A theoretical study on the reaction of ozone with aqueous iodide

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Abstract

Atmospheric iodine chemistry plays a key role in tropospheric ozone catalytic destruction, new particle formation, and as one of the possible sinks of gaseous polar elemental mercury. Moreover, it has been recently proposed that reaction of ozone with iodide on sea surface could be the major contributor to the chemical loss of atmospheric ozone. However, the mechanism of the reaction between aqueous iodide and ozone is not well known. The aim of this paper is to improve the understanding of such mechanism. In this paper, it is presented an *ab initio* study of the reaction of aqueous iodide and ozone, evaluating thermodynamic data of the different reactions proposed in previous experimental studies. In addition, the structures, energetics and possible evolution of the key IOO⁻ intermediate are discussed for the first time.

1. Introduction

Atmospheric iodine chemistry has received special attention in the last decades (see Saiz-Lopez, Plane et al. 2012¹ and references therein), since it plays a relevant role in tropospheric ozone catalytic destruction^{2,3} and new particle formation.⁴ Moreover, in the polar atmosphere, iodine has also been suggested as one of the possible sinks of gaseous elemental mercury.⁵

Ozone is a key atmospheric molecule. In the stratosphere, it prevents us from the damaging short-wave ultraviolet rays. In the troposphere, ozone absorbs infrared radiation as a greenhouse gas, and it has adverse effects in air quality and public health (see e.g.: Arlene et al., 2015⁶). In the lower atmosphere, ozone is mainly produced over the continents (due to the oxidation of organic compounds during daytime in the presence of nitrogen oxides), and transported to the marine boundary layer where major destruction occurs, mainly by its own photolysis. However, the ozone loss calculated for all the known processes, excluding halogens, accounts for only about 50 % of total loss. In this context, iodine has been proposed as the main contributor to halogen-mediated destruction of ozone.²

Up to date, biogenic sources such as marine macroalgae and phytoplacton have been assumed to be the main supplier of atmospheric iodine compounds, mainly I₂ and iodine-containing organic molecules.⁷ However, these sources cannot account for the total amount of gas-phase iodine oxide concentration observed.^{8,9} Recently, it has been proposed that the reaction of ozone with iodide on the sea surface could be the major contributor to the chemical loss of atmospheric ozone, and that it could also account for about 75 % of the observed iodine oxide levels over tropical Atlantic Ocean.¹⁰

The reaction of aqueous iodide with ozone yields I₂ according to the following previously proposed basic mechanism (aqueous phase is assumed for reactants and products excepted where explicitly indicated):¹¹⁻¹³

Recent studies have pointed that reaction R1 would occur in the air/water interface,¹⁴⁻¹⁶ where I⁻ concentration is enriched in relation to the bulk phase.^{17,18} It is worth to highlight that in fine sea salt aerosol particles the I⁻ concentration observed was about 2 and 4 orders of magnitude higher than in seawater,¹⁹⁻²² consequently it is expected that these reactions could happen into aerosols too, although there are no experimental studies up to date.

Apart from I₂ (g), a previous study revealed that IO (g) was also detected as a product of this reaction, although its release was about 100 times lower than I₂ (g).¹³ In this work, it was proposed that the reaction progresses via an IOO⁻ intermediate, in accord with the identification of an analogous BrOO⁻ intermediate in the reaction of Br⁻ and O₃ at the air/aerosol interface.²³ Taken this into account, reaction R1 could be rewritten as:

IO(g) was suggested as product resulting from the evolution of the IOOO⁻ intermediate by several step reactions, although no experimental confirmation of this mechanism was provided.¹³

More recently, it has been shown that HOI (g) is also emitted to the gas phase (reaction R7) in the reaction between iodide and ozone, even at much higher concentration than I₂ (g) (around 500 times more), therefore hypoiodous acid has been suggested to be the main carrier of iodine from oceans to the atmosphere.^{10, 24}

Furthermore, other experiments conducted on this reaction in aqueous microdroplets have recently revealed that oxidation of iodide by ozone leads to formation in the aqueous phase of different species such as IO₃⁻, IO₂⁻ and I₃⁻, with increasing concentration at higher ozone levels.²⁵ In that work, a possible mechanism for the production of these species in the air/water interface was also suggested:

Nevertheless, there are no systematic kinetic and thermodynamic studies of reactions R1-R10. Such information is desirable to assess the validity of these proposed processes. In this regard, and aiming to gain insight into the mechanism of the reaction between aqueous iodide and ozone, we present here, for the first time, an *ab initio* study of reactions proposed in previous experimental works, paying special attention to their thermodynamic features. In addition, a first theoretical investigation about possible structures and evolution of the key IOOO⁻ intermediate is also presented. As discussed below, the complexity of this system revealed by our *ab initio* study led us to consider the current report as a first piece of evidence on the chemical behavior of the IOOO⁻ intermediate on one side, and as a motivation for future theoretical and/or experimental works on the other side.

2. Methods

Quantum calculations on iodinated species were performed using a shape-consistent averaged relativistic effective potential (AREP)²⁶ to replace the 46-electron core of the iodine atom.²⁷ The AREP formalism has been shown to properly account for relativistic effects encapsulated in the core potential when used with flexible basis sets optimized for AREP operators.²⁸ Valence-only aug-cc-pVTZ and aug-cc-pVQZ (i.e. aug-cc-pVXZ, X = 3 and 4, respectively) basis sets were optimized for the iodine AREP²⁹ following the procedure prescribed for generating correlated consistent basis sets for relativistic core potentials.³⁰ Conventional aug-cc-pVXZ basis sets were employed for H and O atoms.

