Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A theoretical study on the reaction of ozone with aqueous iodide

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Supplementary Information

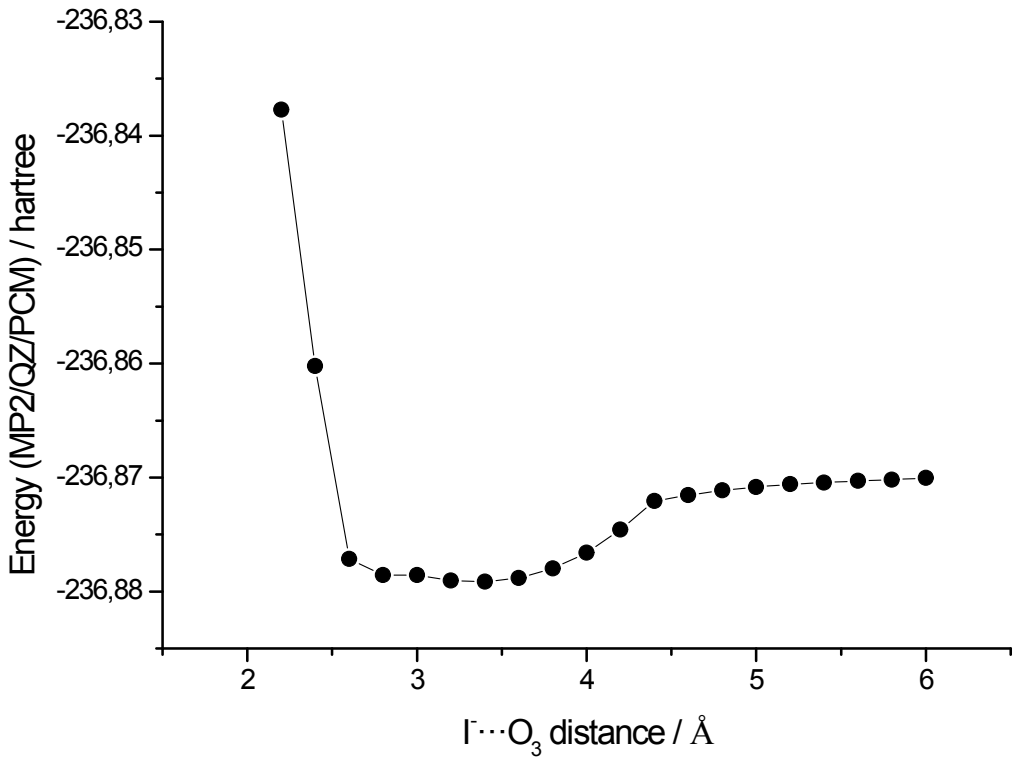
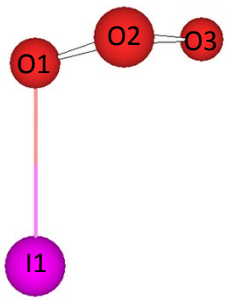
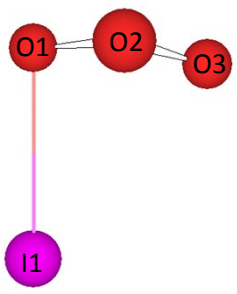


Figure S1. Energy curve at the MP2/aug-cc-pVQZ level including solvation effects with PCM, scanning the I⁻···O2 distance in conformation C1 in Fig. 1.

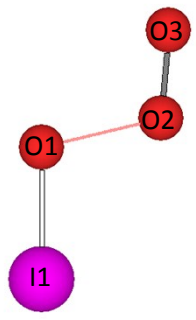


C1 / CCSD(T)

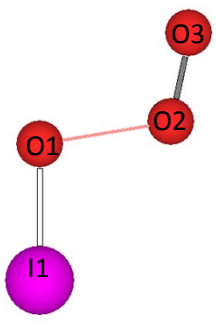


C1 / MP2

	CCSD(T)/TZ	MP2/QZ
R_{I1-O1}	2.642	2.720
R_{O1-O2}	1.303	1.371
$A_{O1-O2-O3}$	108.1	98.4
R_{O2-O3}	1.308	1.286
$A_{I1-O1-O2}$	114.3	113.3
$D_{I1-O1-O2-O3}$	73.6	65.9

