A Mechanism for the Oxidation of SO_2 by a Derivative of the Criegee Intermediate

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Introduction

Sulfur dioxide is present in the atmosphere as a result of a number of both natural and unnatural processes. The presence of SO_2 in the atmosphere contributes heavily to the formation of sulfuric acid aerosol particles through a variety of oxidation pathways. Sulfuric acid can be immensely harmful to the atmosphere. It is implicated in both the formation of acid rain and the depletion of ozone. Although SO_2 emissions are nowhere near as large as man-made CO_2 emissions, the two are estimated to have an impact of similar magnitude upon the environment. On the other hand, sulfate aerosol particles can also have cooling effects on the air. It is thus very important to understand the oxidation processes of atmospheric SO_2 to the very best of our ability.

There are a wide variety oxidants for SO_2. The most common of these is hydroxyl radical. Up to half of the sulfuric acid formed by SO_2 oxidation is thought to come from an oxidant other than OH[1]. There are a number of other oxidants that make up this other 50%, such as NO_2, RO_2 and criegee intermediates. Criegee intermediates are often produced as byproducts of alkene ozonolysis in plants, and are thus atmospherically relevant to our discussion of SO_2 oxidation. There are two possible outcomes for the reaction of SO_2 with a criegee intermediate – oxidation of SO_2 and isomerization of the intermediate:

Fig. 1: SO_2 Oxidation

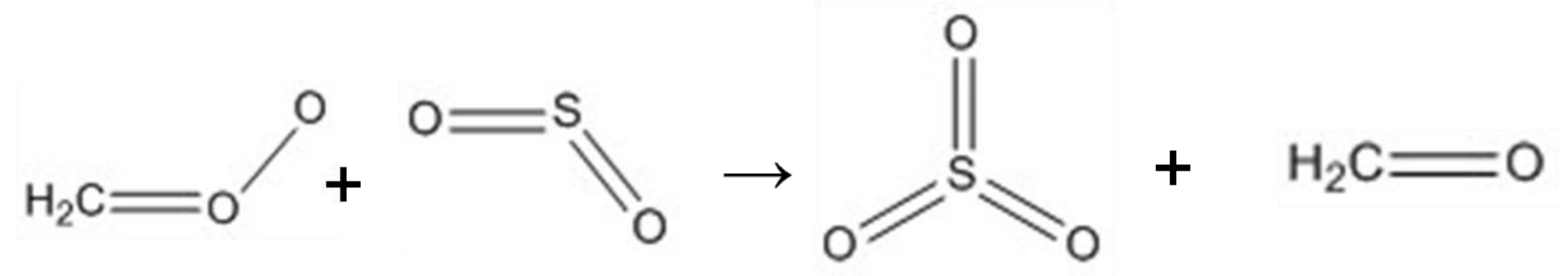
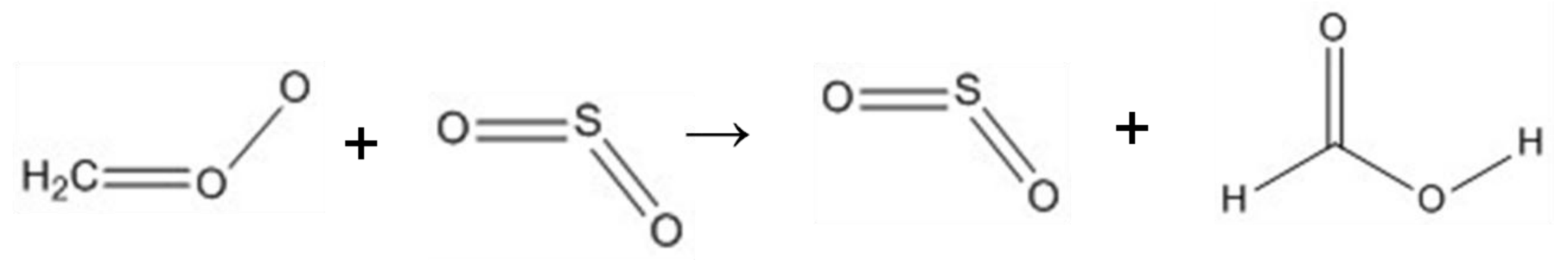


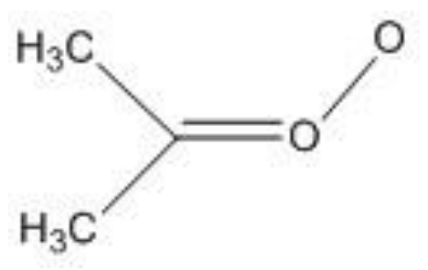
Fig 2: CI Isomerization



RRKM/Master simulations of this reaction based upon CBS-QB3 optimized energies of the reaction mechanism show a 98% yield of SO_3, with the CI isomerizing only 2% of the time.

