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The Reaction of Ozone with the Hydroxide Ion: Mechanistic Considerations Based on Thermokinetic and Quantum Chemical Calculations and the Role of HO_4^- in Superoxide Dismutation

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Abstract: The reaction of OH^- with O_3 eventually leads to the formation of $^{\bullet}OH$ radicals. In the original mechanistic concept (J. Staehelin, J. Hoigné, *Environ. Sci. Technol.* **1982**, *16*, 676–681), it was suggested that the first step occurred by O transfer: $OH^- + O_3 \rightarrow HO_2^- + O_2$ and that $^{\bullet}OH$ was generated in the subsequent reaction(s) of HO_2^- with O_3 (the peroxone process). This mechanistic concept has now been revised on the basis of thermokinetic and quantum chemical calculations. A one-step O transfer such as that mentioned above would require the release of O_2 in its excited singlet state ($^1O_2$, O_2-($^1\Delta_g$)); this state lies $95.5\ \text{kJ mol}^{-1}$ above the triplet ground state ($^3O_2$, O_2-($^3\Sigma_g^-$)). The low experimental rate constant of $70\ \text{M}^{-1}\text{s}^{-1}$ is not incompatible with such a reaction. However, according to our calculations, the reaction of OH^- with O_3 to form an adduct ($OH^- + O_3 \rightarrow HO_4^-$; $\Delta G = 3.5\ \text{kJ mol}^{-1}$) is a much better candidate for the rate-determining step as compared with the significantly more endergonic O transfer ($\Delta G = 26.7\ \text{kJ mol}^{-1}$). Hence, we favor this reaction; all the more so as numerous precedents of similar ozone adduct formation are known in the literature. Three potential decay routes of the adduct HO_4^- have been probed: $HO_4^- \rightarrow HO_2^- + {}^1O_2$ is spin allowed, but markedly endergonic ($\Delta G = 23.2\ \text{kJ mol}^{-1}$). $HO_4^- \rightarrow HO_2^- + {}^3O_2$ is spin forbidden ($\Delta G = -73.3\ \text{kJ mol}^{-1}$). The decay into radicals, $HO_4^- \rightarrow HO_2^{\bullet} + O_2^{\bullet -}$, is spin allowed and less endergonic ($\Delta G = 14.8\ \text{kJ mol}^{-1}$) than $HO_4^- \rightarrow HO_2^- + {}^1O_2$. It is thus $HO_4^- \rightarrow HO_2^{\bullet} + O_2^{\bullet -}$ by which HO_4^- decays. It is noted that a large contribution of the reverse of this reaction, $HO_2^{\bullet} + O_2^{\bullet -} \rightarrow HO_4^-$, followed by $HO_4^- \rightarrow HO_2^- + {}^3O_2$, now explains why the measured rate of the bimolecular decay of $HO_2^{\bullet}$ and $O_2^{\bullet -}$ into $HO_2^- + O_2$ ($k = 1 \times 10^8\ \text{M}^{-1}\text{s}^{-1}$) is below diffusion controlled. Because k for the process $HO_4^- \rightarrow HO_2^{\bullet} + O_2^{\bullet -}$ is much larger than k for the reverse of $OH^- + O_3 \rightarrow HO_4^-$, the forward reaction $OH^- + O_3 \rightarrow HO_4^-$ is practically irreversible.

Keywords: density functional calculations · kinetics · ozone · radicals · reactive intermediates

Introduction

The reaction with OH^- that eventually leads to the formation of $^{\bullet}OH$ is one of the most often cited reactions of ozone in aqueous solution. It was discovered by Staehelin and Hoigné in their excellent paper on the formation of $^{\bullet}OH$ by O_3/H_2O_2 (the peroxone process).[1] Equations (1)–(6) have been used to describe the mechanism of this process.

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \tag{1}$$

$$HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet -} \quad \text{(electron transfer)} \tag{2}$$

$$HO_2^{\bullet} \rightleftharpoons O_2^{\bullet -} + H^+ \tag{3}$$

$$O_3^{\bullet -} + H^+ \rightleftharpoons HO_3^{\bullet} \tag{4}$$

$$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2 \tag{5}$$

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$$O_2^{\bullet -} + O_3 \rightarrow O_2 + O_3^{\bullet -} \quad (6)$$

This mechanism implies that in the sequence of events two $^{\bullet}OH$ are formed per one H_2O_2 and two O_3 molecules consumed.