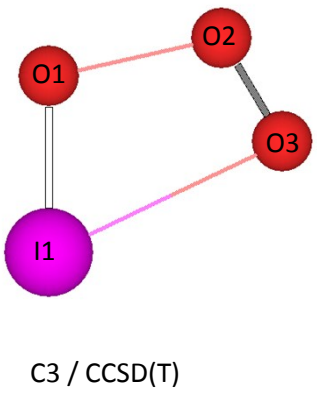


C2 / CCSD(T)

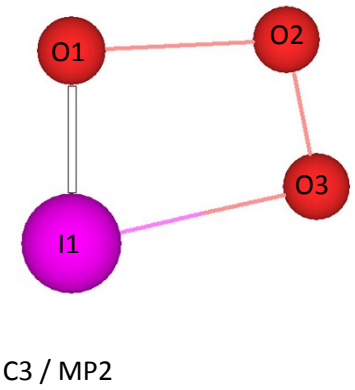


C2 / MP2

	CCSD(T)/TZ	MP2/QZ
R_{I1-O1}	1.952	1.927
R_{O1-O2}	1.812	1.888
$A_{O1-O2-O3}$	103.6	1.275
R_{O2-O3}	1.301	99.6
$A_{I1-O1-O2}$	108.4	111.0
$D_{I1-O1-O2-O3}$	180.00	180.0



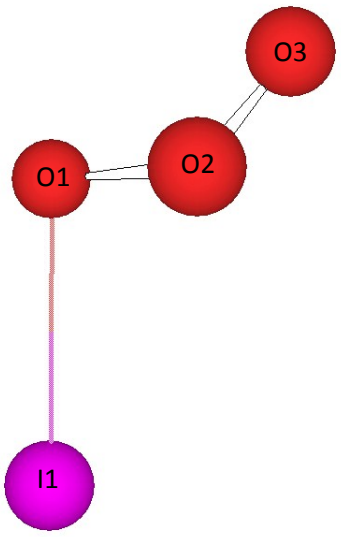
C3 / CCSD(T)



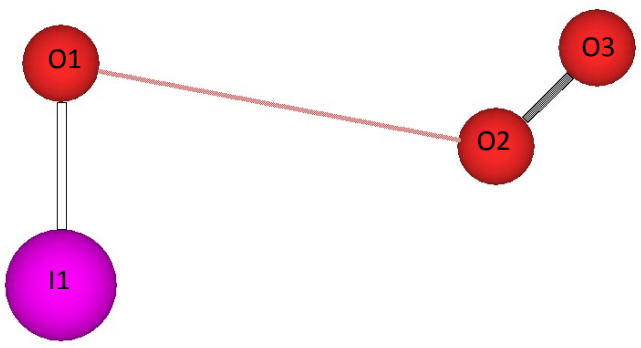
C3 / MP2

	CCSD(T)/TZ	MP2/QZ
R_{I1-O1}	1.917	1.863
R_{O1-O2}	1.916	2.082
$A_{O1-O2-O3}$	102.5	92.8
R_{O2-O3}	1.306	1.449
$A_{I1-O1-O2}$	108.1	98.6
$D_{I1-O1-O2-O3}$	0.1	0.0

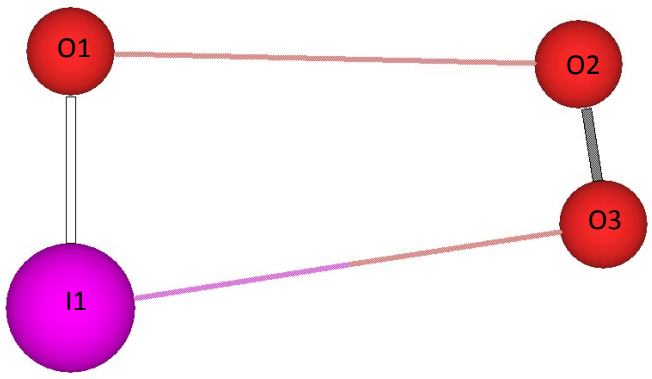
Figure S2. Equilibrium geometries of the three conformation of $IOOO^-$ intermediate obtained at CCSD(T)/aug-cc-pVTZ/PCM and MP2/aug-cc-pVQZ/PCM levels. Distances bonds (in Å) and angles (in degrees) of the conformers are included in the table at the right panel.



