

Supplementary materials for:

Gas-Phase Reaction of CeVO_5^+ Cluster Ions with C_2H_4 : Reactivity of Cluster Bonded Peroxides

Jia-Bi Ma,^{*[a]} Jing-Heng Meng,^[b] and Sheng-Gui He^{*[b]}

Contents:

1. Table S1: Bond energies by experiments and different functionals.
2. Figure S1: DFT calculated infrared spectra of IS1-IS5.
3. Figure S2: The intrinsic reaction coordinate calculations for the steps of **1** → **TS1/2** → **2**, and **3** → **TS3/4** → **4** in Fig. 4 of the main text.
4. Figure S3-S7, S9: DFT calculated potential energy profiles for the reactions of IS1-IS3 and IS5 with C_2H_4 , and intrinsic reaction coordinate calculations, or relaxed potential-energy curves.
5. Figure S8: The relaxed potential-energy curves formed by decreasing the distances between O atom and H atom in IS1-IS3.

[a] Dr. J.-B. Ma
Key Laboratory of Cluster Science, The Institute for Chemical Physics, School of Chemistry
Beijing Institute of Technology, 100081, Beijing (People's Republic of China)
E-Mail: majiabi@bit.edu.cn

[b] Jing-Heng Meng, and Prof. Dr. S.-G. He
State Key Laboratory for Structural Chemistry of Unstable and Stable Species
Institute of Chemistry, Chinese Academy of Sciences
100190 Beijing (People's Republic of China)
E-Mail: shengguihe@iccas.ac.cn

Table S1: Bond energies by experiments and different functionals. The values are in unit of eV.

| | | Ce-O | V-O | O-O | CH ₂ CH-H |
|-----------------------|--------------|--------------|--------------|--------------|----------------------|
| Experiments | Value | 8.219±0.08 | 6.44±0.2 | 5.116 | 4.757±0.03 |
| | Reference | 1 | 2 | 3 | 4 |
| Hybrid Functionals | B3LYP | 8.020 | 6.592 | 5.150 | 4.629 |
| | B3P86 | 8.752 | 7.063 | 5.379 | 4.734 |
| | B1B95 | 8.683 | 6.508 | 5.151 | 4.643 |
| | B1LYP | 8.385 | 6.156 | 4.826 | 4.576 |
| | B3PW91 | 8.488 | 6.890 | 5.168 | 4.577 |
| | PBE1PBE | 8.493 | 6.637 | 5.127 | 4.554 |
| | M06 | 8.905 | 6.602 | 4.952 | 4.589 |
| | M062X | 8.202 | 5.390 | 4.999 | 4.658 |
| | M05 | 7.772 | 6.545 | 5.034 | 4.582 |
| | X3LYP | 8.648 | 6.493 | 5.089 | 4.630 |
| M052X | 8.747 | 5.188 | 4.907 | 4.697 | |
| Pure Functionals | M06L | 8.794 | 6.401 | 5.170 | 4.511 |
| | BPW91 | 8.814 | 7.593 | 5.768 | 4.503 |
| | BLYP | 8.827 | 7.247 | 5.680 | 4.552 |
| | BP86 | 9.030 | 7.654 | 5.939 | 4.662 |
| | TPSS | 8.608 | 7.197 | 5.284 | 4.620 |
| | PBE | 9.061 | 7.693 | 6.009 | 4.546 |
| | BPBE | 8.828 | 7.612 | 5.791 | 4.493 |

Supplementary References

1. M. Dulick, E. Murad, R. F. Barrow, *J. Chem. Phys.* 1986, **85**, 385.
2. G. L. Gutsev, L. Andrews, C. W. Bauschlicher, *Theor. Chem. Acc.* 2003, **109**, 298.
3. J. B. Pedley, E. M. Marshall, *J. Phys. Chem. Ref. Data* 1983, **12**, 967.
4. J. Berkowitz, G. B. Ellison, D. Gutman, *J. Phys. Chem.* 1994, **98**, 2744.