The peroxone process has recently been re-investigated,[2] and it is now clear that the $^{\bullet}OH$ yield is only 50 % of the formerly assumed value.[3] In the new mechanistic concept, Equations (4)–(6) are replaced by Equations (7) and (8), and, more importantly, the electron-transfer reaction [Eq. (2)] is now suggested to be preceded by formation of an adduct [Eq. (9)].

$$O_3^{\bullet -} \rightleftharpoons O^{\bullet -} + O_2 \quad (7)$$

$$O^{\bullet -} + H_2O \rightleftharpoons {}^{\bullet}OH + OH^- \quad (8)$$

$$HO_2^- + O_3 \rightarrow HO_5^- \ \text{(adduct formation)} \quad (9)$$

The reaction of OH^- with O_3 has been suggested to produce H_2O_2 (HO_2^-) according to Equation (10),[1] and thus to trigger the peroxone process. It will be shown in the present paper that this reaction is also in need of further scrutiny.

$$OH^- + O_3 \rightarrow HO_2^- + O_2 \ \text{(O transfer)} \quad (10)$$

There is now increasing evidence to suggest that adducts must be important intermediates in the reactions of O_3 in aqueous solution, and many reactions, previously assumed to be O-transfer and electron-transfer reactions, probably involve adducts as short-lived intermediates. The branching of these two processes in the O_3 chemistry of tertiary amines led to the first suggestion of an adduct as an intermediate in these two reactions [Eq. (11)–(13)].[4] It is recalled that the ground state of O_2 is a triplet state ($O_2(^3\Sigma_g^-)$, $^3O_2$). Its release is a spin-forbidden process. The spin-allowed reaction requires that O_2 is formed in its (excited) singlet state ($O_2(^1\Delta_g)$, $^1O_2$), which lies 95.5 kJ mol^{-1} above the ground state, and when O transfer is the only process, the $^1O_2$ yield is 100 % as long as the reaction is sufficiently exergonic and other effects do not lower its yield (see below).[5]

$$R_3N + O_3 \rightarrow R_3N^+OOO^- \quad (11)$$

$$R_3N^+OOO^- \rightarrow R_3NO + O_2(^1\Delta_g) \quad (12)$$

$$R_3N^+OOO^- \rightarrow R_3N^{\bullet +} + O_3^{\bullet -} \quad (13)$$

The observation of a marked heavy-atom effect in the $^1O_2$ yield in the O transfer from O_3 to the halide ions Br^- and I^-, for example, Equations (14)–(16), gave strong support to this mechanism.[5] In Equation (16), the heavy atom facilitates the intersystem crossing by spin–orbit coupling with concomitant release of ground-state triplet O_2 ($^3O_2$).

$$I^- + O_3 \rightarrow IOOO^- \quad (14)$$

$$IOOO^- \rightarrow IO^- + {}^1O_2 \ \text{(spin allowed)} \quad (15)$$

$$IOOO^- \rightarrow IO^- + {}^3O_2 \ \text{(spin forbidden)} \quad (16)$$

Finally, kinetic evidence for an adduct was obtained when it was shown that the relatively slow $O_3 + Br^-$ reaction is reversible [Eq. (17)].[6]

$$Br^- + O_3 \rightleftharpoons BrOOO^- \quad (17)$$

Recent quantum chemical calculations showed that the Gibbs energy of the formation of this adduct is indeed very low and that in other cases, in which no reversibility is observed, it is high.[7] In the peroxone process, this adduct can decompose according to Equation (18).

$$HO_5^- \rightarrow HO_2^{\bullet} + O_3^{\bullet -} \quad (18)$$

The radical pair $HO_2^{\bullet}$ and $O_3^{\bullet -}$ is held together for a short period of time by the solvent cage, where it may react by disproportionation [Eq. (19)] in competition with diffusion out of the cage.

$$HO_2^{\bullet} + O_3^{\bullet -} \rightarrow O_2 + HO_3^- \quad (19)$$

It has also been considered that the adduct may decompose in competition with the radical-forming process [Eq. (18)] by the spin-allowed O_2-elimination reaction [Eq. (20)] and/or the thermodynamically favored but kinetically disfavored spin-forbidden reaction [Eq. (21)].

$$HO_5^- \rightarrow HO_3^- + {}^1O_2 \ \text{(spin allowed)} \quad (20)$$

$$HO_5^- \rightarrow HO_3^- + {}^3O_2 \ \text{(spin forbidden)} \quad (21)$$

HO_3^- is in equilibrium with H_2O_3 [Eq. (22); for a discussion of its pK_a value see below], and it is the decay of HO_3^- [Eqs. (23) and (24)] in equilibrium with H_2O_3 that determines the lifetime of H_2O_3 in aqueous solution at pH > 2.[8–10] Equations (19)–(24) now explain why the $^{\bullet}OH$ yield of the peroxone process is only 50 %.

