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Research Paper

Ab initio Study on the Reaction Kinetics of IO+ClO and IO+BrO

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Abstract: *Ab initio calculations have been performed to investigate various geometries, vibrational frequencies and reaction kinetics of the reactions IO with ClO and IO with BrO, which play a crucial role in atmospheric ozone depletion. Geometries and frequencies have been obtained at the MP2 using SDB(Stuttgart-Dresden-Bonn)TZ basis set for bromine, iodine and cc-pVTZ basis sets for chlorine and oxygen along with (s,p) diffuse functions for all the atoms. The energetics have been studied at the QCISD(T) level of theory at the MP2 optimized geometries. We obtained consistent heat of reactions of the various channels for both the reactions. Calculated heat of formations of the different species are in good agreement with the available data and may serve as future references.*

Keywords: Ab initio calculation, Halogen radicals, Molecular properties, Thermo-chemical properties.

Introduction

The halogen monoxide radicals have recently received much attention both in experimental and theoretical investigations because of their direct involvement in atmospheric ozone depletion, especially in the lower stratosphere. The occurrence of IO with XO (X=Cl, Br) would lead to ozone loss via the reactions:

$IO + XO \rightarrow I + X + O_2$ (X = Cl, Br)
$I + O_3 \rightarrow IO + O_2$ (i)
$X + O_3 \rightarrow XO + O_2$
Net: $2\,O_3 \rightarrow 3\,O_2$

It has been estimated that the chemistry involving iodine is of particular importance as small amount of it can make a significant contribution to ozone depletion[1-3]. The role of iodine in atmospheric ozone depletion depends upon several factors and one of them is kinetic data of rate coefficients of the key reactions of IO with ClO, BrO and HO_2[1]. These reactions have also a potential contribution in tropospheric chemistry where ozone depletion events observed in recent years in polar spring and in marine boundary layer[4-6]. Solomon et al.[1] discussed in a model calculation that iodine is 1000 times more efficient than chlorine in destroying ozone in the lower stratosphere. But Bedjanian et al. [7,8], Gilles et al. [9] and also Turnip seed et al. [10] claimed from their experimental investigations on IO+XO (X=Cl, Br) that efficiency of iodine in ozone depletion is about 3-5 times lower than that of the model prediction by Solomon et. al. [1].

The reaction between IO and ClO radicals may proceed through following thermodynamically feasible channels[7]:

$IO + ClO \rightarrow I + OClO$ Δ_rH_{298}= -(4.0±0.2) kcal/mol (2a)
$\rightarrow I + ClOO \rightarrow I + Cl + O_2$ = 2.3±1.2 kcal/mol) (2b)
$\rightarrow ICl + O_2$ = -(47.5±1.2) kcal/mo (2c)
$\rightarrow Cl + OIO$ (2d)

The channel (2a) is the major channel having maximum rate constant, but it is the null cycle for ozone depletion[1]. ClOO is thermodynamically more stable than OClO and it readily dissociates to Cl + O_2. Model calculation of Solomon et. al. [1] considered only the reaction channel (2b) to form I + Cl + O_2 , whereas Bedjanian et al. [7] considered the first three (2a-2c) channels, moreover, they[7] mentioned the possibility of the fourth channel (2d). Rowley et al.[11] from photoisomerization study using R-matrix isolation technique suggested a Y-shaped isomer for thermodynamically favored product IX + O_2 (X= Cl,Br). In a photodissociation study, Ingham et al. [12] detected a strong absorption band of OIO molecule. So the possibility of the fourth channel can not be ruled out. Later, Bedjanian and Poulet[13] reported kinetics and reaction mechanism of halogen oxide radicals of stratospheric importance and reviewed thermochemical data of XO radicals. According to Bedjanian et al. [7], the channel(2a) is exothermic, channel (2b) is endothermic to form I+Cl+O_2 and channel (2c) is highly exothermic. The heat of reactions, as predicted by Bedjanian et al. [7], are quoted above along with the channels (2a-2c). But the values will be changed slightly, if one uses recently recommended experimental values of heat of formation of different species.

