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Computational Investigation of HIO and HIO_2 Isomers

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The theoretical study of hypoiodous and iodous acid isomers, which can be written in the common form HIO_n ($n = 1,2$), is presented. For this purpose, several basis sets and several computational methods are tested. The best fitting with the values known in the literature is achieved using density functional theory at the level of Gill96 exchange and Perdew-Wang91 correlation functional (G96PW91) method, with Lanl2DZ basis set augmented with p and d diffuse and polarization functions for oxygen, relativistic effective core potential of Hay and Wadt combined with Lanl2DZ basis set augmented with diffuse (s and p) and polarization (d and f) functions for iodine, and 6-311++G(3df,3pd) basis set for hydrogen. Using this method for the calculation of bond lengths, vibrations, and energies, the mentioned species are analyzed. The justification of the calculated values is performed by thermochemical calculations of enthalpy of formation of mentioned species. We found that between hypoiodous acid isomers HOI is more stable then HIO, and that between iodous acid isomers HOIO is the most stable isomer. Therefore, they are the most probable ones in the reactions where they take part. All calculations are performed for the species in the gaseous phase. As far as we know, these calculations give the first such information for iodous acid isomers and HIO.

1. Introduction

Working on the elucidation of the Bray−Liebhafsky oscillatory reaction,[1] the reaction where hydrogen peroxide decomposes into water and oxygen in the presence of iodate and hydrogen ions by a very complex mechanism,[2−6] we felt a necessity to know the structure and stability of possible isomers of some intermediate species.[7] Particularly, we are interested in isomers of two key intermediate species that appears in all models: hypoiodous (HIO) and iodous (HIO_2) acids.[1−6] (In the considered system, the experimental investigations of the particular reactions existing in the model are very difficult (sometimes impossible). Therefore, if experimental determinations of some kinetic parameters are impossible, the theoretical calculations would be of great importance.) These compounds have not been the object of theoretical studies, and there are very few experimental results related to them. (The mentioned hydrogen-oxy-iodous species are also of crucial importance in the pollution problem related with reactions between iodine-containing compounds in the marine boundary layer.[8]) Therefore, the necessity to select a suitable method and basis set for the investigation of these species appeared. For this purpose, several basis sets and several computational methods that are commonly used in similar cases[9] are tested. The computed results are compared with the experimental results where they exist. As it will be shown in the following text, the best fit with the experimental values is achieved with the G96PW91 method. Using this method for the calculation of bond lengths, vibrations and energies, the hypoiodous and iodous acid isomers are analyzed.

Our calculations are also compared with the theoretical studies of the oxy-iodine species without hydrogen (I_xO_y where $x = 1$, 2 and $y = 1$, 2) in gaseous phase, published by Misra and Marshall.[10]

The additional justification of the results obtained is performed by thermochemical calculations of enthalpy of formation of mentioned species.

2. Methods

The first part of our task is to select a suitable method for investigation of hypoiodous and iodous acid isomers. For this purpose, the bond lengths and vibrational frequencies for the test species with similar kind of bonds as mentioned ones (HI, $IO^\bullet$, IO^-, O_2, I_2, $HO^\bullet$, and HOOH) are investigated using density functional theory (at the level of Becke three-parameter hybrid functional B3LYP[11] and Gill96[12] exchange and Perdew-Wang91[13] correlation functional G96PW91) and Moller−Plessett second-order correlation energy correction method (MP2). The 6-311++G(3df,3pd), 6-31G(d) and double-ζ valence basis sets augmented with p and d, diffuse and polarization

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TABLE 1: Experimental (exp) and Computed Bond Lengths (in 10^{-10} m) for Different Computational Methods and Basis Sets

bond	B3LYP/ Lanl2DZdp^a Lanl2DZspdf + ECP^b 6-311++G(3df,3pd)^c	G96PW91/ Lanl2DZdp^a Lanl2DZspdf + ECP^b 6-311++G(3df,3pd)^c	MP2=FC/ 6-311++G(3df,3pd)^a 6-311++G(3df,3pd)^b 6-311G^c	exp
H−I	1.610	1.619	1.622	1.609^e
O−I$^\bullet$	1.859	1.867	1.888^d	1.868^f
O−I$^-$	1.920	1.926	1.924	1.929^f
O=O	1.219	1.230	1.219^d	1.208^e
I−I	2.675	2.671	2.680^d	2.665^e
H−O$^\bullet$	0.976	0.982	0.968	0.970^e
HO−OH	1.452	1.464	1.444^d	1.475^g
H−OO−H	0.967	0.974	0.966	0.950^g
ARE (%)	0.78	0.92	0.95	
R	0.9997	0.9998	0.9996	

[a] The basis set used for O. [b] The basis set used for I. [c] The basis set used for H. [d] From reference 10. [e] From reference 20. [f] From reference 21. [g] From reference 22.