C1 (triplet)	MP2/QZ
R_{I1-O1}	2.548
R_{O1-O2}	1.389
$A_{O1-O2-O3}$	113.8
R_{O2-O3}	1.256
$A_{I1-O1-O2}$	100.7
$D_{I1-O1-O2-O3}$	130.2



C2 (triplet)	MP2/QZ
R_{I1-O1}	1.918
R_{O1-O2}	3.8275
$A_{O1-O2-O3}$	124.9
R_{O2-O3}	1.216
$A_{I1-O1-O2}$	79.2
$D_{I1-O1-O2-O3}$	180.5



C3 (triplet)	MP2/QZ
R_{I1-O1}	1.918
R_{O1-O2}	3.820
$A_{O1-O2-O3}$	100.2
R_{O2-O3}	1.216
$A_{I1-O1-O2}$	88.6
$D_{I1-O1-O2-O3}$	0.0

Figure S3. Equilibrium geometries of the three conformation of $IOOO^-$ intermediate in the triplet spin state obtained at MP2/aug-cc-pVQZ/PCM level. Distances bonds (in Å) and angles (in degrees) of the conformers are included in the table at the right panel.

Table S1. Absolute energies obtained at each level of theory (MP2 optimization or CCSD(T) single point calculations), for all aqueous species studied in this work. Energies values are in hartree except entropies that are in cal.mol^{-1}.K^{-1}. PCM and COSMO refer to the solvation models considered to treat all the species studied in the aqueous phase.

	IO_3^- PCM	**IO_3^- COSMO**	**O_3 PCM**	**O_3 COSMO**	**I^- PCM**	**I^- COSMO**
E_0 MP2/QZ	-236,9724194	-236,9812726	-225,2911296	-225,2919197	-11,5780247	-11,5780247
E_{ZPE} MP2/QZ	0,00787	0,007815	0,009882	0,009486	0	0
H_{corr} MP2/QZ	0,013067	0,013033	0,01377	0,013373	0,00236	0,00236
G_{corr} MP2/QZ	-0,0207340000	-0,020796864	-0,013275	-0,014312459	-0,016848	-0,016848631
E_{SO} B3LYP/QZ	-0,0035218562	-0,0035218562	0	0	-0,004270848	-0,004270848
S MP2/QZ	71,141	71,201	56,921	58,269	40,428	40,428
E_0 CCSD(T)/TZ	-236,8597816	-236,8685259	-225,1977733	-225,198576	-11,5717606	-11,57456471
E_0 CCSD(T)/QZ	-237,0029814	-237,0120396	-225,3040466	-225,3049362	-11,6008974	-11,6042262
E_0 CCSD(T)/CBS	-237,0962294	-237,1054921	-225,373249	-225,3741952	-11,61987053	-11,623541
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ	-237,0883594	-237,0976771	-225,363367	-225,3647092	-11,61987053	-11,623541
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ	-237,0918813	-237,1011989	-225,363367	-225,3647092	-11,62414138	-11,62781185
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + H_{corr} MP2/QZ	-237,0788143	-237,0881659	-225,349597	-225,3513362	-11,62178138	-11,62545185
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + G_{corr} MP2/QZ	-237,1126153	-237,1219958	-225,376642	-225,3790217	-11,64098938	-11,64466048

	IO$^-$ PCM	**IO$^-$ COSMO**	**IO PCM**	**IO COSMO**	**I_2 PCM**	**I_2 COSMO**
E_0 MP2/QZ	-86,664909	-86,6985765	-86,4555398	-86,4892073	-22,8001205	-22,80064962
E_{ZPE} MP2/QZ	0,001522	0,001476	0,001341	0,001295	0,000524	0,000525
H_{corr} MP2/QZ	0,004953	0,004914	0,004812	0,004773	0,004344	0,004342
G_{corr} MP2/QZ	-0,021637	-0,021677705	-0,022412	-0,022452705	-0,025155	-0,02579799
E_{SO} B3LYP/QZ	-0,00470112	-0,00470112	-0,0062599200	-0,00625992	-0,010517761	-0,010517761
S MP2/QZ	55,963	55,967	57,298	57,302	62,086	63,435
E_0 CCSD(T)/TZ	-86,6280583	-86,63421465	-86,4447831	-86,45093945	-22,7905179	-22,79131164
E_0 CCSD(T)/QZ	-86,6924813	-86,6985765	-86,5057612	-86,5118564	-22,8434529	-22,84399208
E_0 CCSD(T)/CBS	-86,73443189	-86,74048728	-86,54546856	-86,55152395	-22,8779228	-22,87829622
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ	-86,73290989	-86,73901128	-86,54412756	-86,55022895	-22,8773988	-22,87777122
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ	-86,73761101	-86,7437124	-86,55038748	-86,55648887	-22,88791657	-22,88828898
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + H_{corr} MP2/QZ	-86,73265801	-86,7387984	-86,54557548	-86,55171587	-22,88357257	-22,88394698
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + G_{corr} MP2/QZ	-86,75924801	-86,7653901	-86,57279948	-86,57894157	-22,91307157	-22,91408697

