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The Reactions of Bromide with Ozone Towards Bromate and the Hypobromite Puzzle: A Density Functional Theory Study

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Taking the solvent water into account, the energetics of the reactions of O_3 with Br^- leading to BrO_3^- have been calculated by Density Functional Theory at the B3LYP/6–311+G(d)/ SCRF = COSMO level. Br^- reversibly forms an adduct, $BrOOO^-$, ($\Delta G = +6\ kJ\ mol^{-1}$) that decays spin allowed into BrO^- and $O_2(^1\Delta_g)$ ($\Delta G = +13\ kJ\ mol^{-1}$). BrO^- undergoes an oxidation to BrO_2^- and a reduction to Br^-. This may be accounted for if two different adducts, $OBrOOO^-$ and $BrOOOO^-$, decay into BrO^- plus O_2 and Br^- plus $2\ O_2$. After cyclization, $OBrOOO^-$ may also lead to Br^- plus $2\ O_2$.

Keywords Bromide, Hypobromite, Bromite, Bromate, Ozone, Reduction, Ozone Adducts, Singlet Dioxygen, DFT Calculation, Thermodynamics, Reaction Mechanism

INTRODUCTION

In drinking water treatment with O_3, the amount of O_3 that can be applied to bromide-containing waters is restricted by the formation of bromate, BrO_3^-. Bromate is potentially carcinogenic, and thus its concentration in drinking water must not exceed 10 μg/L (EU Directive, 1998; US EPA, 2006). Bromate formation by O_3 is a multi-step process ($Br^- \rightarrow BrO^- \rightarrow BrO_2^- \rightarrow BrO_3^-$) that requires at least three molecules of O_3. The various steps that are involved in BrO_3^- formation have been studied in detail (Haag et al., 1982; Haag and Hoigné, 1983; von Gunten and Hoigné, 1992, 1994, 1996; von Gunten et al., 1995; Liu et al., 2001). In drinking water treatment, there is always a contribution by $^\bullet OH$ radical in addition to

the O_3 reactions (von Gunten and Hoigné, 1994, 1996). Here, we deal only with the latter.

There is now increasing evidence that in the oxidation of inorganic ions by O_3 an adduct is the first intermediate. For Br^-, the evidence is twofold. First, there is kinetic evidence that the addition of O_3 to Br^- is reversible (Liu et al., 2001). The reaction products provide the second evidence. Br^- and O_3 are singlet molecules in their ground states and so is the Br^-/O_3 adduct. The spin conservation rule demands, that the overall multiplicity of the products should also be a singlet. For fulfilling this requirement, O_2 must be formed in its (excited) singlet state, $O_2(^1\Delta_g)$. This state lies 94 kJ mol^{-1} above the (triplet) ground state, $O_2(^3\Sigma_g^-)$. Heavy atoms can weaken the spin conservation rule by spin orbit coupling, and when the adduct is sufficiently long-lived, some of the O_2 may be released as (triplet) ground state O_2. In the Br^- plus O_3 reaction, the $O_2(^1\Delta_g)$ yield is only 54% giving evidence for an adduct of a certain lifetime (Muñoz et al., 2001). For a heavier atom such as I^-, the effect is even more dramatic. Here, the $O_2(^1\Delta_g)$ yield is only 14%. Without a heavy atom as a catalyst, $O_2(^1\Delta_g)$ yields indeed reach 100% (Muñoz et al., 2001). Substrate/O_3 adducts are now also well documented for amines (Muñoz and von Sonntag, 2000) and sulfur(II) compounds (Muñoz et al., 2001), and recently have been postulated for the peroxone process (Sein et al., 2007).

En route to BrO_3^-, Br^- is oxidized to BrO^- in the first step (reactions [1] and [2]). This reaction is slow ($k_{obs} = 160$ M^{-1} s^{-1} at 20 °C (Haag and Hoigné, 1983); $k_{obs} = 258$ M^{-1} s^{-1} at 25 °C including reaction of water yielding HOBr (Liu et al., 2001)) and reversible (Liu et al., 2001).
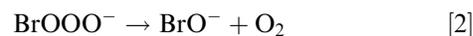
$$Br^- + O_3 \rightleftarrows BrOOO^- \qquad [1]$$

$$BrOOO^- \rightarrow BrO^- + O_2 \qquad [2]$$

The reaction of O_3 with BrO^- gives rise to two products, BrO_2^- plus O_2, the trivial and *oxidative* pathway (reactions [3] and [4]; $k_{obs} = 110$ M^{-1} s^{-1} (Haag and Hoigné, 1983)), but there is also a *reductive* pathway that gives rise to Br^- plus 2 O_2 (reactions [5] and [6]; $k_{obs} = 330$ M^{-1} s^{-1} (Haag and Hoigné, 1983)). It is tempting to assume also an adduct / two different adducts as intermediates in these reactions.

