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Peculiar Structure of the $HOOO^-$ Anion

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Abstract: The $HOOO^-$ anion (**1**) can adopt a triplet state (**T-1**) or a singlet state (**S-1**), where the former is 9.8 kcal/mol ($\Delta H(298) = 10.3$ kcal/mol) more stable than the latter. **S-1** possesses 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, **S-1** adopts a geometry closely related to that of HOOOH (OO(O), 1.388 Å; (O)OO(H), 1.509 Å; τ(OOOH), 78.3°), justifying that **S-1** is considered the anion of HOOOH. Dissociation into HO anion and $O_2(^1\Delta g)$ requires 15.4 ($\Delta H(298) = 14.3$; $\Delta G(298) = 8.9$) kcal/mol. Structure **T-1** corresponds to a van der Waals complex between HO anion and $O_2(^3\Sigma g^-)$ having a binding energy of 2.7 ($\Delta H(298) = 2.1$) kcal/mol. Modes of generating **S-1** in aqueous solution are discussed, and it is shown that **S-1** represents an important intermediate in ozonation reactions.

Introduction

Reactions of ozone with saturated organic materials are at the focus of current research interests. Ozonation reactions play an important role in the polluted atmosphere (reactions of ozone with air pollutants),[1,2] for wastewater purification and drinking water processing (oxidation of contaminants with ozone),[3−6] in toxicity studies of ozone and activity investigations of medical ozone,[7] in polymer degradation (aging of polymers by ozone),[8] and in chemical synthesis[9] as for example the low-temperature ozonation of organic substrates.[10,11] Although these topics have been investigated for the last 3 decades,[12,13] the mechanism of the ozonation of saturated compounds is still unclear. Three possible reactions of ozone are presented in Scheme 1:[1−13] (a) oxygen transfer via a possible intermediate I (reaction 1 in Scheme 1); (b) electron transfer leading to ion pair II (reaction 2, Scheme 1), which can leave the solvent cage or collapse to yield the O-transfer product of reaction 1; (c) H abstraction by the radical anion of ozone formed in reaction 2 (reaction 3) or ozone itself (reaction 4, Scheme 1). In these reactions, the radicals $HO_3^\bullet$ and $RO_3^\bullet$ or alternatively the anions HO_3^- and RO_3^- occur as intermediates, which can be considered as derivatives of hydrogen trioxide, HOOOH, or ozone. The existence of HOOOH and ROOOH as intermediates in the low-temperature ozonation of various saturated organic compounds[14,15] was recently confirmed by ^{17}O NMR spectroscopy.[14e] HOOOH is presently discussed as an intermediate in the antibody catalysis of the oxidation of water by singlet dioxygen yielding a quasi-unlimited amount of hydrogen peroxide.[16]

Although the HOOO radical has been the subject of several theoretical[17] and experimental studies[18] that led to convincing evidence for its existence,[18] much less attention was devoted to the elusive hydrotrioxide anion, $HOOO^-$ (**1**) and its deriva-

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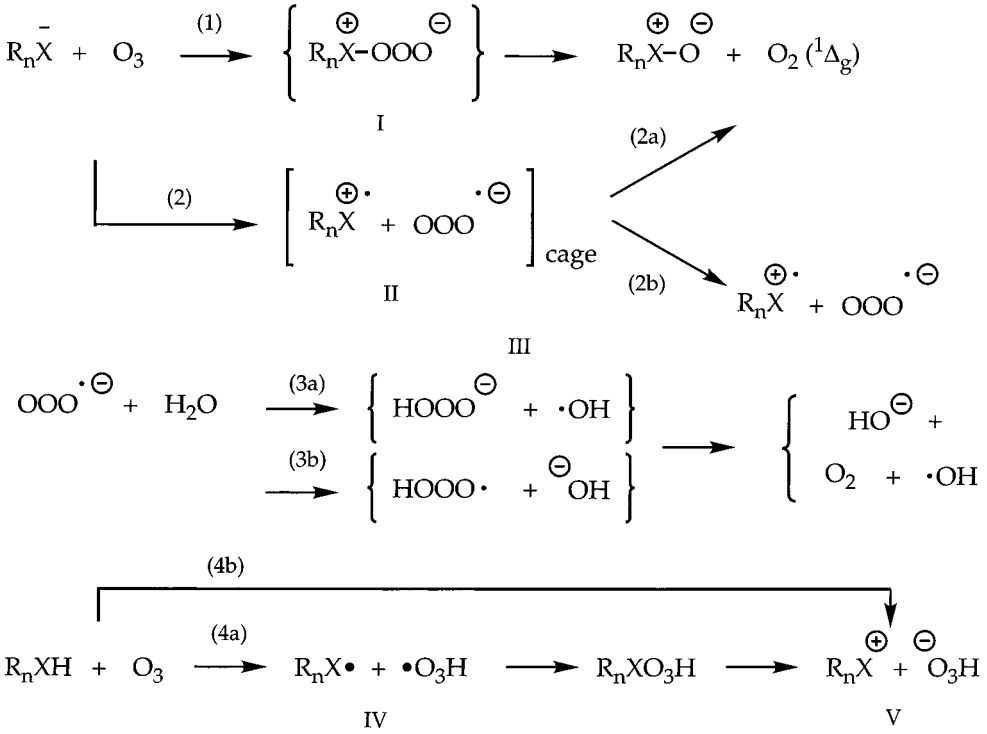
Scheme 1. Possible Mechanism of Ozonation Reactions



tives ROOO⁻. Trioxide anions were invoked in mechanistic explanations of ozonation reactions since the 1960s (for a review of the early work, see refs 12 and 13). Nangia and Benson[19] suggested anion **1** as an intermediate in the first step of the ozonation of saturated C−H bonds (hydrocarbons, alcohols, ethers, acetals) formed by the transfer of the hydride ion to ozone to form an anion pair, $R^{+-}OOOH$. Cacace et al.[18a] provided in their recent neutralization−reionization (NR) mass spectrometric study on HOOO radicals, using protonated ozone ($HOOO^+$) as the charged precursor, experimental evidence for the existence of anion **1**. Formally, anion **1** could be generated from hydrogen trioxide acid in a basic environment.