	H_2O PCM	**H_2O COSMO**	**H^+ PCM**	**H^+ COSMO**	**O_2 PCM**	**O_2 COSMO**
E_0 MP2/QZ	-76,3893985	-76,39368993	-0,448447915	-0,448447915	-150,2201186	-150,2202576
E_{ZPE} MP2/QZ	0,021412	0,021255	0	0	0,003394	0,003394
H_{corr} MP2/QZ	0,025192	0,025033	0	0	0,006704	0,006703
G_{corr} MP2/QZ	0,003774	0,002967401	0,02972981	0,02972981	-0,016587	-0,016194555
E_{SO} B3LYP/QZ	0	0	0	0	0	0
S MP2/QZ	45,078	46,441	-62,5717	-62,5717	49,02	48,192
E_0 CCSD(T)/TZ	-76,3639895	-76,36816693	-0,448447915	-0,448447915	-150,169143	-150,1690802
E_0 CCSD(T)/QZ	-76,4017629	-76,40597405	-0,448447915	-0,448447915	-150,2399331	-150,2399336
E_0 CCSD(T)/CBS	-76,42635996	-76,43059307	-0,448447915	-0,448447915	-150,2860298	-150,2860716
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ	-76,40494796	-76,40933807	-0,448447915	-0,448447915	-150,2826358	-150,2826776
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ	-76,40494796	-76,40933807	-0,448447915	-0,448447915	-150,2826358	-150,2826776
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + H_{corr} MP2/QZ	-76,37975596	-76,38430507	-0,448447915	-0,448447915	-150,2759318	-150,2759746
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + G_{corr} MP2/QZ	-76,40117396	-76,40637067	-0,418718105	-0,418718105	-150,2992228	-150,2988721

	O_2^- PCM	**O_2^- COSMO**	**HOI PCM**	**HOI COSMO**	**HIO_2 PCM**	**HIO_2 COSMO**
E_0 MP2/QZ	-150,3460159	-150,3461549	-87,1422863	-87,14513545	-162,2529291	-162,2589932
E_{ZPE} MP2/QZ	0,002565	0,002565	0,012483	0,012435	0,015676	0,015701
H_{corr} MP2/QZ	0,005892	0,005892	0,016446	0,016397	0,020547	0,02053
G_{corr} MP2/QZ	-0,017229	-0,016835933	-0,012458	-0,012496719	-0,012122	-0,012059295
E_{SO} B3LYP/QZ	0	0	0,005944128	0,005944128	0,005274816	0,005274816
S MP2/QZ	48,663	47,835	60,833	60,812	68,757	68,59
E_0 CCSD(T)/TZ	-150,2942072	-150,2941444	-87,1120384	-87,11486393	-162,1871319	-162,1934072
E_0 CCSD(T)/QZ	-150,3671465	-150,367147	-87,1740435	-87,1768464	-162,287197	-162,293252
E_0 CCSD(T)/CBS	-150,4146427	-150,4146845	-87,21441962	-87,21720778	-162,3523568	-162,3582684
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ	-150,4120777	-150,4121195	-87,20193662	-87,20477278	-162,3366808	-162,3425674
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ	-150,4120777	-150,4121195	-87,19599249	-87,19882865	-162,331406	-162,3372926
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + H_{corr} MP2/QZ	-150,4061857	-150,4062275	-87,17954649	-87,18243165	-162,310859	-162,3167626
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + G_{corr} MP2/QZ	-150,4293067	-150,4289554	-87,20845049	-87,21132537	-162,343528	-162,3493519