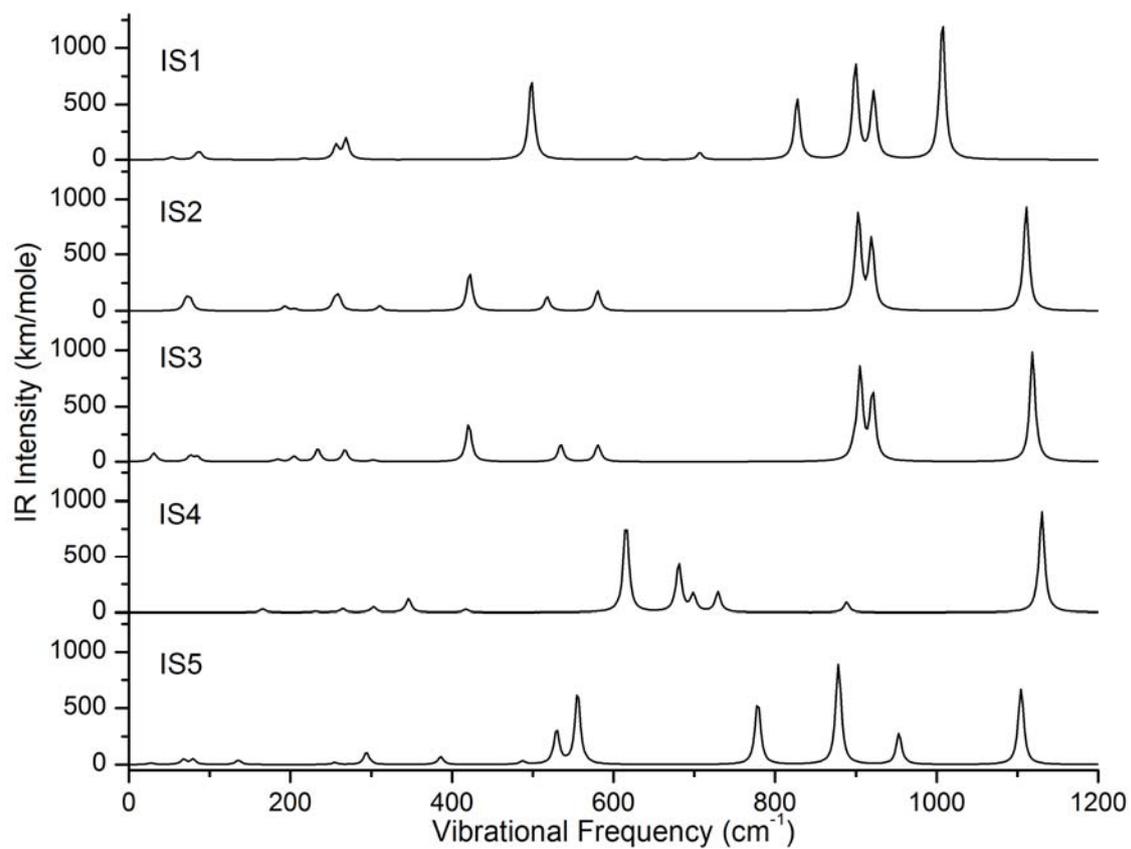


Figure S1: Density functional theory calculated infrared spectra of IS1-IS5.

