

## *Ab initio* Study of the Transition State of Direct Isomerization from *CIOCl* to *CICIO* on the $S_0$ and $S_1$ State

Heesun An, Kunhye Lee, and Kyoung Koo Baeck\*

Department of Chemistry, Gangneung-Wonju National University, Gangneung, Gangwon-do 210-702, Korea

\*E-mail: baeck@gwnu.ac.kr

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There have been many experimental studies of the photolysis of dichlorine monoxide ( $Cl_2O$ ),<sup>1-8</sup> partially because it is the anhydride of *HOCl*, an important chlorine reservoir species in the stratosphere. A rather unusual chemical species, *CICIO*, was detected in even the very earliest studies of *CIOCl*. After the detection of two of the vibration modes (962 - 952  $cm^{-1}$  and 368 - 377  $cm^{-1}$ ) of *CICIO* in 1967,<sup>1</sup> the third vibration mode (241  $cm^{-1}$ ) was also reported in 1973.<sup>2</sup> In 1995, Johnsson *et al.* investigated the properties of *CICIO* by using irradiation of light between 320 and 428 nm, refined all three of the vibrational properties,<sup>3</sup> and suggested that the geminate recombination of *CIO* and *Cl*, which are the products of the initial dissociation of *CIOCl*, is the main photoisomerization pathway to *CICIO*.<sup>3</sup> This proposal seems to be further supported in 1999 by a resonance Raman study of *CICIO* photochemistry in solution with radiation with a wavelength of 282.4 nm (4.39 eV).<sup>4</sup>

Meanwhile, the direct isomerization from *CIOCl* into *CICIO* through a transition state ( $TS_{S_0}$ ) of  $S_0$  was also suggested in 1998,<sup>5</sup> as another possible explanation for the isomer, but the role of  $TS_{S_0}$  in actual dynamical process has not yet been clearly studied theoretically. A later theoretical study in 2001 with reduced two-dimensional space at fixed bond angle showed that the initial dynamics of excited electronic states is the direct dissociation of *CIOCl* to *CIO* and *Cl*,<sup>6</sup> but the possibility of isomerization through angular motion in either the ground or the excited electronic state was not explicitly studied there. Neither the validity of the  $TS_{S_0}$  nor the possibility of the direct isomerization has been explicitly examined yet.

In addition, Nickolaisen *et al.* observed unknown vibrational series in their absorption spectrum in the energy region of 20,000 - 22,000  $cm^{-1}$ ; 'We have identified fragmentary series having 110, 325, and 786  $cm^{-1}$  spacing in this region ... but we have been unable to establish a unique origin for the bands in this region.'<sup>7</sup> No theoretical result has been reported yet about the state responsible to this observation.

Since the energies of the light sources (irradiation of light 320 - 428 nm corresponds to 3.9 - 2.9 eV) used in the detection of *CICIO* correspond to the first excited singlet state,  $S_1$  ( $^1B_1$ ), of *CIOCl*,<sup>2,7</sup> the detailed dynamical behavior of the  $S_1$  state of *CIOCl* and *CICIO* deserves to be studied too. In other word, the possibility of direct isomerization through the potential energy surface (PES) of not only the  $S_0$  state but also the  $S_1$  state deserve to be explored further. However, no reliable theoretical study of the stability, stationary structure, and vibration pro-

erties of the  $S_1$  electronic states of *CIOCl* and *CICIO* has previously been explicitly reported yet. Because the photolysis with higher photon energies opens up more complicated and distinct pathways,<sup>4,7-9</sup> a clearer understanding of the characteristics of  $S_1$  is an indispensable prerequisite of further rigorous dynamical study of the higher excited states of  $Cl_2O$  systems.

To provide additional insights on the matters, i.e., the validity and role of the transition state structure involved in the direct isomerization along  $S_0$  PES from *CIOCl* to *CICIO* isomer is re-examined in the present work by using highest level of theory applied so far. The stability of the first excited singlet state,  $S_1$ , of both *CIOCl* and *CICIO* are also studied here, at first.

**Details of Computations.** The coupled-cluster singles and doubles (CCSD) method<sup>10</sup> and its extended CCSD(T) method<sup>11</sup> including non-iterative triples were used for the study of the ground singlet state ( $S_0$ ), whereas the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) method<sup>12</sup> was used for the first excited singlet states ( $S_1$ ). The molecular orbitals (MOs) corresponding to the core atomic orbitals of O (1s) and Cl (1s, 2s, and 2p) atoms were frozen (dropped) in the post Hartree-Fock calculations. The analytic gradient method for the CCSD and EOM-CCSD energies with the dropped MO space not only for the ground state<sup>13</sup> but also for excited states,<sup>14</sup> as implemented in the ACES-2 suit of programs,<sup>15</sup> was used in the present study.