Optimized geometries and frequencies were obtained in second order Moller-Plesset calculations (MP2) with both X = 3, 4 correlated consistent basis sets checking in all cases that the geometries were true minima. Single point coupled cluster calculations, using single and double substitutions and including triple excitations, CCSD(T), energies were then computed at those optimized geometries, and complete basis set (CBS) extrapolation for these energies and aug-cc-pVXZ basis sets was determined with the two-point T-Z extrapolation formula: $E^{\text{corr}}(\infty) = E^{\text{corr}}(X) + B/(X+1/2)^3$, X = 3 and 4.³¹ Zero-point energies (ZPEs), enthalpy corrections and absolute entropies were determined at MP2/aug-cc-pVQZ frequencies calculations.

Additionally to gas phase calculations, two solvation models were also considered to treat all the species studied in the aqueous phase: (i) the polarizable continuum model (PCM)³², which is one of the most widely used self-consistent reaction field models; and (ii) the COnductor-like Screening MOdel (COSMO) continuum solvation model which describes dielectric screening effects in solvents.^{33, 34} The same set of calculations employed for the gas phase was used for both solvation models.

Spin-orbit (SO) corrections were obtained with the pseudopotential spin-orbit density functional theory (SODFT) method implemented in NWChem.³⁵ This approach uses a relativistic two-component Hamiltonian that can be developed in either a basis set framework based on the zeroth-order regular approximation, or a SO pseudopotential framework.³⁶ We used the latter procedure that requires the definition of an effective core potential and a matching SO potential, as that already constructed within the shape-consistent AREP formalism.^{26, 28} After exploring different functionals customarily recommended for SODFT calculations³⁷ (namely ACM, PBE0, and B3LYP) together with our AREP-SO operators for iodine in some benchmark molecules,³⁸ we selected the B3LYP hybrid functional together with the aug-cc-pVQZ basis set for computing SO corrections in the gas phase of all the iodine species addressed in this work.

For the particular case of the ionic intermediate IOOO⁻, transition structures (TSs) between pairs of equilibrium geometries (see below) were also located by means of the QST2 (quadratic synchronous transit) approach³⁹ from reactant and product input structures. These TS geometries were obtained at the MP2/AREP/aug-cc-pVQZ level of theory in both gas phase, and PCM solvated phase, and CCSD(T) energies (including CBS extrapolation) were then computed in single-point calculations at these MP2 QST2 geometries. Aimed to characterize the bonding nature of the IOOO⁻ intermediate, topological analysis of the electron density $\rho(\mathbf{r})$ of the three gas phase equilibrium structures was also conducted. $\rho(\mathbf{r})$ was obtained in all-electron MP2/TZVPP calculations and critical points of $\rho(\mathbf{r})$ were located and characterized according to the Atoms in Molecules (AIM) theory^{40, 41} with the AIMAll package,⁴² which was also used to compute AIM atomic charges. In addition, atomic charges to fit the electrostatic potential according to the CHelpG scheme,⁴³ and those corresponding to the natural population analysis (NPA) phase of natural bond orbital (NBO)⁴⁴

calculations, were also obtained in both MP2/AREP/aug-cc-pVQZ and all-electron MP2/TZVPP calculations. An atomic radius 2.4 Å for iodine obtained by multiplying its standard Van der Waals radius 2.0 Å by the factor 1.2 used in CHelpG calculations for the Van der Waals radius of oxygen⁴² was employed to obtain CHelpG charges.

Geometries, frequencies, and energies regarding gas phase and PCM solvated phase as well as QST2, CHelpG and NBO calculations were performed with Gaussian 09.⁴⁵ SODFT and COSMO calculations were carried out with NWChem 6.5.³⁵

Thermodynamic data (enthalpies and Gibbs free energies of the studied reactions) were calculated using the following procedure: (i) first, geometries were optimized at the MP2/aug-cc-pVQZ level and ZPE, entropy and enthalpy corrections calculated at these structures; (ii) then single point CCSD(T)/aug-cc-pVXZ (X= T,Q) calculations were carried out at these geometries to include CBS correction; (iii) finally, SO corrections obtained as described above were added to total energies.

3. Results and Discussion

3.1. Thermodynamic study of aqueous phase reactions of iodide with ozone.

In order to assess the reliability of our methodology, especially that concerning evaluation of thermodynamic properties in aqueous solution, we used different approaches to compute the standard enthalpy of reaction R11:

for which a reliable experimental value is available in aqueous solution.⁴⁶ The reason to test just enthalpy instead of Gibbs free energy, is that inaccuracies in these energies are the main source of errors in *ab initio* determination of Gibbs free energies of reactions, as entropies are usually rather well estimated. The results of this test are presented in Table 1, where it can be seen that both PCM and CPCM enthalpies provide reasonable estimates, and COSMO result is in excellent agreement with the experimental value. With the support provided by this result, PCM and COSMO schemes were chosen to compute Gibbs free energies of the aqueous reactions studied in this work.

Table 1. Computed and experimental standard enthalpy of reaction R11 in kcal.mol⁻¹

	PCM	CPCM	SMD	COSMO	Experimental ^a
$\Delta_f H^0$	-67.42	-67.03	-79.21	-69.89	-69.81

^a Values calculated using experimental standard free enthalpies of formation in aqueous solution from West et al, 1984:⁴⁶ $\Delta_f H^0$ (I⁻) = -13.19, $\Delta_f H^0$ (O₃) = 30.1 and $\Delta_f H^0$ (IO₃⁻) = -52.9 in kcal.mol⁻¹.

