

## On the Reaction Mechanism of Br<sub>2</sub> with OCS

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**Abstract:** The reaction mechanism of photochemical reaction between Br<sub>2</sub> (<sup>1</sup>Σ) and OCS (<sup>1</sup>Σ) is predicted by means of theoretical methods. The calculated results indicate that the direct addition of Br<sub>2</sub> to the CS bond of OCS molecule is more favorable in energy than the direct addition of Br<sub>2</sub> to the CO bond. Furthermore, the intermediate isomer *syn*-BrC(O)SBr is more stable thermodynamically and kinetically than *anti*-BrC(O)SBr. The original resultant *anti*-BrC(O)SBr formed in the most favorable reaction channel can easily isomerize into the final product *syn*-BrC(O)SBr with only 31.72 kJ/mol reaction barrier height. The suggested mechanism is in good agreement with previous experimental study.

**Keywords:** Reaction mechanism, reaction of Br<sub>2</sub> with OCS, CCSD(T) method.

In the experiment performed by Romano and coworkers<sup>1</sup>, they explored the photochemically induced reaction between Br<sub>2</sub> and OCS in an Ar matrix at 15 K followed by the assignment for the FTIR spectrum of the matrix, and the existence of a novel (bromocarbonyl) sulfenyl bromide, *syn*-BrC(O)SBr, is confirmed. Furthermore, two computational models, MP2 and B3LYP with 6-31+G(d) basis set, predict the *syn* conformer to be more stable than the *anti* one, in agreement with all the available experimental and theoretical evidences<sup>2-4</sup>. Because the reactants in Romano's experiments are Br<sub>2</sub> and OCS, an *anti* product is expected, which is not in agreement with the final experimental observation. And then, a structure arrangement or conformer conversion is suggested to exist in the photochemical reaction. In this work, we will explore the reaction mechanism of Br<sub>2</sub> with OCS for predicting the intermediates, products, and their reaction channels and understanding the available experimental results by means of theoretical methods.

All calculations are performed using Gaussian 98 program running on the SGI/Origin300 server. The geometries of reactants, intermediate isomers, products, and transition states are optimized at the B3LYP/6-311G(d) level of theory, and the CCSD(T) energies including zero-point energy correction obtained from B3LYP geometries with 6-311G(2df) basis set are used in all discussion of this letter.

Four intermediate isomers, *anti*- and *syn*-BrC(O)SBr, *anti*- and *syn*-BrC(S)OBr, and

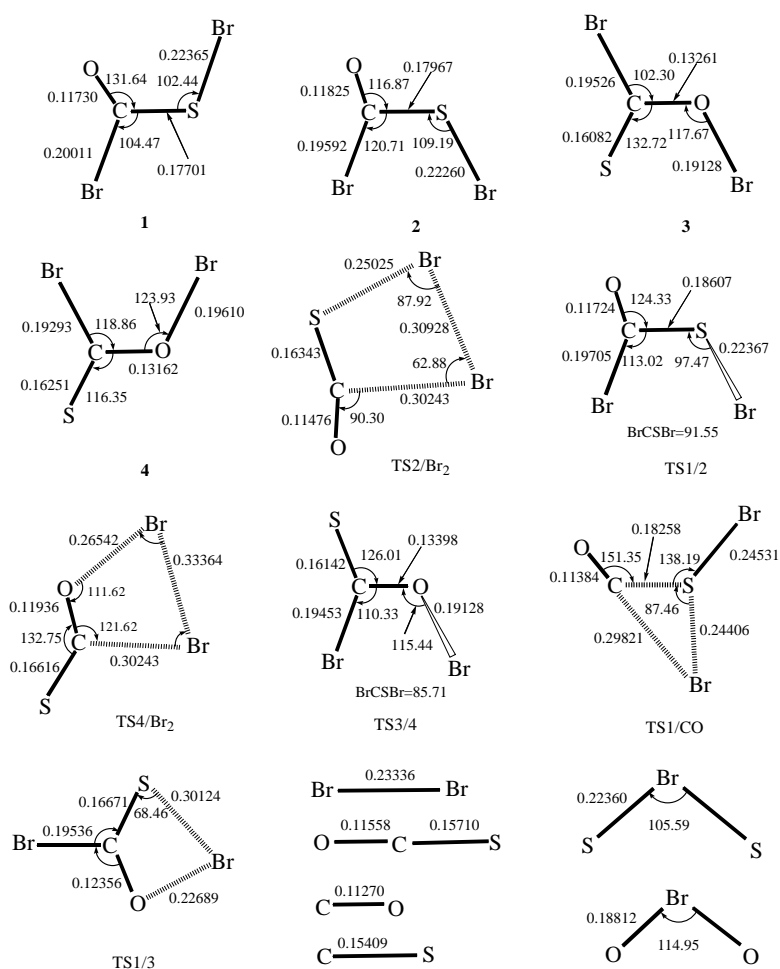
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six reaction transition states are obtained in the optimizations. Their geometries are indicated in **Figure 1**, while the reaction channels are plotted in **Figure 2**.