Objectives and Methods

The mechanism has previously characterized in detail for the reaction of SO_2 with the simplest CI, CH_2OO (shown in Figures 1 and 2). Our research was an attempt to characterize a similar mechanism for the reaction of SO2 with a similar CI, $C(CH_3)_2OO$:



We used Gaussian 09 to carry out all calculations. We used B3LYP/6-31+G(d,p) calculations to find and precisely optimize the geometry of each individual species in the proposed mechanism. Local minima were typically located by drawing the molecules by hand and running a B3LYP optimization on the molecule. Transition states were located through a combination of interpolation calculations and potential energy scans along bond lengths, bond angles and dihedral angles, using the minima as starting points. We then used larger CBS-QB3 calculations to find accurate energies for each species. Relative CBS-QB3 energies are shown in kcal/mol the results section in red.

References and Acknowledgements

References:

1) Mauldin III et al (2012) A New Atmospherically Relevant Oxidant of Sulphur Dioxide, *Nature 488*, 193–196

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Future Work

Goals for future work include:

- Locating the 3 missing transition states: TS XIVb, TS XVa and TS XVb, or rationalize their non-existence if they cannot be located.
- Carrying out successful CBS-QB3 calculations on all species for which this information is missing.
- Eventually, once the mechanism has been completed, we may carry out simulations similar to those mentioned above. This will allow us to predict relative yields of SO_3 and isomerized CI for this reaction and compare it to other oxidations of SO_2.