There are only two theoretical studies (HF and MP) on the structure of the $HOOO^-$ anion,[20,21] which both assumed the ground state of the $HOOO^-$ anion (**1**) to be a singlet state. However, if one considers **1** to be formed from a combination of $H(^2S)$ and the $O_3^-(^2B_1)$ anion, both a singlet and a triplet state can result. In this work we will show that **1** possesses two low-lying states where the triplet state **T-1** is lower in energy than the singlet state **S-1**. These two states have strongly differing geometries so that the question has to be answered whether one can speak of two different states of the same species or two different molecules with different geometries and different electronic structures. We will investigate the peculiar bonding situation in these anions to see whether they can be related to HOOOH. Also, we will discuss the role of **1** (or its derivatives $ROOO^-$) in the ozonation reactions shown in Scheme 1, where aqueous solutions (wastewater purification, drinking water processing, toxicity of ozone for the human body, etc.) or humid (fog) atmospheres (ozone reactions at the surface of water droplets) are considered.

Computational Methods

In this work, MP2, MP4,[22] density functional theory (DFT),[23] and coupled cluster (CC) calculations[24] were carried out with a variety of basis sets. These calculations revealed that calculated properties of **1** strongly depend on the method and basis set employed because both the triplet and the singlet potential energy surface (PES) are rather flat in the vicinity of the equilibrium geometries of **S-1** and **T-1**. The most reliable description of **1** was obtained using CCSD(T) (inclusion of all single and double excitations and adding triple excitations in a perturbative way[25]) in combination with Pople's triple ζ basis 6-311++G-(3df,3pd) basis set,[26a] which contains a set of diffuse functions to

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describe the anionic charge in an appropriate way and a set of f functions found necessary in the case of peroxide bonds.[27] CCSD(T)/6-311++G-(3df,3pd) calculations were also used to characterize the stationary points found on the PES by vibrational frequencies and to determine the infrared spectrum of **1**.

The triplet states were determined by UHF−CCSD(T), which has been shown to lead to the complete annihilation of the first spin contaminant in the complete space of the S and D excitations.[26b] Accordingly calculated $\langle S^2 \rangle$ values were close to the ideal value of 2 (UHF, 2.049, and UHF−CCSD(T), 2.000 (**T-1**); B3LYP, 2.015 (**T-1**) and 2.012 (**T-2**)), thus reflecting only negligible contributions from S+2 and higher contaminants.

Results of the MP calculations turned out to be less reliable and will not be discussed in the following (although CCSD(T) geometry optimizations were started from preliminary MP2 or MP4 geometries). DFT employed with the same basis set and the B3LYP hybrid functional[28] turned out to be more reliable although it does not provide the accuracy of the CCSD(T) calculations in the case of **1**. Because of the high calculational cost of the CCSD(T) calculations, the water complex of **1** and all solution calculations were carried out at the B3LYP/6-311++G(3df,3pd) level of theory.

Binding energies of the van der Waals complexes investigated in this work were corrected for basis set superposition errors (BSSEs) using the counterpoise method of Boys and Bernardi.[29] For all gas-phase structures considered vibrational frequencies were calculated at the B3LYP/6-311++G(3df,3pd) level of theory to determine enthalpies at 298 K and to predict heats of formation $\Delta H_f^0(298)$ for the compounds considered. In this connection, CCSD(T) calculations were carried out for appropriate reference compounds.

Nonspecific solvation was described with the self-consistent reaction field (SCRF) approach by employing Tomasi's continuum model.[30] For the situation in aqueous solution, the dielectric constant of water at room temperature was chosen ($\epsilon = 78.39$[31]) while the situation of a typical organic solvent was modeled with the dielectric constant of cyclohexane ($\epsilon = 2.023$ [31]). Geometries were reoptimized for a given value of ϵ to determine the influence of the solvent. The united atom model for Hartree−Fock (UAHF)[30b] was used to build the molecular cavities. The error due to the effect of the electronic charge of the solute being located outside the cavity (escaped charge) was minimized by normalizing the polarization charge on the cavity surface in two different ways. During geometry optimization all calculated charges on the cavity surface were scaled by a constant factor.[30c] For the optimized geometry of the solute, a single point calculation was carried out, in which the effect of the escaped charge was accounted for by means of additional effective charges distributed over the cavity surface according to the solute electron density.[30d] As has been shown[30b] the latter charge normalization method is more accurate in the case of anions.

Changes in the gas phase geometry when using the dielectric constant ϵ(cyclohexane) were small, and therefore, the geometry optimization in solution was only carried out for anion **1**.[30c] Both in cyclohexane and aqueous solution reoptimization of **T-1** led to its dissociation while solvated **S-1** occupies a minimum under solvation conditions. Dissociation of **S-1** into HO^- and $O_2(^1\Delta_g)$ in solution was tested by stretching the distance (H)O−O(O) stepwise by 0.05 Å and determining geometry and solvation energy for each new interaction distance. At a critical distance of 1.8 Å, SCRF optimizations did no longer converge because of the well-known problems observed in general for anions.[30b] We note in this connection that the SCRF descriptions of the anion **1** depend on basis set, geometry, and the charge renormalization model used. It was necessary to employ a large basis and the procedure described above to obtain reasonable solvation energies. It was not feasible to calculate under these conditions the vibrational frequencies of the solute.

The free energy G^s of a solute is influenced by the solute−solvent interactions (electrostatic, exchange repulsion, and dispersion interactions plus cavity work) but also by the thermal motions of the solute in solution. The solvation energy ΔG_{solv} is given as the difference $G^s - G°$, where $G°$ is the free energy of the molecule in the gas phase: $G°(298) = H(298) - TS$; i.e., $G°$ depends on the energy and the thermal motions of the molecule in the gas phase. In this work, we used the *reduced* solvation energy ΔG^*_{solv},[30e] for which the difference in the contributions arising from the molecular motions in the gas phase and in solution is neglected.

The electronic structure of **1** was investigated by (a) determining atomic charges with the natural bond orbital (NBO) analysis of Weinhold[32] and (b) analyzing the electron density distribution with the help of bond critical points[33] and difference density distributions. The two criteria for covalent bonding (existence of a bond critical point and a negative, stabilizing energy density at the bond critical point) given by Cremer and Kraka[34] were applied to investigate bonding in anion **1**. Use of the Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$ is not useful in this connection because it describes for bonds between electronegative atoms depletion rather than concentration of the density in the bond region as is well documented for F_2.[34]

Results and Discussion

The most stable structure of **1** is the **T-1** state, which according to geometry and electronic structure corresponds to a van der Waals complex between the HO anion and molecular oxygen, $O_2(^3\Sigma g^-)$, rather than a triplet state of the anion of HOOOH (Figure 1). **T-1** is linear, and the distance O2O3 is 2.613 Å, which is 0.2−0.4 Å larger than the normal O···O van der Waals distance (2.2−2.4 Å[31]). The PES close to the equilibrium geometry is flat so that distortion of the linear structure requires little energy. We note in this connection that B3LYP/6-311++G(3df,3pd) predicts a nonlinear van der Waals complex **T-1** (O2O3 = 2.609 Å) with a T structure (O_2 on top of the HO bond), in which atom O2 can establish van der Waals interactions with both O3 and the H atom. Because of the known deficiencies of DFT to describe weakly bound van der Waals complexes,[35] the CCSD(T) structure is more reliable.