$$H_2O_3 \rightleftharpoons HO_3^- + H^+ \quad (22)$$

$$HO_3^- \rightarrow OH^- + {}^1O_2 \ \text{(spin allowed)} \quad (23)$$

$$HO_3^- \rightarrow OH^- + {}^3O_2 \ \text{(spin forbidden)} \quad (24)$$

In light of the above, the reaction of OH^- with O_3 may also be much more complex than hitherto believed. Again, we may have to consider an adduct in the first place [Eq. (25)]. The rate of reaction of OH^- with O_3 is so slow ($k = 70\,\text{M}^{-1}\text{s}^{-1}$) that Equation (25) may be reversible, as has been found for the slow reaction of Br^- with O_3 [Eq. (17)].

$$OH^- + O_3 \rightleftharpoons HO_4^- \quad (25)$$

HO_4^- may release O_2, but we have to consider two processes, the energetically expensive spin-allowed and the spin-forbidden reactions [Eqs. (26) and (27)].

$HO_4^- \rightarrow HO_2^- + {}^1O_2$ (spin allowed) (26)

$HO_4^- \rightarrow HO_2^- + {}^3O_2$ (spin forbidden) (27)

As the final products HO_2^- and O_2 are concerned, these reactions are equivalent to the present concept, the O-transfer reaction [Eq. (10)]. There is, however, also another route, the decay into two radicals [Eq. (28)].

$HO_4^- \rightleftharpoons HO_2^{\bullet} + O_2^{\bullet -}$ (28)

In the present paper, we have evaluated these reactions by thermokinetic and quantum chemical approaches, and it will be shown that the reaction of OH^- with O_3 leads to the formation of free radicals via an adduct, that is, the present mechanism has to be revised.

Experimental Section

DFT calculations were carried out using Becke's three-parameter functional (B3)[11] in combination with the Lee, Yang, and Parr (LYP)[12] correlation functional with the 6-311+(d,p) basis set,[13] Gaussian 03.[14] The molecular geometries, energies and frequency calculations of all calculated structures were obtained at the same B3LYP/6-311+(d,p) level of theory. By using unscaled vibrations, frequency analyses were done to characterize the stationary points on the potential surface and to obtain zero point energies (ZPE) and thermochemical properties, such as entropy (*S*), enthalpy (*H*), and Gibbs energy (*G*) at standard temperature (298.15 K) and pressure (1 atm). The ground state of O_2 is a triplet state, and the electronic structure of O_3 is a "pathological case" for electronic structure theory.[15,16] Therefore, the keyword Guess = Mix was used to avoid possible RHF-UHF instability by triplet molecular oxygen and singlet ozone. To take the solvent effect of water on the molecular structure and energy of molecules into account, especially important in the case of anions, geometry optimizations were carried out using self-consistent reaction field SCRF = CPCM[17,18] models as implemented in the Gaussian 03 packages. Gaussian-1 (G1) was used for the calculation of the O–O bond dissociation energy (BDE).[19,20] The G1 method reproduces O–O BDE in good agreement with the experiment,[21] whereas DFT underestimates it (see below). As to the choice of the level of the DFT calculations, diffuse functions at the heteroatoms are of major importance, especially in the case of anions. Beyond this, only minor further improvements are obtained upon raising the basis set.

The free-energy difference between ${}^1O_2$ and ${}^3O_2$ has been calculated at 95.5 kJ mol^{-1} based on $\Delta G_f^0({}^1O_2)$[22] = 112 kJ mol^{-1} and the solubility of ${}^3O_2$ in water (1.3×10^{-3} mol bar^{-1}; $\Delta G_f^0({}^3O_2) = -5.706\times\log(1.3\times10^{-3}\,\text{M}) = 16.5$ kJ mol^{-1}).

Results and Discussion

Thermokinetic calculations and the likely mechanism of the reaction $OH^- + O_3$: Formation of $HO_2^{\bullet}$ with $O_2^{\bullet -}$ from $O_3 + OH^-$ is formally a three-electron transfer (O^+ transfer). Such a process would appear unlikely in a single step. On the other hand, assuming the formation of an adduct as an intermediate (here HO_4^-), several cleavage patterns, not least the formation of these products, can be easily envisaged. Customarily, and based on much experimental evidence, combination of peroxyl radicals is thought to proceed by way of an intermediate tetroxide.[23] Hence, one might expect HO_4^- to be the immediate product of OH^- reacting with O_3, provided it is thermodynamically accessible. In the following, we shall make a thermodynamic assessment of the free energy of HO_4^-. In addition, we shall try to describe the likely mechanism of the entire reaction and estimate the product yields of the different channels.