$$BrO^- + O_3 \rightarrow [OBrOOO] \rightarrow BrO_2^- + O_2 \qquad [3]/[4]$$

$$BrO^- + O_3 \rightarrow [OBrOOO^-/BrOOOO^-] \rightarrow Br^- + 2\,O_2 \qquad [5]/[6]$$
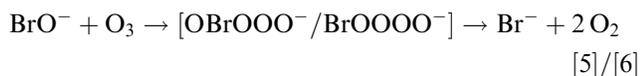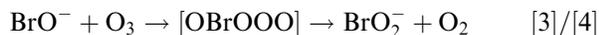
We were attracted by this reaction, as in the reaction of Mn^{2+} with O_3 *en route* to MnO_4^- reduction processes that consume much more O_3 than stoichiometrically required also occur (Reisz et al., 2004b; Reisz et al., 2004a; Reisz et al., 2008).

The last step is reported to be fast (reactions [7] and [8]; $k_{obs} > 1 \times 10^5$ M^{-1} s^{-1}) and without a competition.

$$BrO_2^- + O_3 \rightarrow [O_2BrOOO^-] \rightarrow BrO_3^- + O_2 \qquad [7]/[8]$$

Here we report Density Functional Theory (DFT) calculations on the thermodynamics of the above reactions, and these data now provide a better understanding of the complex reaction scheme.

COMPUTATIONAL METHODS

DFT calculations were carried out using Becke's three-parameter functional (B3) (Becke, 1993) in combination with the Lee, Yang, and Parr (LYP) (Lee et al., 1988) correlation functional with the $6–311+(d)$ basis set (McGrath and Radom, 1991 Gaussian 03: Frisch et al., 2003). The molecular geometries, energies and frequency calculations of all calculated structures were obtained at the same B3LYP/$6–311+(d)$ level of theory. 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). Reaction parameters such as ΔH and ΔG were calculated as a balance of the electronic energies (ΔE) and total Gibbs energies (ΔG; $G = H - TS$). No attempt has been made to calculate activation energies.

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 (Schlegel and McDouall, 1991; Foresman and Frisch, 1995). Therefore, the keyword Guess = Mix was used to avoid possible RHF-UHF instability by triplet molecular oxygen and singlet ozone. Nevertheless, the eigenfunctions of the optimized complexes of BrO^- and BrO_2^- with O_3 are not pure spin states, but contain considerable amounts of spin

contamination from higher spin states. For this reason, the structures and stabilities of these complexes should be discussed only qualitatively. 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 (Barone and Cossi, 1998; Cossi et al., 2003) models as implemented in the Gaussian 03 packages. Test calculations have also been done using Coupled Cluster calculations with single and double substitutions (CCSD) followed by single point calculations with triple excitations (CCSD(T) method) (Pople et al., 1987; Scuseria and Schaefer, 1989) both in the gas phase and in water (SCRF = CPCM). Ozone bond lengths (1.267 Å) and bold angle (116.7°) and the BrO^- bond length (1.868 Å) are only marginally closer to the experimental values than the DFT calculations. Moreover, the energy of the $BrOOO^-$ intermediate comes out very similar (–15 kJ mol^{-1}) in the gas phase. Such calculations are computationally expensive and an attempt to implement solvent effects to larger complexes failed because of convergence problems upon geometry optimization. We thus felt that the more robust DFT approach is adequate for the present study. Here, only calculations in water are reported, as with ions gas phase calculations are inappropriate.

RESULTS AND DISCUSSION

According to our DFT calculations, reaction (1) is practically thermoneutral (for a compilation of the calculated reaction enthalpies and Gibbs energies see Table 1). This is in very good agreement with the reported reversibility. The Gibbs energy of the subsequent decay into BrO^- plus $O_2(^1\Delta_g)$, spin allowed, is $+6$ kJ mol^{-1}. Within experimental error of the DFT calculations, this reaction is thermoneutral, and the observation that 54% of the oxygen that is released is in its $^1\Delta_g$ state (Muñoz et al., 2001) further supports this view.

The structures of O_3 and of the intermediate O_3 adduct to Br^- are shown in Figure 1.

The Br–O bond length of this adduct is large (1.78 Å as compared to 1.27 Å in O_3) as one would expect for a reaction that is reversible at room temperature. Only 69% of the negative excess charge remains at bromine and 31% are found at the oxygens, and this intermediate is hence a charge transfer complex.