The reaction of IO with BrO may proceed through the following channels[8]:

IO + BrO $\rightarrow$ Br + OIO
$\Delta_r H_{298} < 0.0$ kcal/mol (3a)
$\rightarrow$ I + BrOO $\rightarrow$ I + Br +O_2= -(4.1±2.6) kcal/mol) (3b)
$\rightarrow$IBr+ O_2 = -(46.5±2.6) kcal/mol (3c)
$\rightarrow$ I + OBrO = 5.5±8.6 kcal/mol (3d)

Bedjanian et al. [8] performed an extensive study on this IO + BrO reaction using mass spectrometric discharge flow technique and predicted that the major channel is (3a), and in channel (3b) the stable BrOO is responsible for forming Br+O_2. The fourth channel (3d) is the minor channel having least branching ratio. Gilles et al. [9] studied the above reaction using pulsed laser photolysis with discharge flow technique and predicted that the non-iodine atom producing channels (i.e., 3a and 3c) are the dominant ones. Rowley et al. [11] mentioned that the potential impact of channel (3a) and (3d) on ozone depletion depends on the fate of OXO species, whether they are photostable or not. Note that, as Bedjanian et al. [8] reported, the channel (3a) is exothermic, channel (3b) is also exothermic to form I+Br+O_2, channel (3c) is highly exothermic, but channel (3d) is endothermic.

Various experimental investigations were performed mainly for determining the thermal rate constant of these radical-radical reaction[4-13], but the theoretical investigations along this line are limited. Among the theoretical calculations, Peterson group reported geometry, frequency and thermochemistry on XO[14] and IX[15] (X=C, Br, I) at the QCISD(T) level of theory. Lee[16] performed ab initio study of X_2, IX, and OXO systems at the level of CCSD(T)-Full/AE and ECP method using 6-311+G(3d,f) basis sets. Recently, Grant et al. [17] reported an extensive study of the thermochemistry of XO, X_2, IX, XO, OXO, XOO at CCSD(n) level of theories using augmented basis sets. Papayannis et al. [18] performed ab initio calculations on the BrO + ClO reaction and suggested several reaction pathways. Pacios and Gomez[19] carried out ab initio calculations of the different isomers of XOO using UMP2/AREP/TZ(2df). Misra and Marshall[20] also reported ab initio study of OIO isomers at the QCISDT)/6-311G-3df level of theory. At the same level of theory, McGrath and Rowland[21] studied geometry, electron affinity ionization energy etc. of XO systems. Guha and Francisco[22], Gomez and Pacios[23], Peterson and Werner[24] and few others carried out ab initio calculations of the different isomers of XOOY and studied their geometries, frequencies and energetics.

In this article, we are going to report various optimized geometries of the reactants and products, their vibrational frequencies, heat of reactions of different product channels and finally heat of formations of different species. We obtained consistent heat of reaction and heat of formation. As the structures and vibrational frequencies of XO, OXO and XOO are still somewhat speculative, our data may serve as future references. To get a complete phase out of these reactions information of intermediate states, transitions states, energy barriers and reaction pathways are needed and obviously these require sufficient computing facility. Part of them is under our consideration as future work. In the following sections we explain the computational schemes used followed by results and discussion of the present investigation.