The values of $\Delta H_f^0(H_2O_4,g)$[24] and $S^0(H_2O_4)$[25] have, by Benson, been estimated as -13 kJ mol^{-1} and 322 J mol^{-1} K^{-1}, respectively. These values yield $\Delta G_f^0(H_2O_4,g) = 52.6$ kJ mol^{-1}. The free energy of hydration of H_2O_2 is given as -28.5 kJ mol^{-1}.[26] Now, upon hydration, the H_2O_4 species forms four more hydrogen bonds to the water solvent than does H_2O_2, and the increment in free energy of hydration for each extra hydrogen bond introduced is approximately -7.5 kJ mol^{-1}.[27] Hence, ΔG^0 of hydration of H_2O_4 is predicted to be approximately $-28.5 + [4\times(-7.5)] = -58.5$ kJ mol^{-1}. We then calculate $\Delta G_f^0(H_2O_4,aq) = -6.0$ kJ mol^{-1}. It is reasonable to assume that $pK_a(H_2O_4) \approx pK_a(HO_2^{\bullet}) = 4.8$, with the ratio of O/H being the same in the two species (see below). This yields $\Delta G_f^0(HO_4^-,aq) = 21.4$ kJ mol^{-1}. With this value at hand, we can now probe the reaction mechanism.

We first consider Equation (25). From the literature, one finds $\Delta G_f^0(O_3,g) = 163$ kJ mol^{-1},[28] and the Henry's law constant of O_3 is 0.008 M bar^{-1}. This yields $\Delta G_f^0(O_3,aq) = 163.2 - 5.706\times\log(0.008) = 175.2$ kJ mol^{-1}.[29] By combining this value with $\Delta G_f^0(HO_4^-,aq) = 21.4$ kJ mol^{-1} and $\Delta G_f^0(OH^-,aq) = -157.24$ kJ mol^{-1}, we obtain $\Delta G_{25}^0 = 3.5$ kJ mol^{-1}. From this value we obtain $K_{25} = k_{25}/k_{-25} = 0.24\,\text{M}^{-1}$. This K value suggests that, thermodynamically, HO_4^- is readily accessible. Since $70\,\text{M}^{-1}\text{s}^{-1}$ is the experimental rate constant of the $O_3 + OH^-$ reaction, we assign this value to k_{25}, the rate-determining step in the reaction of O_3 with OH^-. As will be shown, Reaction (25) is practically irreversible since Reaction (−25) is far too slow to compete with subsequent steps. The aqueous free energies of all species (except for HO_4^-) involved in these steps are experimentally known[22,28] to have the following values (all in kJ mol^{-1}): $\Delta G_f^0(HO_2^{\bullet}) = 4.4$, $\Delta G_f^0(O_2^{\bullet -}) = 31.8$, $\Delta G_f^0(HO_2^-) = -67.4$, $\Delta G_f^0({}^3O_2) = 16.5$, and $\Delta G_f^0({}^1O_2) = 112$. These data yield the ΔG^0 values given below.

Once formed, HO_4^- might decompose as shown in Equation (26) with $\Delta G_{26}^0 = 23.2$ kJ mol^{-1} and $k_{26}/k_{-26} = K_{26} = 9\times10^{-5}\,\text{M}$; as shown in Equation (27) with $\Delta G_{27}^0 = -72.3$ kJ mol^{-1} and $k_{27}/k_{-27} = K_{27} = 5\times10^{12}\,\text{M}$; and in Equation (28) with $\Delta G_{28}^0 = 14.8$ kJ mol^{-1} and $k_{28}/k_{-28} = K_{28} = 2.7\times10^{-3}\,\text{M}$.

Equations (27) and (28) are related to each other in that they share a common intermediate. This is the geminate radical pair, formed upon homolysis of HO_4^-. The geminate pair can either diffuse out of the solvent cage, which completes Equation (28) and forms the free $HO_2^{\bullet}$ and $O_2^{\bullet -}$ radicals. Alternatively, it can undergo an in-cage electron transfer to produce almost exclusively ${}^3O_2 + HO_2^-$, which completes Equation (27). This is because in the geminate radical pair, efficient intersystem crossing can occur and formation of ${}^3O_2$ rather than ${}^1O_2$ is energetically favorable. Finally,

HO_4^- can decompose concertedly as in Equation (26). This is a one-step reaction and requires spin conservation; hence it can only produce $^1O_2$.