To make direct comparisons with previous theoretical works, exactly the same two basis sets (Basis-1 and Basis-2) of them were used in the present study too. Basis-1 is the TZV2d sets, consisted of 5s3p2d and 5s4p2d contracted GTO for oxygen and chlorine, respectively, as used by Chaquin and colleagues for their B3LYP calculations.<sup>5,16</sup> Basis-2 is the TZ2P sets having 5s3p2d and 6s5p2d contracted GTO for oxygen and chlorine, respectively, and was used by Lee with the CCSD(T) method.<sup>17</sup> All six components of the Cartesian d-functions were included in Basis-1 and -2. In order to get nearest result to the one-electron basis set limit, the aug-cc-pVQZ sets (Basis-3) is used for the B3LYP-DFT method while the aug-cc-pVTZ sets for the CCSD and CCSD(T) methods. Only five pure spherical d-type functions were used in Basis-3 and -4.

**The Ground State,  $S_0$  ( $X^1A_1$ ,  $X^1A'$ ).** The vibrational properties of the ground states of *CIOCl* and *CICIO* are relatively well established,<sup>3</sup> with reliable theoretical results.<sup>16,18</sup> The theoretical results for *CIOCl* and *CICIO* with various functional forms (BLYP, BP86, BPW91, B3LYP, and SVWN) of DFT

**Table 1.** Bond lengths ( $\gamma$  in Å), angles ( $\angle$  in degrees), vibrational frequencies ( $\omega$  in  $\text{cm}^{-1}$ ), and total energies ( $E_{\text{tot}}$  in a.u.) of the ground electronic states ( $S_0$ ) of *CIOCl*, *CICIO*, and the transition state ( $\text{TS}_{S_0}$ ) connecting the  $S_0$  states of the two isomers. The structures of the isomers and  $\text{TS}_{S_0}$  are depicted in Figure 1

Method-	1	2	3	4	5	
Theory	B3LYP		CCSD	CCSD(T)		Exp. <sup>b</sup>
Basis <sup>a</sup>	Basis-1	Basis-2	Basis-3	Basis-4	Basis-3	
<i>CIOCl</i> ( $S_0, X^1A_1$ )						
$\gamma_{Cl-O}$	1.724	1.709	1.699	1.731	1.715	1.696
$\angle_{Cl-O-Cl}$	112.4	112.8	111.3	110.7	110.9	110.9
$\omega_1$ (asym. str.)	651	669	763	667(4)	699(1.4)	686
$\omega_2$ (sym. str.)	649	657	674	624(1)	642(1.1)	640
$\omega_3$ (bend)	290	294	305	288(0.1)	293(0.1)	300
$E_{\text{tot}}^c$ (a.u.)	-1.5711	-1.6095	-0.4466	-0.3569	-0.4791	
$\Delta E_{\text{bind}}^d$ (eV)	1.25	1.38	1.23	1.26	1.44	1.40
<i>CICIO</i> ( $S_0, X^1A'$ )						
$\gamma_{Cl-Cl}$	2.186	2.147	2.108	2.232	2.167	
$\gamma_{Cl-O}$	1.533	1.517	1.518	1.545	1.532	
$\angle_{Cl-O-Cl}$	114.0	113.4	112.2	114.2	113.2	
$\omega_1$ ( <i>Cl-O</i> str.)	949	976	970	918(38)	957(56.2)	962
$\omega_2$ ( <i>Cl-Cl</i> str.)	393	403	431	336(33)	371(45.1)	375
$\omega_3$ (bend)	240	250	256	214(5)	231(5.1)	239
$\Delta E_{\text{iso}}^e$ (eV)	0.68	0.56	0.90	0.82	0.74	
$\text{TS}_{S_0}$ <i>CIOCl</i>						
$\gamma_{Cl-O}$	1.552	1.535	1.550	1.618	1.598	
$\gamma_{O-Cl}$	2.603	2.574	2.604	2.821	2.886	
$\angle_{Cl-O-Cl}$	76.8	77.6	76.3	114.6	113.6	
$\omega_1$ (str.)	925	948	899	753	786	
$\omega_2$ (str.)	227	229	211	80	64	
$\omega_3$ (bend)	566 i	583 i	683 i	192 i	193 i	
$\Delta E_{\text{iso}}^e$ (eV)	2.11	2.12	2.46	1.16	1.36	
$\Delta E_{\text{bind}}^d$ (eV)	+0.86	+0.73	+1.23	-0.10	-0.08	

<sup>a</sup>Basis-1, Basis-2, Basis-3, and Basis-4 are the TZV2d, aug-cc-pVQZ, aug-cc-pVTZ, and TZ2P sets, respectively. <sup>b</sup>Ref. 19 for bond lengths and angles, Ref. 22 for  $\Delta E_{\text{bind}}$ , and Ref. 3 for vibration frequencies. <sup>c</sup>The total energies are given with respect to -994.0 Hartrees. <sup>d</sup>The binding energy (in eV) with respect to the dissociation limit of  $\text{Cl}(\text{P})$  and  $\text{ClO}(\text{P})$ . <sup>e</sup>The relative energy (in eV) with respect to the  $S_0$  of *CIOCl*.