As mentioned in the introduction, the reaction between iodide and ozone in aqueous phase has been postulated to evolve by forming an IOO⁻ intermediate. Different conformations for this species characterized as real minima in the potential energy surface were found in geometry optimizations and are depicted in Figure 1. Two different situations with three different conformers can be distinguished, one for which the geometry resembles an I⁻...O₃ adduct with a van der Waals-type interaction (conformation C1 in what follows), and another for which an IO⁻...O₂ geometry either in trans or cis arrangement (herein conformations C2 and C3, respectively) were found. A topological analysis on the nature of bonding for the interactions underlying those structures is presented below.

Considering the existence of these three conformers for the anionic IOO⁻ intermediate, we postulate a mechanism in which reaction R4 initially progresses via formation of the adduct I⁻...O₃ (C1), which then undergoes an internal restructuring to yield an IO⁻...O₂ conformations, C2 (R12a) or C3 (R12b), which they could also be in equilibrium between them (R12c):

Thermodynamic data calculated for the previous reactions together with other reactions that have been proposed in previous experimental studies are summarized in Table 2. The initial reaction between iodide and ozone to give IOO⁻ (C1) presents a large positive Gibbs free energy (approx. 20 kcal mol⁻¹), while small negative values are obtained in the intramolecular conversion from C1 to C2 conformation or even to C3. These results suggest that after I⁻...O₃ complex formation it is expected a spontaneous evolution towards the IO⁻...O₂ structure, which also shows a much larger negative free energy for the final release of IO⁻ in the aqueous phase (approx. -42 kcal mol⁻¹, reaction R5). The $\Delta_r G$ for the global reaction $\text{I}^- + \text{O}_3(\text{g}) \rightarrow \text{IO}^- + \text{O}_2$ is finally a large negative value around -25 kcal.mol⁻¹, even larger than the analogous value for the reaction with bromine, around -17 kcal.mol⁻¹

^{1, 47} In consequence, it is expected that the first step of this reaction (R4b) to be thermodynamically limited if there is not an extra source of energy, but once IOOO⁻ (C1) is formed the process is expected to be very fast. It has been proposed before that I⁻ + O₃ reactions happen mainly in the water interface,²⁵ which is in line with these results, since the extra energy required for C1 formation could be supplied by the kinetic energy of ozone in its uptake to water in the interface.⁴⁸ Moreover, it is expected that other sources of energy such as light or temperature could activate this process, too.

Previous experimental studies about the effect of temperature into the rate coefficient of this reaction present contradictory results. In fact, while Magi et al.⁴⁹ give a positive value of 17±7 kcal.mol⁻¹ for the activation energy that would be in line what it is observed in this work, other studies indicate a null or negative activation energy.²⁴ However, we need to take into account that different experimental techniques and different species were monitored in those studies. While in the first study ozone was monitored, in the second one final products, HIO and I₂, were measured. Further experimental and theoretical research that includes determination of rate coefficients in function of temperature would be desirable to confirm whether these reactions are barrierless or not.

Once IOOO⁻ complex (C2 or C3 conformers) is formed, in addition to formation of IO⁻ and O₂ (g), it could yield IO(g) and O₂⁻ anion by the following reactions:

which could be a possible pathway for IO(g) formation, product observed in previous experiments.¹³ This possible pathway is further discussed in next section.

Additionally, IO⁻ could be formed in R5a or R5b:

IO⁻ is the conjugate base of the weak hypoiodous acid (HOI), which is expected to be mainly in its protonated form at pH typical of sea water (pH_{OCEAN} ≈ 8).¹⁰ Our computed value for Gibbs free energy of this reaction shows a fair agreement with the experimental value obtained from its pK_a.¹³ HOI could escape from the aqueous phase according to reaction R7, resulting in a slightly endergonic process, in nice agreement with the experimental value (see Table 2). However, aqueous HOI could further react with more iodide (R2) and/or dissolved ozone (R8) to generate new species being both processes predicted spontaneous in our study. Consequently, and in agreement with experimental findings, the HOI(g) concentration is expected to be larger than I₂(g) concentration at low I⁻ and O₃ concentration.¹⁰

Table 2. Calculated and estimated Gibbs free energy of reactions studied in kcal.mol⁻¹.