	IO_2^- PCM	IO_2^- COSMO	I_3^- PCM	I_3^- COSMO	$IOOO^-$ C3 PCM	$IOOO^-$ C3 COSMO
E_0 MP2/QZ	-161,7934457	-161,8014344	-34,4004702	-34,40139523	-236,8807763	-236,88918
E_{ZPE} MP2/QZ	0,004055	0,004002	0,000693	0,000743	0,009471	0,008547
H_{corr} MP2/QZ	0,008476	0,008443	0,00667	0,007131	0,014611	0,013719
G_{corr} MP2/QZ	-0,022708	-0,023436923	-0,025774	-0,031650689	-0,019611	-0,020513776
E_{SO} B3LYP/QZ	0,004589568	0,004589568	0,014597377	0,014597377	0,004748928	0,004748928
S MP2/QZ	65,632	67,097	68,286	81,623	72,026	72,049
E_0 CCSD(T)/TZ	-161,7211942	-161,7295221	-34,3796379	-34,38085061	-236,7551301	-236,7650996
E_0 CCSD(T)/QZ	-161,823565	-161,8316071	-34,4625481	-34,4635431	-236,8885542	-236,8989892
E_0 CCSD(T)/CBS	-161,8902262	-161,8980822	-34,51653708	-34,51739031	-236,9754365	-236,9861747
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ	-161,8861712	-161,8940802	-34,51584408	-34,51664731	-236,9659655	-236,9776277
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ	-161,8815817	-161,8894906	-34,5012467	-34,50204993	-236,9612166	-236,9728788
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + H_{corr} MP2/QZ	-161,8731057	-161,8810476	-34,4945767	-34,49491893	-236,9466056	-236,9591598
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + G_{corr} MP2/QZ	-161,9042897	-161,9129276	-34,5270207	-34,53370062	-236,9808276	-236,9933926

	$IOOO^-$ C1 PCM	$IOOO^-$ C1 COSMO	$IOOO^-$ C2 PCM	$IOOO^-$ C2 COSMO	$IOOO^-$ TS_{C1C2} PCM	$IOOO^-$ TS_{C2C3} PCM
E_0 MP2/QZ	-236,8791701	-236,8817486	-236,8498758	-236,8549141	-236,8370658	-236,8486861
E_{ZPE} MP2/QZ	0,013538	0,011982	0,007148	0,006621	0,006205	0,006903
H_{corr} MP2/QZ	0,018991	0,017475	0,013253	0,01204	0,011342	0,012205
G_{corr} MP2/QZ	-0,016643	-0,018281999	-0,023519	-0,023098377	-0,023198	-0,022638
E_{SO} B3LYP/QZ	0,005689152	0,005689152	0,004876416	0,004876416	0,005282784	0,004812672
S MP2/QZ	74,998	75,257	77,394	73,955	72,695	73,334
E_0 CCSD(T)/TZ	-236,7655454	-236,7685109	-236,7592907	-236,7644425	-236,7601564	-236,7583391
E_0 CCSD(T)/QZ	-236,899172	-236,9026626	-236,8929838	-236,8977777	-236,8931267	-236,8921231
E_0 CCSD(T)/CBS	-236,9861862	-236,9900187	-236,9800413	-236,9846022	-236,9797135	-236,9792398
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ	-236,9726482	-236,9780367	-236,9728933	-236,9779812	-236,9735085	-236,9723368
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ	-236,966959	-236,9723476	-236,9680169	-236,9731048	-236,9682257	-236,9675241
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + H_{corr} MP2/QZ	-236,947968	-236,9548726	-236,9547639	-236,9610648	-236,9568837	-236,9553191
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + G_{corr} MP2/QZ	-236,983602	-236,9906296	-236,9915359	-236,9962031	-236,9914237	-236,9901621

	$IOOO^-$ C1 triplet PCM	$IOOO^-$ C2 triplet PCM	$IOOO^-$ C3 triplet PCM
E_0 MP2/QZ	-236,8220044	-236,8859164	-236,8860567
E_{ZPE} MP2/QZ	0,008349	0,005281	0,005492
H_{corr} MP2/QZ	0,014321	0,012624	0,012732
G_{corr} MP2/QZ	-0,02375	-0,032103	-0,030994
E_{SO} B3LYP/QZ	0,0052358	0,00503861	0,00515295
S MP2/QZ	80,127	94,134	92,03
E_0 CCSD(T)/TZ	-236,7525084	-236,7981412	-236,7982426
E_0 CCSD(T)/QZ	-236,8830938	-236,8866983	-236,8865738
E_0 CCSD(T)/CBS	-236,9681276	-236,9443644	-236,9440928
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ	-236,9597786	-236,9390834	-236,9386008
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ	-236,9545428	-236,9340448	-236,9334478
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + H_{corr} MP2/QZ	-236,9402218	-236,9214208	-236,9207158
E_0 CCSD(T)/CBS +E_{ZPE} MP2/QZ + E_{SO} B3LYP/QZ + G_{corr} MP2/QZ	-236,9782928	-236,9661478	-236,9644418