Now, given that Equation (−28) is slightly exergonic, it is expected to be diffusion controlled, and we tentatively assume (based on known precedents in the literature) $k_{-28} \approx 5\times10^9\,\text{M}^{-1}\,\text{s}^{-1}$. By way of an example, it should be recalled that, for the well-investigated exergonic ($\Delta G^0 = -55\,\text{kJ}\,\text{mol}^{-1}$) reaction $^{\bullet}NO_2 + O_2^{\bullet-} \rightarrow O_2NOO^-$, the rate constant ($k$) is $4.5\times10^9\,\text{M}^{-1}\,\text{s}^{-1}$, and similarly, for the equally exergonic ($\Delta G^0 = -65\,\text{kJ}\,\text{mol}^{-1}$) reaction $^{\bullet}NO + O_2^{\bullet-} \rightarrow ONOO^-$ it is $(5\pm1)\times10^9\,\text{M}^{-1}\,\text{s}^{-1}$.[30]

With our assumed k_{-28} value, k_{28} comes out as approximately $10^7\,\text{s}^{-1}$, that is, it is very large, much larger than the estimated $k_{-26} \approx 70/0.24 \approx 300\,\text{s}^{-1}$. This shows that Equation (25) is practically irreversible. Furthermore, it is known that $HO_2^{\bullet}$ reacts with $O_2^{\bullet-}$ to yield almost exclusively $^3O_2 + HO_2^-$ [Eq. (29)].[31]

$$HO_2^{\bullet} + O_2^{\bullet-} \rightarrow HO_2^- + {}^3O_2 \qquad (29)$$

These latter experiments were conducted at initial radical concentrations of the order of $10^{-5}\,\text{M}$ or so, and under these conditions the equilibrium in Equation (28) is strongly shifted to the right. Since the experimental rate constant of radical recombination is found to be only $10^8\,\text{M}^{-1}\,\text{s}^{-1}$,[32] this implies that only approximately $10^8/5\times10^9 = 2\,\%$ of the geminate pair undergoes electron transfer, with the rest diffusing out of the solvent cage. It then follows that k_{28} is much larger, by a factor of 50 or so, than k_{27}.

Clearly, the reaction between $HO_2^{\bullet}$ and $O_2^{\bullet-}$, that is, Equation (−28), yields primarily HO_4^-. The final products form in Equations (26) and (27) [which make up a part of Eq. (29)]. Now, since in this reaction sequence practically no $^1O_2$ could be observed, it is clear that $k_{27} \gg k_{26}$, and hence $k_{28} \gg k_{26}$. To conclude, it would appear that Equation (25), that is, the formation of HO_4^- from O_3 and OH^-, is mainly followed by Equation (28), yielding the $HO_2^{\bullet}$ and $O_2^{\bullet-}$ radicals. No more than approximately 2 % of HO_4^- is expected to undergo Equation (27), and Equation (26) appears to be blocked.

Quantum chemical calculations: There is already a quantum chemical study on the reaction of OH^- with ozone,[33] but it is at low level (AMI) and inadequate for elucidating a complex reaction such as $OH^- + O_3$ in aqueous solution. Density functional theory (DFT) with B3LYP/6-311+G(d)/SCRF=COSMO basis sets were applied for the study of the reaction of Br^- with O_3 in water [cf. Eq. (17)] and showed a very good agreement with the experiment. Apparently, the solvation energies of Br^- and $BrOOO^-$ are sufficiently similar to cause little problems despite the fact that DFT markedly underestimates the solvation energies of ions such as OH^-, HO_2^-, and $O_2^{\bullet-}$. Experimental[34] and calculated solvation energies for these ions are compiled in Table 1.

Table 1. Compilation of experimental[34] and calculated (B3LYP/6-311+G(d,p)/COSMO) solvation energies, their deviations (ΔE), and the estimated solvation energy of HO_4^- (all in kJ mol^{-1}).

Species	Exptl	Calcd	Estimated	ΔE
OH^-	435	368	–	67
HO_2^-	414	365	–	49
$O_2^{\bullet-}$	355	319	–	36
HO_4^-	–	332	370	38

There is the tendency for the deviation (ΔE) between experimental and calculated solvation energies to be larger the larger the experimental solvation energy. This allowed us to estimate by graphical interpolation the solvation energy of HO_4^- on the basis of our calculations (Figure 1). This value, also given in Table 2, has been used for the corrections. For OH^- and HO_2^-, the corrections were based on the experimental values.

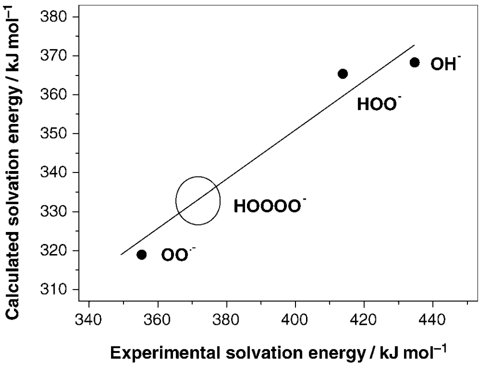

Figure 1. Calculated versus experimental solvation energies of OH^-, HO_2^-, and $O_2^{\bullet-}$. The "experimental" value for HO_4^- may be obtained from the calculated one by interpolation.

