

**Supporting Information for**  
**Singlet ( $^1\Delta_g$ )  $O_2$  as an Efficient Tropospheric**  
**Oxidizing Agent: Gas Phase Reaction with**  
**Simplest Criegee Intermediate**

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In the MESMER program, kinetic calculations are carried out through construction of stochastic energy gained master equation by describing the time dependent rovibrational population density  $[p_m(E)]$  for a particular isomeric species ( $m$ ) on the PES having total rovibrational energy  $E$ . For one dimensional master equation  $E$  is independent variable. The energy gained master equation keeping  $E$  as continuous variable can be expressed by the following differential equation-

$$\begin{aligned} \frac{dp_m(E)}{dt} = & \omega \int_{E_{0m}}^{\infty} P(E|E')p_m(E')dE' - \omega p_m(E) + \sum_{n \neq m}^M k_{mn}(E)p_n(E) - \sum_{n \neq m}^M k_{nm}(E)p_m(E) \\ & - k_{Sm}(E)p_m(E) + K_{Rm}^{eq}k_{Rm}(E) \frac{\rho_m(E)e^{-\beta E}}{Q_m(\beta)} n_{APB} - k_{Rm}(E)p_m(E) \end{aligned} \quad (1)$$

There are seven terms in right hand side on the above equation. Among them, positive terms corresponds to the population flux into the energy grain associated with the chemical species  $m$   $[m, E]$  and negative terms corresponds to the population flux out of  $[m, E]$ . The first term in right hand side of the above equation represents the population increase in  $[m, E]$  through collisional energy transfer.  $\omega$  represents Lennard-Jones collision frequency and  $P(E|E')$  represents the probability of the collision with bath gas (considering  $N_2$  for our investigation) results in a transition from a grain with energy  $E'$  to a grain with energy  $E$ . The second terms in the above equation corresponds to the population loss from  $[m, E]$  due to collision. The reversible population gain for  $p_m(E)$  at a constant energy  $E$  through the reactions that population from isomer  $n$  to isomer  $m$  is described by the third term whereas the fourth term represents the population loss for  $p_m(E)$  at a constant energy  $E$  through the reactions that population from isomer  $m$  to isomer  $n$ . The  $k_{mn}(E)$  and  $k_{nm}(E)$  terms represent the microcanonical rate coefficient for population transfer from isomer  $n$  to isomer  $m$  and isomer  $m$  to isomer  $n$ , respectively. The fifth term corresponds to the irreversible population loss from  $[m, E]$  through the reactions that transferring population from isomer  $m$  to products  $S$  having microcanonical rate coefficient  $k_{Sm}(E)$ . The sixth and seventh terms represent the so-called bimolecular source term and apply only to those isomers which are populated

via bimolecular association reactions. It is assuming that two bimolecular reactants say A and B are maintained in a Boltzmann distribution and the reactant A is in sufficient large amount compare to reactant B and under this condition pseudo first order kinetics is considered to be appropriate and in this condition the sixth and seventh terms describe the population gain by  $[m, E]$  due to bimolecular association of reactants A and B (altogether denoted as R) and the population from  $[m, E]$  via redissociation to the reactants. Here, the  $k_{Rm}(E)$  is the rate coefficient at which  $[m, E]$  redissociates to give the bimolecular reactants, R, and  $K_{Rm}^{eq}$  represents the equilibrium constant between isomer m and the reactants. The rovibrational partition function for isomer m ( $Q_m(\beta)$ ) is given by  $Q_m(\beta) = \int dE \rho_m(E) e^{-\beta E}$ . In the sixth term,  $n_A$  corresponds to the number density of reactant A and  $p_B$  represents the population in reactant B. The phenomenological rate coefficients are calculated from the eigenvalues and eigenvectors of the system using Bartis-Widom method.