TABLE 2: Experimental and Computed Vibrational Frequencies in cm^{-1} for Different Computational Methods and Basis Sets

bond	B3LYP/Lanl2DZdp^b Lanl2DZspdf + ECP^c 6-311++G(3df,3pd)^d	G96PW91/Lanl2DZdp^b Lanl2DZspdf + ECP^c 6-311++G(3df,3pd)^d	MP2=FC/^{a} 6-31G(d)^b 6-31G(d)^c 6-31G^d	exp
H−I	2335.7	2276.9	2231.0	2309.0^f
O−I$^\bullet$	685.9	689.7	724.0^e	681.6^g
O−I$^-$	592.3	596.2	608.2	581.0^g
O=O	1617.9	1548.6	1360.0^e	1580.2^f
I−I	216.4	217.5	217.0^e	214.5^h
H−O$^\bullet$	3705.7	3623.7	3589.0	3737.8^f
HOOH	379.6	380.3	332.7	371.0^i
	956.6	915.1	896.0^e	877.0^i
	1430.7	1385.2	1408.5	1402.0^i
	3771.5	3677.6	3593.1	3599.0^i
	1313.3	1275.3	1276.6	1266.0^i
	3773.1	3678.4	3594.5	3608.0^i
ARE(%)	2.9	2.0	4.0	
R	0.9991	0.9992	0.998	

[a] Scaled by 0.9646. [b] The basis set used for O. [c] The basis set used for I. [d] The basis set used for H. [e] From reference 10. [f] From reference 20. [g] From reference 21. [h] From reference 23. [i] From reference 24.

functions, hereafter called Lanl2DZdp, are used for oxygen.[14] The 6-311++G(3df,3pd),[15] 6-31G(d),[15,16] and double-ζ valence basis sets combined with the relativistic effective core potential of Wadt and Hay[17] and augmented with uncontracted diffuse s and p functions (exponents 0.0569 and 0.0330, respectively),[18] and d and f polarization functions (exponents 0.292 and 0.441, respectively),[18] hereafter called Lanl2DZspdf + ECP, are used for iodine. The 6-311++G(3df,3pd), 6-311G and 6-31G basis sets are used for hydrogen (for hydrogen, 6-31G(d) basis set is identical to 6-31G). The complete listing of basis sets used in calculations can be found in Supporting Information.

For open-shell and closed-shell systems, the spin-unrestricted and spin-restricted methods are used, respectively. Geometries for stationary points are identified by minimization of energy with respect to all geometrical parameters. Vibrational frequencies are calculated for all structures in order to show whether structures are real minima on the respective potential energy surface, or not. All quantum chemical calculations are performed by means of the Gaussian 98 program package,[19] with tight option for optimization and ultra fine grid for integration.

3. Results and Discussion

3.1. Selection of the Method. To determine the most suitable method and basis set for investigation of hypoiodous and iodous acid isomers, geometries are optimized and vibrational frequencies are calculated for the test species HI, IO$^\bullet$, IO$^-$, O$_2$, I$_2$, HO$^\bullet$ and HOOH, using several methods and basis sets. The experimental and computed values for bond lengths and vibrational frequencies are given in Tables 1 and 2, respectively. As a measure of the quality of the correlation between experimental and calculated values for bond lengths and vibrational frequencies, the average relative error (ARE) and correlation coefficient (R) are used (Tables 1 and 2). By inspecting the values of the correlation coefficients and average relative errors one can conclude that all methods and basis sets applied in this work yield satisfactory correlation between the experimental and calculated results. Regarding bond lengths, slightly better fitting is achieved by means of the B3LYP method, whereas the values of vibrational frequencies are better reproduced by means of G96PW91. Analyzing these results, we decided to use the G96PW91 method with Lan2DZdp basis set for oxygen, Lanl2DZspdf + ECP for iodine, and 6-311++G(3df,3pd) for hydrogen for the further investigation of the HIO$_n$ species.

3.2. Hypoiodous Acid Isomers. The structures of both obtained hypoiodous acid isomers (HOI and HIO) are presented in Figure 1. The computed bond lengths in 10^{-10} m (Figure 1) and vibrational frequencies in cm^{-1} for HOI, presented in Table 3, are in a good accordance with experimentally obtained values (ARE = 0.47% and ARE = 1.8%, respectively).[25] As far as we know, there are no experimental data for the HIO molecule that could be compared to the calculated values. The computed values for HIO are given in Figure 1 and Table 3.

On the basis of the bond lengths presented in the Figure 1, it can be concluded that HOI isomer is more stable than HIO,

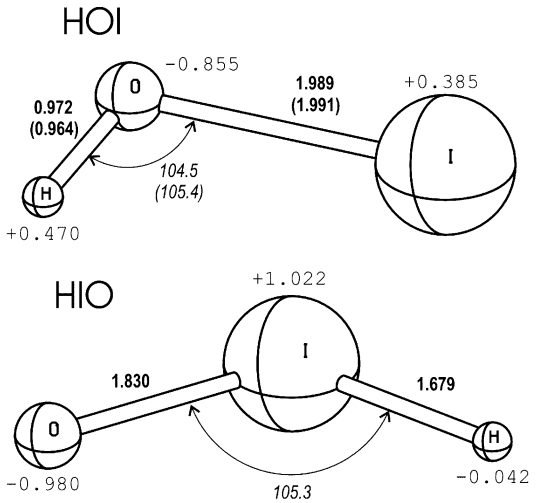

Figure 1. G96PW91 natural charges (normal) from NBO, geometries of hypoiodous acid isomers with bond lengths in 10^{-10} m (bold) and angles in degrees (italic). In brackets are given the experimental values[21] for HOI.

since the H−O bond is stronger then H−I bond. This assumption is confirmed by the energy calculation (Table 4). The Natural Bond Orbital Analysis (NBO)[26] shows that I−O bonds are polarized in both isomers. The natural charge distribution (Figure 1) from NBO shows that I−O bond is more polarized in the HIO than in the HOI isomer. This causes significant shortening of the I−O bonds in the HIO isomer. Regarding the bond order, one can conclude that both molecules have only single bonds. The HOI molecule has one lone pair on oxygen and two on iodine, whereas HIO has one lone pair on iodine and two on oxygen. More precisely, the NBO calculations for HOI indicate an important role of the valence non-Lewis orbitals (i.e., two valence antibonds) relative to the extra-valence orbitals (the 50 Rydberg) in the slight departures from a localized Lewis structure model. The oxygen lone pair is the lowest occupancy (1.82214 electrons) and highest energy Lewis NBO, and it is primarily delocalized into σ^*_{IO}.