Complex **T-1** is 2.7 kcal/mol ($\Delta H(298) = 2.1$ kcal/mol, given in bold print in Scheme 2) more stable than the separated

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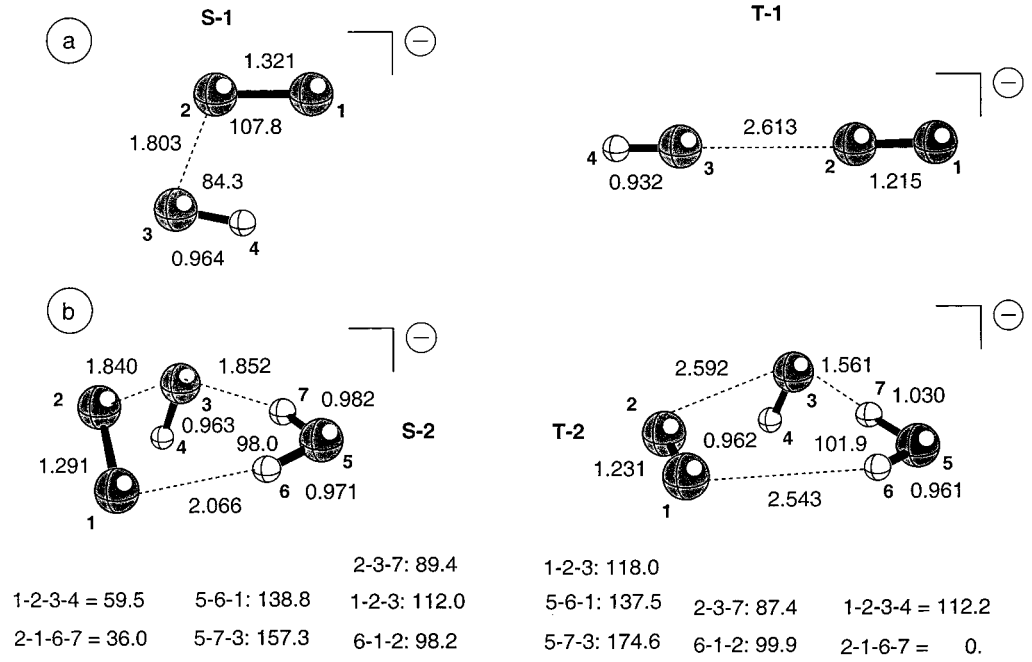
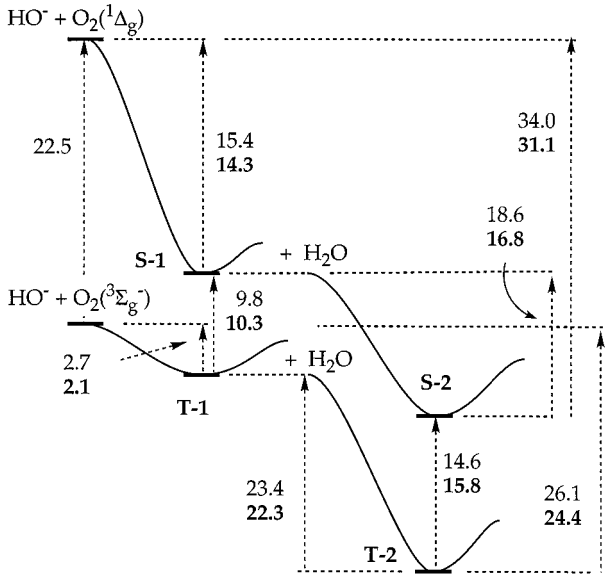


Figure 1. CCSD(T)/6-311++G(3df,3pd) geometries of **1** and B3LYP/6-311++G(3df,3pd) geometries of **2**. Distances are in Å, and angles are in deg.

Scheme 2. Relative Energies (Normal Print) and Enthalpies $\Delta H(298)$ (Bold Print) of **1** and **2** According to CCSD(T)/6-311++G(3df,3pd) Calculations with All Values in kcal/mol



monomers. Its structure and stability is a result of (destabilizing) exchange repulsion between the oxygen lone pair electrons, (stabilizing) dispersion interactions, and (stabilizing) dipole-induced dipole interactions, where the latter can be rationalized by utilizing calculated NBO charges (Scheme 3).

The singlet state **S-1** adopts a planar syn form that is 9.8 ($\Delta H(298) = 10.3$) kcal/mol less stable than the **T-1** form but 15.4 ($\Delta H(298) = 14.3$) kcal/mol more stable than HO^- anion and $O_2(^1\Delta g)$. Although **S-1** also possesses a relatively long O2O3 distance (1.803 Å; B3LYP, 1.798 Å; Figure 1), the molecule is no longer a van der Waals complex. Considering that a normal OO bond in a peroxide is about 1.45 Å[36] and that the lengthening of the van der Waals distance for O2, O3 (normal, 2.2−2.4 Å;[31] **T-1**, 2.6 Å) in **T-1** is 0.2−0.4 Å, an OO distance of 1.8 Å does not seem to exclude covalent bonding. In favor of covalent bonding are the following observations:

(a) The bond O1O2 is significantly lengthened ($O_2(^1\Delta g)$, 1.215 Å;[37] **S-1**, 1.321 Å), while the corresponding change in **T-1** is rather small ($O_2(^3\Sigma g^-)$, 1.207 Å;[37] **T-1**, 1.217 Å). Hence interactions between the HO and O_2 part are much stronger in **S-1** than in **T-1**. (b) There is a bond critical point between O2 and O3 (B3LYP/6-311++G(3df,3pd), 0.75 e/Å^3; HOOH, 1.93 e/Å^3), and the energy density is negative (−0.10 hartree/Å^3; HOOH, −1.41 hartree/Å^3) at this point. According to the criteria established by Cremer and Kraka,[34] a very weak covalent bond should exist between O2 and O3. (c) Simple electronic structure considerations suggest a donor bond between O3 and O2 (see Scheme 3). The $O_2(^1\Delta g)$ state is a two-configurational state with the character of an open shell singlet biradical (see, e.g., ref 36). The negative charge of the HO anion polarizes the π-electrons of $O_2(^1\Delta g)$ in the way that the spin-coupled single electrons occupy the in-plane π-orbitals and are pushed from O2 to O1. Hence, O3 can donate negative charge to O2 via the in-plane π-orbitals thus establishing a weak covalent bond.

