), or methyl *tert*-butyl ether ( $\epsilon = \text{ca. } 4$ ) due to the fact that a larger amount of isopropyl alcohol ( $0.3\text{--}0.5 \text{ M}$ ;  $\epsilon = 18.3^{46}$ ) is in the reaction mixture and, in addition, a considerable amount of water ( $\epsilon = 78.5^{46}$ , Figure 4) is formed in the reaction (see point b below). This is in line with the fact that, for the solvents

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mentioned, about the same product ratios were observed experimentally.

According to the calculations carried out in this work, the ion-pair **8** should play a central role for the reaction mechanism:

(a) Collapse of the ion pair yields hydrotrioxide **10** of isopropyl alcohol (see Figure 4, possibility a) in a strongly exothermic reaction ( $\Delta E(\text{solv}) = -54.3$  kcal/mol, Figure 2). Even when considering dissipation, a sufficient amount of energy should be available to cleave the (C)O–O(OH) bond to yield an alkoxy radical and the HOO• radical, which by abstraction of an H atom forms hydrogen peroxide (Figure 4). If the alkoxy radical abstracts a H atom from OOH radical (in the solvent cage), a diol and molecular oxygen ( $^1\text{O}_2/^3\text{O}_2$ ) could be formed.<sup>24</sup> Although singlet oxygen was actually detected among the decomposition products by typical  $^1\text{O}_2$  acceptors (1,3-diphenylisobenzofuran, 9,10-dimethylanthracene, and tetraphenylcyclopentadienone<sup>2,3</sup>) and by chemiluminescence in the infrared region,<sup>58</sup> the diol was not detected.<sup>1,2</sup> Loss of a methyl radical would convert the alkoxy radical into acetic acid (Figure 4), which was observed experimentally.<sup>1,2</sup>

(b) The HOOO<sup>−</sup> anion can decompose into hydroxy anions and singlet oxygen, provided its excess energy of  $13.5 + 8.3 = 21.8$  kcal/mol (Figure 2) is not dissipated and suffices for the dissociation reaction, which requires 14.3 kcal/mol.<sup>5</sup> If this is the case for acetone plus water, its enol tautomer plus water or a diol (see Figure 4) could be formed. Singlet oxygen  $\text{O}_2(^1\Delta_g)$  has been observed,<sup>2,3,58</sup> thus suggesting that path b is likely. This is confirmed by the generation of an appreciable amount of water in the reaction (also see above).<sup>2</sup>

(c) If the HOOO<sup>−</sup> anion abstracts a proton from the OH group of **8a**, acetone and HOOOH will be generated (path c, Figure 4). The anion could also abstract a proton from one of the methyl groups to give the enol, which then rearranges to acetone.

We also considered the possibility that a proton is abstracted from the alcohol group by ozone, although such a reaction would be in contradiction with the known electrophilic character of ozone. Proton abstraction would lead to an alkoxy anion **14a**

and the cation HOOO<sup>+</sup> **14b** shown in Figure 3. Ion-pair **14** would be destabilized relative to ion-pair **8** by 134 kcal/mol (difference in enthalpies) and, therefore, can be truly excluded from the reaction mechanism.

All solution-phase products of the ozonation of isopropyl alcohol can be explained with the help of the ion-pair **8**. An ozone–alcohol complex such as **2** does not play any role in the solution phase. NBO charges<sup>47</sup> and an analysis of the electron density distribution<sup>48</sup> reveal that TS **3** in acetone solution obtains more polar, although not ionic, character. Nevertheless, it facilitates the ion-pair formation. The formation of the radical pair **5** should be largely suppressed in the solution-phase mechanism of the alcohol ozonation. However, it cannot be excluded that in the course of the alkyl hydrotrioxide decomposition free radicals are generated. This would involve homolytic cleavage of the RO–OOH bond as the weakest bond (see ref 3 and references therein).

Ozone accelerates the conversion of alcohols to aldehydes (ketones), which is clearly a factor increasing the toxicity of ozone. Alcohol consumption during the time of an increase of ozone concentrations in industrial areas during the summer is known to lead to considerable health risks, and the reactions discussed in this work are relevant in this connection. Also, the administration of medical ozone may be accompanied by unwanted side effects if alcohol is consumed.

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**Supporting Information Available:** Geometries and energy data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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