Results

HOZ Formation

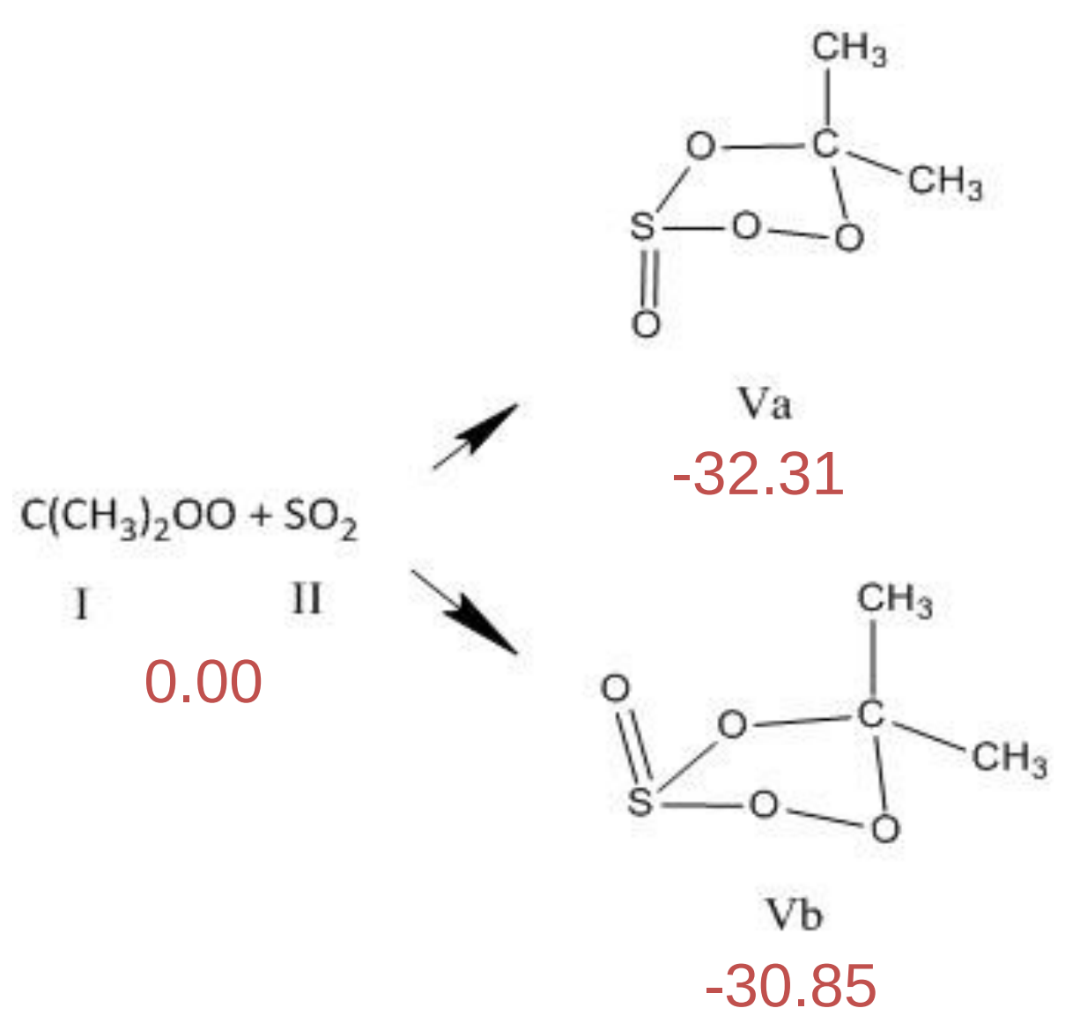
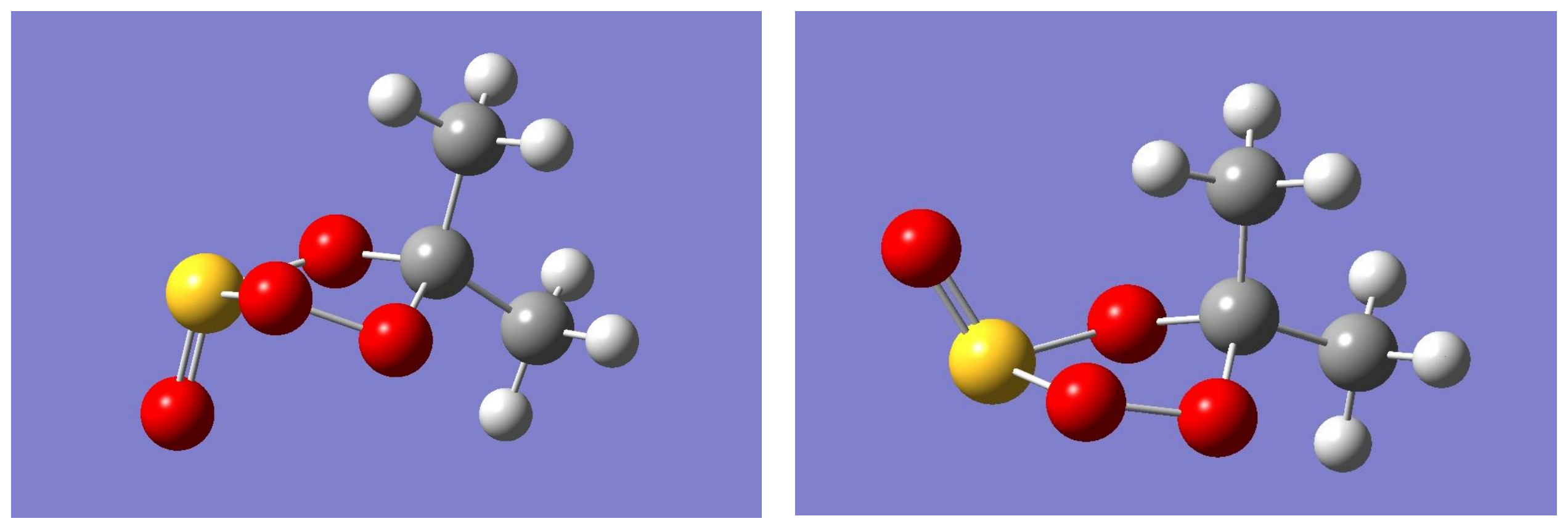


Fig. 4: *HOZ Formation*
The two reactants form a five-membered ring. *Anti*-heteroozonide (Va) and *syn*-heteroozonide are distinguished by the position of the *sp*² hybridized oxygen atom relative to the ring, as seen in Figure 5.



Va *Vb*

Fig. 5: *syn- and anti-HOZ*
In each iteration of HOZ, the sulfur atom bonds to the terminal oxygen from the CI. One of the O atoms from SO_2 bonds to the central C atom. In Va, the other O atom points opposite the pseudo-axial methyl group. In Vb, it points in the same direction as the pseudo-axial group.

