

**Supporting Information**

**for**

**New Mechanistic Insights: Why Do Plants Produce  
Isoprene?**

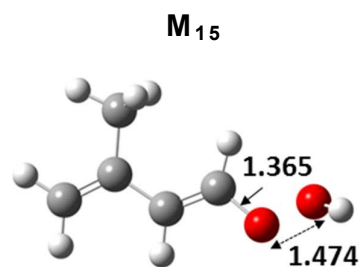
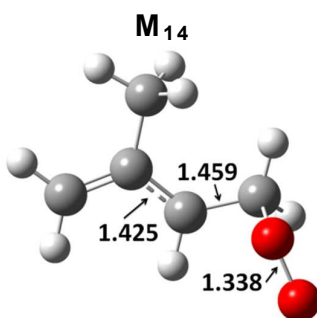
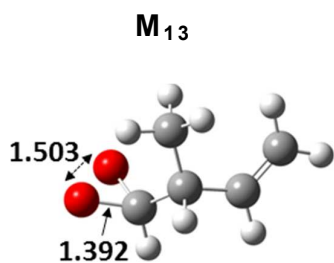
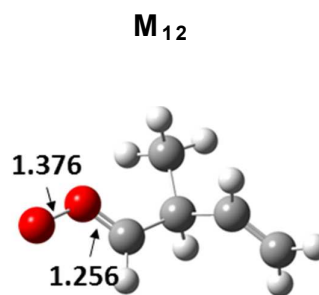
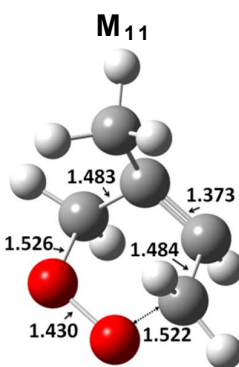
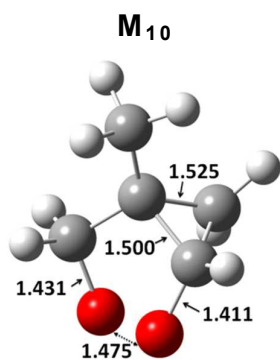
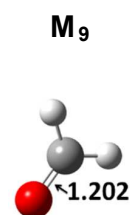
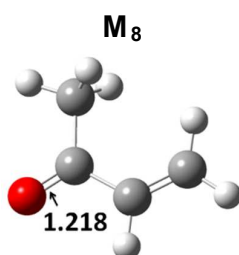
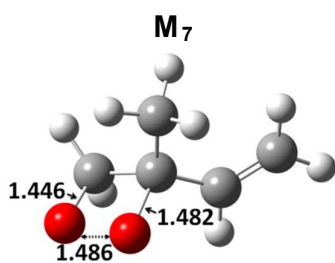
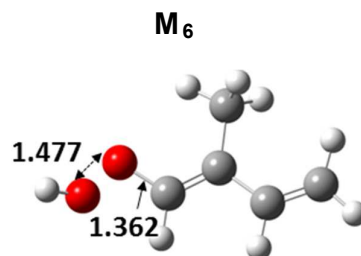
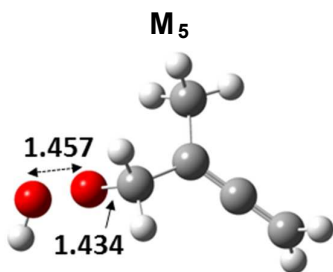
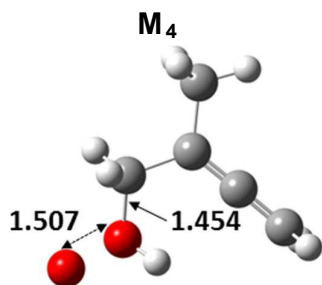
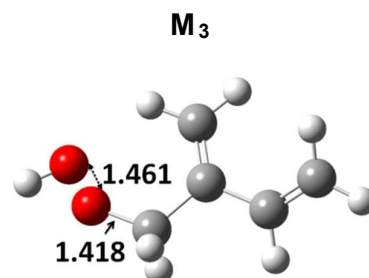
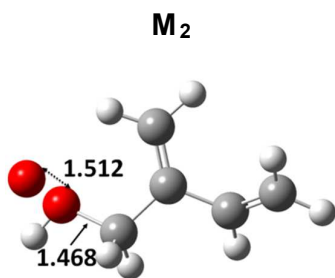
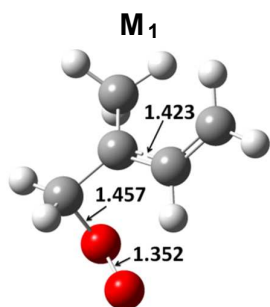
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Jomana Al-Nu'airat,<sup>1</sup> Bogdan Z. Dlugogorski<sup>1</sup>

