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Research Paper

Ab initio Study on the IOOCl Isomers and Reaction Pathways of the IO+ClO Reaction

***T. K. Ghosh[1] and S. Yabushita[2]**
[1]Department of Physics, Diamond Harbour Women's University, Sarisha
DH Road, South 24-Pgs, West Bengal-743368, INDIA
[1]Department of Chemistry, Faculty of Science and Technology, Keio University,
3-14-1 Hiyoshi, Kohoku-ku, Yokohama, 223-8522, JAPAN

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Abstract: *Ab initio calculations have been performed to investigate various minimum energy geometries, transition state geometries of the reaction between IO and ClO radicals. Geometries and frequencies have been identified at the MP2 level of theory using SDB(Stuttgart-Dresden-Bonn)TZ basis set for iodine and cc-pVTZ basis sets for chlorine and oxygen along with (s,p) diffuse functions for all the three atoms. The energetics have been studied at the QCISD(T) level of theory. Most of the data are reported to be new in literature. Possible reaction pathways for the different product formations have been discussed on the basis of geometries and energetics along with the results of IRC calculations.*

Keywords: Ab initio study, Halogen radicals, Equilibrium geometries, Transition state geometries, Frequency, Relative energy.

Introduction

In recent years the halogen monoxide radicals have received much attention both in experimental and theoretical investigations because of their direct involvement in atmospheric ozone depletion, especially in the lower stratosphere[1-3]. Solomon et al.[1] discussed in model calculation that iodine is 1000 times more efficient than chlorine in destroying ozone in the lower stratosphere. But, Bedjanian et al.[4,5] predicted from the study of thermal rate constants of IO + XO (X=Cl or Br) reactions using mass spectrometric discharge flow technique, that efficiency of iodine in lower stratosphere ozone depletion is about 3 or more times lower than the model prediction. Turnipseed et al.[6] also suggested from a study of the IO + ClO reaction that iodine is about 5 times less efficient than chlorine at destroying ozone. Thus the reaction of IO with ClO is an important key reaction in determining the efficiency of iodine species in atmospheric ozone depletion.

The reaction between IO and ClO radicals may proceed through the following different channels:

$IO + ClO \rightarrow I + OClO \quad \Delta_r H_{298} = 0.67$ (kcal/mol) (1)
$\rightarrow I + ClOO\ (\rightarrow I + Cl + O_2) = -2.85$ (2)
$\rightarrow ICl + O_2 = -51.77$ (3)
$\rightarrow Cl + OIO. = 5.24$ (4)

The major channel (1) has maximum rate constant at room temperature and it is the null cycle for ozone depletion[4,5]. ClOO is thermodynamically more stable than OClO but it readily dissociates to Cl+O_2. Channels (2) and (3) have intermediate rate constants[4] and the thermal rate constant of the fourth channel is yet unknown. The heat of reaction are reported here from our previous report[12]. Model calculation of Solomon et al.[1] assumed a value of 1×10^{10} $cm^{-3} molecule^{-1} s^{-1}$ for the rate constant IO + ClO reaction and considered only the reaction channel (2). Bedjanian et al.[4], in his experimental investigation of this IO + ClO reaction, considered only the first three channels (1-3), however they mentioned the possibility of the fourth channel (4) forming Cl + OIO. Potential influences of halogen containing compounds are also reported in some recent communications[7].

Although, several experimental investigations have been performed for determining the thermal rate constant of this radical-radical reaction[4-6], information on the intermediate states, energy barriers and the reaction pathways for the different product formations is completely unknown. Johnsson et al. from a photoisomerization study using the R-matrix isolation technique and Grant et al. using theoretical approach also suggested that a Y-shaped compound[8] for the channel (3). Among the theoretical calculations along this line, Guha and Francisco[9] and Gomez and Pacios[10] carried out ab initio calculations of the different isomers of XOOY, XOYO, XYO_2 where X, Y=Br and Cl atoms. Papayannis et al.[11] performed ab initio calculations on the reactions BrO + ClO and suggested possible reaction pathways. Very recently, we have reported spectroscopic constants and thermochemical properties of various reactants and products of the IO+ClO and IO+BrO reactions using extensive basis set at the QCISD//MP2 method[12]. Geometries, vibrational frequencies, heat of formation of different diatomic and triatomic species involved in these reactions have been reported.