Closed-Shell Decomposition

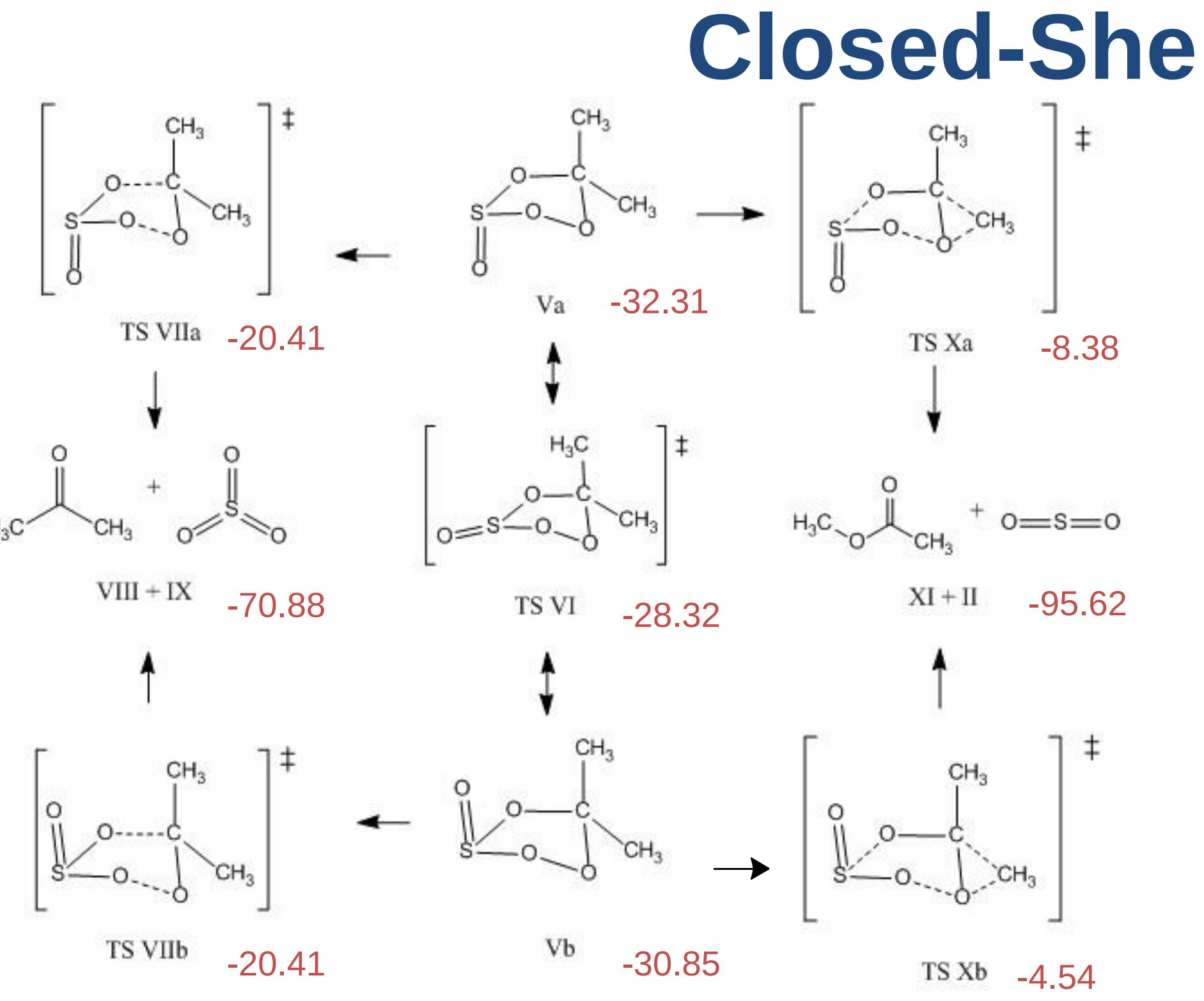


Fig. 6: *Closed-shell decomposition of HOZ*
HOZ has a relatively low energy (~10 kcal/mol) transition state for the formation of SO_3, in which an O-O bond and a C-O bond are broken. There is also a high energy (~25 kcal/mol) transition state in which the O-O bond is broken, the bond between the central carbon and a methyl group is broken, and a new bond is formed between the methyl group and an oxygen atom. This leads to the isomerization of the CI. Additionally, there is a low energy (~3 kcal/mol) transition state for the interconversion of *syn*-HOZ and *anti*-HOZ.