The I−O σ bond is formed from a p-reach hybrid ($sp^{6.69}$) on iodine and practically from a p orbital on oxygen (the contribution of the s orbital is only 8.19%). This bond is slightly polarized. On the other side, the H−I σ bond is formed from a p orbital on iodine and 1s atomic orbital on hydrogen. This bond is not polarized.

For HOI the role of the non-Lewis orbitals is not important (0.041%). The I−O σ bond is formed from a p-reach hybrid orbital $sp^{6.69}$ on oxygen and a p orbital on iodine (the contribution of the s orbital is only 5.49%), whereas the H−O σ bond is formed from the $sp^{3.61}$ orbital on oxygen and 1s atomic orbital on hydrogen. Both bonds are strongly polarized.

3.3. Iodous Acid Isomers. The optimized structures of five iodous acid isomers denoted by HOIO, HOOI, HI(O)O, singlet HO(O)I, and triplet HO(O)I are presented in Figure 2. The computed bond lengths and vibrational frequencies are given in Figure 2 and Table 3. Unfortunately, we did not find any experimental value for iodous acid isomers.

As in previous cases, regarding the bond lengths, we could conclude that HOIO and HOOI isomers are more stable than HI(O)O, singlet HO(O)I, and triplet HO(O)I isomers. A stability calculation for all molecules under investigation was performed. The calculation revealed that only in the case of the HO(O)I molecule was there a UHF function which is lower in energy than the RHF wave function, RHF → UHF instability, without internal instability. This implies that the triplet state of mentioned molecule is more stable than the singlet state (Table 4).

The conclusion that HOIO and HOOI isomers are more stable than HI(O)O, singlet HO(O)I, and triplet HO(O)I isomers is of particular importance for modeling the chemical processes where iodous acid isomers take part as different species in parallel reactions. Of these parallel reactions, the one with the most stable, and therefore the most probable, species will determine the most important pathway. In trying to construct a model as small as possible but flexible enough to describe the essential features of the mechanism, the parallel reactions with less probable isomers will be canceled in the first approximation.

TABLE 3: Calculated Vibrational Frequencies in cm^{-1} and IR Intensities (in brackets) by G96PW91 for Hypoiodous and Iodous Acid Isomers

species	frequencies					
HOI	571.9	1071.9	3721			
	575[a]	1068[a]	3625.8[a]			
HIO	704.2 (11.82)	746.2 (36.73)	1930.7 (90.63)			
HOIO	213.2 (6.92)	384 (93.98)	536.9 (71.53)	790 (45.25)	1004.1 (47.14)	3694.4 (76.96)
HOOI	247.9 (4.81)	406.6 (76.78)	502.2 (19.77)	844.5 (132.35)	1337.2 (35.91)	3616 (34.25)
triplet HO(O)I	17.1 (1.18)	64.3 (10.04)	119.3 (93.54)	1126.0 (71.40)	1359.9 (43.87)	3488.2 (31.37)
HI(O)O	265.6 (17.24)	675.8 (7.99)	708.8 (8.47)	812.2 (24.74)	847.8 (106.12)	1748.3 (161.07)
singlet HO(O)I	160.1 (4.65)	339.2 (19.04)	578.1 (74.95)	1075.5 (209.95)	1320.9 (82.33)	3349.1 (54.99)

[a] From reference 25.

TABLE 4: Energies (in hartrees), Enthalpy of Formation at 0 and 298 K, Temperature Corrections, and Dipole Moments (in Debye) for Hypoiodous and Iodous Acid Isomers

	computed values					experimentally known values	
species	energy (E_0) (electronic + ZPE)	$\Delta_f H_0$ (kJ mol^{-1})	$\Delta_f H_{298}$ (kJ mol^{-1})	$H_{298} - H_0$ (kJ mol^{-1})	dipole moment (Debye)	$\Delta_f H_0$ (kJ mol^{-1})	$\Delta_f H_{298}$ (kJ mol^{-1})
HOI	−87.222595	−68.4	−73.1	10.5	1.4408	−64.9±5.4[a]	−69.6±5.4[a]
HIO	−87.143968	138.2	133.5	10.5	4.0709		
HOIO	−162.387178	−22.4	−28.8	13.0	3.5539		
HOOI	−162.366415	32.2	25.5	12.8	1.7327		
triplet HO(O)I	−162.326759	136.4	133.2	16.3	2.0340		
HI(O)O	−162.324239	143.0	135.6	12.1	4.2774		
singlet HO(O)I	−162.322433	147.7	141.3	13.1	1.9914		

[a] From reference 30.