In this article, we are going to report possible minimum energy geometries, transition state geometries, their harmonic frequencies and relative energy difference with respect to the reactants for the above (1-4) channels of the IO+ClO reaction. Most of the data are reported to be new in literature. Intrinsic reaction coordinate (IRC) calculations have been performed to investigate possible reaction pathways for the different channels. In the following sections we explain the computational schemes used followed by results and discussion of the present investigation.

Computational Details

The computational scheme is the same that we used in our previous article[12]. We employed the large-core pseudo-potential and correlation-consistent type SDB(Stuttgart-Dresden-Bonn)-cc-pVTZ basis set for iodine[13] with the valence shell being 5s5p. For chlorine and oxygen we took cc-pVTZ basis sets[14]. The basis sets for all the atoms were then augmented by a set of s and p type diffuse functions[13,14]. All equilibrium geometries and transition state geometries were optimized at the MP2 level of theory. The harmonic frequencies were also calculated at the MP2 level of theory. Single point energy calculations were performed using QCISD(T) level of theory at the MP2 optimized geometries. The relative energy difference with respect to the reactant (IO+ClO)[12] has been estimated using electronic energy at the QCISD(T) level, the ZPE correction obtained using our calculated frequencies and the experimental spin orbit coupling correction (ΔSOC) of IO (3.33 $kcal.mol^{-1}$) and ClO (0.45 $kcal.mol^{-1}$ [16,17]. For several transition states, the intrinsic reaction coordinate (IRC) method was used to get the minima of both sides of the transition states. We used MP2 method for the IRC calculations with step size 0.1-0.2 $amu^{1/2}$ bohr. The geometries of the different species, their energetics and the results of the IRC calculations assist us to have a qualitative idea of the possible reaction pathways for the different channels. All the calculations described above were performed employing the Gaussian 03W program[15].

Results and Discussion

A: Minimum energy geometries

Several minimum energy geometries and transition state geometries have been identified in the singlet potential energy surface of the IO + ClO reaction. The minimum energy geometries along with the vibrational frequencies calculated at the MP2 levels are listed in Table. We obtained skewed ClOOI, Y-shaped $IClO_2$ and $ClIO_2$, and two linear chain-typed IOClO and OIOCl geometries. Guha and Francisco[9], Gomez et al.[10] and also Papayannis et al.[11] obtained similar isomeric geometries for the $BrClO_2$ compound.

The first isomer is the skewed ClOOI, represented by MG(a), and it has a ClOOI dihedral angle of 84.1°. The OOI bond angle (110.5 °) is a bit larger than the ClOO bond angle (109.2 °). Each oxygen atom has two lone pairs of electrons, which has repulsive effects with neighboring halogen atoms. Iodine being larger than chlorine has larger repulsion with the lone pairs of oxygen than chlorine, which makes the OOI bond angle slightly larger than ClOO bond angle. Possibly, due to the better overlap of 5p orbital of iodine and 3p orbital of chlorine with 2p orbital of oxygen than the similar 2p orbitals of oxygen atoms make the I-O and Cl-O distances greater than O-O distance.

The second isomer MG(b) is the Y-shaped $IClO_2$, which has a plane of symmetry (C_S symmetry). The I-Cl bond distance is 2.707 Å, which is much larger than the Cl-O bond length of 1.452 Å. This is because of the multiple bonding characteristic of Cl=O, which occurs due to the resonance between lone pair electrons of terminal oxygen atoms with Cl-O bond pair. The OClO angle is formed by the repulsion of lone pair electrons of chlorine, the two oxygen atoms and the Cl=O bonding electrons. This repulsion is greater than the repulsion due to I-Cl and Cl=O bonds with the lone pairs of terminal oxygen atoms, which form the IClO angle. As a result, the OClO angle becomes greater than the IClO angle.