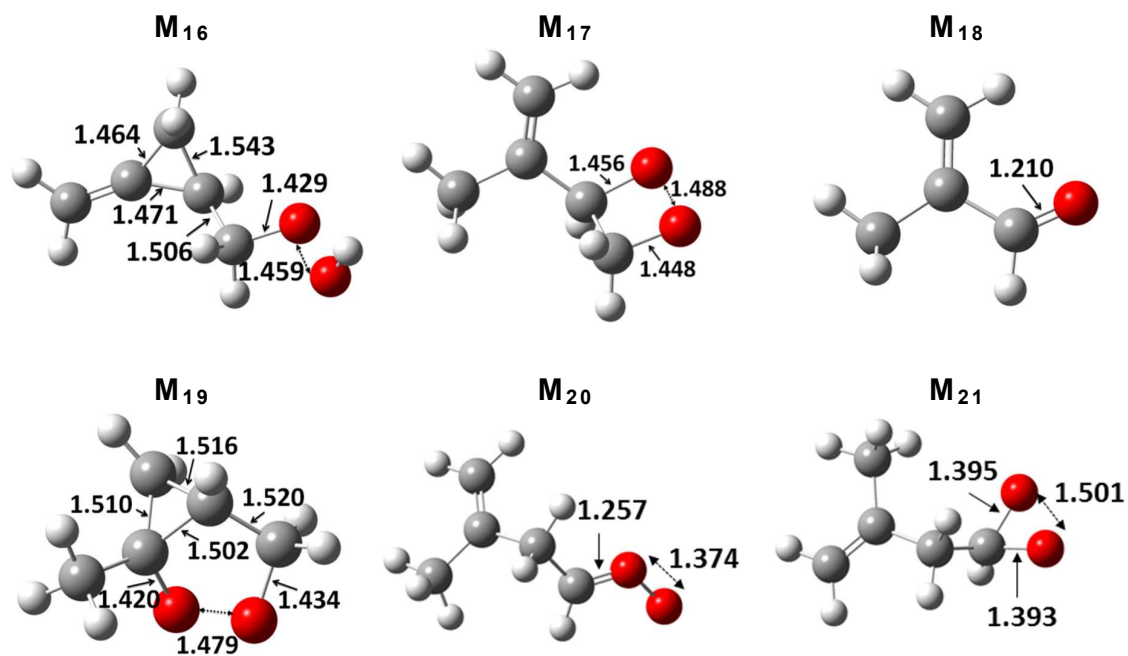
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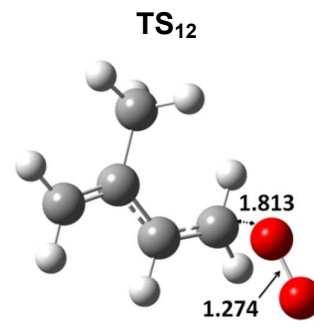
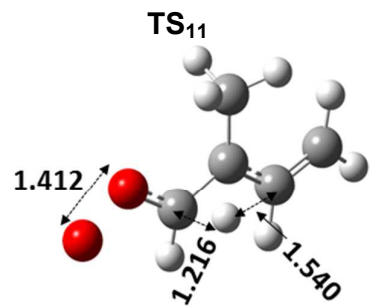
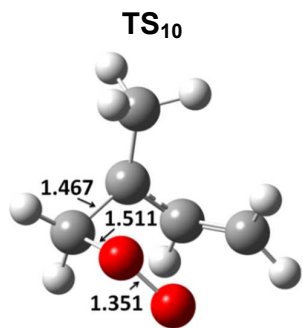
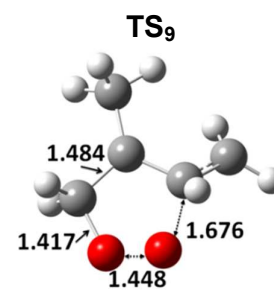
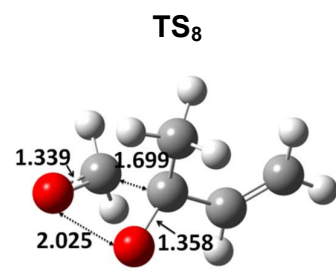
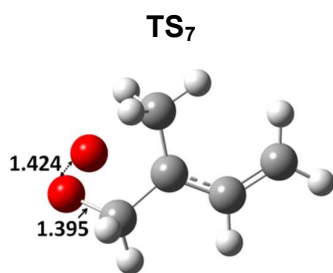
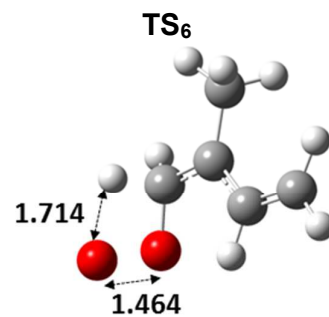
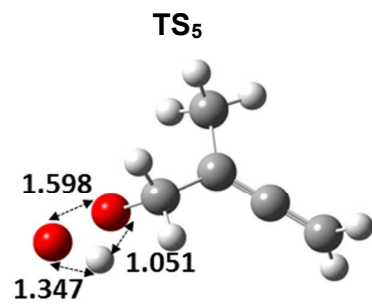
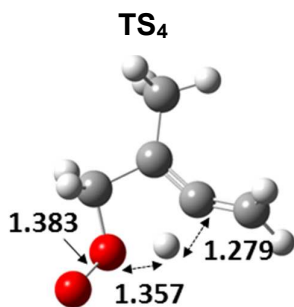
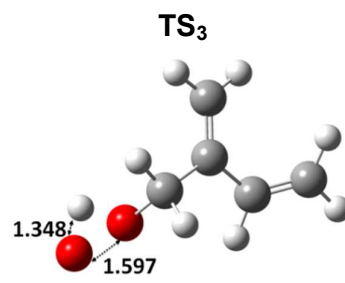
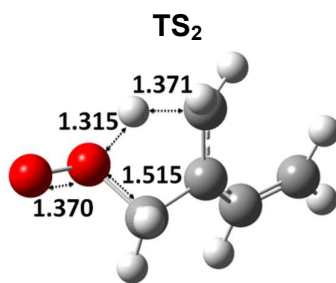
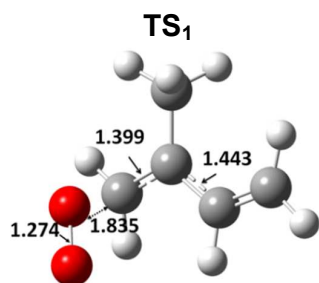
**Table S1:** Calculated thermal enthalpies (in Hartree) and expected spin contaminations;  $\langle S^2 \rangle$ ..