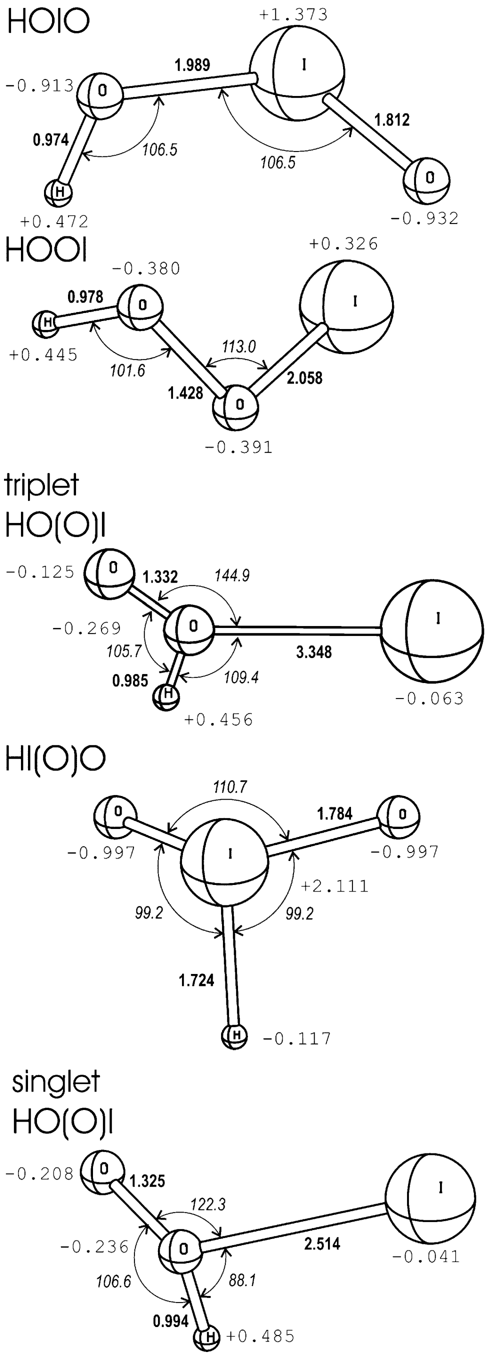

Figure 2. G96PW91 natural charges (normal) from NBO, geometries of iodous acid isomers with bond lengths in 10^{-10} m (bold) and angles in degrees (italic). They are ordered with respect to stability, where the HOIO is the most stable.

Therefore, the detailed examinations of HOIO and HOOI will be given in the following, mostly.

Moreover, according to calculations done by Misra and Marshall,[10] the OIO isomer is more stable than OOI, and by our theoretical investigation, which showed that the O−I bond in OOI is significantly elongated (Figure 2) with respect to the same bond in OIO, we could expect that the HOIO isomer is more stable than HOOI one. The IOO can be described as a complex between I and O_2.[27]

By inspecting the geometries of these compounds (Figure 2), one can conclude that new OH bonds are as strong as the corresponding bonds in hydrogen peroxide. The consequence of the formation of the O−H bond is that the corresponding neighboring O−I and O−O bonds are elongated as compared to those in the oxides. For example, the O−O bond length in HOOI becomes similar to that in HOOH.

Regarding the natural charge distribution (Figure 2), from NBO it is clear that the I−O bonds are much more polarized in the HOIO and especially in the HI(O)O than those in other isomers. As a consequence, the I−O bonds are significantly shorter in those isomers than the corresponding bonds in HO(O)I and HOOI species.

Regarding the bond order, one can conclude that all molecules, except HO(O)I, have only single bonds. The NBO analysis also shows that HOIO has two lone pairs on terminal oxygen and one on another oxygen and iodine. The same analysis reveals that in HOOI exist two lone pairs on iodine and one on each oxygen. In the case of HOIO and HOOI, the non-Lewis orbitals play a significant role (0.644 and 0.218%, respectively). Concerning HOIO, the lone pare on the terminal oxygen is the lowest-occupancy (1.67164 electrons) NBO, and it is primarily delocalized into σ^*_{IO} orbital. The lone pair on the other oxygen atom also shows low occupancy (1.93088 electrons). This orbital has the highest energy, and it is primarily delocalized into σ^*_{IO} orbital. The terminal I−O σ bond is formed from hybrid orbitals $sp^{7.47}$ and $sp^{9.07}$ on iodine and oxygen, respectively. The other I−O σ bond is formed from hybrid orbital $sp^{8.59}$ on oxygen and practically from the p orbital on iodine (the contribution of the s orbital is only 5.37%). The H−O σ bond is formed from $sp^{3.46}$ on oxygen and the 1s atomic orbital on hydrogen. All bonds are highly polarized.

As mentioned above, the contribution of non-Lewis orbitals in HOOI is smaller than in HOIO. The lone pair on oxygen bonded to hydrogen is the lowest-occupancy (1.91076 electrons) NBO, and it is primarily delocalized into the σ^*_{OI} orbital. The lone pair on iodine is the highest-energy and somewhat higher-occupancy NBO (1.97145 electrons), and it is primarily delocalized into the σ^*_{OO} orbital. The O−O σ bond is formed from p-reach hybrid orbitals $sp^{7.78}$ and $sp^{7.08}$ on oxygen, whereas the O−I bond is formed from p orbitals on oxygen and iodine. These p orbitals have a small contribution of s orbitals (6.90 and 3.95%, respectively). As in the previous cases, the OH bond is formed between hybrid sp orbital (sp^4) on oxygen and s orbital on hydrogen. As expected, the HO and OI bonds are highly polarized.