From **Figure 2**, we can note that the intermediate isomers **3** and **4** are two high-lying species relative to intermediates **1** and **2**. The isomerization barriers from **4** to **3**, and **3** to **1** *via* transition states TS3/4 and TS1/3, are only 28.50 kJ/mol and 44.16 kJ/mol, respectively, which indicate that they have lower kinetic stability. Furthermore, considering very high direct dissociation energy 497.83 kJ/mol from **3** to dissociation fragments SC ( $^1\Sigma$ ) and OBr<sub>2</sub> ( $^1A_1$ ), we can consider that the intermediate isomers **3** and **4** are kinetically unstable, *viz.*, they are very difficult to be observed experimentally. But low-lying isomers **1** and **2** can be predicted to be kinetically more stable than **3** and **4** considering that they lie in a deeper potential well because of higher dissociation barrier (164.37 kJ/mol) and isomerization energies (231.32 kJ/mol for **1** → **3** and 197.18 kJ/mol for **2** → Br<sub>2</sub> ( $^1\Sigma$ ) + OCS ( $^1\Sigma$ )).

**Figure 1** Predicted geometries of intermediate isomers, fragments, and transition states. Bond lengths are in nanometers, and bond angles in degrees.

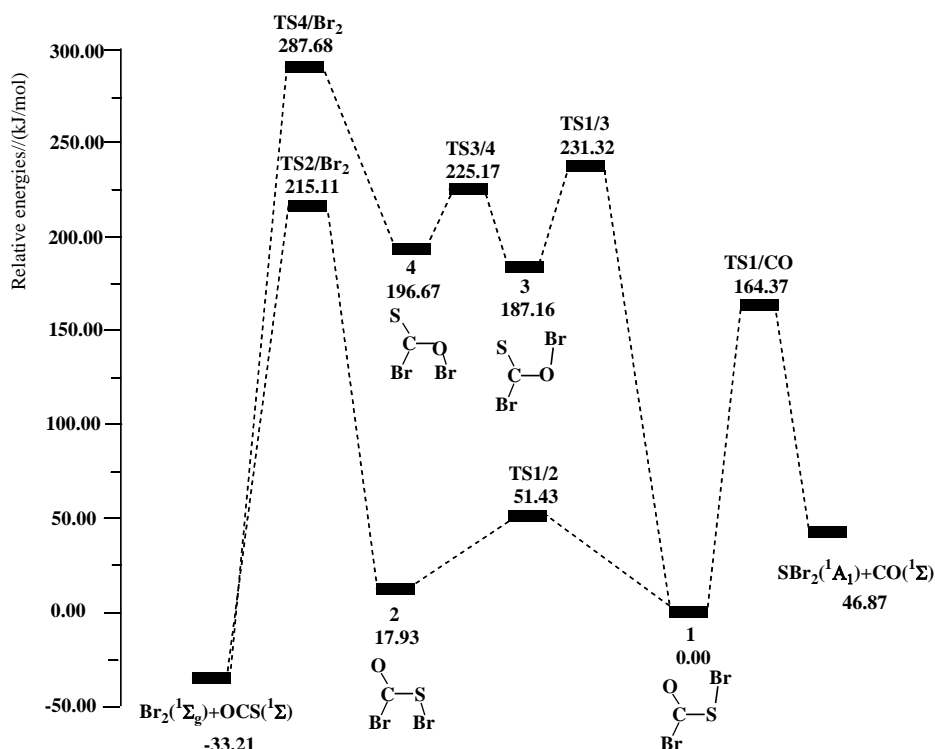


In conformers **1** and **2**, C-O bond lengths are very close to the normal C-O double bond distance (0.11999 nm in H<sub>2</sub>CO at the B3LYP/6-311G(d) level), and then, they can be regarded as normal double bond. The C-S bond lengths are slightly shorter than the normal C-S single bond length (0.18354 nm in CH<sub>3</sub>SH at the B3LYP/6-311G(d) level), and are obviously longer than the C-S double bond distance (0.16152 nm in H<sub>2</sub>CS at the B3LYP/6-311G(d) level). Therefore, we can consider that the C-S bonds in **1** and **2** are single bond with some double bond characters.

