**Work on locating the Enolate - Ene Transition State**

Hf "[A Enolate.arc](A%20enolate.arc)" = -32947.8 kcal∙mol-1 and "[G Ene.arc](G%20ene.arc)" = -32959.2 kcal∙mol-1.

### Starting point: <Locate-TS.mop>

This uses stationary points "[A Enolate.mop](A%20enolate.mop)" and "[G Ene.mop](G%20ene.mop)" and produces an output file "[Locate‑TS.out](Locate-TS.out)" and a geometry near to the transition state: "[Locate-TS 140p0 average.mop](Locate-TS%20140p0%20average.mop)"

### First refinement: "[Locate-TS Sigma 140 Set 1 TS.mop](Locate-TS%20Sigma%20140%20Set%201%20TS.mop)"

"Locate-TS 140p0 average.mop" was edited as follows:

* All "+1" were changed to "+0"
* Optimization flags for C4N, H42N, and C9 were changed back to "+1"
* Keywords replaced with "mozyme output EPS=78.4 T=1W CHARGE=-5 HTML ts gnorm=5"

This ran a simple TS gradient minimization. The [output](Locate-TS%20Sigma%20140%20Set%201%20TS.out) showed that this failed due to "TRUST RADIUS", but produced "[Locate-TS Sigma 140 Set 1 TS.arc"](Locate-TS%20Sigma%20140%20Set%201%20TS.arc) that had Hf = -32914.68 kcal∙mol-1, and looked like a [transition state geometry](Locate-TS%20Sigma%20140%20Set%201%20TS.html).

### Second refinement: "[Locate-TS Sigma 140 Set 1 TS 2.mop](Locate-TS%20Sigma%20140%20Set%201%20TS%202.mop)"

The only edit made to "[Locate-TS Sigma 140 Set 1 TS.arc](Locate-TS%20Sigma%20140%20Set%201%20TS.arc)" was to delete all the arc-specific text. The resulting file was run, and produced "[Locate-TS Sigma 140 Set 1 TS 2.out](Locate-TS%20Sigma%20140%20Set%201%20TS%202.out)" and "[Locate-TS Sigma 140 Set 1 TS 2.arc](Locate-TS%20Sigma%20140%20Set%201%20TS%202.arc)" that had Hf = -32914.84 kcal∙mol-1, and was a valid [transition state geometry](Locate-TS%20Sigma%20140%20Set%201%20TS%202.html).

### Third refinement: "[Locate-TS Sigma 140 Set 1 TS 2 LBFGS.mop](Locate-TS%20Sigma%20140%20Set%201%20TS%202%20LBFGS.mop)"

"[Locate-TS Sigma 140 Set 1 TS 2.arc](Locate-TS%20Sigma%20140%20Set%201%20TS%202.arc)" was edited to delete all the arc-specific text, and keyword "TS" was replaced by "INVERT". The resulting file was run, and produced "[Locate-TS Sigma 140 Set 1 TS 2 LBFGS.out](Locate-TS%20Sigma%20140%20Set%201%20TS%202%20LBFGS.out)" and "[Locate-TS Sigma 140 Set 1 TS 2 LBFGS.arc](Locate-TS%20Sigma%20140%20Set%201%20TS%202%20LBFGS.arc)" that had Hf = -32925.48 kcal∙mol-1, and was a valid [transition state geometry](Locate-TS%20Sigma%20140%20Set%201%20TS%202%20LBFGS.html).

### Fourth refinement: "[Locate-TS Sigma 140 Set 1 TS 3 LBFGS.mop](Locate-TS%20Sigma%20140%20Set%201%20TS%203%20LBFGS.mop)"

"[Locate-TS Sigma 140 Set 1 TS 2.arc](Locate-TS%20Sigma%20140%20Set%201%20TS%202.arc)" was edited to delete all the arc-specific text, and keyword "TS" was replaced by "INVERT". The resulting file was run, and produced "[Locate-TS Sigma 140 Set 1 TS 3 LBFGS.out](Locate-TS%20Sigma%20140%20Set%201%20TS%203%20LBFGS.out)" and "[Locate-TS Sigma 140 Set 1 TS 3 LBFGS.arc](Locate-TS%20Sigma%20140%20Set%201%20TS%203%20LBFGS.arc)" that had Hf = -32926.74 kcal∙mol-1, and was a valid [transition state geometry](Locate-TS%20Sigma%20140%20Set%201%20TS%203%20LBFGS.html).