The HI(O)O has two lone pairs on oxygen and no lone pair on iodine. For HI(O)O there is an important contribution of the non-Lewis orbitals (1.029%). The lone pairs on both oxygen atoms are lowest-occupancy (1.78657 and 1.86838 electrons) and highest-energy NBO, and they are primarily delocalized into two σ^*_{IO} and one σ^*_{IH} orbitals. The O−I σ bonds are built from $sp^{7.97}$ and $sp^{6.68}$ orbitals on oxygen and iodine, respectively, whereas the H−I bond is formed from the p orbital on iodine with small contribution of s orbital (7.14%) and 1s atom orbital of hydrogen. The H−I bond is not polarized, while both O−I bonds are polarized.

The singlet HO(O)I molecule has the same distribution of lone pairs as the HOOI molecule. The NBO analysis showed that a triplet HO(O)I molecule exists like two fragments and can be best described as $I^\bullet + OOH^\bullet$, which I−O bond length was confirmed (Figure 2). In the case of singlet HO(O)I, it was found that the antibonding molecular orbital was occupied with two electrons, resulting in prolongation of the I−O bond in the singlet state.

3.4. Thermochemical Calculations. Thermochemical calculations would be necessary to justify the computed values. For this purpose, the calculations having the aim to compare

TABLE 5: Energies (in hartrees), Enthalpy of Formation at 0 and 298 K, and Temperature Corrections for I$_x$O$_y$ Isomers

	computed values				known values	
species	energy (E_0) (electronic + ZPE)	$\Delta_f H_0$ (kJ mol^{-1})	$\Delta_f H_{298}$ (kJ mol^{-1})	$H_{298} - H_0$ (kJ mol^{-1})	$\Delta_f H_0$ (kJ mol^{-1})	$\Delta_f H_{298}$ (kJ mol^{-1})
IO$^•$	−86.574905	117.8	115.9	9.0	117.8^a	115.9^a 126 ± 18^c
OIO$^•$	−161.766319	93.3	89.6	11.6	80.4^b	76.7^b 159.3 ± 25^{c,d}
OOI$^•$	−161.756034	120.3	117.3	12.2	104.1^b	96.6^b; 116.5 ± 40^{c,d}
IOI	−98.016176	115.8	111.2	13.0	97.0^b	92.4^b 119.5 ± 25^{c,d}
IIO	−98.010324	131.2	127.0	13.4	138.2^b	134.1^b 106.7 ± 40^{c,d}

[a] Experimentally ordered value from reference 28. [b] Calculated values from reference 10. [c] Estimated values from Burcat tables (reference 32). [d] Estimated values from NIST-JANAF tables (reference 31).

the obtained values to those available in the literature are performed. (The literature known value can be both experimentally obtained and estimated values.) With the aim to conserve bond types and spin, as well as possible, the following isogyric reaction is used to predict the heat of formation of HOI:

$$\mathrm{HOOH} + \mathrm{IO}^\bullet \rightarrow \mathrm{HOO}^\bullet + \mathbf{HOI} \qquad (1)$$

All calculations are done at 0 K by the following procedure:

$$\Delta_r H_{0,\,\mathrm{calc}} = \sum_{\beta_i} \nu_{\beta_i} E_0(\beta_i) - \sum_{\alpha_i} \nu_{\alpha i} E_0(\alpha_i) = \mathrm{E}_0\,(\mathrm{HOO}^\bullet) + \mathrm{E}_0\,(\mathrm{HOI}) - \mathrm{E}_0\,(\mathrm{HOOH}) + \mathrm{E}_0\,(\mathrm{IO}^\bullet)$$

where α_i and β_i denote reactants and products, respectively, and ν is the stoichiometric coefficient. The value for the enthalpy of reaction 1 is calculated as $\Delta_r H_{0,\ \mathrm{calc}} = -0.016622$ hartrees $= -43.7$ kJ mol^{-1}. Using this value and the values for enthalpies of formation of IO$^•$, HOOH, and HOO$^•$, available in the literature, {$\Delta_f H_0(\mathrm{IO}^\bullet) = 117.8$ kJ mol^{-1} (ref 28), $\Delta_f H_0(\mathrm{HOOH}) = -129.9$ kJ mol^{-1} (ref 29), and $\Delta_f H_0(\mathrm{HOO}^\bullet) = 12.6$ kJ mol^{-1} (ref 29)}, the enthalpy of formation for HOI is calculated in the common manner:

$$\Delta_f H_0(\mathrm{HOI}) = \Delta_f H_0(\mathrm{HOOH}) + \Delta_f H_0(\mathrm{IO}^\bullet) - \Delta_f H_0(\mathrm{HOO}^\bullet) + \Delta_r H_0 = -68.4\ \mathrm{kJ\ mol^{-1}}$$

(As far as we know among species having iodine and oxygen atoms, IO$^•$ is only one with a value for the enthalpy of formation obtained directly from experimentation.) The obtained value of −68.4 kJ mol^{-1} is in good accordance with the measured value of −64.9 ± 5.4 kJ mol^{-1} (ref 30). The appropriate $\Delta_f H_{298}$ value is obtained via the relation $\Delta_f H_{298} = \Delta_f H_0 + (H_{298} - H_0)_{\mathrm{compound}} - (\mathrm{H}_{298} - \mathrm{H}_0)_{\mathrm{elements}}$. The values for $\Delta_f H_{298}$ obtained in this manner are given in Table 4. The obtained result for HOI (Table 4) of −73.1 kJ mol^{-1} is in agreement with the value for $\Delta_f H_{298}$ (−69.6 ± 5.4 kJ mol^{-1}) given by Berry et al.[30]

The enthalpy of formation for HIO [$\Delta_f H_0$(HIO)] is calculated from $\Delta_f H_0$(HOI) using our computed value for the energy difference between two isomers at zero temperature.