Inverse Laplace transform (ILT) method has used to obtain microcanonical rate coefficients from an existing Arrhenius form. Generally the required Arrhenius parameters for the ILT method in MESMER are usually obtained from experimental data through the fitting process. But there exist no experimental studies on the kinetics of the reaction of SCI and  $^1\text{O}_2$ . So, we have calculated the rate coefficient of the bimolecular barrierless association step using KTOOLS from Multiwell at different temperatures. Molecular geometry optimization and normal mode vibrational frequency calculations of reactant and trial transition state along the unimolecular dissociation reaction path have been carried out at M06-2X/aug-cc-pVTZ level of theory. Further the energetics of the unimolecular dissociation reaction path have been extrapolated up to reported all the corrected energy limits using a two point fitting method. And then by fitting these rate coefficient values we have calculated the Arrhenius parameter for the studied reaction. At high pressure condition the equilibrium constant for bimolecular association ( $\text{A} + \text{B} \xrightleftharpoons[k_d]{k_a} \text{C}$ ) can be expressed as-

$$K = \frac{k'_a}{k_d} = \frac{\chi_C}{\chi_B} \quad (2)$$

Where forward rate coefficient  $k'_a = k_a A$ .  $\chi_C$  and  $\chi_B$  are the equilibrium fraction of C and B, respectively. The canonical high pressure rate coefficient may be expressed as-

$$k_d(\beta) = K_e(\beta)k_a(\beta) \quad (3)$$

In case of  $k_a(\beta)$  having a modified Arrhenius expression then the equation becomes-

$$\frac{W(E)}{h} = k(E)\rho(E) = A_0\beta_0^n L^{-1}\left[K_e(\beta)\frac{Q(\beta)}{\beta^n}e^{-\beta E_a}\right] \quad (4)$$

And the final results is-

$$k(E)\rho(E) = \frac{A_0\beta_0^n}{\Gamma(n+1.5)}\left(\frac{2\pi\mu}{h^2}\right)^{3/2}\left(\frac{g_A g_B}{g_C}\right) \int_0^E d\tau \rho_R(E-\tau)(\tau - E_a - \Delta H_0^0)^{n+0.5} u(\tau - E_a - \Delta H_0^0) \quad (5)$$

where  $\rho_R E$  is the convolved density of states for the associating pair,  $\Delta H_0^0$  is the enthalpy of reaction,  $\mu$  is the reduced mass of the system and  $g_X$  is the spin degeneracy of species  $X$ .

**Table S1:** T1-diagnostic values of all the studied species calculated at CCSD(T)/aug-cc-pVTZ//CCSD(T)-F12/cc-pVDZ-F12 level of theory

| species           | T1-Diagnostic |
|-------------------|---------------|
| SCI               | 0.04467895    |
| $^1\text{O}_2$    | 0.01560213    |
| RC                | 0.01952569    |
| TS                | 0.03990966    |
| PC                | 0.02363846    |
| CH <sub>2</sub> O | 0.01564981    |
| O <sub>3</sub>    | 0.02761454    |

**Table S2:** Concentrations of  $^1\text{O}_2$  (molecules  $\text{cm}^{-3}$ ) at different altitudes in troposphere calculated following the method described in the main article

| Altitude (km) | T (K) | P (atm) | $^1\text{O}_2$    |
|---------------|-------|---------|-------------------|
| 0             | 298   | 1       | $1.7 \times 10^8$ |
| 5             | 259   | 0.535   | $1.0 \times 10^8$ |
| 10            | 230   | 0.266   | $5.8 \times 10^7$ |
| 15            | 213   | 0.120   | $2.8 \times 10^7$ |

**Table S3: Absolute electronic energies, ZPE corrections and thermal corrections to Gibbs free energies at 298 K of all the studied species calculated at CCSD(T)-F12/cc-pVDZ-F12 level and absolute electronic energies calculated at the CCSD(T)/CBS level of theory (All values are in Hartree)**

| Species   | CCSD(T)-F12/<br>cc-pVDZ-F12 | CCSD(T)/<br>CBS | ZPE correction | Thermal Correction<br>to Gibbs free<br>energy |
|---|-----------------------------|-----------------|----------------|---|
| SCI   | -189.36003690601            | -189.4103435614 | 0.0307459      | 0.00768935                                    |
| <sup>1</sup> O <sub>2</sub>                             | -150.1181611968             | -150.1552496715 | 0.00342033     | -0.01553033                                   |
| RC  | -339.5469146015             | -339.6359255276 | 0.04072497     | 0.01426163                                    |
| TS  | -339.526905454              | -339.6143804229 | 0.03756435     | 0.0112065                                     |
| PC  | -339.5560867875             | -339.6417395716 | 0.03536668     | 0.0051679                                     |
| CH <sub>2</sub> O                                       | -114.3614503635             | -114.3907955897 | 0.02666747     | 0.00500717                                    |
| O <sub>3</sub>  | -225.190170886408           | -225.2463263153 | 0.00681628     | -0.0163367                                    |
| <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> O <sub>2</sub> | -150.1673469228             | -150.2018837248 | 0.00363196     | -0.02226021                                   |