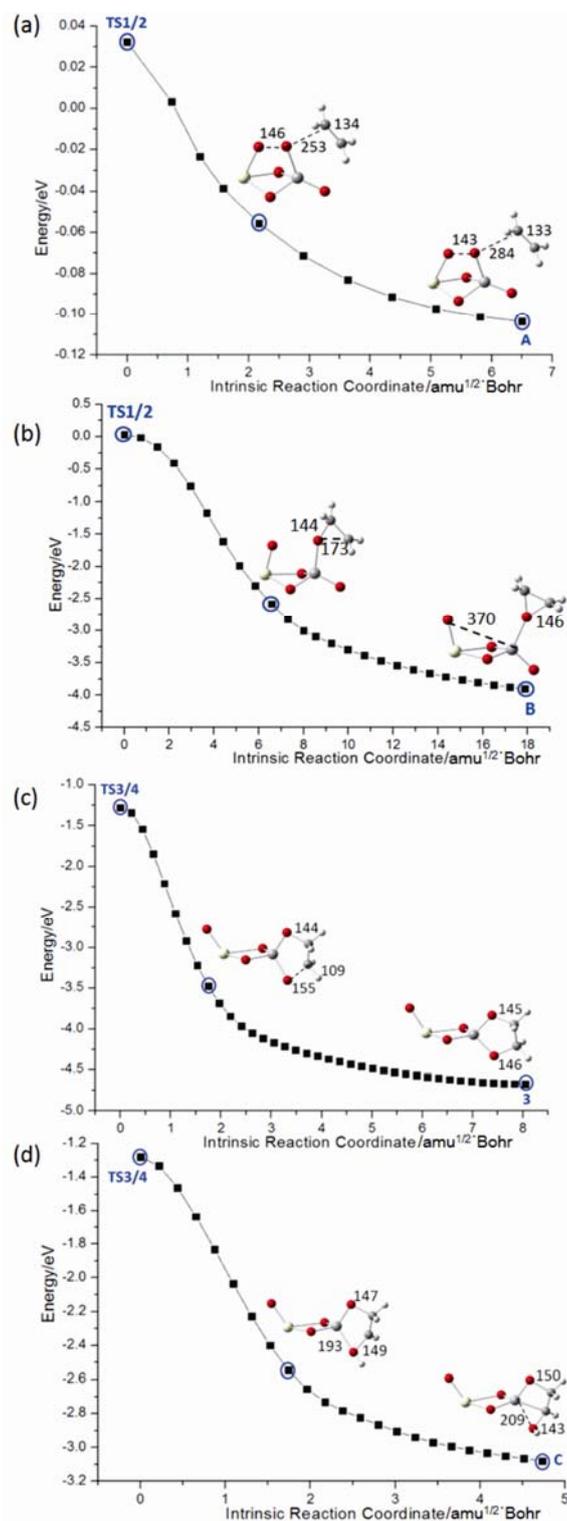


Figure S2: The intrinsic reaction coordinate (IRC) calculations for the steps of **1** \rightarrow **TS1/2** \rightarrow **2** (a and b), and **3** \rightarrow **TS3/4** \rightarrow **4** (c and d) in Fig. 4 of the main text. Bond lengths are in pm. The energies are with respect to the separated reactants/4 without zero-point vibration corrections. Intermediates **1**, **2** and **4** can be obtained by optimizing the geometries of points A, B and C in panels a, b and d, respectively.