For the reaction between Br<sub>2</sub> and OCS, two reaction channels are suggested from **Figure 2**. The first is the direct addition of Br<sub>2</sub> to the C-O bond of OCS molecule, followed by the isomerization pathway **4** → TS3/4 → **3** → TS1/3 → **1**, with a reaction barrier height of 320.89 kJ/mol. The other is a direction addition process of Br<sub>2</sub> to the C-S bond of OCS molecule, followed by the interconversion reaction **2** → TS1/2 → **1**, and the initial reaction barrier is 248.32 kJ/mol. Obviously, the former reaction channel is very favorable to compete with the latter by comparing their reaction barrier height. Therefore, the direct addition reaction of Br<sub>2</sub> to the CS bond of OCS molecule should be the most possible initial reaction step in Romano's experiment<sup>1</sup>.

The calculated results show that *syn*-BrC(O)SBr **1** is lower in energy than *anti*-BrC(O)SBr by 17.37 kJ/mol, *i.e.*, *syn* conformer is more stable thermodynamically than *anti* one. Based on the suggested reaction pathways above, we can easily know that

**Figure 2** Schematic reaction channels



*anti* species is firstly formed in the reaction of Br<sub>2</sub> with OCS *via* transition state TS2/Br<sub>2</sub>. And the *anti* conformer can isomerize into *syn* isomer *via* transition state TS1/2 with a 31.72 kJ/mol reaction barrier height. Note that the 49.09 kJ/mol reverse barrier and dissociation barrier of 164.37 kJ/mol from **1** to fragments SBr<sub>2</sub> (<sup>1</sup>A<sub>1</sub>) and CO (<sup>1</sup>Σ), we can say that the *syn* isomer is more stable kinetically than *anti* one, and the main product in Romano's experiment<sup>1</sup> is *syn*-BrC(O)SBr, but not *anti*-BrC(O)SBr. The theoretical prediction is in good agreement with the experimental observation<sup>1</sup>.

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### Correction

J. G. YANG, X. Y. YU, H. H. WU, Z. L. CHENG, Y. M. LIU, M. Y. HE, "The Synthesis of 2, 4, 6-Triisopropyl-1, 3, 5-trioxane Catalyzed by Ionic Liquids", Vol. 16 No. 3, pp299-302. On page 300, 18th line "C<sub>10</sub>H<sub>21</sub>O<sub>3</sub>" should be "C<sub>12</sub>H<sub>24</sub>O<sub>3</sub>".