The evaluation of the energetics of Equation (28) requires the calculation of the O−O bond dissociation energy (BDE) of HO_4^-. DFT is not a good method for calculating BDEs. This has been shown for the BDE of the O−O bond of pernitrous acid,[21] ONO−OH, calculated at 61 kJ mol^{-1}, for which reliable experimental data (83 kJ mol^{-1}) is available.[35] However, the ONO−OH BDE is calculated very satisfactorily by the G1 method (87 kJ mol^{-1}),[21] and yields data of similar quality as the very time-consuming MRCI method (79 kJ mol^{-1}).[36] The G1 method does not allow the calculation of anions. We were thus restricted to the calculation of the energetics of the decomposition of HOO−OOH [Eq. (30)] and to take the pK_a values of $HO_2^{\bullet}$ and HOOOOH [Eqs. (3) and (31)] into account.

$$HOOOOH \rightarrow 2\,HO_2^{\bullet} \qquad (30)$$

$$HOOOOH \rightleftharpoons HOOOO^- + H^+ \qquad (31)$$

It will be shown below that the pK_a values of $HO_2^{\bullet}$ and H_2O_4 coincide. With this in mind, the BDEs of HOO−OOH and HOO−OO$^-$ are identical, that is, $\Delta G = 12.4\,\text{kJ}\,\text{mol}^{-1}$ (calculated with SCRF=COSMO to account for effects of the solvent water).

The thermokinetic data and the quantum chemical data are compiled in Table 2. The DFT calculations differ from the thermokinetic data systematically by some 15 kJ mol^{-1}. This is not very much considering that the solvation energy of anions is very poorly calculated by DFT, and the corrections that have to be applied are very large (up to 66 kJ mol^{-1}, Table 1). Moreover, the solvation energy of the important intermediate HO_4^- cannot be based on experimental data, and its value is necessarily fraught with a great uncertainty. In contrast, the calculation using the G1 method that has been applied for the calculation of ΔG of Equation (28) (Table 2) is in very good agreement with the thermokinetic value. It should be recalled that this method cannot be applied to the other entries in Table 2, as the G1 method does not allow the calculation of charged species. Despite the above uncertainties, the quantum chemical calculations support the above conclusions that were based on reliable thermokinetic data.

Table 2. Compilation of ΔG values (in kJ mol^{-1}) obtained by thermokinetic and quantum chemical calculations.

Reaction	Eq.	Thermokinetic	DFT	DFT-corrected	G1
$OH^- + O_3 \rightarrow HO_4^-$	(25)	3.5	−38	−9	–
$HO_4^- \rightarrow HO_2^- + {}^1O_2$	(26)	23.2	−4.4	5.6	–
$HO_4^- \rightarrow HO_2^- + {}^3O_2$	(27)	−72.3	99.9	−89.9	–
$HO_4^- \rightarrow HO_2^{\bullet} + O_2^{\bullet -}$	(28)	14.8	67.3	–	12.4

The pK_a values of compounds/radicals of the general formula H_xO_y: Pauling's rule relates the pK_a values of oxy acids to their oxygen content (ca. 4 pK_a units per O atom).[37] As a consequence of this, a linear relationship between the pK_a value and the O/H ratio of H_xO_y compounds was expected. This indeed turned out to be the case, and the relationship pK_a = 19–7([O]/[H]) was established.[9] For example, H_2O_2 and $^{\bullet}OH$ that have the same O/H ratio (1.0) also have the same pK_a values (11.8). There are four experimental values: H_2O, $H_2O_2/^{\bullet}OH$, and $HO_2^{\bullet}$. They are spread over 11 pK_a units and cover a factor of 4 in the O/H ratio (Figure 2). This allowed us to estimate the pK_a values of several short-lived intermediates that we are interested in here. From this plot we arrived at the pK_a values of the O/H compounds that are compiled in Table 3.

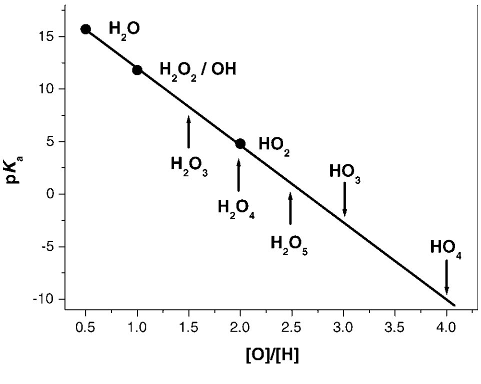

Figure 2. Plot of experimental (●) and estimated (arrows) pK_a values of H_xO_y compounds that are relevant for the ozone chemistry in aqueous solution.