The third one MG(c) is IOClO of linear chain-type structure with oxygen as terminal atom and has a dihedral angle IOClO of 67.7°. The OClO bond angle (113.8°) is larger than the IOCl bond angle (112.3°), which is due to the larger O-O' repulsion than the I-Cl repulsion (O’ is O-atom to Cl-side). The Mulliken atomic charges on the atoms are 0.31 for I, -0.40 for O, 0.59 for Cl and -0.50 for O’ respectively, suggest that it has X^+O^- (X=I, Cl) resonant structures.

Table 1: Optimized Minimum Energy Geometries (A^o, degree), Harmonic Frequencies (cm^{-1}) of IOOCl isomers at the MP2 level

Species	Geometry		Frequency	
	Coordinate	Present Calc.	Mode Description	Present Calc.
MG(a) ClOOI	ClO	1.7164	OO str	769.3
	OO	1.4158	ClO str	667.0
	OI	2.0358	IO str	552.5
	ClOO	109.2	ClOO bend	410.4
	OOI	110.5	IOO bend	261.6
	ClOOI	84.1	Torsion	89.5
MG(b) $IClO_2$	ICl	2.7071	ClO str sym	1299.6
	ClO	1.4522	ClO str asym	1170.0
	IClO	105.2	OClO bend	507.7
	OClO	115.2	ICl str	365.0
	IClOO	-115.3	IClO bend	179.5
			umbrella	140.5
MG(c) IOClO	IO	2.0190	ClO’ str	1180.8
	OCl	1.7631	IO str	557.8
	ClO’	1.4942	OCl str	444.7
	IOCl	112.3	OClO’	323.9
	OClO’[a]	113.8	IOCl bend	189.7
	IOClO’	67.7	Torsion	70.8
MG(d) $ClIO_2$	ClI	2.4066	IO str asym	981.6
	IO	1.7700	IO str sym	979.0
	ClIO	102.0	ClI str	322.5
	OIO	109.2	OIO bend	310.0
	$ClIO_2$	-107.4	Umbrella	214.2
			ClIO bend	173.6
MG(e) OIOCl	OI	1.8041	OI str	950.3
	IO’	2.0374	O’Cl str	708.4
	O’Cl	1.7110	IO’ str	459.6
	OIO’	107.7	OIO’ bend	231.7
	IO’Cl	113.3	IO’Cl bend	184.1
	OIO’Cl	77.2	Torsion	77.0

Abbreviations: [a] O’ is the O-atom attached to Cl-atom.

The fourth isomer MG(d) is another Y-shaped $ClIO_2$ complex. The Cl-I bond distance is 2.407 Å, which is slightly smaller than the I-Cl bond distance of $IClO_2$. The I-O bond distance is 1.77 A^o, which is much greater than the Cl-O bond length of the $IClO_2$ isomer. Both the ClIO and OIO bond angles are smaller by 3-5^o than the corresponding IClO and OClO bond angles of the $IClO_2$ isomer.

The fifth isomeric geometry MG(e) is the OIOCl, which has a linear chain type structure with a OIOCl dihedral angle of 77.2^o. In this case the Mulliken charges are -0.64 for O, 0.99 for I, -0.40 for O’ and only 0.05 for Cl, respectively. Like the isomer (c), here we also found X^+O^- (X=I, Cl) resonant structures. The O-O’ distance (3.105 Å) being smaller than I-Cl distances (3.136 Å), not tabulated these values, the O-O repulsion is larger than the I-Cl repulsion. But the dominant OI and IO’ (O’ is the O-atom attached to Cl-atom) .resonances decrease the O-O repulsion. This makes OIO’ angle smaller than IO’Cl angle.