ID	Reaction	$\Delta_r G$		
		PCM	COSMO	Exp.
R1	$\text{H}^+ + \text{I}^- + \text{O}_3 \rightarrow \text{HOI} + \text{O}_2$	-44.75	-42.54	
R2	$\text{HOI} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O}$	-28.92	-28.71	
R3	$\text{I}_2 \rightleftharpoons \text{I}_2 (\text{g})$	1.04	1.68	0.66 ^a
R4a	$\text{I}^- + \text{O}_3 (\text{g}) \rightarrow \text{IOOO}^- (\text{C1})$	21.18	19.07	
R4b	$\text{I}^- + \text{O}_3 \rightarrow \text{IOOO}^- (\text{C1})$	21.35	20.74	
R5a	$\text{IOOO}^- (\text{C2}) \rightarrow \text{IO}^- + \text{O}_2$	-42.00	-42.71	
R5b	$\text{IOOO}^- (\text{C3}) \rightarrow \text{IO}^- + \text{O}_2$	-48.72	-44.47	
R5c	$\text{IOOO}^- (\text{C3}) \rightarrow \text{IO} + \text{O}_2^-$	-13.35	-9.10	
R6	$\text{IO}^- + \text{H}^+ \rightleftharpoons \text{HOI}$	-19.13	-17.08	-15.01 ^b
R7	$\text{HOI} \rightleftharpoons \text{HOI (g)}$	3.09	4.90	3.10 ^c
R8	$\text{HOI} + \text{O}_3 \rightarrow \text{IO}_2^- + \text{O}_2 + \text{H}^+$	-23.30	-25.21	
R9	$\text{IO}_2^- + \text{O}_3 \rightarrow \text{IO}_3^- + \text{O}_2$	-82.15	-80.90	
R10	$\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$	16.97	15.72	-3.90 ^d
R11	$\text{I}^- + \text{O}_3 \rightarrow \text{IO}_3^-$	-59.60	-61.69	
R12a	$\text{IOOO}^- (\text{C1}) \rightarrow \text{IOOO}^- (\text{C2})$	-4.98	-3.50	
R12b	$\text{IOOO}^- (\text{C1}) \rightarrow \text{IOOO}^- (\text{C3})$	1.74	-1.73	
R12c	$\text{IOOO}^- (\text{C2}) \rightleftharpoons \text{IOOO}^- (\text{C3})$	6.72	1.76	
R13	$\text{IO} \rightleftharpoons \text{IO (g)}$	2.37	6.23	
R14	$\text{IO}_2^- + \text{H}^+ \rightleftharpoons \text{HIO}_2$	-12.88	-11.11	
R15	$\text{HOI} + 2\text{O}_3 \rightarrow \text{IO}_3^- + 2\text{O}_2 + \text{H}^+$	-105.4	-106.1	
R16	$\text{IO}^- + 2\text{O}_3 \rightarrow \text{IO}_3^- + 2\text{O}_2$	-124.5	-123.2	
R17	$\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$	-70.82	-65.11	

^a Experimental value obtained from K_{eq} = 0.33, Ref. ⁵⁰

^b Experimental value obtained from pK_a(HOI) = 11.05 in Ref. ⁵¹

^c Experimental value obtained from K_{eq} = 5.34×10⁻³, Ref. ⁵²

^d Experimental value obtained from K_{eq} = 721, Ref. ⁵³.

The reaction of HOI with iodide is predicted to be a very exergonic process that would produce the spontaneous formation of I_2 (aq), which in turn it could be also released to the gas phase (R3). Nevertheless, dissolved I_2 could additionally react with more iodide to produce I_3^- anions (R10). In this case, our calculated value is far from the experimental one, which predicts formation of this anion as a favorable process (see Table 2). Considering that the estimates for the values of other reactions involving I^- and I_2 are in good agreement with experiment (e.g. R3 and R11), we suspect that our calculated values for the I_3^- anion in the aqueous phase should be the main reason for this discrepancy. Moreover, previous results obtained by our group using a similar methodology to test different properties of I_3^- in the gas phase yielded a nice agreement with experimental data.²⁹ Consequently, we believe that the approximations involved in usual solvation models employed in quantum calculations, such as those used in this work, are not adequate for the particular case of this peculiar anionic molecule. Given that I_3^- is a highly polarizable molecule since it contains three iodine atoms, it can be proposed that continuum approximations to treat the solvent could not describe properly interactions with water molecules. The linear voluminous structure of this anion would suffer significant variations in the aqueous environment making rather difficult to treat theoretically, as it is known that the potential energy surface of I_3^- in water is fairly flat.^{54, 55}

Continuing with the discussion of the different pathways for the reaction of iodide with ozone depending on dissolved ozone concentration, if the concentration is high enough, HOI can be further oxidized and form iodite or iodate species following reactions R8 and R9. From a thermodynamically point of view, both processes are highly favored, especially the transformation of iodite to iodate, which could explain that iodate is the final species that accumulates onto aerosols, and iodite is uniquely observed as a transient species.²⁵ R15-R17 reactions summarize the processes indicated above.

3.2. Nature of bonding in the intermediate ion IOOO⁻

As mentioned above, three stable (true minima) structures were found for the intermediate ion IOOO⁻ with geometries shown in Fig. 1 and Table 3. Except for minor differences regarding some geometry parameters that are below analyzed, these structures are qualitatively similar in the gas phase and in the two solvation models, PCM and COSMO, considered here. Both approaches agree in predicting C2 as the lowest lying structure, but PCM places C1 at ~5 kcal.mol⁻¹ and then C3 at ~7 kcal.mol⁻¹ above C2, whereas COSMO modifies this energetic order predicting C3 as the structure with minimum energy after C2 with only ~2 kcal.mol⁻¹ more, and then C1 at 3.5 kcal.mol⁻¹ above C2 (see Table 2). It must be noted that previous reports of *ab initio* calculations on the BrOOO⁻ intermediate arising from reactions of ozone with bromide either found only one conformer (with structure similar to our C1 geometry of IOOO⁻),^{56, 57} or were unable to find theoretical evidence on the existence of these species, in this case probably due to the level of theory employed.⁴⁷ With the objective to characterize the nature of bonding, as well as the charge balance in these structures, we gather some topological descriptors of bond critical points (BCPs) of $\rho(r)$ in Table 4, together with atomic charges computed with three different population analyses, namely NPA, CHelpG, and AIM, in Table 5. Since the topology of $\rho(r)$ and atomic charges provide information on the electron distribution associated to the nature of bonding in IOOO⁻, these properties are addressed only for geometries in the gas phase.