The above conclusion that H_2O_4 must have the same pK_a value as $HO_2^{\bullet}$ has been derived from these data. But from this plot it also follows that the pK_a of $HO_3^{\bullet}$ must be near −2 and not 6.15,[38] as has been generally assumed to date.[39] Most likely, this high pK_a value has been an experimental artifact (a so-called kinetic pK_a value). The new mechanistic concept of the peroxone process[2] is based on the equilibrium shown in Equation (7) for which a dissociation constant of $K = 5.5 \times 10^{-7}$ M has been determined.[40] H_2O_3 and its anion must also be involved in the peroxone process and $HO_4^{\bullet}$ is a potential intermediate in the $^{\bullet}OH$-induced decomposition of O_3.

Table 3. Compilation of experimental and estimated pK_a values of H_xO_y compounds.

Compound	O/H ratio	pK_a value	Remark
H_2O	0.5	15.7	exptl
$^{\bullet}OH$	1.0	11.8	exptl
H_2O_2	1.0	11.8	exptl
H_2O_3	1.5	8.5	estimated
$HO_2^{\bullet}$	2.0	4.8	exptl
H_2O_4	2.0	4.8	estimated
H_2O_5	2.5	1.5	estimated
$HO_3^{\bullet}$	3.0	−2.0	estimated
$HO_4^{\bullet}$	4.0	−9.0	estimated

Is HO_4^- a more abundant intermediate than hitherto realized? HO_4^- as a short-lived intermediate has been discussed here for the first time. We came to postulate it, when we analyzed the reaction of O_3 with OH^-. As a consequence of the line of thoughts outlined above, we now realize that it must also be the main product in the decay of $HO_2^{\bullet}/O_2^{\bullet -}$. These radicals are the smallest and most abundant peroxyl radicals and play a dominating role in cellular O_2 management and in peroxyl free-radical chemistry.[41] Their slow bimolecular decay rate [$k_{29} = 1 \times 10^8$ M^{-1}s^{-1}; $k(2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2) = 8.5 \times 10^5$ M^{-1}s^{-1}; a bimolecular decay of $O_2^{\bullet -}$ does not take place][32] has always puzzled free-radical chemists. Because of deleterious effects induced by $HO_2^{\bullet}/O_2^-$, nature has invented the superoxide dismutases to reduce their cellular steady state.[42,43] Ischemia is a critical situation in heart attack and heart surgery, and is believed to be due to high levels of $O_2^{\bullet -}$. If our above analysis is correct, the reason for the low k_{obs} of the bimolecular decay of these radicals is due to a competing (and dominating) reaction, that is, Equation (−28). In HO_4^-, the $HO_2^{\bullet}/O_2^{\bullet -}$ radicals are only "parked" as they are re-formed after a very short while in Equation (−28). Above, it has been estimated that the ratio of k_{-28}/k_{29} is near 50. With this and the importance of $HO_2^{\bullet}$/

$O_2^{\bullet -}$, HO_4^- would be one of the most abundant short-lived nonradical intermediates in our biosphere.

Conclusion

According to our calculations, the reaction of OH^- with O_3 gives rise to an adduct, HO_4^-. This adduct is very short-lived and decomposes ($k \approx 10^7\,s^{-1}$) into $HO_2^\bullet + O_2^{\bullet -}$. These radicals undergo only a rather slow bimolecular decay and mainly revert to HO_4^- ($k = 5 \times 10^9\,M^{-1}s^{-1}$; $\approx 98\,\%$) in competition with a disproportionation by electron transfer into $HO_2^- + O_2$ ($k = 10^8\,M^{-1}s^{-1}$; $\approx 2\,\%$).

With these data, the current mechanistic concept of the reaction of OH^- with O_3 has to be revised and HO_4^-, as yet not recognized as a likely intermediate in superoxide dismutation, would be one of the most abundant short-lived nonradical intermediates in our biosphere. The preferred formation of the thermodynamically unfavorable HO_4^- from $HO_2^\bullet$ and $O_2^{\bullet -}$ is not unexpected. Notably in free-radical chemistry, kinetics often overruns thermodynamics. This principle is known as Wilhelm Ostwald's "step rule" (Stufenregel).

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[1] J. Staehelin, J. Hoigné, *Environ. Sci. Technol.* **1982**, *16*, 676–681.

[2] M. M. Sein, A. Golloch, T. C. Schmidt, C. von Sonntag, *ChemPhysChem* **2007**, *8*, 2065–2067.