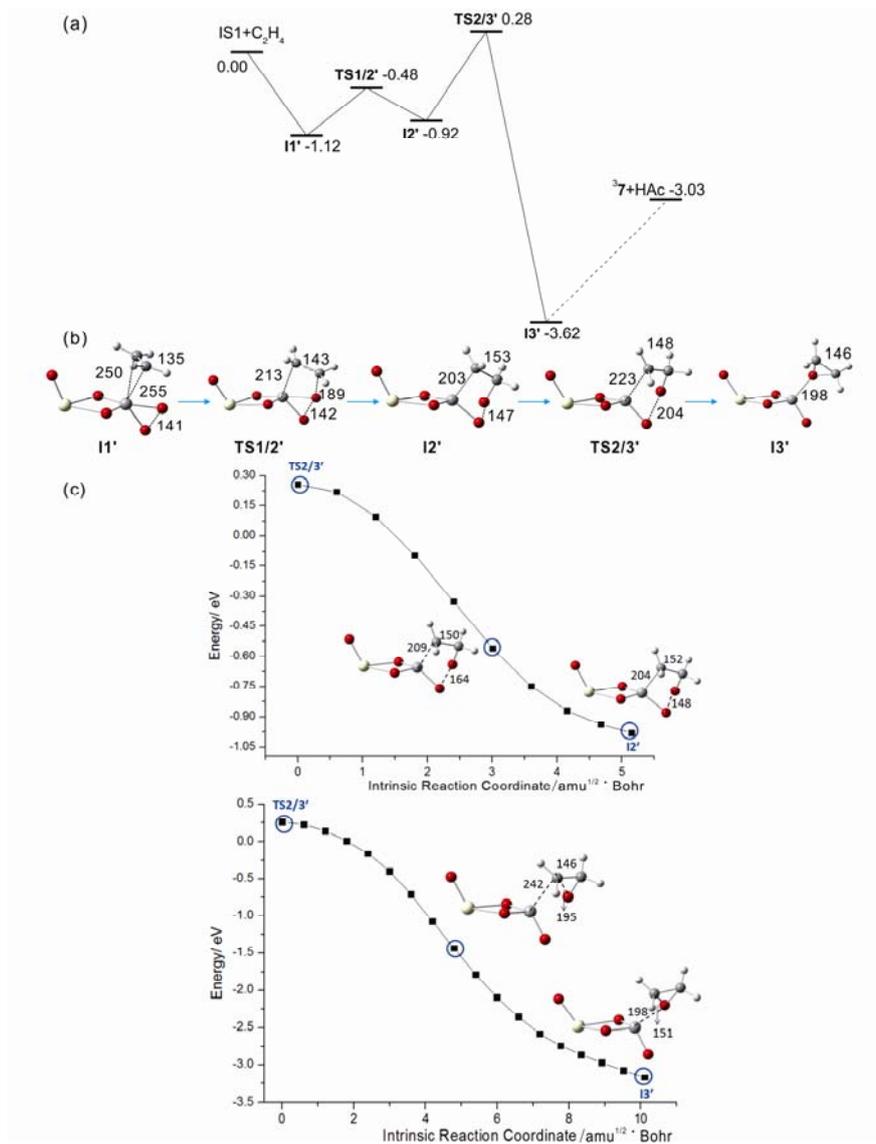


Figure S3: DFT calculated potential energy profile (a), structures (b) for the reaction of IS1 with C₂H₄, and IRC calculations for the step of I2' → TS2/3' → I3' (c). Bond lengths are in pm. In panel a, the zero-point vibration corrected energies (ΔH_{0K} in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. The superscript indicates the spin multiplicities. In panel c, the energies are with respect to the separated reactants without zero-point vibration corrections.

After the formation of the encounter complex I1', the approaching of C₂H₄ and vanadium atom forms V–C bond, which is concomitant with the process that O–O bond is slightly elongated from 141 pm in I1' to 147 pm in I2'. The intrinsic energy barrier TS2/3' hampers the following steps, and therefore no further intermediates and TSs were located to complete this pathway. The intermediate I3' is the same as **2** in Fig. 4 of the main text.