Among the harmonic frequencies of the minimum energy geometries, for the MG(a) ClOOI isomer, the largest frequency is 769.3 cm^{-1} associated with the O-O stretching mode and the least one is 89.5 cm^{-1} associated with a ClOOI torsion mode. The I-O stretching frequency has a smaller value (552.5 cm^{-1}) than the Cl-O stretch (667.0 cm^{-1}) and is consistent with I-O bond length being larger than Cl-O bond length. The IOO bend has a smaller frequency than the ClOO bend and it is also consistent with the larger mass of iodine than that of chlorine. The MG(b) $ICl O_2$ isomer has Cl-O symmetric and asymmetric stretching frequencies of 1299.6 cm^{-1} and 1170.0 cm^{-1}, respectively. The I-Cl symmetric stretching occurs at the frequency of 365.0 cm^{-1}. There is an umbrella mode having a frequency of 140.5 cm^{-1}. The third geometry MG(c) IOClO has the maximum frequency of 1180.8 cm^{-1} associated with the Cl-O' stretch and the O-Cl stretch has a frequency of 444.7 cm^{-1}. The OClO and IOCl bends occur at 323.9 cm^{-1} and 189.7 cm^{-1}, respectively. The least one is the IOClO torsion having frequency of 70.8 cm^{-1}. The MG(d) $ClIO_2$ isomer has IO asymmetric and symmetric stretching frequencies of 981.6 cm^{-1} and 979.0 cm^{-1}, respectively. The I-O symmetric stretching frequency is greater than the Cl-I stretching frequency and it is consistent with I-O bond length being smaller than Cl-I bond length. The Cl-I asymmetric stretching has an umbrella mode with a frequency of 214.2 cm^{-1}. Finally the MG(e) OIO'Cl complex has O-I and I-O' stretching frequencies of 950.3 cm^{-1} and 459.6 cm^{-1} respectively. The OIO'and IO'Cl bends occur at 231.7 cm^{-1} and 184.1 cm^{-1}, respectively. The OIO'Cl torsion has a frequency of 77.0 cm^{-1}.

B: Transition state geometries

Various transition state geometries, which are possibly involved during the course of the IO+ClO reaction, are depicted in Table 2. The first one is IOOCl, represented by TS(a), a chain structure with the IOOCl dihedral angle being 55.8°. The IOO bond angle (108.3 °) is larger than the OOCl bond angle (98.7°) which is due to the similar reason that iodine has larger repulsion with the lone pairs of oxygen than chlorine, as mentioned earlier in the case of Mg(a) ClOOI minimum energy geometry. The transition state TS(b) IOClO has a similar structure as that of the MG(c) IOClO minimum energy geometry and it has X^+O^- resonant structures also. In TS(b), the O-O' repulsion effect is larger than the I-Cl repulsion, which makes OClO' bond angle (118.0°) larger than IOCl bond angle (116.4°) . Note that O' is the O-atom attached to Cl. The transition state TS(c), OIOCl, is another resonant-typed linear structure having an OIO'Cl dihedral angle of 86.0°. The OIO' angle is slightly smaller than IO'Cl angle. Both the O-I and I-O' bond lengths are smaller than O'-Cl bond length, which may be due to the large orbital overlap between I and O (or O') than that of between Cl and O'. The fourth transition state is TS(d) ClOOI, which occurs at the approach of two radicals with the ClOOI dihedral being 180°. It has a large ClOO bond angle of 172.8° compared to OOI bond angle of 125.4°. The harmonic frequencies of all the transition states are also listed in Table 2.