Material and Methods

We employed large-core pseudopotential and correlation-consistent type SDB(Stuttgart-Dresden-Bonn)-cc-pVTZ basis set for bromine and iodine[25] and cc-pVTZ basis set chlorine and oxygen[26]. The basis sets for all the atoms were then augmented by a set of s and p type diffuse functions[25,26]. All the reactants and products are optimized at the second-order Moller-Plesset Perturbation theory level 2 (MP2). The vibrational frequencies were also calculated at the MP2 level. Single point energy calculations were performed using Quadratic Configuration Interaction Single-Double including Triples terms (QCISD(T)) at the MP2 optimized geometries. To study the thermochemical properties, we included our calculated thermal corrections to enthalpy (ΔE_{298}) at 298.15 K (including ZPE correction) at the MP2 level and the experimental spin-orbit coupling corrections (ΔSOC) of Cl (0.84 kcal mol^{-1}), Br (3.51 kcal mol^{-1}), I (7.25 kcal mol^{-1}), ClO (0.45 kcal mol^{-1}), BrO (1.29kcal mol^{1})

[27] and IO (3.33 kcal mol^{-1}) [28] to the energy values obtained based on QCISD(T) level of theory (E_e). Using these corrected enthalpy values (H_{298}^{corr}), we calculated the heat of reactions of different channels for both the reactions. Finally we have calculated heat of formation of various species. In calculating the heat of formation, we used the experimental heat of formations of Cl (28.99 kcal/mol), Br (26.73 kcal/mol), I (25.52 kcal/mol), Cl_2 (0), Br_2 (7.39 kcal/mol), I_2 (14.92 kcal/mol) and O_2 (0) from NIST-JANAF compilations[29]. All the calculations described above were performed employing the Gaussian03W program[30].

Results and Discussion

(A) Geometries and vibrational frequencies: The optimized geometries and vibrational frequencies of all the reactants and products of the reactions (2) and (3) are listed in Table 1 along with the available data for comparison. For diatomic systems XO and IX, we obtained consistent geometries and vibrational frequencies in comparison to the experimental values[28].

Table 1: Optimized geometries (A^{o}, degree), Harmonic Frequencies (cm^{-1}) of various species

Species	Parameters	Present calc.	Expt. Values	Other calcs.
ClO	r_e	1.5678	1.5696^{a}	1.5683^{c}
	Freq	849.4	853.8	856.7
BrO	r_e	1.7057	1.7172^{a}	1.7168^{c}
	Freq	749.0	727.1	733.4
IO	r_e	1.8870	1.8676^{a}	1.8723^{c}
	Freq	685.1	681.4	683.6
ICl	r_e	2.3251	2.3209^{a}	2.3169^{d}
	Freq	404.8	384.3	391.8
IBr	r_e	2.4699	2.4690^{a}	2.4673^{d}
	Freq	283.0	268.6	272.6
O_2	r_e	1.2233	1.2075^{a}	1.2095^{e}
	Freq	1462.5	1580.2	1585
OClO	ClO	1.4891	1.4710^{b}	1.476^{f}
	OClO	117.7	117.6	118.4
	Freq	1007.6, 443.3, 1168.8	945.6, 447.7, 1110.1	975, 324, 1284
OBrO	BrO	1.6388	1.6490^{b}	1.640^{g}
	OBrO	115.1	114.4	115.4
	Freq	899.8, 329.5, 933.2	800, 300, 852	897, 328, 939
OIO	IO	1.8150	[1.80]^{b}	1.811^{h}
	OIO	111.3	[120]	111.4
	Freq	848.0, 267.2, 871.8	765, 192, [800]	826, 260, 867
ClOO	ClO	1.7157	[1.83]^{b}	2.142^{f}
	OO	1.2655	[1.23]	1.154
	ClOO	113.2	[110]	118.3
	Freq	1104.0, 500.5, 1643.1	192.4, 408.3, 1442.8	223, 473, 1950
BrOO	BrO	1.8230	[2.00]^{b}	2.258^{g}
	OO	1.2788	[1.25]	1.168
	BrOO	113.6	[115]	118.3
	Freq	1016.6, 434.9, 1686.7	[160], [250], [1487]	156, 439, 1581
IOO	IO	2.5326	[2.40]^{b}	3.346^{h}
	OO	1.1709	[1.25]	1.219
	IOO	120.5	[120]	121.0
	Freq	129.5, 395.6, 1854.3	[150], [275], [1500]	84, 205, 1669