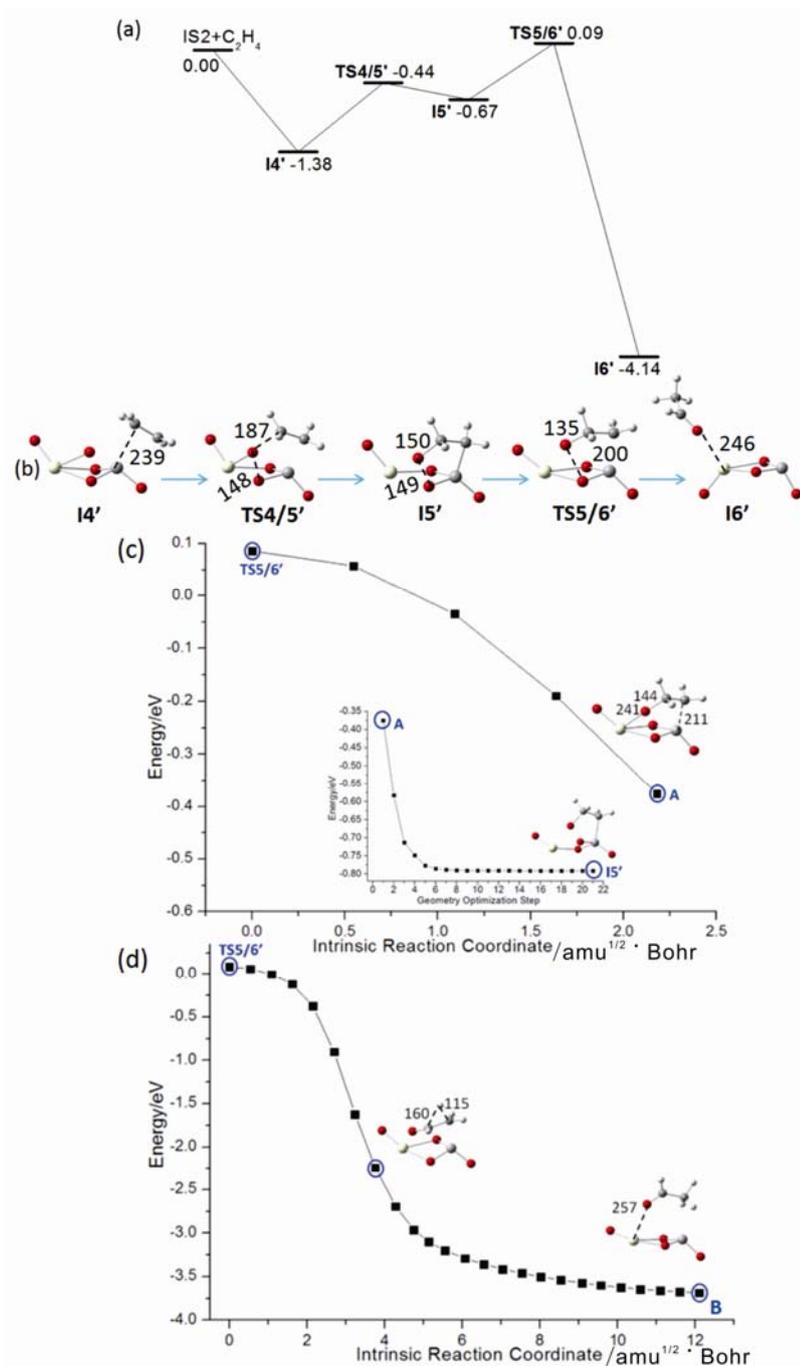


Figure S4: DFT calculated potential energy profiles for the reaction of IS2 with C₂H₄, and IRC calculations for the step of I5' → TS5/6' → I6' (c). Bond lengths are in pm. In panel a, the zero-point vibration corrected energies (ΔH_{0K} in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. In panels c and d, the energies are with respect to the separated reactants without zero-point vibration corrections. Intermediates I5' and I6' can be obtained by optimizing the geometries of points A and B in panels a and b, respectively. In the inset of panel c, the optimization of the geometry of point A is given.

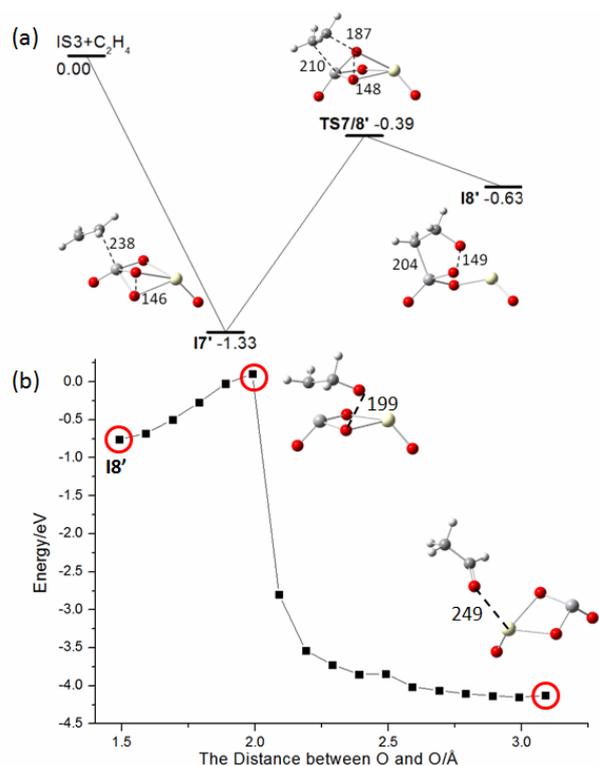


Figure S5: DFT calculated potential energy profile for the reaction of IS3 with C₂H₄ (a), and the relaxed potential-energy curve by increasing the distance of O–O bond in **18'** (b). Bond lengths are given in pm. The zero-point vibration corrected energies (ΔH_{0K} in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given for (a). The relative electronic energies without zero-point vibration correction are given for (b).

As shown in panel b, the abrupt change in energy is because more than one dimension are as active coordinates along the reaction path, that is, the O–O and C–H distances. For this complicated case, the multicoordinate driven (MCD) method⁵ can be applied to get the initial TS structure. Considerable efforts have been devoted to obtaining a smooth potential-energy surface between **18'** and the product (aldehyde) by using MCD method; however, such a potential-energy curve cannot be obtained. Therefore, it is likely that the actual barrier is much higher than calculated herein, which further supports the conclusion that the path originating from IS3 and C₂H₄ is unfavorable. It is noteworthy that the TSs, shown in other figures of both the main text and Supporting Information, only involve one dimension as active coordinate. According to the IRC calculations and relaxed potential-energy curves of the key steps in all the other potential energy profiles, no abrupt changes in energy are obtained.