|                  | Singlet     |                       | Triplet     |                       | Broken symmetry |                       | Corrected Values |
|------------------|-------------|-----------------------|-------------|-----------------------|-----------------|-----------------------|------------------|
|                  | $H$         | $\langle S^2 \rangle$ | $H$         | $\langle S^2 \rangle$ | $H$             | $\langle S^2 \rangle$ |                  |
| ${}^1O_2$        | -150.301953 | 0.00                  | -150.363389 | 2.008759              | -150.346987     | 1.004215              | -150.330590      |
| TS <sub>1</sub>  | -345.550147 | 0.00                  | -345.564149 | 2.045935              | -345.562577     | 0.848535              | -345.561463      |
| M <sub>1</sub>   | -345.556864 | 0.00                  | -345.549324 | 2.027056              | -345.564592     | 0.624026              | -345.571383      |
| TS <sub>2</sub>  | -345.515397 | 0.00                  | -345.496082 | 2.023639              | -345.51764      | 0.358908              | -345.522288      |
| TS <sub>4</sub>  | -345.505453 | 0.00                  | -345.490141 | 2.023973              | -345.510165     | 0.477675              | -345.516351      |
| TS <sub>6</sub>  | -345.536945 | 0.00                  | -345.529636 | 2.027746              | -345.543565     | 0.577776              | -345.549115      |
| TS <sub>7</sub>  | -345.545167 | 0.00                  | -345.552767 | 2.028868              | -345.558432     | 0.793882              | -345.562074      |
| TS <sub>9</sub>  | -345.506566 | 0.00                  | -345.523154 | 2.013826              | -345.525541     | 0.880574              | -345.527396      |
| TS <sub>10</sub> | -345.548596 | 0.00                  | -345.51661  | 2.02142               | -345.549688     | 0.237078              | -345.554083      |
| TS <sub>11</sub> | -345.527425 | 0.00                  | -345.506650 | 2.023080              | -345.530340     | 0.378196              | -345.535787      |
| M <sub>12</sub>  | -345.588972 | 0.00                  | -345.51532  | 2.008477              | -345.588972     | 0.00                  | -345.588972      |
| TS <sub>12</sub> | -345.546836 | 0.00                  | -345.612085 | 2.008755              | -345.576251     | 0.980291              | -345.542095      |
| M <sub>14</sub>  | -345.55129  | 0.00                  | -345.556071 | 2.029797              | -345.565151     | 0.768368              | -345.570682      |
| TS <sub>13</sub> | -345.530018 | 0.00                  | -345.529133 | 2.029474              | -345.540927     | 0.685598              | -345.546944      |
| TS <sub>14</sub> | -345.51712  | 0.00                  | -345.495887 | 2.010277              | -345.519784     | 0.378033              | -345.525319      |
| TS <sub>15</sub> | -345.540663 | 0.00                  | -345.551614 | 2.030691              | -345.556965     | 0.836647              | -345.560714      |
| TS <sub>17</sub> | -345.528554 | 0.00                  | -345.495021 | 2.049148              | -345.528942     | 0.096354              | -345.530616      |
| TS <sub>18</sub> | -345.545713 | 0.00                  | -345.527941 | 2.029334              | -345.549951     | 0.479511              | -345.556761      |
| TS <sub>19</sub> | -345.522261 | 0.00                  | -345.511206 | 2.026078              | -345.528652     | 0.543562              | -345.535049      |
| M <sub>20</sub>  | -345.592235 | 0.00                  | -345.520301 | 2.008033              | -345.592235     | 0.000000              | -345.592235      |