Table 3. MP2/AREP/aug-cc-pVQZ optimized geometries of the three equilibrium structures of the intermediate ion IOOO⁻ in gas and solvated phases obtained in PCM and COSMO calculations

Parameter	Gas	PCM	COSMO
<i>C1 geometry</i>			
$r(I1-O2)$	2.754	2.720	2.704
$r(O2-O3)$	1.374	1.371	1.362
$r(O3-O4)$	1.282	1.286	1.279
$\alpha(I1-O2-O3)$	100.4	98.4	100.8
$\alpha(O2-O3-O4)$	114.2	113.3	113.9
$d(I1-O2-O3-O4)$	69.6	65.9	69.9
<i>C2 geometry (trans-)</i>			
$r(I1-O2)$	1.908	1.927	1.927
$r(O2-O3)$	1.950	1.888	1.936
$r(O3-O4)$	1.274	1.275	1.274
$\alpha(I1-O2-O3)$	99.3	99.6	97.3
$\alpha(O2-O3-O4)$	111.4	111.0	113.1
$d(I1-O2-O3-O4)$	180.0	180.0	180.0
<i>C3 geometry (cis-)</i>			
$r(I1-O2)$	1.856	1.863	1.870
$r(O2-O3)$	2.104	2.082	2.082
$r(O3-O4)$	1.441	1.449	1.425
$r(O4-I1)$	2.411	2.429	2.446
$\alpha(I1-O2-O3)$	91.3	92.8	92.9
$\alpha(O2-O3-O4)$	99.0	98.6	99.1
$\alpha(O3-O4-I1)$	91.31	91.5	91.7
$\alpha(O4-I1-O2)$	78.45	77.1	76.2
$d(I1-O2-O3-O4)$	0.0	0.0	0.0

Atom numbering and geometry labels refer to Fig. 1. Bond lengths r in Å, bond angles α and dihedrals d in degrees.

Table 4. Topological descriptors of critical points of the all-electron MP2/TZVPP electron density computed at gas phase MP2/AREP/aug-cc-pVQZ optimized geometries of three equilibrium structures of the intermediate ion IOOO⁻

Bond	ρ_c	$\nabla^2\rho_c$	ϵ	G_c	V_c	H_c
<i>C1 geometry</i>						
I1-O2	0.0316	0.0779	0.1503	0.2076	-0.2205	-0.0129
O2-O3	0.3371	0.1529	0.0438	0.3251	-0.6119	-0.2868
O3-O4	0.4372	-0.3229	0.0607	0.4113	-0.9034	-0.4921
<i>C2 geometry (trans-)</i>						
I1-O2	0.1511	0.3089	0.0279	0.1606	-0.2441	-0.0835
O2-O3	0.0805	0.2645	0.1857	0.0732	-0.0803	-0.0071
O3-O4	0.4424	-0.3461	0.0407	0.4200	-0.9266	-0.5066
<i>C3 geometry (cis-)</i>						
I1-O2	0.1672	0.4385	0.0041	0.2062	-0.3028	-0.0966
O2-O3	0.0571	0.1848	0.1196	0.0494	-0.0525	-0.0031
O3-O4	0.2749	0.2835	0.0010	0.2537	-0.4364	-0.1827
O4-I1	0.0602	0.1043	0.2450	0.0398	-0.0536	-0.0138
RCP	0.0272	0.1457		0.0329	-0.0294	+0.0035

Atom numbering and geometry labels refer to Fig. 1. All values (atomic units) correspond to (3,-1) bond critical points except RCP that is the (3,+1) ring critical point in the C3 geometry. Topological descriptors are the following variables computed at the critical points: electron density ρ_c , Laplacian of the electron density $\nabla^2\rho_c$, ellipticity ϵ , kinetic energy density G_c , potential energy density V_c , and total energy density $H_c = G_c + V_c$

The main feature of IOOO⁻ structures is that C1 can be regarded as a (I...O₃)⁻ arrangement that would directly arise from reaction of iodide with ozone, whereas both C2 and C3 structures might be viewed as trans and cis isomers of a (IO...O₂)⁻ arrangement, respectively, being the trans isomer more stable. To analyze these geometries, it is helpful to take into account the following results obtained at same levels of theory for the components of those two arrangements (they are given in the following order: gas, PCM and COSMO). Bond lengths (Å) in IO⁻: 1.899, 1.918, 1.919. *Ibid.* in O₂: 1.216, 1.216, 1.216. *Ibid.* in O₃: 1.275, 1.274, 1.272 and bond angle (°) in O₃: 116.9, 116.7, and 116.7. In what follows, we discuss C1, C2, and C3 structures in turn addressing together geometries (Table 3), topological properties of BCPs (Table 4) and atomic charges (Table 5).

Table 5 All-electron MP2/TZVPP atomic charges computed at gas phase MP2/AREP/aug-cc-pVQZ optimized geometries of three equilibrium structures of the intermediate ion IOOO⁻

Atom	NPA	CHelpG	AIM
<i>C1 geometry</i>			
I1	-0.600	-0.668	-0.572
O2	-0.345	-0.224	-0.335
O3	+0.160	+0.079	+0.133
O4	-0.215	-0.187	-0.226
<i>C2 geometry</i>			
I1	+0.260	-0.295	+0.289
O2	-0.836	-0.312	-0.859
O3	-0.196	-0.108	-0.172
O4	-0.228	-0.285	-0.258
<i>C3 geometry</i>			
I1	+0.607	-0.081	+0.630
O2	-0.838	-0.344	-0.869
O3	-0.304	-0.280	-0.311
O4	-0.465	-0.295	-0.450

Atom numbering and geometry labels refer to Fig. 1.
All values in atomic units.