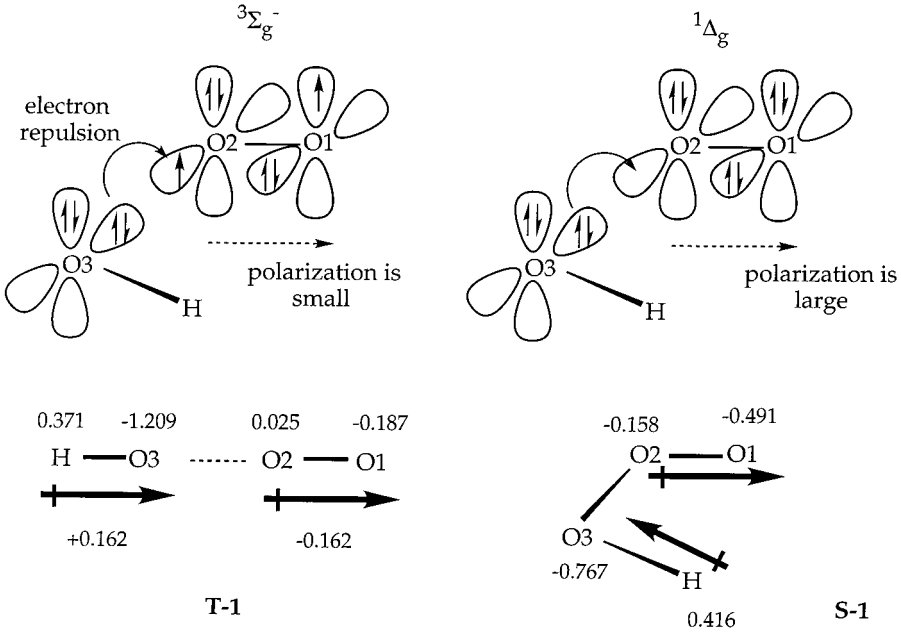
π-Polarization is also responsible for the fact that the syn planar **S-1** form is more stable than the trans form by 2.2 kcal/mol. In the syn form dipole-induced dipole interactions (supported by attraction between O1 and H) are stronger than in the trans form. The induction forces stabilizing **S-1** are much weaker in **T-1** due to stronger exchange repulsion between the in-plane π-electrons that keep the two monomers in **T-1** at larger distance (Scheme 3). If **T-1** is forced into the geometry of **S-1**, its energy raises by 13 kcal/mol so that it becomes less stable than the **S-1** state.

Deprotonation of HOOOH can only lead to the **S-1** state, which could dissociate to the HO anion and $O_2(^1\Delta g)$ provided an excess enthalpy of 14.3 kcal/mol is available for **S-1** (Scheme 2). Although such processes may occur in the gas phase, it is

(36) Cremer, D. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; p 1.

(37) Huber, K. P.; Herzberg, G. H. *Molecular Spectra and Molecular Constants of Diatomic Molecules*; Van Nostrand-Reinhold: New York, 1979.

Scheme 3. Orbital Diagrams and Electron Configuration for the Interaction of the HO Anion with Molecular Oxygen in Its $^3\Sigma g^-$ (Left) or $^1\Delta g$ State (Right) To Give **T-1** and **S-1** with NBO Atomic Charges for the CCSD(T) Geometries



more realistic to consider the situation in solution where due to solvation the relative energies of **T-1** and **S-1** can change. We considered first specific solvation by one water molecule, which yields complexes **T-2** (**T-1**·H_2O) and **S-2** (**S-1**·H_2O) (see Figure 1). In complex **2**, one water molecule forms with **1** a six-membered ring hold together by a stronger and a weaker H-bond in both cases water being the donor while the OH bond of **1** (O3H4) is exocyclic oriented. Similar structures were found for the complex of the HOOO radical with water although in this case the OH group established the short H-bond and one of the water OH bonds was exocyclic.[38,39]

Water stabilizes **S-1** by another 18.6 ($\Delta H(298) = 16.8$) kcal/mol, i.e., **S-2** is 34.0 ($\Delta H(298) = 31.1$) kcal/mol more stable than the separated monomers, while in the triplet state the stabilization energy is even 23.4 ($\Delta H(298) = 22.3$) kcal/mol, i.e., **T-2** becomes 26.1 ($\Delta H(298) = 24.4$) kcal/mol more stable than the separated monomers. The energy difference between the **T-2** and the **S-2** complex is 14.6 ($\Delta H(298) = 15.8$) kcal/mol according to CCSD(T) energies calculated at B3LYP geometries.

The calculated geometries reveal that the stronger of the two H-bonds is directed toward the oxygen of the HO anion. In the case of **S-2,** this leads to a weakening of the O2O3 bond (the bond length increases from 1.803 to 1.840 Å, Figure 1) while in the case of **T-2** van der Waals interactions between HO anion and $O_2(^3\Sigma g^-)$ are increased (shortening of the distance O2O3 from 2.613 to 2.592 Å). These changes are a result of the different bonding situations in **S-1** and **T-1**. The hydrogen bond in **S-2** polarizes the negative charge at O3 in the direction of atom H7. The OH group becomes a weaker lone pair donor, and this leads to a weakening of the O3O2 bond. At the same time exchange repulsion is lowered so that in **T-2** van der Waals interactions with $O_2(^3\Sigma g^-)$ can become stronger where the weak hydrogen bond H6···O1 plays a supportive role.

Anion **S-1** can be generated in four different ways: (a) proton abstraction from HOOOH in the presence of a reaction partner of sufficient basic character; (b) hydride abstraction from a hydrocarbon by ozone; (c) capture of an electron by the HOOO radical; (d) capture of an electron by ozone yielding $O_3^{\bullet-}(^2B_1)$ (see Figure 2), which by reaction with $H(^2S)$ leads to **S-1**. In Table 1, heats of formation $\Delta H_f^0(298)$ based on the quantum chemical calculations carried out in this work (for details of the calculation see footnotes of Table 1) are listed for **1** and **2** and suitable reference compounds so that the four possible formation modes of **S-1** can be considered in detail.