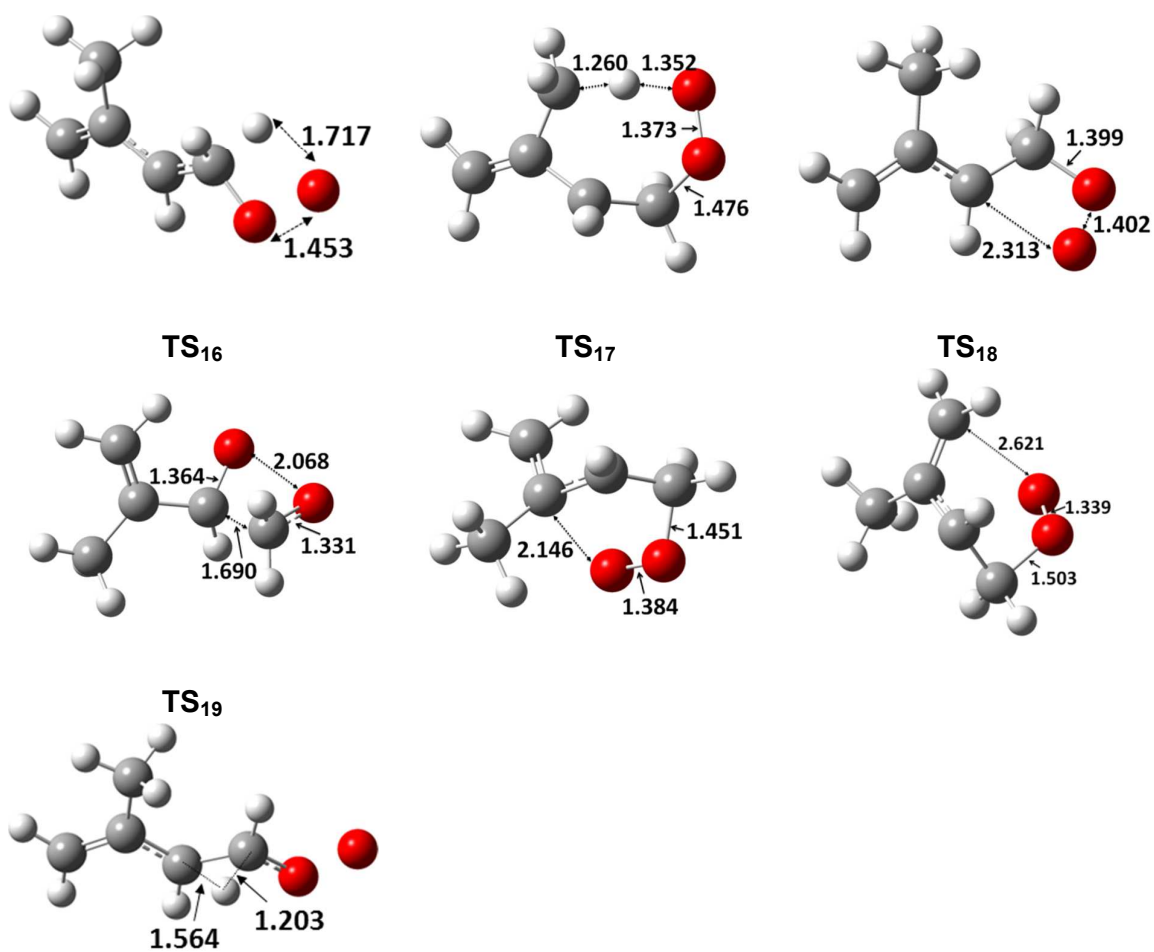
**Figure S1:** Optimized structures of reaction products from oxidation of isoprene by singlet delta oxygen (distances are in  $\text{\AA}$ ).



**TS<sub>13</sub>**

**TS<sub>14</sub>**

**TS<sub>15</sub>**



**Figure S2:** Optimized structures of transition states formed in the oxidation of isoprene by singlet delta oxygen (distances are in Å).