### Fifth refinement: "[Locate-TS Sigma 140 Set 1 TS 4 LBFGS.mop](Locate-TS%20Sigma%20140%20Set%201%20TS%204%20LBFGS.mop)"

"[Locate-TS Sigma 140 Set 1 TS 3 LBFGS.arc](Locate-TS%20Sigma%20140%20Set%201%20TS%203%20LBFGS.arc)" was edited to delete all the arc-specific text. The resulting file was run, and produced "[Locate-TS Sigma 140 Set 1 TS 4 LBFGS.out](Locate-TS%20Sigma%20140%20Set%201%20TS%204%20LBFGS.out)" and "[Locate-TS Sigma 140 Set 1 TS 4 LBFGS.arc](Locate-TS%20Sigma%20140%20Set%201%20TS%204%20LBFGS.arc)" that had Hf  ‑32926.02 kcal∙mol-1, and was a valid [transition state geometry](Locate-TS%20Sigma%20140%20Set%201%20TS%204%20LBFGS.html).

### Summary

|  |  |  |
| --- | --- | --- |
| System | Hf (kcal∙mol-1) | Hf' (kcal∙mol-1) |
| "[A Enolate](A%20enolate.arc)" | -32947.8 | 0.0 |
| "[D Transition state](Locate-TS%20Sigma%20140%20Set%201%20TS%204%20LBFGS.arc)" | -32926.0 | 21.8 |
| "[G Ene](G%20ene.arc)" | -32959.2 | -11.4 |

### FORCE calculation: "[FORCE for Ene-Enolate.mop](FORCE%20for%20Ene-Enolate.mop)"

A calculation to verify that the system was a genuine transition state was run. This used GEO\_DAT pointing to "[Locate‑TS Sigma 140 Set 1 TS 4 LBFGS.arc](Locate-TS%20Sigma%20140%20Set%201%20TS%204%20LBFGS.arc)" and had the following keywords:

|  |  |
| --- | --- |
| **Keyword(s)** | **Significance** |
| **EPS=78.4, T=1W CHARGE=-5 MOZYME** | Keywords common to this system. |
| **GEO\_DAT="Locate-TS Sigma 140 Set 1 TS 4 LBFGS.arc"** | By using GEO\_DAT, the source of the geometry is defined, and it's obvious that it has not been modified. |
| **FORCETS** | Run a FORCE calculation using only the atoms that had optimization flags "+1". |
| **OUTPUT(N)** | Suppress all large data-blocks, but because "N" is present, print the normal coordinates. |
| **ISOTOPE** | Save the results in a <file>.res restart file, so that other jobs can use the results of this job. |

The output file, "[FORCE for Ene-Enolate.out](FORCE%20for%20Ene-Enolate.out)" showed that the system was indeed a transition state, the lowest vibrational frequency being *i*1899.5 cm-1. This value is very large, and indicates that the curve of the reaction path at the transition state is very steep.

### IRC calculation: "[Ene-Enolate IRC (plus direction).mop](Ene-Enolate%20IRC%20(plus%20direction).mop)" and "[Ene‑Enolate IRC (minus direction).mop](Ene-Enolate%20IRC%20(minus%20direction).mop)"

"[Locate‑TS Sigma 140 Set 1 TS 4 LBFGS.arc](Locate-TS%20Sigma%20140%20Set%201%20TS%204%20LBFGS.arc)" was edited to delete all the arc-specific text and replace the keywords with " EPS=78.4 T=1W CHARGE=-5 MOZYME FORCETS restart mini x-priority=0.1 IRC=1 HTML"

|  |  |
| --- | --- |
| **Keyword(s)** | **Significance** |
| **EPS=78.4, T=1W CHARGE=-5 MOZYME** | Keywords common to this system. |
| **FORCETS** | Run a FORCE calculation using only the atoms that had optimization flags "+1". |
| **RESTART** | Restart the job at the end of the FORCE calculation. |
| **MINI** | In the IRC, only print the atoms that have coordinate flags "+2" and "+1" In this run, that would be the groups with residue sequence number 1301 and 1302. |
| **X-PRIORITY=0.1** | Use a step-size of 0.1 Å in the IRC. |
| **IRC=1** | Generate an IRC in the positive direction |
| **HTML** | Generate a web-page for this IRC. |

All optimization flags for residues 1301 and 1302 that were "+0" were replaced with "+2". The edited file was named "[Ene-Enolate IRC (plus direction).mop](Ene-Enolate%20IRC%20(plus%20direction).mop)". "FORCE for Ene-Enolate.res" from the previous job was copied and the copy re‑named "Ene-Enolate IRC (plus direction).res". A second IRC job was also prepared, in this job "IRC=1" was replaced by "IRC=-1" . This job was named "[Ene-Enolate IRC (minus direction).mop](Ene-Enolate%20IRC%20(minus%20direction).mop)" A restart file for this job was made by copying the

JSmol graphics of the Ene-Enolate reaction path (IRC)

[Graphic](Ene-Enolate%20IRC.html)