Abbreviations: ^{a}Reference[28], ^{b}reference[29], ^{c}reference[14], ^{d}reference[15], ^{e}reference[31], ^{f}reference[18], ^{g}reference[19], ^{h}reference[20], [.…] values are speculated from the anticipated trends of similar halogen families

Results of other theoretical calculations are also tabulated for comparison[14,15]. For O_2, our bond length is overestimated to the experimental value[28] as well as to the theoretical value by Hassenzadeh et al. at the level of multi-reference CASPT2/6-311+G(3df) [31]. For triatomic systems, the optimized geometries at the MP2 level are in good agreement with the experimental values quoted from NIST-JANAF compilations[29].We obtained consistent vibrational frequencies (tabulated frequencies are in the order of symmetric stretching, bending and asymmetric stretching) at the MP2 level for OXO (X=Cl, Br, I) systems. Our values are supported by the listed theoretical values[18-20]. But MP2 provides poor vibrational frequencies for XlOO systems in comparison to NIST-JANAF compilations, which are the speculated values anticipated from the trends of similar halogen families[29]. For ClOO and BrOO, the ClO and BrO symmetric stretching frequency values are about 6 times of the experimental values. The OO asymmetric stretching frequency values are also higher by 200-354cm^{-1}. An analysis of the Mulliken population reveals that there is a large charge transfer from O to X (X=Cl, Br). This increases the force constant for the O-O stretching mode and hence we obtained a larger O-O stretching frequency. Papayannis et al. [18], Pacios and Gomez[19] as well as Peterson and Werner[24] pointed out a similar charge transfer to explain the increment of O-O asymmetric frequency. It is to be noted that Papayannis et al. [18] used ROMP2/6-311++G (3df) method for obtaining frequency values of OClO, ClOO, Pacios and Gomez's usedUMP2/AREP/TZ(2df) for OBrO and BrOO and Mishra and Marshall used MP2-FC/6-31G(d) for OIO and IOO systems. Probably, due to their used basis sets an anomalous change in the optimized geometries is observed. This overestimated geometrical shape decreases the frequency values. It is to be mentioned that our higher frequency values for OClO, OBrO and OIO systems cause an increase of ZPE by only 0.17, 0.30 and 0.33 kcal/mol, respectively. For ClOO, BrOO and IOO systems the increments are 1.72, 1.77 and 0.65 kcal/mol, respectively. These will accordingly affect the heat of reaction and heat of formation values. One may expect better prediction for these triatomic systems by a multi-configuration methodology using more extensive basis sets.

(B) Energetics and thermochemistry

In Table 2, we have listed our energy (E_e) obtained at the QCISD (T) level of theory. It is to be noted that the QCIST(T) level has predicted correct energy ordering between OXO and XOO (X=Cl, Br, I) systems, that the XOO radical is thermodynamically more stable than OXO radical by 4-5 kcal/mol. In Table 2, the experimental spin-orbit coupling corrections (ΔSOC) of Cl, Br, I, ClO, BrO[27], IO[28] and the MP2 thermal corrections to enthalpy at 298.15 K (ΔE_{298}) (including ZPE correction)are listed, which are added to E_e to obtain corrected enthalpy values H_{298}^{corr}. These values are used to obtain heat of reaction ($\Delta_r H_{298}$) of different channels at 298.15 K (Table 3) and heat of formations ($\Delta_f H_{298}$) of the different species (Table 4).