**Table S4: Optimized geometries in Cartesian coordinates and normal mode frequencies of all species calculated at CCSD(T)-F12/cc-pVDZ-F12 level of theory**

| Compound name   | Cartesian Coordinate (Å)  | Frequencies (cm <sup>-1</sup> )   |
|---|---|---|
| SCI   | C 1.06679279605099 -0.21349548804398 -0.00000000136524<br>O -0.00287527500476 0.46857254252080 0.00000000088710<br>O -1.17218973609944 -0.19189670615906 -0.00000000037351<br>H 0.99492532637891 -1.29361193165170 0.00000000066770<br>H 1.97712488867430 0.36714458333395 0.00000000018396   | 535.59 648.19 877.51<br>932.18 1241.42 1324.01<br>1494.64 3140.29 3302.07   |
| <sup>1</sup> O <sub>2</sub>                             | O 0.00000000000000 0.00000000000000 0.60991785293585<br>O 0.00000000000000 0.00000000000000 -0.60991785293585   | 1501.35   |
| RC  | C 1.15677958060376 0.00059324704770 0.00138514443250<br>O 0.30190984760762 1.13273888258259 0.18023122714987<br>O -0.95880338033315 0.62713396166920 -0.31008424563632<br>H 1.75909492046029 0.07406131855321 -0.90429496792405<br>H 1.75357162489949 -0.07239974595049 0.91076870879391<br>O 0.30397075043144 -1.13138289138998 -0.18295232852508<br>O -0.95660334366943 -0.62936977251224 0.31128546170917  | 41.88 502.19 670.93<br>702.93 752.31 813.51<br>915.06 985.04 1034.24<br>1142.57 1189.38 1382.9<br>1542.55 3064.47 3136.24   |
| TS  | C 0.00948411587886 0.00723386062137 0.01734078472610<br>O -0.01732687780428 0.08511900586922 1.78549207673867<br>O 1.31434847567091 -0.04540901675071 2.04425289531407<br>H -0.55356830627988 -0.92273724459142 -0.09530364763435<br>H -0.56483254662256 0.93794118951062 -0.06907234279919<br>O 1.22193136018324 0.07098554221411 -0.34777599994796<br>O 1.81840761897370 -0.94898136687320 1.29972707360266 | -501.33 221.03 305.86<br>462.69 580.07 732.33<br>832.41 914.66 1101.2<br>1161.05 1202.58 1373.36<br>1504.84 2997.84 3098.93 |
| PC  | C 2.00019967491196 -0.00154492055017 0.44941799155429<br>O -1.09119531625401 -1.08101438448813 0.20937883134354<br>O -1.45668441961781 0.00057905645349 -0.34212774383827<br>H 1.34471080679004 -0.00900137646353 1.33469536081030<br>H 3.08705378250550 0.00254803803795 0.63238121838586<br>O 1.54901656069959 0.00180006618213 -0.67105329761053<br>O -1.09268508903527 1.08194052082827 0.21082763935481  | 36.12 89.74 110.3<br>131.62 169.36 237.34<br>729.74 1099.83 1173.97<br>1196.3 1278.01 1539.06<br>1776.25 2939.71 3016.84    |
| O <sub>3</sub>  | O 0.00000000000000 0.00000000007109 0.44076780944482<br>O 0.00000000000000 1.08320924900671 -0.22038440470084<br>O 0.00000000000000 -1.08320924907780 -0.22038440474398   | 725.02 1098.09 1168.89  |
| CH <sub>2</sub> O                                       | C -0.53156980077869 0.00003314813746 0.00000808298529<br>O 0.67503804235864 -0.00007171038749 -0.00000355524908<br>H -1.11128297506264 0.93796197490546 0.00001323674031<br>H -1.11143626651731 -0.93780141265543 0.00001323552348  | 1186.47 1271.50 1536.92<br>1778.81 2930.21 3001.76  |
| <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> O <sub>2</sub> | O 0.00000000000000 0.00000000000000 0.60434714469308<br>O 0.00000000000000 0.00000000000000 -0.60434714469308   | 1594.25   |