Acrolein Dimerization

Acrolein (1) thermally dimerizes to give one of the two possible products 2 and 3. The "polarity" model predicts that the dimerization should occur through resonance forms 4 and 5 to give product 3. In fact, product 2 is formed.

Products 2 and 3 are formed through two separate and independent chemical reactions, each of which has a different activation energy. Apparently, the activation energy to form product 2 is lower than the activation energy to form product 3. Recall that the activation energy has a molecular orbital component, and that we can make a relative estimate of the size of that molecular orbital component using perturbation theory. Thus, a large filled orbital/empty orbital mixing contribution (large $\Delta \varepsilon$) lowers the overall activation barrier more than a small $\Delta \varepsilon$ value does.

The HOMO and LUMO for acrolein are shown below. Since this reaction is a dimerization, the HOMO/LUMO gap is the same for both possible HOMO/LUMO pairings.
We can apply these numerical values in the perturbation equation to calculate the overall energy savings at each reaction's transition state; the bigger the value, the lower the transition state (= the faster the reaction). Although the energy savings values are very close, the value from reaction 1, which produces product 2, is greater. Note that these mathematical values actually have to be modified by multiplication by a constant to convert them into actual energy units.

**Reaction 1**

\[
\frac{[(-0.58)(-0.39) + (0.58)(0.59)]^2}{2.5 - (-14.5)} + \frac{[(0.51)(0.48) + (0.59)(0.58)]^2}{2.5 - (-14.5)} = 0.0393
\]

**Reaction 2**

\[
\frac{[(-0.58)(-0.59) + (0.58)(0.39)]^2}{2.5 - (-14.5)} + \frac{[(0.51)(0.58) + (0.59)(0.48)]^2}{2.5 - (-14.5)} = 0.0387
\]