theory as well as various levels (SCF, MP2, and CCSD[T]) of *ab initio* theory have been compared there.<sup>18</sup> The transition state ( $\text{TS}_{S_0}$ ) connecting the two ground states,  $S_0$  ( $^1A_1$ ) of *CIOCl* and  $S_0$  ( $^1A'$ ) of *CICIO* has been investigated with a DFT method only, and the possibility of isomerization through  $\text{TS}_{S_0}$  was suggested and discussed there with the DFT results for the  $\text{TS}_{S_0}$ .<sup>5</sup>

In order to verify the validity of the previous results, especially for the reliability of the  $\text{TS}_{S_0}$ , we have applied five different methodologies, and the results are shown with some available experimental values and previous theoretical results in Table 1. The results by Method-1 (B3LYP/TZV2d) are included here because the method is what used in the previous work by Chaquin *et al.*,<sup>5,16</sup> whereas the results by Method-4 (CCSD(T)/TZ2P) are shown here because they are used as the most reliable theoretical values at the time.<sup>17</sup> We have tested many different combinations of DFT methods and basis sets, and the results by B3LYP/aug-cc-pVQZ (Method-2) are included in Table 1

as typical basis set-limit results of DFT methods. Method-3 and Method-5 correspond to the CCSD/aug-cc-pVTZ and the CCSD(T)/aug-cc-pVTZ method, respectively.

The calculated bond lengths and angles as well as vibrational frequencies of our five methodologies are all in excellent agreement with experiment values.<sup>3,19</sup> Especially, the vibration frequencies by CCSD(T)/aug-cc-pVTZ method are almost in perfect agreement with experimental values. Therefore, the results by Method-2 (B3LYP/aug-cc-pVQZ) and Method-5 (CCSD(T)/aug-cc-pVTZ) correspond to the ones obtained with one of the highest levels of theory applied so far to these systems. The calculated isomerization energies ( $\Delta E_{\text{iso}}$ ) shown in the middle part of Table 1 – 0.56 and 0.74 eV by Method-2 and Method-5, respectively – are all comparable to the most reliable value provided previously, 0.685 eV, which was obtained with the CCSD(T)/ANO4 method.<sup>20</sup> The positive values of the isomerization energies correspond to the fact that *CIOCl* isomer structure is more stable than the *CICIO* isomer. The binding energy ( $\Delta E_{\text{bind}}$ ) with respect to the dissociation limit of  $\text{Cl}(\text{P})$  and  $\text{ClO}(\text{P})$  is 1.44 [1.38] eV according to the CCSD(T)/aug-cc-pVTZ [B3LYP/aug-cc-pVQZ] method, whereas the experimental value is 1.40 eV.<sup>21</sup> The previous theoretical study by the CAS-PT2-Cl/cc-pVTZ+2s2p method produced 1.44 eV.<sup>22</sup> The results by the DFT calculations are reasonably good so far, not only for the spectroscopic properties but also energetic properties,  $E_{\text{bind}}$  and  $\Delta E_{\text{iso}}$ .

The question about the reliability of the transition state ( $\text{TS}_{S_0}$ ) structure connecting the stationary  $S_0$  structures of *CIOCl* and *CICIO* is one of the main motivations of the present work. The results by our five methodologies are given in the lowest part of Table 1. Two important facts can be noticed from the results. First, the structure and vibration frequencies by Method-1, Method-2, and Method-3 are basically all alike. The bond angles ( $\angle_{Cl-O-Cl}$ ) are around  $77^\circ$ , and the magnitudes of the imaginary frequency are around  $600 \text{ cm}^{-1}$ . The results by the CCSD(T) method (Method-4 and Method-5), however, disclose a rather different structure ( $\angle_{Cl-O-Cl} \approx 114^\circ$ ) and the magnitude of the imaginary frequency ( $\sim 190 \text{ cm}^{-1}$ ). The second important difference is the binding energy ( $E_{\text{bind}}$ ) of the  $\text{TS}_{S_0}$  structure with respect to the dissociation limit of ' $\text{Cl}(\text{P}) + \text{ClO}(\text{P})$ ' fragments. Method-1, -2, and -3 produced negative binding energies, and it imply that the  $\text{TS}_{S_0}$  structure has higher energy than the dissociation limit. The length of one *Cl-O* bond of  $\text{TS}_{S_0}$  structure is about 2.6 Å, about 150% of equilibrium bond length. It seems unreliable result, due to the limitation of DFT methods (Method-1 and Method-2) and the limitation of the single-reference CCSD method (Method-3). The CCSD(T) seems to remedy the problem, and the binding energy by Method-4/Method-5 is just around 0.1 eV. If we consider the possible basis-set-superposition-error (BSSE) effect, the binding energy would become zero. The large *Cl-O* bond distance ( $\sim 2.9$  Å) also implies that the  $\text{TS}_{S_0}$  structure by the CCSD(T) method is nothing but a kind of van der Waals complex between the dissociated fragments,  $\text{Cl}(\text{P})$  and  $\text{ClO}(\text{P})$ . More detailed study on the van der Waals complex should include much higher theoretical levels for electron correlation with even larger basis sets and relativistic spin-orbit coupling, but the study is out of the scope of the present work.



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