Supplementary Reference:

1. Berente and G. Náray-Szabó, *J. Phys. Chem. A* 2006, **110**, 772.

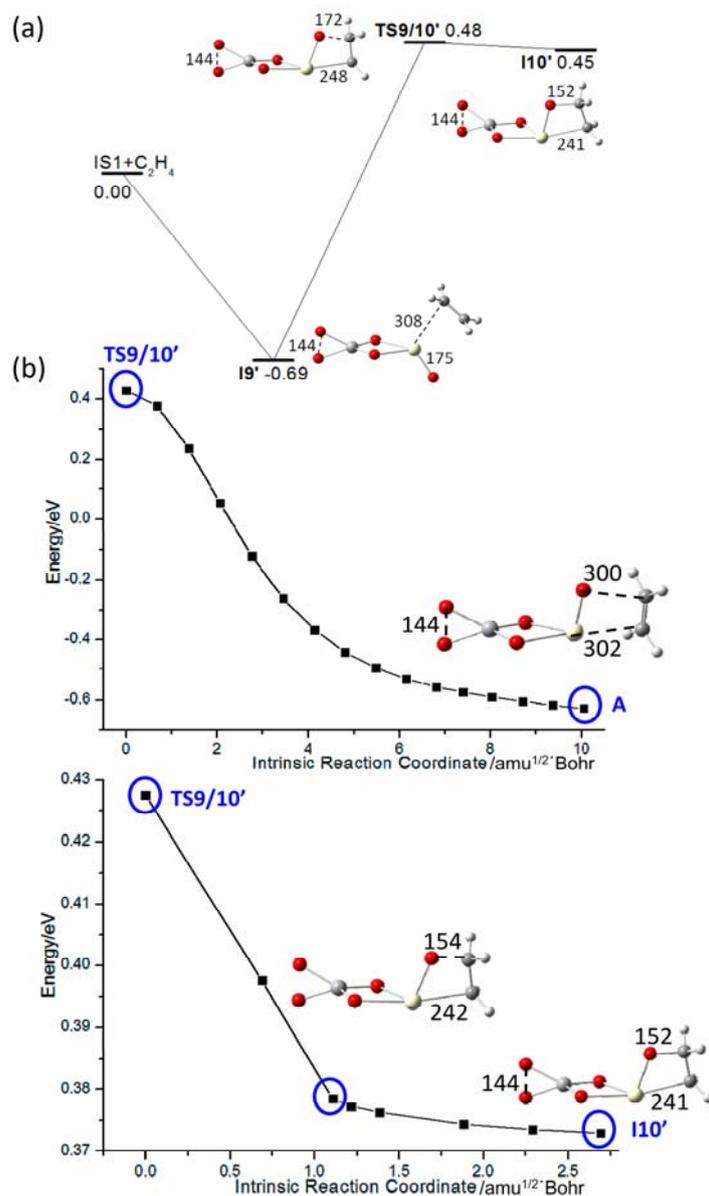


Figure S6: DFT calculated potential energy profile for the reaction of IS1 with C₂H₄ (a), and the IRC calculations for the step of I9' → TS9/10' → I10' (b). Bond lengths are given in pm. In panel a, the zero-point vibration corrected energies (ΔH_{0K} in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. In panel b, the energies are with respect to the separated reactants without zero-point vibration corrections. Intermediate I9' can be obtained by optimizing the geometry of point A in panel b.