The heat of reactions ($\Delta_r H_{298}$) at 298.15 K of the various channels are listed in Table 3 along with the estimated experimental values for comparison. The tabulated experimental heat of reactions are estimated using the experimental heat of formation of various specious from NIST-JANAF compilation[29]. Note that for ClO, BrO, IO, we list the recently recommended values by Bedjanianand Poulet[13] and for OIO by Bedjanian et al. [8] (listed in Table 4). It is clear from Table 3, that for channel (2a) we obtained a small endothermic value of 0.67 kcal/mol for the heat of reaction compared to the experimental estimation of exothermicity by -(4.59±0.12)kcal/mol. This large deviation occurred probably due to the computational scheme used in our calculation. For channels (2b) our calculated value is slightly underestimated compared to the experimental estimation. One of the reasons of this underestimation is due to our higher ZPE correction of ClOO (by 1.72 kcal/mol). Our calculated value for (2c) is in close agreement with the experimental prediction. The channel (2d) is found to be endothermic by 5.24 kcal/mol, which is also within the range of experimental prediction. It is to be mentioned that in our calculation, we did not include the spin-orbit coupling (SOC) correction of OIO. The Mulliken population analysis shows that the radical side of OIO is on I atom and the spin density of I atom is greater than that of O atoms. Thus the SOC correction of OIO, is not negligible. Thus the inclusion SOC of OIO may improve the result of (2d).

For the reaction IO+BrO, our calculated heat of reaction for the channels (3a) and (3b) are slightly exothermic and in good agreement with the experimental predictions. However, an error is encountered in channel (3b) due to our higher ZPE of BrOO (by 1.77 kcal/mol). The channel (3c) is found to be highly exothermic by -50.33 kcal/mol, which is in agreement with the experimental value. The endothermicity of the channel (2d) is also consistent with the experimental range.

Finally, we have calculated heat of formations ($\Delta_f H_{298}$) of XO, IX, OXO and XOO (X=Cl, Br, I) systems using the corrected enthalpy H_{298}^{corr} (from Table 2) of different species and using the following reaction schemes:

$$\frac{1}{2}X_2+\frac{1}{2}O_2 \rightarrow XO \quad \text{with X = Cl, Br, I} \qquad (4a)$$

$$\frac{1}{2}I_2+\frac{1}{2}X_2 \rightarrow IX$$

$$IO+XO \rightarrow I+OXO, \quad \text{with X = Cl, Br} \qquad (4b)$$
$$IO+XO \rightarrow I+XOO,$$

$$IO+XO \rightarrow X+OIO \quad \text{with X = Cl} \qquad (4c)$$
$$IO+XO \rightarrow X+IOO$$

In calculating these, we have used experimental heat of formations of Cl, Br, I, Cl_2, Br_2, I_2 and O_2 as mentioned[29] in Section 2.

Our calculated values are listed in Table 4 along with experimental and theoretical values for comparison. Our calculated heat of formation for ClO and BrO are in good agreement with the experimental predictions. We obtained a value of 30.63kcal mol^{-1} for IO, which is within the range of recently recommended value of 29±2 kcal/mol by Bedjanianand Poulet[13]. For ICl and IBr the heat of formations are consistent with reported experimental values. Note that, our calculated heat of formations for the diatomic systems are supported by the theoretical calculation of Grant et al. [17] at the level of CCSD(T)/aug-cc-pVTZ.

Table 2: QCISD (T) Energies (E_e), SOC corrections (SOC), enthalpy corrections (ΔE_{298}) at 298.15 K and corrected enthalpy values (H_{298}^{corr}) of various species

Species	E_e (au)	ΔSOC (au)	ΔE_{298} (au)	H_{298}^{corr} (au)
Cl	-459.672246	-0.001338[a]	0.002360	-459.671224
Br	-13.292615	-0.005597[a]	0.002360	-13.295852
I	-11.329531	-0.011547[a]	0.002360	-11.338718
O_2	-150.132943		0.006642	-150.126301
Cl_2	-919.427863		0.004795	-919.423068
Br_2	-26.658191		0.004450	-26.653741
I_2	-22.723564		0.004343	-22.719221
ClO	-534.738089	-0.000724[a]	0.005305	-534.733508
BrO	-88.351497	-0.002050[a]	0.005106	-88.348441
IO	-86.385528	-0.005308[a]	0.004984	-86.385852
ICl	-471.080070		0.004532	-471.075538
IBr	-24.692559		0.004391	-24.688168
OClO	-609.789646		0.010069	-609.779577
OBrO	-163.402491		0.009190	-163.393301
OIO	-161.448681		0.008892	-161.439789
ClOO	-609.796603		0.011427	-609.785176
BrOO	-163.410534		0.011240	-163.399294
IOO	-161.455977		0.010192	-161.445785

Abbreviations: [a] Reference[27].