The proton affinity of **S-1** is 365.7 kcal/mol, which means that HOOOH is clearly more acidic than HOOH ($\Delta H(298) = 376.7$) and HOH ($\Delta H(298) = 391.3$, Table 1) (see also ref 21). Solvation in aqueous solution will reduce these differences as the HO^- and HOO^- anions possessing a more localized negative charge can be better solvated than the $HOOO^-$ anion (see for the reduced solvation energies ΔG^*_{solv} in Table 2). For hydrocarbons, which can stabilize positive charge, a hydride transfer to ozone will be an exothermic reaction leading, as suggested by Nangia and Benson,[17] to ion pairs $R^{+-}OOOH$. The electron affinity of the $HOOO^\bullet$ radical is 1.188 eV (27.4 kcal/mol, Table 1), which is considerably smaller than that of the $HO^\bullet$ radical (1.828 eV; 43.0 kcal/mol) but somewhat larger than that of the $HOO^\bullet$ radical (1.078 eV; 24.8 kcal/mol).[40] Complexation of the $HOOO^\bullet$ radical by one water molecule increases the electron affinity to 2.29 eV (37.7 kcal/mol), which simply reflects the fact that the complexation energy of **S-1** is higher (18.6 kcal/mol) than that of $HOOO^\bullet$ (8 kcal/mol).[38] Similar observations were made for the $HO(H_2O)$ (EA: <2.95 eV; <68 kcal/mol[41]).

In Figure 3, the infrared (IR) spectra of **T-1** and **S-1** calculated at CCSD(T)/6-311G++(3df,3pd) are shown. The triplet state can be identified by the OH stretching band (3799 cm^{-1};

(38) Aloisio, S.; Francisco, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 8592.
(39) Cerkovnik, J.; Erzen, E.; Koller, J.; Plesničar, B. *J. Am. Chem. Soc.* **2002**, *124*, 404.
(40) (a) Schulz, P. A.; Mead, R. D.; Jones, P. L.; Lineberger, W. C. *J. Chem. Phys.* **1982**, *77*, 1153. (b) Oakes, J. M.; Harding, L. B.; Ellison, G. B. *J. Chem. Phys.* **1985**, *83*, 5400.
(41) Golub, S.; Steiner, B. *J. Chem. Phys.* **1968**, *49*, 5191.

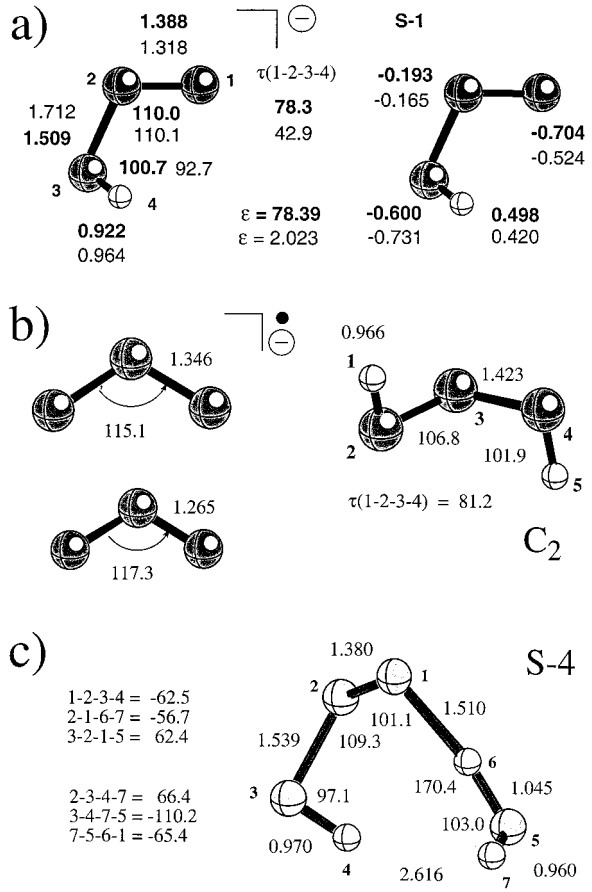


Figure 2. (a) PISA/B3LYP/6-311++G(3df,3pd) geometries (left side) of **S-1** for dielectric constant $\epsilon = 2.023$ (normal print, cyclohexane) and $\epsilon = 78.39$ (bold print, water). Also shown are NBO charges (right side) in electrons. (b) CCSD(T)/6-311++G(3df,3pd) geometries of O_3, $O_3^{\bullet -}$, and HOOOH. (c) B3LYP/6-311++G(3df,3pd) geometry of **S-4**. Distances are in Å, and angles are in deg.

intensity $I = 103$ km/mol), which is comparable to that of the HO radical (3738 cm^{-1} [37]) or the HO^- anion (3700 cm^{-1} [37]), and the OO stretching frequency (1549 cm^{-1}; intensity $I = 54$ km/mol) similar to that of $O_2(^3\Sigma g^-)$ (1580 cm^{-1} [37]). **S-1** is easy to recognize by the OO stretching bands at 1144 and 973 cm^{-1} ($I = 185$ and 63 km/mol; ozone: 1110 and 1042 cm^{-1} [42]).

We also studied nonspecific solvation of **S-1**, **S-2, T-1,** and **T-2** in aqueous solution (yielding **S-3** and **T-3**; see Figure 4) modeling the solvent effect by a polarizable continuum[30] for a typical organic solvent (cyclohexane, $\epsilon = 2.023$) and aqueous solution ($\epsilon = 78.39$). In general, nonspecific solvation will be larger if the anion is smaller; i.e., the OH^- anion will be stronger solvated than **1** and **1**, in turn, will be stronger solvated than **2**, because in the latter cases the negative charge is more delocalized than in the former cases thus reducing stabilizing electrostatic interactions. This is confirmed by the calculated reduced solvation energies listed in Table 2. With increasing dielectric constant of the solvent, the free energy difference ΔG between **T-1** and **S-1** increases from 10.3 ($\epsilon = 1$) to 13.8 ($\epsilon = 2.0$) and 25.4 kcal/mol ($\epsilon = 78.4$, Figure 4) because the triplet state leads to larger solvation energies (Table 2).

Interactions with the solvent will lead to immediate dissociation of van der Waals complex **T-1** ($\Delta G^*_{solv} = -69$ kcal/mol, Table 2) to the strongly solvated HO^- anion ($\Delta G^*_{solv} = -112$ kcal/mol, Table 2) and molecular oxygen; i.e., **T-1** is not stable in solution. This however is also true when in the gas phase the thermal motion of the molecules is considered: the $\Delta G(298)$ value of anion **T-1** is 3.3 kcal/mol larger than that of $HO^- + O_2(^3\Sigma g^-)$ (see Figure 4).