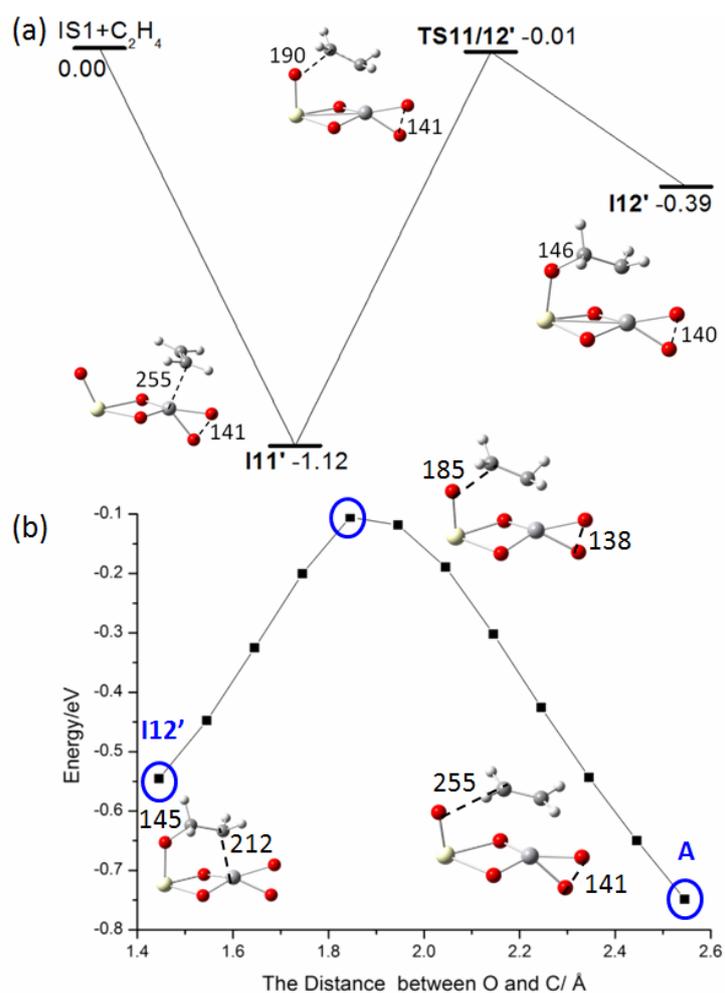


Figure S7: DFT calculated potential energy profile for the reaction of IS1 with C₂H₄ (a), and the relaxed potential-energy curves by variation of the distance between O and C in **I12'** (panel b). Bond lengths are given in pm. In panel a, the zero-point vibration corrected energies (ΔH_{0K} in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. Starting from **I12'**, paths including hydrogen-atom transfer and breaking the Ce–O or O–O bonds involve large barriers which are at least 1 eV higher in energy than the separated reactants. In panel b, the energies are with respect to the separated reactants without zero-point vibration corrections. Intermediate **I11'** can be obtained by optimizing the geometry of point A in panel b.