Hypobromous acid is a weak acid (pK_a(HOBr) = 8.8 (Haag and Hoigné, 1983)). As O_3 is a strongly electrophilic agent (Hoigné and Bader, 1983), anions react generally much faster than their conjugate acids (for example: $k(O_3 + H_2S) = 3 \times 10^4$ M^{-1} s^{-1}; $k(O_3 + HS^-) = 3 \times 10^9$ M^{-1} s^{-1} (Hoigné et al., 1985)). Thus, BrO^- is the O_3-reactive species at ambient pH (Haag and Hoigné, 1983). For the reactions of BrO^- with O_3 there

TABLE 1. Calculated Reaction Enthalpies (ΔH) and Gibbs Energies (ΔG) Taking the Solvent Water into Account (B3LYP/6–311+G(d)/ SCRF = COSMO)

No.	Reaction	ΔH/kJ mol^{-1}	ΔG/kJ mol^{-1}
[1]	$Br^- + O_3 \rightarrow BrOOO^-$	−13	+6
[2a]	$BrOOO^- \rightarrow BrO^- + O_2(^1\Delta_g)$ spin allowed	+50	+13
[2b]	$BrOOO^- \rightarrow BrO^- + O_2(^3\Sigma_g^-)$ spin forbidden	−46	−81
[1]/[2a]	$Br^- + O_3 \rightarrow BrOOO^- \rightarrow BrO^- + O_2(^1\Delta_g)$ spin allowed	+37	+19
[1]/[2b]	$Br^- + O_3 \rightarrow BrOOO^- \rightarrow BrO^- + O_2(^3\Sigma_g^-)$ spin forbidden	−61	−75
[3]/[4a]	$BrO^- + O_3 \rightarrow$ Adduct $\rightarrow BrO_2^- + O_2(^1\Delta_g)$ spin allowed	−32	−36
[3]/[4b]	$BrO^- + O_3 \rightarrow$ Adduct $\rightarrow BrO_2^- + O_2(^3\Delta_g)$ spin forbidden	−126	−130
[5]/[6]	$BrO^- + O_3 \rightarrow$ Adduct $\rightarrow Br^- + 2\,O_2(^3\Sigma_g^-)$ spin allowed	−318	−347
[7]/[8a]	$BrO_2^- + O_3 \rightarrow$ Adduct $\rightarrow BrO_3^- + O_2(^3\Sigma_g^-)$ spin allowed	−98	−93
[7]/[8b]	$BrO_2^- + O_3 \rightarrow$ Adduct $\rightarrow BrO_3^- + O_2(^3\Sigma_g^-)$ spin forbidden	−194	−187
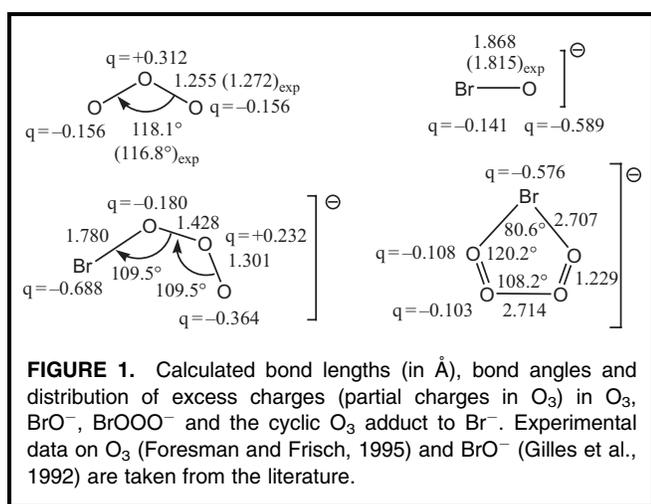
FIGURE 1. Calculated bond lengths (in Å), bond angles and distribution of excess charges (partial charges in O_3) in O_3, BrO^-, $BrOOO^-$ and the cyclic O_3 adduct to Br^-. Experimental data on O_3 (Foresman and Frisch, 1995) and BrO^- (Gilles et al., 1992) are taken from the literature.

are two competing reactions (reactions [3] and [5]). The competition may occur on the way to two different adducts [Scheme 1, reactions [a]/[c] vs. [b]/[d]], or there may be one adduct that can decays into two directions, reactions [c] vs. [e]/[f].