All the four transition states have one imaginary frequency, suggesting that these are first-order saddle points. For the transition state TS(a) IOOCl, the O-O stretching mode has the maximum frequency of 1247.1 cm^{-1}. The ClOO bend occurs at 661.8 cm^{-1}. It has a ClOO wag having a frequency of 393.9 cm^{-1}. The O-Cl and I-Cl stretches are associated with frequencies of 286.0 cm^{-1} and 136.1 cm^{-1}, respectively. The second transition state, TS(b) IOClO, has Cl-O' and O-Cl stretching frequencies of 1253.5 cm^{-1} and 862.8 cm^{-1}, respectively. The OClO' and IOCl bends occur at 243.4 cm^{-1} and 82.5 cm^{-1}, respectively. Third one, the TS(c) OIOCl has larger frequencies associated with OI and IO' stretches. Two bends OIO' and IO'Cl occur at 297.2 cm^{-1} and 125.3 cm^{-1}, respectively. It has a torsional mode with frequency 81.3 cm^{-1}. The fourth transition state, TS(d) ClOOI, has larger frequencies associated with Cl-O and I-O. The ClOO bend occurs at a higher value than the IOO bend, because of lighter mass of chlorine than of iodine. It has a torsion mode having a frequency of 80.0 cm^{-1}. The magnitude of the imaginary frequency of TS(d) is very large 1152.9i.

The trans- and cis- forms of the ClOOI intermediate have also been examined and their geometrical parameters are listed in Table 2. The trans- conformer, TS(f), has the largest distance between the halogen atoms and the cis- conformer, TS(e), has the smallest distance between the halogen atoms in the plane. The XOO (X=Cl, I) angles are larger in cis- geometry, which is due to the larger repulsion between two halogen atoms in the cis- geometry. The increase in ClOO and OOI bond angles from trans- to cis- configurations through ClOOI minimum energy geometry are 103.1° → 109.2° →115.5° and 103.1° → 110.5° →118.6°, respectively. The O-O distance decreases from ClOOI minimum through trans- to cis- conformers as 1.527 Å → 1.502 Å →1.416 Å. The corresponding decrease in Cl-O and I-O bonds are 1.7164 Å → 1.6828 Å → 1.6693 Å and 2.0358 Å → 1.9898 Å → 1.9858 Å, respectively. Such changes of geometrical patterns suggest that these trans- and cis- conformers of ClOOI may be characterized as saddle points for rotation around O-O bond. Similar geometrical changes have also been found earlier for the BrOOCl isomer[11]. These trans- and cis- configurations have one imaginary frequency along the reaction coordinate, suggesting that these are first order saddle points. The trans- configuration is a loose transition state because of having a very small imaginary frequency along the reaction coordinate of only 7.7i cm^{-1} as compared to cis- configuration. Details of all frequency values are listed in Table 2.

Table 2: Optimized Transition State Geometries (A°, degree), Harmonic Frequencies (cm^{-1}) of various transition states at the MP2 level

Species	Geometry		Frequency	
	Coordinate	Present Calc.	Mode Description	Present Calc.
TS(a) IOO'Cl	IO	1.9366	OO str	1247.1
	OO	1.3381	ClOO bend	661.8
	OCl	2.6166	ClOO wag	393.9
	IOO	108.3	OCl str	286.0
	OOCl	98.7	ICl str	136.1
	IOOCl	55.8	reaction coord	384.9i
TS(b) IOClO	IO	2.7029	ClO' str	1253.5
	OCl	1.4851	OCl str	862.8
	ClO'	1.4583	OO str	476.1
	IOCl	116.4	OClO'	243.4
	OClO'	118.0	IOCl bend	82.5
	IOClO'	80.9	reaction coord	112.9i
TS(c) OIOCl	OI	1.7809	OI str	981.5
	IO'	1.8053	IO' str	723.1
	O'Cl	2.4010	OIO' bend	297.2
	OIO'	111.5	IO'Cl bend	125.3
	IO'Cl	112.3	torsion	81.3
	OIO'Cl	86.0	reaction coord	302.6i
TS(d) ClOOI	ClO	1.8561	ClO str	862.2
	OO	1.6641	OI str	664.7
	OI	1.9198	ClOO bend	493.6
	ClOO	172.8	IOO bend	317.1
	OOI	125.4	torsion	80.0
			reaction coord	1152.9i
TS(e) trans-COOI	ClO	1.6828	ClO str	777.5
	OO	1.5021	OO str	748.0
	OI	1.9998	ClOO bend	633.5
	ClOO	103.1	IOO bend	255.3
	OOI	103.1	IO str	181.0
			reaction coord	7.7i
TS(f) cis-COOI	ClO	1.6693	ClO str	772.8
	OO	1.5266	ClOO bend	608.4
	OI	1.9858	IO str	537.5
	ClOO	115.5	OO str	384.7
	OOI	118.6	IOO bend	159.8
			reaction coord	209.7i