Specific solvation by one water molecule does not enhance but decreases the stability of **T-1** in solution (by 24.1 kcal/mol, Table 2) because of the lower solvation energy of **T-2** compared to **T-1**. Dissociation of **T-2** into $HO(H_2O)^-$ and $O_2(^3\Sigma g^-)$ is exothermic: 14.6 (ΔE, gas phase) − 28.2 (difference in ΔG^*_{solv}

Table 1. Experimental and Calculated Heats of Formation, Proton Affinities, and Electron Affinities at 298 K[a]

molecule	$\Delta H_f^0(298)$	molecule	$\Delta H_f^0(298)$
	Experimental Values[b]		
$O(^3P)$	58.98	$O_3^{\bullet -}$	−14.4
$OH^\bullet$	9.31	$HOO^\bullet$	1.7
OH^-	−33.67; −54.97	$O_2(^1\Delta_g)$	22.5
H_2O	−57.8; −68.31	HOOH	−32.6; −45.7
O_3	34.1; 30.1	H^+	367.16; 0
$H^\bullet$	52.09	H^-	33.39
	Calculated Values		
$HO_3^\bullet$	1.9 (-1 ± 5)[c]	HOOOH	−22.7 (-26 ± 3)[c]
HO_3^- (**S-1**)	−25.5	HO_3^- (**T-1**)	−35.8
$HO_3(H_2O)^-$ (**S-2**)	−100.1	$HO_3(H_2O)^-$ (**T-2**)	−115.9
HOO^-	−23.1		
	Proton Affinities		
HO^-	391.3	HOO^-	376.7
S-1	364.4	**S-2**	356.5
$O_3^{\bullet -}$	350.9		
	Electron Affinities		
$HO^\bullet$	43.0[d]	$HOO^\bullet$	24.8[e]
$HO_3^\bullet$	27.4	$HO_3(H_2O)^\bullet$	37
$O_3^{\bullet -}$	48.5		

[a] All values in kcal/mol. The second entry for the experimental values[31] corresponds to the heat of formation in aqueous solution. $\Delta H_f^0(298)$ of $HO_3^\bullet$ is from the dissociation energy of HOOOH (B3LYP, 76.6 kcal/mol) using the calculated $\Delta H_f^0(298)$ of HOOOH and the experimental $\Delta H_f^0(298)$ of $H^\bullet$. $\Delta H_f^0(298)$ of HOOOH is from the formal reaction $2HOOH \rightarrow HOH + HOOOH$ (B3LYP, −22.6; CCSD(T), −22.7 kcal/mol). $\Delta H_f^0(298)$ of HOO^- is from the formal reaction $HOOH + HO^- \rightarrow HOH + HOO^-$ (B3LYP, −23.6; CCSD(T), −23.1 kcal/mol). $\Delta H_f^0(298)$ of **1** and **2** is from Scheme 2 using the reference data of this table. $\Delta H_f^0(298)$ of **S-1** is from the formal reaction $HOOOH + HO^- \rightarrow HOOO^- + HOH$; the experimental values are for HOH and HO as well as the calculated $\Delta H_f^0(298)$ for HOOOH (B3LYP, −25.2; CCSD(T), −24.3 kcal/mol). All calculations are with the 6-311++G(3df,3pd) basis set. [b] Reference 31. [c]Reference 18c. [d]Reference 40a. [e]Reference 40b.

Table 2. Reduced Solvation Energies ΔG^*_{Solv} Calculated at SCRF/B3LYP/6-311++G(3df,3pd) for Cyclohexane ($\epsilon = 2.023$) and Water ($\epsilon = 78.39$)[a]

molecule	geometry	$\epsilon = 2.023$	geometry	$\epsilon = 78.39$
T-1	CCSD(T)/gas[b]	−34.7	CCSD(T)/gas[b]	−69.3
T-2	DFT/gas	−26.0	DFT/gas	−51.8
S-1	DFT/solvent	−31.9	DFT/solvent	−70.2 (−54.2)[c]
S-2	DFT/gas	−25.1	DFT/gas	−42.3
$O_3^-(^2B_1)$	CCSD(T)/gas	−31.9	DFT/solvent	−71.1
OH^-	CCSD(T)/gas	−46.1	DFT/solvent	−112.1
$OH^-\cdots H_2O$	DFT/gas	−33.4	DFT/solvent	−81.4
$O_2(^3\Sigma_g^-)$	CCSD(T)/gas	0.5	DFT/solvent	1.4
$O_2(^1\Delta_g)$	exptl[d]	0.4	DFT/solvent	0.8
H_2O	CCSD(T)/gas	−1.4	DFT/solvent	−6.6

[a] Reduced solvation energies ΔG^*_{solv} are given in kcal/mol. UAHF charges were used for the cavity, and the normalization of the polarization charge on the cavity was performed according to ref 30b. CCSD(T)/6-311++G(3df,3pd) (CCSD(T)/gas), B3LYP/6-311++G(3df,3pd) (DFT/gas), and experimental geometries were used in those cases in which a SCRF/B3LYP/6-311++G(3df,3pd) geometry optimization was superfluous ($\epsilon = 2.0$) or not feasible. [b] Optimization leads to dissociation. [c]Solvation energy in parentheses calculated at the CCSD(T)/gas-phase geometry. [d]$R(OO) = 1.2156$ Å.[37]

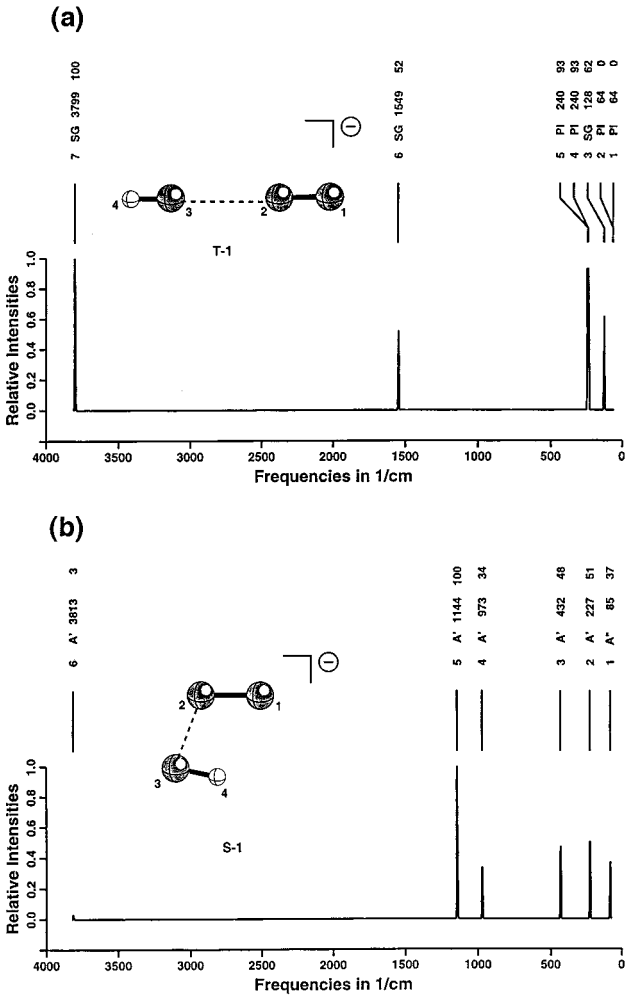


Figure 3. CCSD(T)/6-311++G(3df,3pd) infrared spectra of (a) **T-1** and (b) **S-1**.