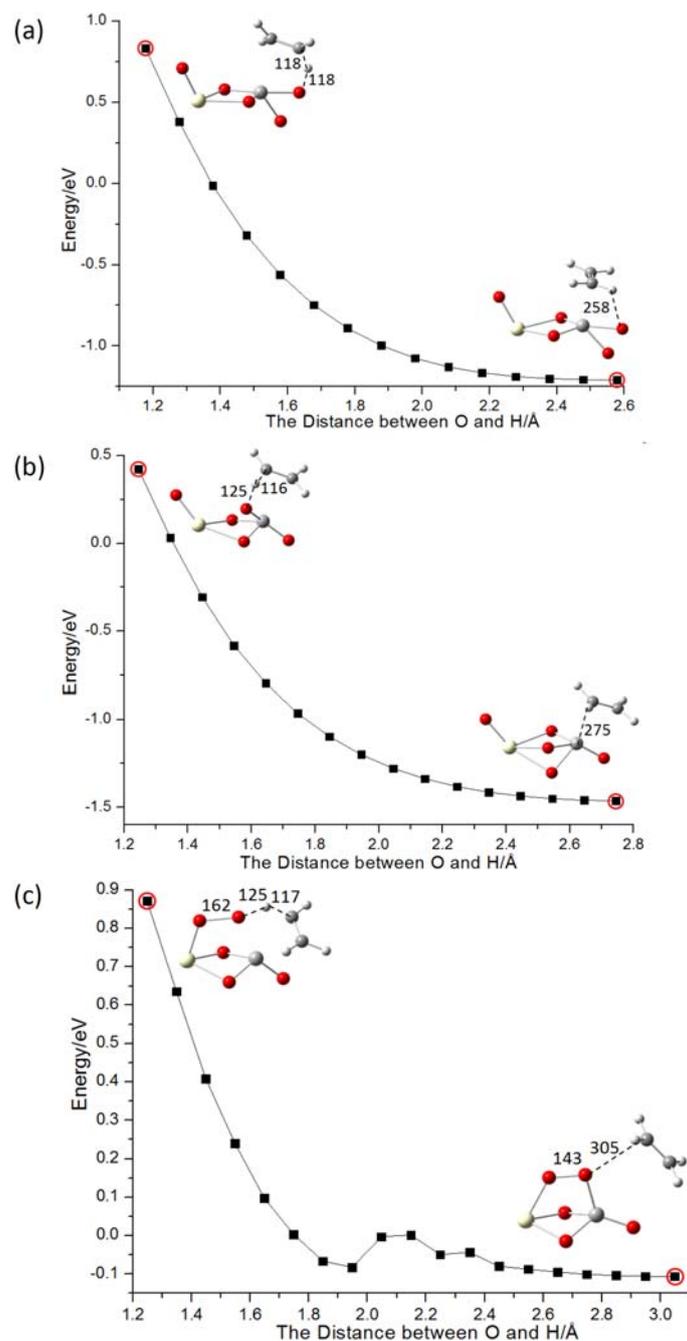


Figure S8: The relaxed potential-energy curves are formed by decreasing the distances between O atom and H atom in IS1 (a), IS2 (b), and IS3 (c). Bond lengths are given in pm. The electronic energies with respect to the separated reactants without zero-point vibration corrections are given.

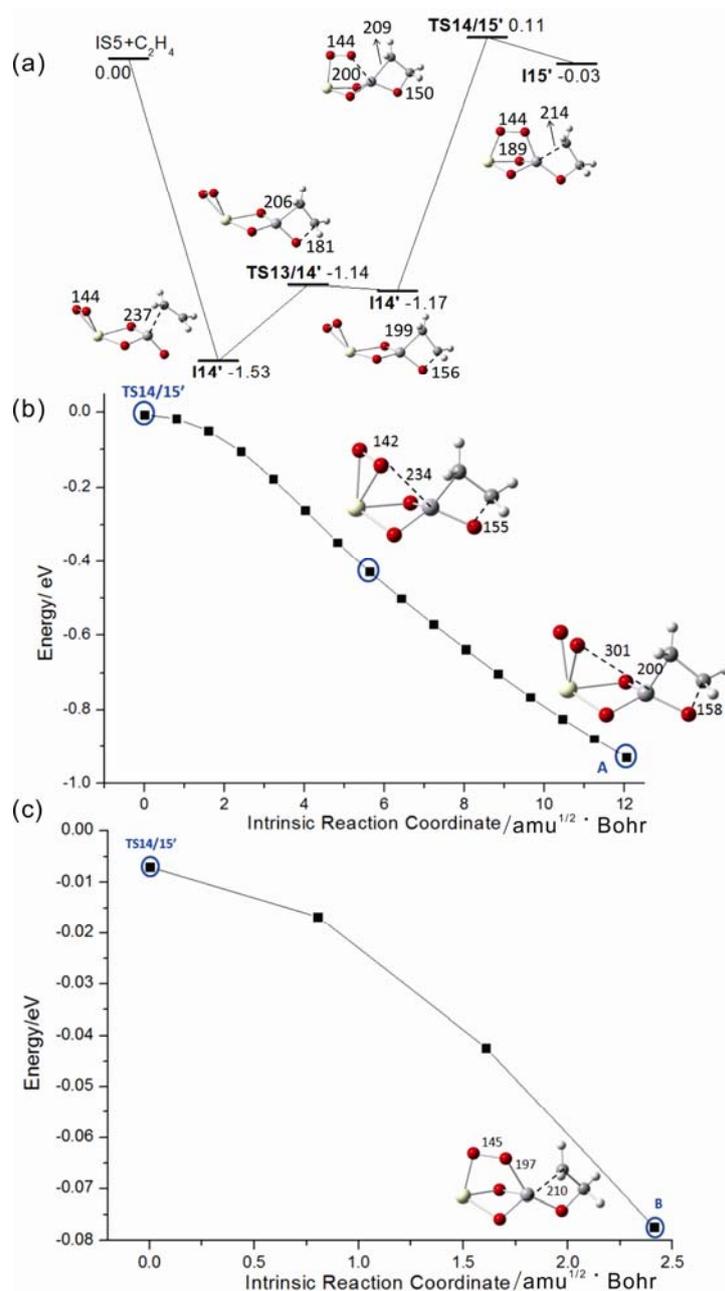


Figure S9: DFT calculated potential energy profile for the reaction of IS5 with C₂H₄ (a) and the IRC calculations for the step of I14' → TS14/15' → I15' (b and c). Bond lengths are given in pm. In panel a, the zero-point vibration corrected energies (ΔH_{0K} in eV) of the reaction intermediates, transition states, and products with respect to the separated reactants are given. In panels b and c, the energies are with respect to the separated reactants without zero-point vibration corrections. Intermediates I14' and I15' can be obtained by optimizing the geometries of points A and B in panels b and c, respectively.