C: Energetics and Reaction pathways

The total energies of the minimum energy geometries and transition state geometries at the MP2 and QCISD(T) levels are listed in Table 3. The MP2 energies predict inconsistent relative energies, which has been found to calculate thermochemical data for the different channels[12]. The energy difference with respect to the reactant (IO+ClO)[12] has been estimated using electronic energy at the QCISD(T) level, the ZPE correction obtained using our calculated frequencies and using experimental spin orbit coupling correction (ΔSOC) of IO 3.33 kcal.mol^{-1}) and ClO (0.45 kcal.mol^{1} [16,17].

Among the five minimum energy geometries, the MG(d) ClIO$_2$ is the most stable isomer and it is 31.97 kcal mol^{-1} below the reactants. The MG (a) ClOOI, (e) OIOCl, (b)IClO$_2$ and (c) IOClO are less stable than ClIO$_2$ by 15.23 kcal mol^{-1}, 17.59 kcal mol^{-1}, 26.59 kcal mol^{-1} and 29.36 kcal mol^{-1}, respectively.

The transition states TS(a) IOOCl and TS(b) IOClO lie at 13.77 kcal mol^{-1} and 8.89 kcal mol^{-1}, respectively, above the reactants. The TS(a) IOOCl represents the energy barrier for the isomeric interconversion process from ClOOI to IClO$_2$. This can be visualized by the geometrical change that the shrinkage of I-Cl bond, viz., 3.5893 A° → 3.1954 A° → 2.7071 A° and a corresponding increase of I-O bond (O is the oxygen at the I side) as 2.8586 A° → 2.6777 A° → 3.3910 A°. The results of the IRC calculation for the TS(a), shown in Figure 1, where we have shown the above trends of the mentioned bond lengths and potential energy along the minimum energy path (E_{MEP}). We found another isomeric interconversition $IClO_2$ → IOClO via TS(b). This isomeric interconversion process can be visualized by the geometrical change that approaching far of I and Cl atoms, viz., 2.7071 A° → 3.6160 A° → 3.1446 A° and the shrinkage of I-O bond (O is the oxygen on the I side), viz., 3.3910 A° → 2.7029 A° → 2.0190 A°. This is also supported by the IRC results of the TS(b) shown in Figure 2. In Figure 2, the I-Cl distance at the minimum reaction coordinate is greater than the I-Cl distance of the $IClO_2$ intermediate. We we can not proceed further through IRC calculation. However, the equal values of Cl-O and Cl-O' will expect to confirm the structure at the further IRC calculation by other method.

Table 3: Total Electronic Energies (a.u.), ZPE (kcal mol^{-1}) and SOC Corrections (kcal mol^{-1}) and Relative Energy (kcal mol^{-1}) of Various Species Involved in IO+ClO Reaction