Open-Shell Decomposition

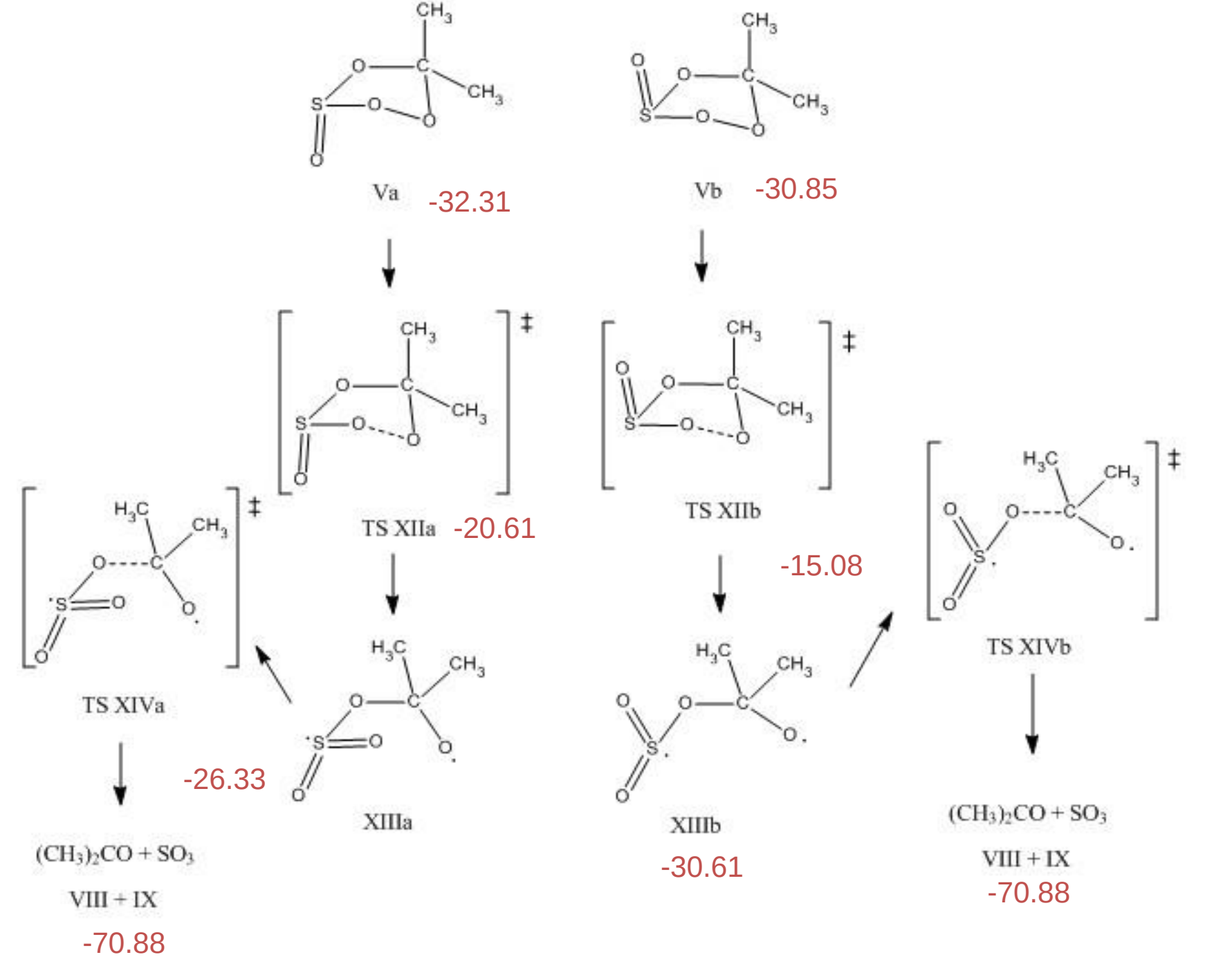


Fig. 7: *Open-shell decomposition of HOZ*
Transition states XIIa and XIIb, which must be reached to initiate the open-shell decomposition, are much higher in energy than the transition states in the closed-shell decomposition, due to their nature as open-shell diradicals. This makes the open-shell decomposition of HOZ much less likely than closed-shell, but still possible. All open-shell species were treated with UB3LYP calculations to find geometry. The initial energy barriers are lower than those for the closed-shell isomerization of CI. As of yet, we have been unable to locate the geometry of TS XIVb, but we do still believe that it exists. While we have located XIIIa geometrically, we have yet to successfully calculate its CBS-QB3 energies.