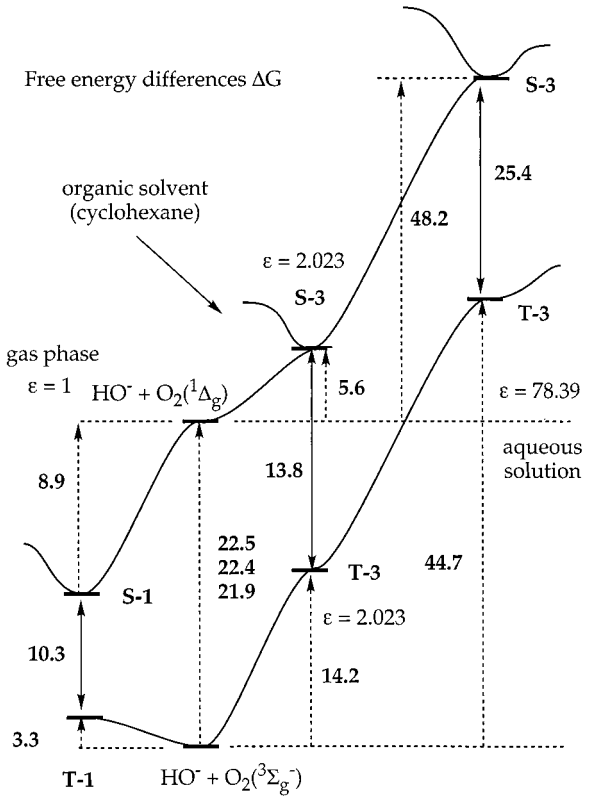


Figure 4. Relative free energies $\Delta G(298)$ of **T-1** and **S-1** for the gas phase (left side) and the solvent phase (right side). Reference for $\epsilon = 1$ (gas phase), $\epsilon = 2.023$ (cyclohexane), and $\epsilon = 78.39$ (water) is always the system $HO^- + O_2$. Reduced solvation energies from Table 2 are used. Note that the larger solvation energy of HO^- leads to more positive free energies on the right side. All values in kcal/mol.

values) = −13.6 kcal/mol. Under normal conditions, there is no chance that either **T-1** or **T-2** can be observed in solution.

Anion **S-1** has a reduced solvation energy of 31.2 kcal/mol in cyclohexane and 54.2 kcal/mol in aqueous solution, which increases to 70.2 kcal/mol (Table 2) when the geometry is relaxed in water. The solvent supports the formation of a normal covalent O2O3 bond by initiating a charge transfer from the O3H to the O1O2 fragment of **S-1** (see Figure 2a). In this way, the terminal atoms carry the larger charges, the negative charge is more equally distributed, and stabilizing electrostatic interactions between solvent and solute are enhanced. The O2O3 bond length decreases from 1.80 (Figure 1) to 1.71 (cyclohexane, Figure 2a) and 1.51 Å (water, Figure 2a) while the bond O1O2 lengthens from 1.32 to 1.39 Å. In this way, the O2O3 bond is shortened and anomeric interactions increase and stabilize the anion in a nonplanar form (HOOO angle, 78°; Figure 2a). The PES of **S-1** in solution is also rather flat. Enforced dissociation of **S-1** to the HO^- anion and $O_2(^1\Delta g)$ leads, contrary to the situation in **T-1**, to an increase in the free energy both for $\epsilon =$ 2.0 and 78.4. The dissociation reaction in aqueous solution could only be investigated to a distance R(O2−O3) of 1.8 Å (increase in the free energy, 2 kcal/mol) so that a barrier to dissociation could not be determined. Specific solvation of **S-1** by one water molecule leads to a thermoneutral reaction ($\Delta G = -0.1$ kcal/mol) in aqueous solution because the stablization energy of **T-2** (−18.6 kcal/mol, Scheme 2) is canceled out by the difference in the reduced solvation energies (+18.5 kcal/mol, Table 2). There may be, however, a contribution due to the difference in the thermal motions in the gas and in the solution phase.

There are several possibilities how **1** or **2** can react to give other products. Structures **T-1** and **T-2** will preferentially dissociate into the monomers. We did not find any pathway how these species could form HOOOH by proton transfer from a water molecule (see below). In view of our results, there is also little chance of finding **T-1** when solving molecular oxygen in an aqueous solution with pH > 7. This is in line with the experimental observation that the solubility of molecular oxygen is strongly decreased in basic solutions. Hence, **T-1** and **T-2** will not be considered any further in the following discussion.

There is the possibility that complex **S-2** rearranges to give HOOOH and a OH anion. We calculated a precursor of the proton transfer step, namely **S-1** H-bonded via its terminal O atom to a water molecule (**S-4**, Figure 2). Structure **S-4**, just 1 kcal/mol less stable than **S-2**, possesses however a geometry that reminds one of HOOOH (B3LYP/6-311++G(3df,3pd): O2O3, 1.539 Å; O1O2, 1.380 Å; Figure 2). The barrier for the proton transfer is rather high because the reaction is endothermic by 43.7 kcal/mol in the gas phase. In aqueous solution, the barrier can be strongly reduced considering the fact that the HO anion has a reduced solvation energy of −112 kcal/mol but **S-2** just −42 kcal/mol (Table 2). Hence, the formation of HOOOH from **S-4** in water cannot be excluded. If either **S-1**

or **S-2** is protonated, this will occur, in view of the calculated charge distribution (Figure 2), at the position of O1 or O3. thus leading to HOOOH or alternatively to water and molecular oxygen in the singlet state.

Chemical Relevance of Results

The HOOO anion can be formed in a singlet state (**S-1**) as the deprotonation product of hydrogen trioxide. The existence of the latter has been recently documented.[39] Although **S-1** in the gas-phase possesses according to CCSD(T) calculations the longest OO bond ever found for a peroxide (O2O3, 1.80 Å),[36] the anion is remarkably stable in the gas phase at 298 K (14.3 kcal/mol). Despite its peculiar structure with the long OO bond, **S-1** is a covalently bonded molecule rather than a van der Waals complex, which can be concluded from the analysis of its geometry, electron density distribution, and simple bonding models.