Table 3: Corrected enthalpy values (H_{298}^{corr}) and heat of reactions ($\Delta_r H_{298}$) for the various product channels of IO+ClO and IO+BrO reactions

Reactions		H_{298}^{corr} (au)	$\Delta_r H_{298}$ (kcal/mol)	
			Present calc.	Expt. values[a]
Reactant	IO + ClO	-621.119360		
Products (2a)	I + OClO	-621.118295	0.67	-(4.59±0.12)
(2b)	I + ClOO	-621.123894	-2.85	-(4.35±1.07)
(2c)	ICl + O_2	-621.201839	-51.77	-(49.11±2.00)
(2d)	Cl + OIO	-621.111013	5.24	7.90±2.03
Reactant	IO + BrO	-174.734293		
Products (3a)	Br + OIO	-174.735641	-0.85	-(0.27±2.40)
(3b)	I + BrOO	-174.738012	-2.33	-(7.87±7.16)
(3c)	IBr + O_2	-174.814469	-50.33	-(49.40±2.37)
(3d)	I + OBrO	-174.732019	1.43	2.65±3.57

Abbreviations: [a]Estimated using experimental heat of formations ($\Delta_f H_{298}$) of various species-ClO, BrO and IO from reference[13], OIO from reference[8] and others from reference[29].

Our calculated value for OClO is about 8.4 kcal/mole larger than the experimental value, but for OBrO and OIO the values are in good agreement with the recommended values by Bedjanian et al. [8,13]. Particularly for this OClO molecule a large error is encountered also in the heat of reaction of channel (2a). As we have obtained consistent geometry and frequency for OClO, the error encountered may be due to the computational scheme used for energetics. A multiconfiguration calculation may improve this result. The heat of formation for ClOO is overestimated by 4.7 kcal/mol, but for BrOO and IOO these are within the range of experimental predictions. As the thermochemistry of these XO, OXO and XOO systems is not yet well known, in view of satisfactory agreement with the available experimental data, our reported values may serve as future references.

Table 4: Heat of Formations ($\Delta_f H_{298}$) of different species

Species	$\Delta_f H_{298}$ (kcal/mol)		
	Present calc.	Expt. values	Others
ClO	25.85	24.29±0.03 [a]	24.8 [d]
BrO	29.80	30.20±0.40 [a]	30.8 [d]
IO	30.63	29.00±2.00 [a]	30.6 [d]
ICl	4.70	4.18±0.03 [b]	4.5 [d]
IBr	10.10	9.77±0.03 [b]	9.9 [d]
OClO	32.88	23.18±1.91 [b]	23.9 [d]
OBrO	37.71	36.33±5.97 [b]	40.6 [d]
OIO	31.47	$\leq$ 32.2 [c]	28.6 [d]
ClOO	29.37	23.42±0.96 [b]	25.1 [d]
BrOO	33.95	25.81±9.56 [b]	28.9 [d]
IOO	27.70	27.84±9.56 [b]	20.9 [d]

Abbreviation: [a]Reference[13], [b]reference[29], [c]reference[8], [d]reference[17]

Conclusion

In summary, we presented spectroscopic and thermochemical properties of various reactants and products of the IO+ClO and IO+BrO reactions, which are potentially important for atmospheric ozone depletion. We obtained consistent heat of reactions of the different channels for both the reactions. The heat of formations of various species are in satisfactory agreement with the available data and may serve as future references.

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