Such good agreement of the G96PW91 method with experimental results indicates that it will, hopefully, produce satisfactory results for a wider range of compounds containing iodine and oxygen. To confirm this assumption, the $\Delta_f H_0$ and $\Delta_f H_{298}$ for HOOI, OIO$^•$, IOI, and IO$^•$ are calculated via the appropriate isogyric reactions.

Using a procedure analogous to that used for hypoiodous acid isomers, the enthalpy of formation of HOOI [$\Delta_f H_0$ (HOOI)] was obtained via the following isogyric reaction:

$$\mathrm{HOOH} + \mathrm{IO}^\bullet \rightarrow \mathrm{HO}^\bullet + \mathbf{HOOI} \qquad (2)$$

For this calculation the known values of $\Delta_f H_0$ for HOOH, OI$^•$, and HO$^•$ are used. The enthalpy of formation for the HO$^•$ radical is $\Delta_f H_0$ (HO$^•$) = 39.1 kJ mol^{-1} (ref 29). The enthalpies of formation of other iodine acid isomers [HOIO, HI(O)O, singlet and triplet HO(O)I] are calculated from $\Delta_f H_0$(HOOI) using our computed value for the energy difference between isomers at zero temperature (Table 4).

The obtained enthalpies for hypoiodous and iodous acid isomers at 0 K are justified by analyzing several isogyric reactions where these species participate. We have started with the isogyric reaction

$$\mathrm{HOIO} + \mathrm{IO}^\bullet \rightarrow \mathrm{HOI} + \mathbf{OIO}^\bullet \qquad (3)$$

with the aim to obtain the enthalpy of formation for OIO$^•$. Using a procedure similar to that used for hypoiodous acid isomers, the enthalpies of formation were calculated (Table 5). The enthalpy of formation for OOI$^•$ was calculated from $\Delta_f H_0$ (OIO$^•$) using our computed value for the energy difference between two isomers at zero temperature (Table 5).

For OIO$^•$, the empirical NIST-JANAF[31] $\Delta_f H_{298}$ value of 159.3 ± 25 kJ mol^{-1} lies about 70 kJ mol^{-1} above our value (Table 5). On the other hand, our value is in agreement with Misra and Marshall's[10] result of 76.7 kJ mol^{-1} (obtained by the G2 method). We believe that our and Misra and Marshall's values are more accurate. In particular, our value for OOI of 117.3 kJ mol^{-1} is close to the empirically estimated value[31,32] of 116.5 ± 40 kJ mol^{-1}.

For the IOI enthalpy of formation, the following isogyric reaction was chosen:

$$\mathrm{HOI} + \mathrm{IO}^\bullet \rightarrow \mathrm{HO}^\bullet + \mathbf{IOI} \qquad (4)$$

In this calculation, our computed value for HOI, and those found in the literature for IO$^•$ and HO$^•$ species, were used.[28,29] By applying the analogous procedure once more, the enthalpy of formation for IOI was determined to be $\Delta_f H_0$(IOI) = 111.2 kJ mol^{-1} (Table 5). This result for $\Delta_f H_{298}$ is in good accordance with the literature value of 119.5 ± 25.0 kJ mol^{-1}.[31, 32]

The enthalpy of formation for IIO was calculated from $\Delta_f H_0$(IOI) using our computed value for the energy differ-

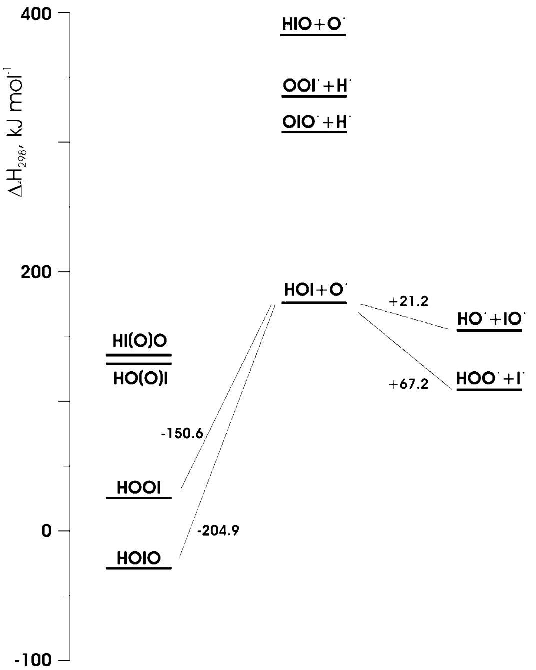

Figure 3. Enthalpies of formation of some combinations of one iodine, one hydrogen, and two oxygen atoms at 298 K. The enthalpies of reactions are presented beside arrows. Between singlet and triplet HO(O)I only the triplet one is considered as more stable form.

ence between two isomers at zero temperature (Table 5). The determined value of 127 kJ mol^{-1} is in a good agreement with the value calculated by the G2 method of $\Delta_f H_0(\mathrm{IIO}) = 134.1$ kJ mol^{-1} given by Misra and Marshall.[10]

An additional test for calculated enthalpies of formation was performed by comparing the known value for IO$^\bullet$ radical[28] at 0 and 298 K with determined one obtained by means of the following isogyric reaction:

$$\mathrm{OOI^\bullet + HO^\bullet \rightarrow HOO^\bullet + \mathbf{IO^\bullet}} \qquad (5)$$

The computed values of $\Delta_f H_0 = 117.8$ kJ mol^{-1} and $\Delta_f H_{298} = 115.9$ kJ mol^{-1} are equal to the known values[28] (Table 5), and approximately equal that in ref 33 where $\Delta_f H_{298}$ (IO$^\bullet$) $\leq$ 117.2 kJ mol^{-1}. The enthalpy of formation for the IO$^\bullet$ radical determined by measurements of ionization energy[34] is $\Delta_f H_{298} = 129.8$ kJ mol^{-1}. Also, the value for $\Delta_f H_{298}$ given by the Alexander Burcat database[32] is 126 kJ mol^{-1}.