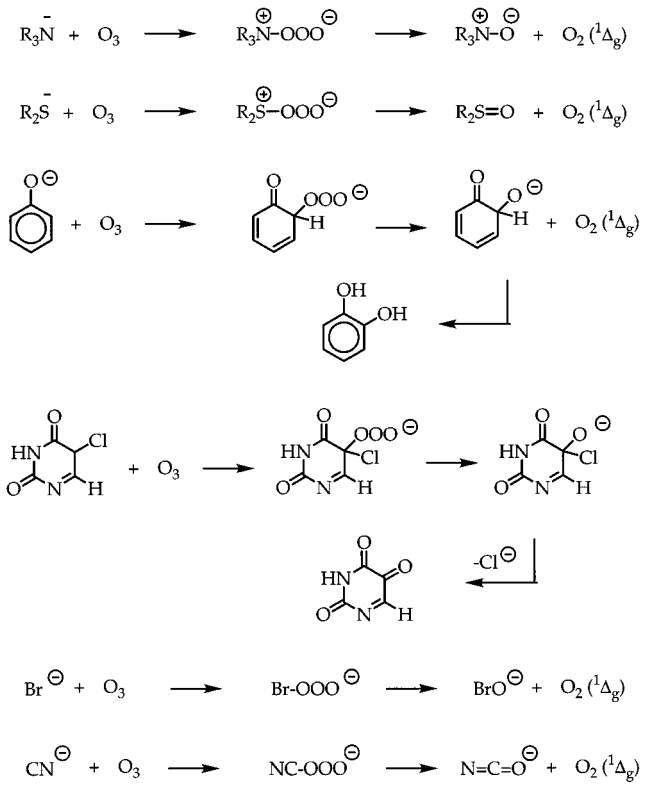
Nonspecific solvation in aqueous solution substantially increases the stability of **S-1** as is reflected by its geometry and in particular an O2O3 bond of 1.51 Å (Figure 2). An experimental detection of **S-1** should be possible in an appropriate solvent when reacting ozone with hydrocarbons that easily form carbenium ions by hydride transfer. Suitable candidates could be acetals such as 1,3-dioxolanes. For example, 2-methyl-1,3-dioxolane forms in the low-temperature ozonation (−78 °C) 2-hydroxy-2methyl-1,3-dioxolane (R−OH) as was confirmed by its NMR spectrum.[43] Experimental evidence excludes the formation of the alcohol R−OH via an intermediate hydrotrioxide (cleavage of the O−O(OH) bond and H abstraction by the alkoxy radical formed). Instead the formation of an ion pair R^+OOOH^- is more likely, which can collapse to a hydroxy compound and $O_2(^1\Delta g)$. There is a chance to detect the ion pair either directly or indirectly at low temperature.[43]

Even more promising for a detection of **S-1** might be the generation of HOOO radicals in the presence of metal atoms. Nelander and co-workers[18b] have shown how the radical can be generated in argon matrixes by various reactions involving the addition of OH radicals to molecular oxygen or the addition of atomic oxygen to peroxy radicals. Laser ablation of metal targets (Al, Fe, In, Li, etc.) to produce electrons can lead to the capture of an electron by OH or O radicals and the formation of **1**.[44]Apriori it is not clear whether this will lead to **S-1** or **T-1**; however, the two species can be easily distinguished by their infrared spectra (Figure 3).

Formally, **S-1** and **T-1** represent two different states of the same molecular species; however, the evidence collected in this work suggests that **S-1** and **T-1** are different species: Despite its unusual gas-phase structure, **S-1** is really the anion of HOOOH while **T-1** corresponds to the van der Waals complex between HO^- and $O_2(^3\Sigma g^-)$ existing only in the gas phase at low temperature. The link between the two species is provided by the ozone radical anion, which by H abstraction could form either **S-1** or **T-1**.

The description of anion **S-1** is directly relevant for the mechanism of the ozonation reaction (Scheme 1). The electron transfer process (2) will take place only in special cases, namely when R_nX has a sufficiently low ionization potential and the process is favored by the solvation of the generated radical ions II (Scheme 1). In aqueous solution, this will lead to a stabilization of about 3 eV[3] while in organic solvents the gain by ion solvation will be just 1−2 eV.[3] The electron affinity of ozone (2.1 eV, 48.5 kcal/mol, Table 1) supports the electron-transfer process; however, if the ionization potential of R_nX in the gas phase is substantially larger than 6 eV ($IP(R_3N) \approx 7$ eV [31]), there will be little chance for an electron transfer. Hence, for normal compounds R_nX dissolved in an organic solvent or in aqueous solution, the O transfer process via I (Scheme 1) is the most likely reaction. In Scheme 4, a number of examples for reaction 1 are listed. They concern the ozonation of tertiary amines, sulfur-containing compounds (sulfides, disulfides, and thiols), phenolates, DNA constituents, nitride and azide ions, halogenide ions, cyanide ions, etc. (see Scheme 4).[3−6] Although I is a zwitterion, its electronic structure closely resembles that of **S-1**. Hence, I can only decompose to R_nXO and $O_2(^1D_g)$ in line with the preferred dissociation route of **S-1** and spin conversation rules. The production of singlet dioxygen directly reflects the existence of I, which should be observable at low temperatures in a matrix.

Scheme 4. Ozonation Reactions Proceeding via the Zwitterion $R_nX^+-OOO^-$



The ozonide radical anion is stable at higher pH values while it is protonated (proton affinity, 350.9 kcal/mol, Table 1), e.g. by water, at lower pH values. In the latter case, $HO_3^\bullet$ is formed (reaction 3b, Scheme 1), which decomposes in a similar way as **S-1** forming $HO^\bullet$ and molecular oxygen. In neutral media, $O_3^{\bullet-}$ can abstract a H atom (reaction 3a, Scheme 1) and form **S-1**. Both protonation and H abstraction are strongly endothermic reactions, which in aqueous solution become less endothermic due to the strong solvation energy of the HO^- anion generated in reaction 3. Ozone is widely used in drinking-water processing and wastewater purification, but the O_3 reactions in water or aqueous solutions (the health risk of inhaled ozone or

(42) Gora, E. K. *Mol. Spectrosc.* **1959**, *3*, 78.
(43) Plesničar, B. To be published. For the currently accepted mechanism of the ozonation of acetals, see: Li, S.; Deslongchamps, P. *Tetrahedron Lett.* **1993**, *34*, 7759 and references therein.
(44) See, e.g.: Liang, B.; Andrews, L. *J. Am. Chem. Soc.* **2001**, *123*, 9848.

injected medical ozone) are yet not adequately understood.[3−7] The present work makes a step to a better understanding of these reactions.

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