Dioxirane Diradical Formation

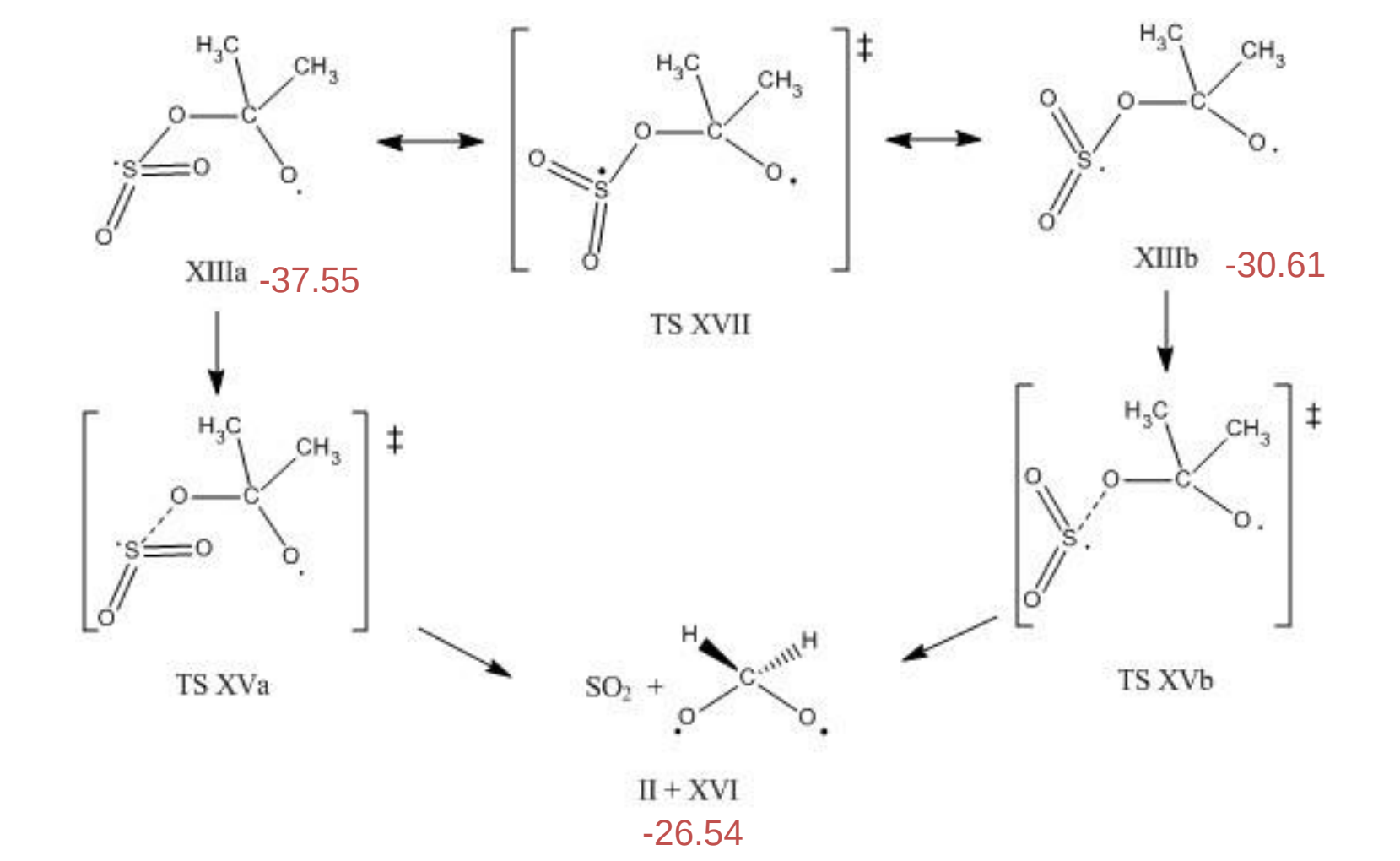


Fig. 8: *Dioxirane diradical formation*
This pathway details the formation of a second CI isomer, the dioxirane diradical. We have yet to locate TS XVa and TS XVb, but previous research leads us to believe that they exist. We have located TS XVII in UB3LYP calculations, but have yet to find its CBS-QB3 energy.