In C1, the long I1-O2 distance ~ 2.7 Å, and O2-O3 and O3-O4 distances ~ 1.37 and 1.28 Å respectively, similar to that of ozone (1.27 Å), clearly suggest that this structure could be considered an $\text{I}\cdots\text{O}_3$ aggregate, as mentioned before. The I1-O2 bond path shows topological properties indicative of a weak interaction:^{40, 41} small values of the electron density (ρ_c) and its positive Laplacian (local depletion of electron charge) at the BCP ($\nabla^2\rho_c$), a relatively large ellipticity (ϵ), and small values of kinetic (G_c) and potential (V_c) energy densities, which yield a very small (though still negative) total energy density (H_c) at the BCP that hints at weak covalent features (Table 4). On the contrary, the O3-O4 bond path shows typically covalent values of these descriptors: large ρ_c , large negative $\nabla^2\rho_c$ (local concentration of electron charge), small ϵ (low anisotropy of the electron density at the BCP), and large energy densities G_c , V_c , and H_c with values prototypical of strong covalent bonds. The interaction between I1 and O2 atoms produces an O2-O3 bond distance ~ 1.37 Å, a bit longer than that of ozone (1.27 Å), and an O2-O3-O4 bond angle $\sim 114^\circ$ a bit closer than that of ozone (117°). While still exhibiting clearly covalent features, the topological descriptors of the O2-O3 bond path indicate a slightly weaker interaction when compared to those of the O3-O4 bond path. The basins path map (Fig. 1) of C1 structure reveals a clear separation between the atomic basin of iodine and those of oxygen atoms. Recall that in AIM theory, the nuclei are the attractors of the gradient vector field of $\rho(r)$, and that the region of space traversed by the trajectories terminating at a nucleus defines a basin. An "atom" in AIM theory is just defined by the union of an attractor (nucleus) and its basin, so that the space of a molecule can be unambiguously partitioned into 3D atomic basins. The dihedral angle ~ 66 - 70° gives rise to a sharp separation between the basins of iodine and the three oxygen atoms that lend further support to the " $\text{I}\cdots\text{O}_3$ " picture of this structure. Contrarily to what happens with structures C2 and C3 (Table 5), the three sets of atomic charges are also consistent in predicting a differentiated role for iodine, which bears most of the negative charge of this anionic intermediate.

In relation to the influence of the aqueous environment on C1 structure predicted by PCM and COSMO approaches, geometry data in Table 3 suggest minor changes with respect to the gas phase. Both methods agree in predicting for the solvated phase slightly shorter I1-O2 and O2-O3 distances, and a bit closer O2-O3-O4 bond angle than for the gas phase, while they differ in the changes predicted for O3-O4 bond length, I1-O2-O3 bond angle and the dihedral angle. However, all these differences are so small that it could be stated that the aqueous environment has no significant effect on this C1 geometry, a feature also found for C2 and C3 conformations.

C2 is the most stable of the three IOOO^- equilibrium structures found. In this geometry, I1-O2 and O3-O4 are nearly equal to those of isolated IO^- and O_3 molecules, respectively, while the very long O2-O3 distance 1.89 - 1.95 Å clearly indicates a weak bonding between I1O2 and O3O4 segments. Note that the O3-O4 bond length does not resemble that of oxygen molecule, but rather it is essentially identical to that of ozone, as it happens in C1. Note additionally that I1-O2-O3 and O2-O3-O4 bond angles are not very different to those of the C1 geometry. However, the topological analysis of the electron density establishes a major difference between C1 and C2 structures with regard to the properties of oxygen atoms. In fact, while the O3-O4 bond path exhibits nearly identical features in C2 and C1 geometries (Table 4), the O2-O3 bond path in C2 shows values reminiscent of a weak interaction (small ρ_c , large ϵ , and so small values of G_c , V_c , and H_c that they might barely make one think of a covalent bond), contrarily to what happens in C1 where this bond path may be regarded as conventionally covalent. The basins path maps exhibits the features expected for a plane molecule: tight arrangement of vector field lines in the proximity of the critical points with sharp separatrices between contiguous atomic basins.

In contrast with C1 results, atomic charges in C2 are inconsistently predicted by the three population analyses (Table 5). In spite of following completely different theoretical approaches, NPA and AIM methodologies closely agree in predicting a large negative charge on O2 atom and a positive charge on I1 atom. On the contrary, CHelpG charges (obtained under the condition to reproduce the electrostatic potential) place a similar negative value on those two atoms. The three sets of results agree, however, in predicting a total negative charge about $-0.6e$ for the I1-O2 segment, although it appears that the reproduction of the electrostatic potential poses a constraint in the form of shared contributions from both atoms. No significant differences are noticed in the O3-O4 segment as the three sets of results agree in giving a net charge about $-0.4e$ for it.

The ring C3 structure is that presenting the greatest differences with respect to reference IO^- and O_3 molecules. The spatial constraints imposed by this cyclic structure give place to a short I1-O2 bond distance, and particularly long O2-O3 and O3-O4 distances. In this case, and contrary to C2 conformation, both I1-O2 and O3-O4 are now more similar to IO and O_2^- monomers (1.839 and 1.346 Å, respectively). Although it is not expected a bond between I1 and O4 given their interatomic distance longer than 2.4 Å, the topology of ρ_c reveals not only that a bonding interaction does exist, but also that it shows covalent-like features, even more than the I1-O2 bond in C1 structure. Except for the obvious difference arising from the presence of a ring critical point in C3, the basins path map of this geometry is equivalent to that of C2. Atomic charges show again the same discrepancy as in C2: similar NPA and AIM results predicting a large negative charge on O2, and a significant positive charge on I1 that nearly cancel each other, while CHelpG charges predict a nearly neutral iodine atom and a negative O2 atom with $-0.34e$ charge. Contrary to that found in C2, now the three sets of atomic charges predict more negative values in the segment O3-O4 ($0.76e$ in NPA and AIM, and $0.57e$ for CHelpG) than I1-O2 in concordance with the bond distances analyzed above. This indicates that while the final product from the most stable conformer C2 is HOI while final products from C3 conformer would be $\text{IO} + \text{O}_2^-$. This is in agreement with the fact that experimentally it has been observed that the main gas phase product is HIO , being IO a less important product.²⁴