In contrast to the DFT calculations of $BrOOO^-$ that did not pose any apparent problem, the calculations of the O_3 adducts that contain additional oxygens, $OBrOOO^-$, $BrOOOO^-$ and O_2BrOOO^-, show considerable spin
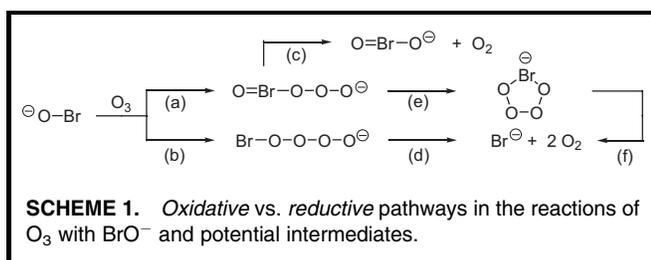
SCHEME 1. *Oxidative* vs. *reductive* pathways in the reactions of O_3 with BrO^- and potential intermediates.

contaminations, and we are hence hesitant to report the data. The cyclic intermediate formed in reaction [e], Scheme 1, could be modeled without spin contaminations only for the calculation of ΔH (–36 kJ mol^{-1}). Possibly due to program problems, a frequency analysis to calculate ΔG could not be done. Yet, the overall energetics is not affected by this caveat. The overall reaction [3]/[4a], spin allowed, is exothermic ($\Delta G = -36$ kJ mol^{-1}), and the spin forbidden reaction [3]/[4b] is even more so ($\Delta G = -130$ kJ mol^{-1}). The reduction reaction that leads to Br^- plus $2\,O_2$, overall reaction [5]/[6], is energetically favored ($\Delta G = -347$ kJ mol^{-1}) over reaction [3]/[4a/b], and this reaction is spin allowed with two ground state (triplet) oxygens, as their common multiplicity is a singlet. Our data do not allow to distinguish between the two envisaged pathways, [a]/[e]/[f] vs. [b]/[d] in Scheme 1.

There is, however, an argument that is in favor of the [a]/[e]/[f] pathway. BrO^- is more negative at oxygen (86% of excess electron density) than at bromine (14%, Fig. 1). The electronic structure of O_3 is largely bipolar with negative charges at the outer oxygens (Fig. 1). An addition to the oxygen as compared to bromine may be disfavored by charge repulsion despite the fact that O_3 is electrophilic. Thus for the oxidative and the reductive pathways in the BrO^- plus O_3 reaction, there may be just one primary adduct, reaction [a] in Scheme 1, and the branching into the two directions would occur at a later stage, [c] vs. [e].

For reaction [c] there may be a certain barrier for the spin allowed process, as this reaction requires the release of O_2 in its excited singlet state. Reaction [e] in Scheme 1 proceeds on the singlet level and the subsequent release of two ground state (triplet) O_2 molecules, reaction [f] in Scheme 1, is spin allowed. This may be the reason, why the reductive pathway is favored over the oxidative one (for rate constants see above).

For the subsequent oxidation of BrO_2^- to BrO_3^- the overall reaction is also exothermic, not only for the spin forbidden reaction ($\Delta G = -187$ kJ mol^{-1}) but also for the spin allowed one ($\Delta G = -93$ kJ mol^{-1}). It has been

mentioned above that a potential intermediate could not be modeled adequately due to spin contaminations.

CONCLUSION

The DFT calculations support some unusual properties of O_3 reactions, that is reversibility (here: $Br^- + O_3$) and reduction (here: $BrO^- + O_3 \rightarrow Br^- + 2O_2$). Intermediate adducts such as $BrOOO^-$ will be found to be much more wide-spread than hitherto discussed. The all too often claimed importance of the high reduction potential of O_3 does not distinguish between the standard two-electron oxidation potential that is given as 2.07 V (Koppenol, 1982) and the one-electron oxidation potential ($E^0 = 2.2$ V; $E^7 = 1.8$ V at pH 7 (Koppenol, 1982)) that has to be quoted, when ozone reactions are compared with $^\bullet OH$ reactions ($E^7 = 1.9$ V at pH 7 (Wardman, 1989)).

In O_3 and $^\bullet OH$ reactions (pollutant abatement) both are usually of little importance as other reactions, neither related to one-electron nor to two-electron transfer reactions, dominate (for a review on $^\bullet OH$ reactions see (von Sonntag, 2006)). For example, O_3 reacts as a reductant in reactions [5]/[6], and in the Criegee reaction the whole O_3 molecule adds to a C–C double bond. One-electron transfer reactions for which the one-electron reduction potential is a measure is only rarely given by O_3 (Flyunt et al., 2003). The two-electron reduction potential could be a measure for O-transfer reactions, but the above value is based on $O_2(^3\Sigma_g^-)$ release, the spin forbidden reaction. As a consequence, when discussing O_3 and $^\bullet OH$ reactions, one has to be much more specific, and basing their outstanding reactivity on their high reduction potentials is usually misleading.

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