SOCO Ring Formation

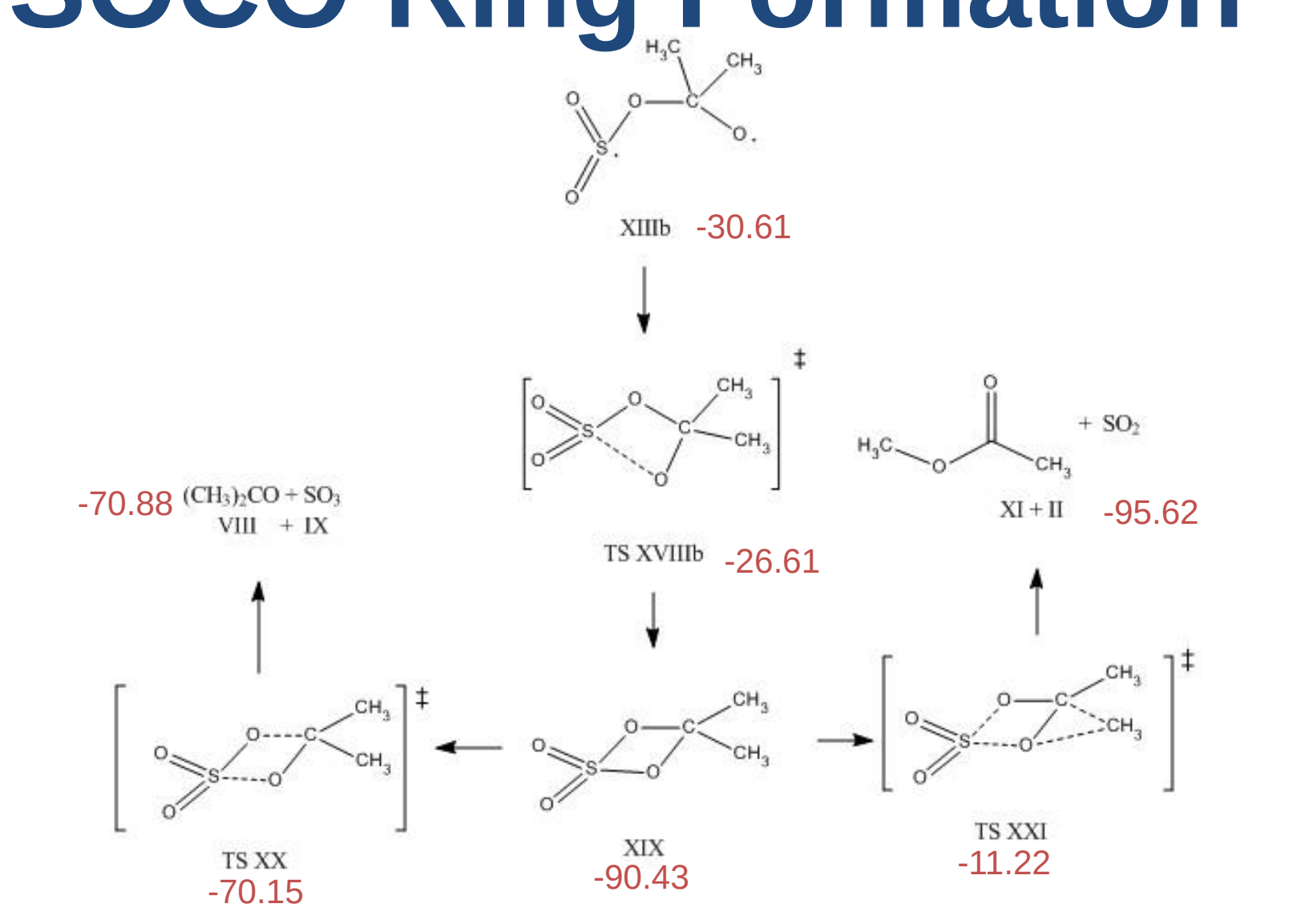


Fig. 9: *SOCO ring formation*
The last pathway results in the formation of an SOCO ring, which can either oxidize SO_2 through a ~20 kcal/mol barrier or isomerize the CI through a very large ~80 kcal/mole barrier.