3.3. Reaction path of changes in the conformations of IOOO^-

In order to explore the formation process of C1 structure of IOOO^- intermediate from addition of O_3 and I^- , we obtained an energy curve at MP2/aug-cc-pVQZ calculations, including solvation effects with PCM, scanning the $\text{I}\cdots\text{O}_2$ distance from as large values as 6 Å ($\text{I}^- + \text{O}_3$ as separated reactants), to a short 2 Å distance (Fig. S1 in Supplementary Information). The main feature found is that I^- and O_3 attract each other until reaching a

flat region between 2.6 and 3.8 Å in which energy varies only ~ 0.5 kcal.mol⁻¹. The ΔE of formation of C1 with respect to the reactants obtained in MP2/aug-cc-pVQZ/PCM calculations is -6.29 kcal/mol (C1 more stable in these *ab initio* results). Analyzing Fig S1, the consequence is that formation of C1 takes place without transition state (TS) formation at the MP2 level of theory. However, the picture changes considerably when CCSD(T) energies are computed. Single point values (at MP2/QZ equilibrium geometries) with TZ and QZ basis sets give $\Delta E = 2.50$ and 3.62 kcal.mol⁻¹, respectively (C1 is now less stable than reactants). Moreover, inclusion of distinct corrections has the effect of increasing the differences. Thus, CBS correction places ΔE at 4.35, ZPE increases it until 6.64 and finally, spin orbit effects give $\Delta E = 12.89$ (all values in kcal.mol⁻¹). If Gibbs free energies are now considered, still larger differences are found, until reaching the value 21.35 kcal/mol, which was that presented in Table 2.

Upon finding these results, we addressed the possibility that the CCSD(T) energy surface could be substantially different to that obtained with MP2 geometries. To this end and taking into account that use of QZ basis sets in CCSD(T) optimizations are computationally prohibitive, we obtained the structure for C1 in CCSD(T)/TZ calculations just trying to localize the minimum. This geometry happened to be similar to the MP2/QZ one (Fig. S2 in Supplementary Information). However, since small differences were observed in those geometries, we evaluated ΔE of the reaction including only CBS correction obtaining a result of 2.44 kcal.mol⁻¹, close to the value found at the MP2/aug-cc-pVQZ optimization (4.35 kcal.mol⁻¹; see above). In this case, the conformational space of the MP2 energy surface should be thus considered equivalent to that obtained at the CCSD(T) level of theory. According to these results, CCSD(T) would predict C1 formation to be an endothermic process, so that the existence of a TS should be considered in this case, and a full treatment to search for the geometry of the TS or alternatively, an energy curve scanning the I-O₂ distance in a similar manner to that done to obtain Fig. S1 had to be carried out. Since CCSD(T) calculations for both possibilities are enormously costly (particularly the frequencies calculation needed to find the TS), such a study is beyond the scope of the current work, and it had to be considered in forthcoming research.

Conversion of C1 in either C2 or C3 is predicted to occur with only one TS in MP2/aug-cc-pVQZ/PCM calculations. Another TS is also found to join C2 and C3. To further explore these conversions, we run minimum energy paths from the TS joining C1 with C2 or C3 (see Fig. 2). Point labelled "TS_{C1-C2/3}" in this curve denotes the origin in the corresponding reaction path. The backward process leads to the C1 state at an energy difference about 24 kcal.mol⁻¹ for the geometry displayed in Fig. 2 (this difference for MP2/aug-cc-pVQZ/PCM fully optimized structures of C1 is 26.42 kcal.mol⁻¹). The curve for the forward process reveals more features. For instance, it shows a first plateau (labelled TS' in Fig. 2) which corresponds to a geometry similar to that found for the TS joining C2 with C3 (also shown in Fig. 2, TS_{C2-C3}): for example the O1...O2 distance is 1.801 Å in TS' and 1.891 Å in TS_{C2-C3}. One might conjecture that going from TS_{C1-C2/3} one could pass through TS_{C2-C3} and there would then be a bifurcation point to reach either C2 or C3 structures. Following that curve and after a slight change of curvature, the final point is C3 structure (see Fig. 2) at an energy difference about 27 kcal.mol⁻¹ (this difference for MP2/aug-cc-pVQZ/PCM fully optimized structures of C3 is 27.43 kcal.mol⁻¹). However, the picture on these conversions again changes drastically upon performing single point CCSD(T) calculations and including CBS, ZPE and SO corrections.