[3] C. von Sonntag, *Water Sci. Technol.* **2008**, *58*, 1015–1021.

[4] F. Muñoz, C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2* **2000**, 2029–2033.

[5] F. Muñoz, E. Mvula, S. E. Braslavsky, C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1109–1116.

[6] Q. Liu, L. M. Schurter, C. E. Muller, S. Aloisio, J. S. Francisco, D. W. Margerum, *Inorg. Chem.* **2001**, *40*, 4436–4442.

[7] S. Naumov, C. von Sonntag, *Ozone Sci. Eng.* **2008**, *30*, 339–343.

[8] G. Czapski, B. H. J. Bielski, *J. Phys. Chem.* **1963**, *67*, 2180–2184.

[9] B. H. J. Bielski, H. S. Schwarz, *J. Phys. Chem.* **1968**, *72*, 3836–3841.

[10] B. H. J. Bielski, *J. Phys. Chem.* **1970**, *74*, 3213–3216.

[11] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[12] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[13] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648.

[14] Gaussian 03, Revision B.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[15] H. B. Schlegel, J. J. W. McDouall in *Computational Advances in Organic Chemistry, NATO-ASI Series C 330* (Eds.: C. Ögretir, I. G. Csismadia), Kluwer Academic, Dodrecht, **1991**, pp. 167–185.

[16] J. B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd ed. Gaussian, Inc., Pittsburgh PA, **1995**.

[17] V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001.

[18] M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669–681.

[19] L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, J. A. Pople, *J. Chem. Phys.* **1990**, *93*, 2537–2545.

[20] J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, L. A. Curtiss, *J. Chem. Phys.* **1989**, *90*, 5622–5629.

[21] R. Sumathi, S. D. Peyerimhoff, *J. Chem. Phys.* **1997**, *107*, 1872–1880.

[22] D. M. Stanbury, *Adv. Inorg. Chem.* **1989**, *33*, 69–138.

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

[24] S. W. Benson, N. Cohen in *Peroxyl Radicals* (Ed.: Z. B. Alfassi), Wiley, New York, **1997**, pp. 49–68.

[25] S. W. Benson, *Thermochemical Kinetics*, 2nd ed. Wiley, New York **1976**.

[26] D. W. O'Sullivan, M. Lee, B. C. Noone, B. C. Heikes, *J. Phys. Chem.* **1996**, *100*, 3241–3247.

[27] H. A. Schwarz, R. W. Dodson, *J. Phys. Chem.* **1984**, *88*, 3643–3647.

[28] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churmey, R. L. Nuttal, *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl 2.

[29] A. K. Bin, *Exp. Therm. Fluid Sci.* **2004**, *28*, 395–405.

[30] S. Goldstein, J. Lind, G. Merenyi, *Chem. Rev.* **2005**, *105*, 2457–2470.

[31] C. S. Foote, F. C. Shook, R. A. Abakerli, *J. Am. Chem. Soc.* **1980**, *102*, 2503–2504.

[32] J. Lin, T. Nakajima, *THEOCHEM* **2003**, *625*, 161–167.

[33] B. H. J. Bielski, D. E. Cabelli, R. L. Arudi, A. B. Ross, *J. Phys. Chem. Ref. Data* **1985**, *14*, 1041–1100.

[34] R. G. Pearson, *J. Am. Chem. Soc.* **1986**, *108*, 6109–6114.

[35] H. Hippler, S. Nasterlack, F. Striebel, *Phys. Chem. Chem. Phys.* **2002**, *4*, 2959–2964.

[36] Y. Li, J. S. Francisco, *J. Chim. Phys.* **2000**, *113*, 7976–7981.

[37] D. F. Shriver, P. W. Atkins, C. H. Langford, *Inorganic Chemistry*, 2nd ed., Oxford University Press, Oxford **1994**, pp. 193–196.

[38] R. E. Bühler, J. Staehelin, J. Hoigné, *J. Phys. Chem.* **1984**, *88*, 2560–2564.

[39] U. von Gunten, *Water Res.* **2003**, *37*, 443–1467.

[40] A. J. Elliot, D. R. McCracken, *Radiat. Phys. Chem.* **1989**, *21*, 69–74.

[41] C. von Sonntag, *Free-Radical-Induced DNA Damage and Its Repair. A Chemical Perspective*, Springer, Berlin, **2006**.

[42] I. Fridovich, *Annu. Rev. Biochem.* **1975**, *44*, 147–159.

[43] L. W. Oberley, *Superoxide Dismutase* (Ed.: L. W. Oberley), CRC Press, Boca Raton, **1982**.

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