Species	E_e		ZPE[b]	SOC[c]	ΔE_{corr}[d]
	MP2	QCISD(T)			
Reactants[a] IO + ClO	-621.026475	-621.123617	2.19	-3.78	0.00
Minimum energy geometries					
MG(a) ClOOI	-621.092207	-621.159091	3.93		-16.74
MG(b) $IClO_2$	-621.071446	-621.125917	5.23		-5.38
MG(c) IOClO	-621.078109	-621.136624	3.96		-2.61
MG(d) $ClIO_2$	-621.131326	-621.183897	4.26		-31.97
MG(e) OIOCl	-621.096870	-621.155005	3.73		-14.38
Transition states					
TS(a) IOOCl	-621.041750	-621.110410	3.89		13.77
TS(b) IOClO	-621.051801	-621.118622	4.17		8.89
TS(c) OIOCl	-621.058093	-621.125206	3.16		3.75
TS(d) ClOOI	-621.011105	-621.062009	3.46		43.72
TS(e) trans-ClOOI	-621.087088	-621.152120	3.71		-12.59
TS(f) cis-ClOOI	-621.077498	-621.143041	3.52		-7.08

Abbreviations: [a]Reference[12], [b] Calculated using our MP2 frequencies, [c]Reference[16], [d]Energy differences with respect to reactants (used QCISD(T) energies including ZPE and SOC corrections).

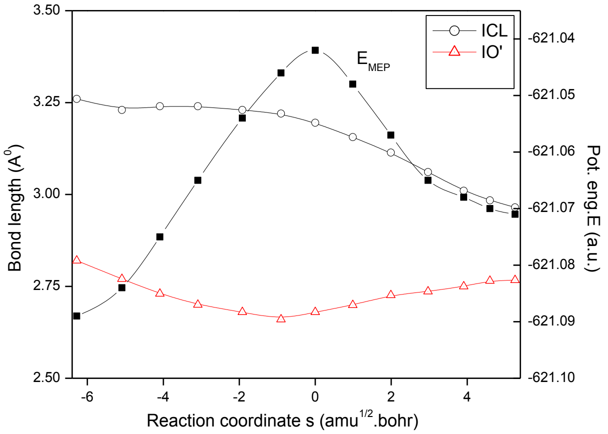

Figure 1: IRC result: MG (a)CIOOI-TS (a)IOOCI-MG (b)ICIOO

The energy barrier for the first isomeric interconversion is 30.51 kcal mol^{-1}, which is very large compared to the second isomeric interconversion barrier of only 3.51 kcal mol^{-1}. Because of the large energy barrier, the first interconversion process is unlikely possible. Therefore, the channel (1) leading to products I + OClO may be formed possibly either by second intermediate interconversion process of $IClO_2$ → IOClO and then to products or following the direct intermediate formation of IOClO and then to products. Note that, the channel (1) is above the reactants by only 0.67 kcal mol^{-1} [12]. As the first isomeric interconversion process is unlikely possible, the MG(a) ClOOI intermediate complex may directly lead to the formation of channel (2) viz. I + ClOO. Similar reaction pathways were suggested by Papayannis et al.[11] for the BrO + ClO reaction. It is to be mentioned here that our predictions are supported by the IRC results.

The results of the IRC calculation of the TS(c) ClOOI, shown in Figure 3, clearly depict the formation of the fourth channel, i.e., Cl + OIO. The Cl + OIO lies at 5.24 kcal mol^{-1} above the reactants. The calculated MP2 energies place the transition state TS(c) above the products Cl + OIO. The relative stability of TS(c) and

Cl + OIO changes at the QCISD(T) level. This implies that the TS(c) may not be stable at this level of theory. Hwang and Mebel[18] reported earlier a similar finding in the study of Cl + O_3 reaction.