A ΔG diagram for minima in the formation and destruction of the IOO⁻ conformers is sketched in Figure 3. Since CCSD(T)/aug-cc-pVTZ/PCM geometries for those minima were similar to the equivalent MP2 geometries, we might consider that diagram is essentially correct. For example, the conversion of C1 to C2 yields a ΔG of -4.98 kcal.mol⁻¹ using optimized MP2 geometries or -3.04 kcal.mol⁻¹ at CCSD(T) minima. The major differences arise from C3 conformation (see Fig. S2 in Supplementary Information), although the order and final energy values of the different conformers in the diagram are essentially similar. Nevertheless and as mentioned above, a detailed description including ΔG values for the different TSs in this diagram would obviously need a complete CCSD(T) treatment, a computational task so demanding that it would require a specific work far beyond the scope of the first report on the problem being presented here. As observed in Fig. 3, after formation of the C1 structure needing around 20 kcal.mol⁻¹, this intermediate could progress to release of IO⁻ and O₂, or IO and O₂⁻ in the aqueous phase without thermodynamic barrier. However, it is important to highlight that in the most energetically favorable case (release of O₂ and IO⁻), our calculated values assume that O₂ is generated in the most stable electronic configuration, namely X³Σ_g⁻, which would imply a change of spin-state from the singlet state of IOO⁻ (produced by addition of the reactants in their most stable singlet states) to the triplet state of oxygen. As another possibility, an internal change of spin state of IOO⁻ intermediate from singlet to triplet (IOO⁻ (¹X) → IOO⁻ (³A)) could release X³Σ_g⁻ O₂ as final product. To explore these possibilities, we performed optimizations at MP2/aug-cc-pVQZ/PCM calculations for the three conformers of IOO⁻ in their triplet states (results shown in Figure S3 in Supplementary Information). The geometry of the conformers underwent different changes, yielding for example larger IO...O₂ distances for C2 and C3 conformers, and a O2-O3 bond length close to the value in X³Σ_g⁻ O₂ molecule (1.216 Å). In any case, the triplet states of these conformers are less stable than singlets: 3.33, 15.93 and 10.28 kcal.mol⁻¹ for C1, C2 and C3, respectively (these values include CBS, ZPE, SO and G corrections as described in Methods section). According to these results, the possible change of the spin state in the IOO⁻ intermediate could occur in the C1 conformation since it would need only an energy about 3 kcal.mol⁻¹. We must stress again that a more exhaustive study accounting for treatment of electron correlation of triplet and singlet electronic states at very high levels of theory is needed in the future to further explore the hypersurface of IOO⁻.

As a general experimental finding, reactions which imply electronic spin changes are usually more hindered,^{58, 59} so alternatively we can assume that the oxygen product could be released in ¹Δ_g state, similarly to what occurs when aqueous solutions of Cl₂ (or hypochlorite ion) and hydrogen peroxide are mixed⁶⁰. For this case, pioneering works date back to 1927 detected the red glow accompanying the OCl⁻ + H₂O₂ reaction, chemiluminescence which subsequent reports attributed to the transition of excited singlet oxygen molecules (¹Δ_g) to ground triplet state. In our reaction, ¹Δ_g oxygen and IO⁻ could similarly be the main products released from C2 or C3 conformations of IOO⁻ both in their ground singlet states. It is well known that excited oxygen is more reactive than the ground triplet state, so it could have an important role in the evolution of the present reaction, although radiation-less relaxation to the ground state from collisional interaction with solvent molecules could also occur.⁶¹ In any case, the destruction of C2 or C3 structures of IOO⁻ via release of ¹Δ_g O₂ + IO⁻ are predicted to be exergonic, with calculated Gibbs free energies -12.65 and -19.37 kcal.mol⁻¹ from C2 and C3, respectively. These results are lower (in absolute value) than those for release of X³Σ_g⁻ oxygen (-42.00 and -48.72 kcal.mol⁻¹ from C2 and C3 respectively, see Table 2).

Conclusions

An *ab initio* study of the reaction of aqueous iodide and ozone, evaluating thermodynamic data of the different reactions proposed in previous experimental studies has been done for the first time. It has been shown that the reaction may progress through a key IOOO⁻ intermediate that presents three different conformers. The formation of this intermediate is the crucial stage in the global reaction, and it is thermodynamically limited and probably it is the rate-limiting step. Our first set of results presented in the current work point to the possibility that formation and destruction of this intermediate could involve different transition states even implying spin-crossing reactions. As other alternative, evolution of the IOOO⁻ intermediate could yield electronic excited products such as ¹Δ_g oxygen. In any case, considering the intricacy of the changes between the possible structures of IOOO⁻, our results should be viewed as a first piece of evidence that has revealed for the first time the complex reaction pathway involved in formation and destruction of a key intermediate in the reaction of iodide and ozone. A further research on this molecular system would need a treatment of electron correlation at CCSD(T) or equivalent very high levels of theory, a demanding computational task which is well beyond the scope of the work reported here. However, the calculations presented in this work are reliable enough to predict that, depending on the conformers of IOOO⁻ formed, the reaction could progress to formation of IO or HOI species. Further reaction with I⁻ or O₃ are thermodynamically favored, leading to formation of iodine, iodite or iodate. Experimental observations of different aqueous and gas phase products are in agreement with the mechanism proposed in this work.

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Figure 1. Three equilibrium structures of the intermediate ion IOOO^- showing the bond paths (thick black lines), bond critical points of the electron density $\rho(r)$ (green spheres), and the ring critical point in C3 geometry (small red sphere inside the cycle). Maps on the right display the gradient vector field lines of $\rho(r)$ that define the atomic basins. Values in parentheses are PCM and COSMO differences (kcal mol^{-1}) in total CCSD(T) energies (that include SO, ZPE, CBD, and thermal corrections to Gibbs free energies) with respect to the lowest lying C2 structure.

Figure 2. Reaction coordinate diagram for evolution from the TS joining C1 with either C2 or C3 along forward and backward reaction paths. Sketches of the structures corresponding to selected conformation are also included. A scheme of the whole process is included at the bottom of the diagram.

Figure 3. Reaction coordinate diagram for the variation of Gibbs free energy in the formation and destruction of IOO^- intermediate. ΔG values are calculated as described in Method section.