In Figure 3 the enthalpies of formation of some species mentioned above, together with some combinations between them, are presented. Analyzing this figure, we can see the possible reaction pathways denoted by arrows. It is obvious that between hypoiodous acid isomers HOI is more stable than HIO, and that between iodous acid isomers HOIO is the most stable isomer. Consequently, in the reaction where all of these isomers appear, HOIO and HOI are more probable products than the others. Moreover, if iodous acid forms from the species HOI, HIO, OOI$^\bullet$, and OIO$^\bullet$ in the presence of H and O, the most probable product will be HOIO. Also, if hypoiodous acid forms from HO$^\bullet$ and IO$^\bullet$, or HOO$^\bullet$ and I$^\bullet$, the most probable product will be HOI. Similarly, other reactions in gaseous phase between species containing I, O, and H could be discussed. For example, if there is HOIO, HI, HOI, and IOI in the presence of water, as is the case in the pollution problem related with reactions between iodine-containing compounds in marine boundary layer,[8] the following reactions between them can be expected:

$$\mathrm{HOIO + HI \rightarrow IOI + HOH} \qquad \Delta_r H_0 = -129.4 \text{ kJ mol}^{-1} \quad (6)$$

$$\mathrm{IOI + HOH \rightarrow 2HOI} \qquad \Delta_r H_0 = -13.7 \text{ kJ mol}^{-1} \quad (7)$$

$$\mathrm{HOI + HI \rightarrow I_2 + HOH} \qquad \Delta_r H_0 = -133.7 \text{ kJ mol}^{-1} \quad (8)$$

$$\mathrm{IOI + HOOH \rightarrow HOI + HOIO} \qquad \Delta_r H_0 = -76.7 \text{ kJ mol}^{-1}$$

In the calculations of $\Delta_r H_0$ we used our calculated enthalpies of formation for IOI, HOI, and HOIO (at 0 K Table 4 and Table 5) and literature values[35] for HI ($\Delta_f H_0 = 28.675$ kJ mol^{-1}), HOH ($\Delta_f H_0 = -238.9$ kJ mol^{-1}), I_2 ($\Delta_f H_0 = 65.5$ kJ mol^{-1}).

In the Bray−Liebhafsky (BL) system, in addition to these four reactions some additional reactions can be expected, although in the water solution. The investigations of these reactions are under intense scrutiny.

4. Conclusion

Hypoiodous and iodous acid isomers are characterized by means of DFT methods. Structural information and vibrational frequencies of these species are presented. A good accordance between the literature known values and calculated data for bond lengths and vibrational frequencies of the test compounds is found. The thermodynamic quantities for the compounds under investigation are derived using appropriate isogyric reactions. Hence, it is reasonable to expect that the G96PW91 method [with Lan2DZdp basis set for oxygen, Lanl2DZspdf + ECP for iodine, and 6-311++G(3df,3pd) for hydrogen] can be successfully applied to other compounds containing iodine, oxygen, and hydrogen. Such compounds and reactions between them are the basis of the Bray−Liebhafsky and Briggs−Rouscher oscillatory reactions that we are interested in. This is, also of particular importance for the examination of the gaseous reaction between iodine-containing compounds released by macroalgae[8] that form in the marine boundary layer, a problem that is well known in pollution and global warming.

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Supporting Information Available: Basis sets used in calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Bray, W. C. *J. Am. Chem. Soc.* **1921**, *43*, 1262. (b) Bray, W. C.; Liebhafsky, H. A. *J. Am. Chem. Soc.* **1931**, *53*, 38. (c) Liebhafsky, H.; Furruichi, R.; Roe, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 51 and references therein.

(2) (a) Sharma, K. R.; Noyes, R. M. *J. Am. Chem. Soc.* **1976**, *98*, 4345. (b) Edelson, D.; Noyes, R. M. *J. Phys. Chem.* **1979**, *83*, 212. (c) Noyes, R. M. *J. Phys. Chem.* **1990**, *94*, 4404. (d) Treindl, L.; Noyes, R. M. *J. Phys. Chem.* **1993**, *97*, 11354. (e) Noyes, R. M.; Kalachev, L. V.; Field, R. J. *J. Phys. Chem.* **1995**, *99*, 3514.

(3) (a) Furrow, S. D. In *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger M., Eds.; J. Wiley: New York, 1985; pp 171. (b) Furrow, S. D. *J. Phys. Chem.* **1987**, *91*, 2129.

(4) (a) Schmitz, G. *J. Chim. Phys.* **1987**, *84*, 957. (b) Schmitz, G. *J. Chim. Phys.* **1991**, *88*, 15. (c) Kolar-Anić, Lj.; Schmitz, G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2343. (d) Kolar-Anić, Lj.; Mišljenović, Đ.; Anić, S.; Nicolis, G. *React. Kinet. Catal. Lett.* **1995**, *54*, 35. (e) Kolar-Anić, Lj.;

Čupić, Ž.; Anić, S.; Schmitz, G. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2147. (f) Čupić, Ž.; Kolar-Anić, Lj. *J. Chem. Phys.* **1999**, *110*, 3951.