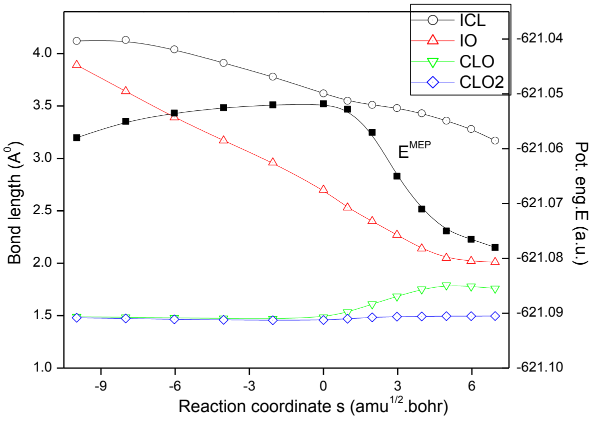

Figure 2: IRC result: MG (b) ICIOO-TS (a)I OCIO –MG (c)IOCIO

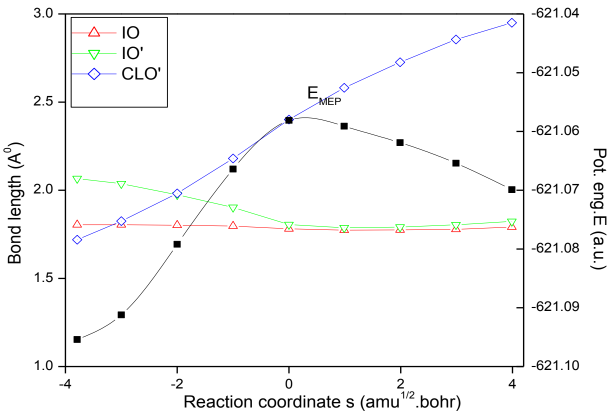

Figure 3: IRC result: MG (e)OIOCI-TS (a) OIOCI –CI+OIO (Ch.4)

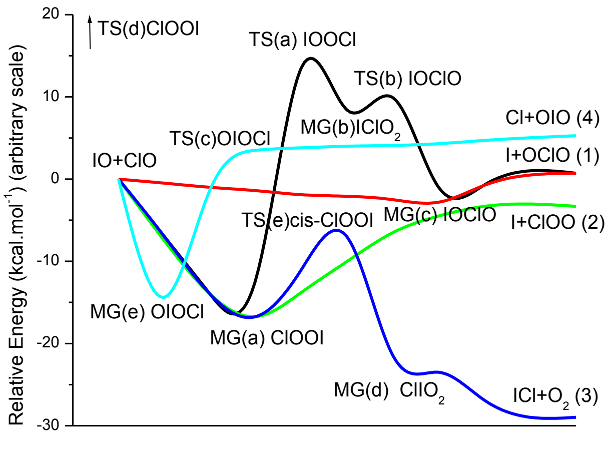

Figure 4: Reaction pathways to different channels

At large O-O distance during the approach of BrO and ClO reactants, Papayannis et al.[12] obtained a transition state ClOOBr, which was just above the reactants and might be responsible for the channel forming ClOO + Br. Following them, we examined a similar transition state TS(d) ClOOI. But this lies at too high 43.71 kcal mol^{-1} above the reactants. This is a tight transition state having a very large imaginary frequency and may be responsible for forming channels like Cl + IOO or else, which is not of our interest.

The results of IRC calculation for TS(f) cis-ClOOI, shows that the geometry changes symmetrically on both sides of the reaction coordinate and so figure obtained from IRC is not shown here. It suggests that it is cyclic conformer of the ClOOI intermediate and one can expect such a cyclic conformer for the production channel (3) i.e., ICl + $^3O_2$, which is well below the reactants. The formation of channel (3) may be depicted to form through the stable cis-ClOOI conformer and/or via the intermediate complex $ClIO_2$. The possibility of such a product formation involving the stable cis- conformer has been mentioned earlier by Papayannis et al.[11] and suggested that a triplet ground state O_2 may be formed by the spin-orbit quenching somewhere in the exit channel or by the removal of spin conservation restriction due to the presence of the heavy atom. Also, the possibility of the formation of ICl + $^3O_2$ via a Y-shaped intermediate has been suggested by Johnsson et al.[8] from a photoisomerization study of IOClO. All the reaction pathways discussed above are shown, in arbitrary scale, in Figure 4.

Conclusion

We investigated various minimum energy and transition state geometries which are involved during the course of the atmospheric important IO + ClO reaction. Possible reaction pathways for different product formations are also discussed. Most of the data are reported to be new and may serve as future references.

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