(5) (a) Valent, I.; Adamčiková, L.; Ševčik, P. *J. Phys. Chem. A* **1998**, *102*, 7576. (b) Kissimonova, K.; Valent, I.; Adamciková, L.; Ševčik, P. *Chem. Phys. Lett*. **2001**, *341*, 345. (c) Kéki, S.; Székely, G.; Beck, M. T. *J. Phys. Chem. A* **2003**, *107*, 73.

(6) (a) Schmitz, G. *Phys. Chem. Chem. Phys*. **1999**, *1*, 1909. (b) Schmitz, G. *Phys. Chem. Chem. Phys*. **2000**, *2*, 4041. (c) Schmitz, G. *Phys. Chem. Chem. Phys*. **2001**, *3*, 4741.

(7) Begović, N.; Marković, Z.; Anić, S.; Kolar-Anić, Lj. In *6th International Conference of Fundamental and Applied Aspects of Physical Chemistry*; Anić, S., Ed.; Society of Physical Chemists of Serbia: Belgrade, 2002; *Physical Chemistry 2002*; p 102.

(8) (a) O'Dowd, C. D.; Jimenez, J. L.; Bahreini, R., Flagan, C. R.; Seinfeld, H. J.; Hämeri, K.; Pirjola, L.; Kulmala, M.; Jennings, S. G.; Hoffmann, T. *Nature* **2002**, *417*, 632. (b) Charles, E. K. *Nature* **2002**, *417*, 597. (c) Jimenez, J. L.; Cocker, D. R.; Bahreini, R.; Zhuang, H.; Varutbangkul, V.; Flagan, R. C.; Seinfeld, J. H.; Hoffmann, T.; O'Dowd, C. *J. Geophys. Res.* **2003**, *108*, D10. (d) Mäkelä, J. M.; Hoffmann, T.; Holzke, C.; Väkevä, M.; Suni, T.; Mattila, T.; Aalto, P. P.; Tapper, U.; Kaupinen, E.; O'Dowd, C. *J. Geophys. Res.* **2002**, *107*, (No. D19).

(9) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure* 1995−96, Gaussian, Inc.; ISBN 0-9636769-3-8.

(10) Misra, A.; Marshall, P. *J. Phys. Chem. A* **1998**, *102*, 9056.

(11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(12) (a) Gill, J. P. W. *Mol. Phys.* **1996**, *89*, 433. (b) Adamo, C.; Barone, V. *J. Comput. Chem.* **1988**, *104*, 1040.

(13) (a) Burke, K.; Perdew, J. P.; Wang, Y. In *Electronic Density Functional Theory: Recent Progress and New Directions*, Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum: New York, 1998. (b) Perdew, J. P. In Electronic Structure of Solids; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991; p 11. (c) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, 46. (d) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1993**, 48. (e) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, 54, 16533.

(14) (a) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure, Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 2. (b) Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352. The database is accessible via the URL http://www.emsl.pnl.gov:2080/forms/basisform.html

(15) (a) Glukhovtsev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 1878. (b) Glukhovtsev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1996**, *104*, 3407.

(16) From: Ashutosh Misra [ashutosh@ti.com], http://www.hyper.com/support/listserv/archive/97.12.txt.

(17) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(18) Glukhovtsev, M. N.; Prossa, A.; Radom, L. *J. Am. Chem. Soc.* **1995**, *117*, 2024.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(20) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold Co.: New York, 1979.

(21) Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *J. Phys. Chem.* **1991**, *95*, 4723.

(22) Redington, R. L.; Olson, W. B.; Cross, P. C. *J. Chem. Phys.* **1962**, *36*, 1311.

(23) Howard, W. F.; Andrews L. *J. Raman Spectrosc.* **1974**, *2*, 447.

(24) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Consolidated Volume I*; Natl. Stand. Ref. Data Ser.; U.S. Natl. Bur. Stand.; NSRDS−NBS 39, 1972.

(25) Klassen, J. J.; Lindner, J.; Leone, S. *J. Chem. Phys.* **1996**, *104*, 7403.

(26) (a) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41. (b) Carpenter, J. E., Ph.D. Thesis, University of Wisconsin, Madison, WI, 1987. (c) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (e) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, 1736. (e) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (f) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (g) Weinhold, F.; Carpenter, J. E. *The Structure of Small Molecules and Ions*; Plenum: New York, 1988; p. 227.

(27) Maier, G.; Bothur, A. *Chem. Ber.* **1997**, *130*, 179.

(28) Bedjanian, Y.; Le Bras, G.; Poulet, G. *J. Phys. Chem. A* **1997**, *101*, 4088.

(29) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*, fourth ed.; Hemisphere: New York, 1989.

(30) Berry, R. J.; Yuan, J.; Misra, A.; Marshall, P. *J. Phys. Chem. A* **1998**, *102*, 5182.

(31) Chase, M. W. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1297.

(32) Burcat, A. *Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion, Technion-Israel Institute of Technology*, Report TEA867; January**,** 2001.

(33) De More, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*; NASA, JPL, California Institute of Technology: Pasadena, CA, 1994.

(34) Zhang, Z.; Monks, P. S.; Stief, L. J.; Liebman, J. F.; Huie, R. E.; Kuo, S.; Klemm, R. B. *J. Phys. Chem.* **1996**, *100*, 63.

(35) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.