JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

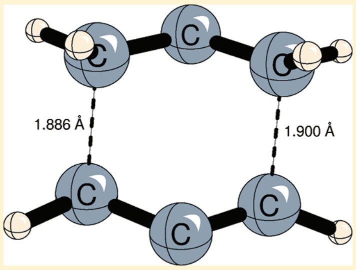
Theoretical Study of Thermal Rearrangements of 1-Hexen-5-yne, 1,2,5-Hexatriene, and 2-Methylenebicyclo[2.1.0]pentane

Uğur Bozkaya*[†,‡] and Ilker Özkan*[‡]

[†]Department of Chemistry, Atatürk University, Erzurum 25240, Turkey

[‡]Department of Chemistry, Middle East Technical University, Ankara 06800, Turkey

Supporting Information

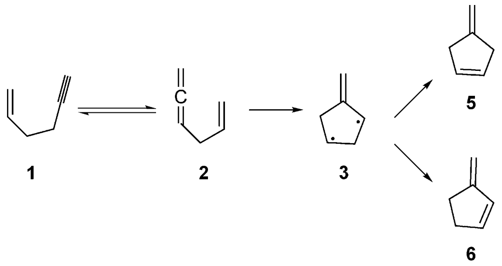


ABSTRACT: In this research, a comprehensive theoretical investigation of the thermal rearrangements of 1-hexen-5-yne, 1,2,5-hexatriene, and 2-methylenebicyclo[2.1.0]pentane is carried out employing density functional theory (DFT) and high level *ab initio* methods, such as the complete active space self-consistent field (CASSCF), multireference second-order Møller−Plesset perturbation theory (MRMP2), and coupled-cluster singles and doubles with perturbative triples [CCSD(T)]. The potential energy surface (PES) for the relevant system is explored to provide a theoretical account of pyrolysis experiments by Huntsman, Baldwin, and Roth on the target system. The rate constants and product distributions are calculated using theoretical kinetic modelings. The rate constant for each isomerization reaction is computed using the transition state theory (TST). The simultaneous first-order ordinary-differential equations are solved numerically for the relevant system to obtain time-dependent concentrations, hence the product distributions at a given temperature. Our computed energy values (reaction energies and activation parameters) are in agreement with Roth's experiments and the product distributions of Huntsman's experiments at 340 and 385 °C with various reaction times, while simulated product fractions are in qualitative accordance with Baldwin's experiment.

INTRODUCTION

Huntsman et al.[1,4−6] carried out the interconversion of 1-hexen-5-yne (**1**) and 1,2,5-hexatriene (**2**) and observed that methelenecyclopentenes (**5** and **6**) were formed at the expense of the triene (Scheme 1). They also estimated the activation energy as 32.7 kcal mol^{-1} for the rearrangement of **1** to **2**. Further, Huntsman et al. predicted an activation energy of 37.2 kcal mol^{-1} for the rearrangement of **2** to **5** and **6**. Moreover, they observed that the ratio of methelenecyclopentenes is [**6**]/[**5**] = 1.27 (Table 1).

Scheme 1. Huntsman's Mechanism

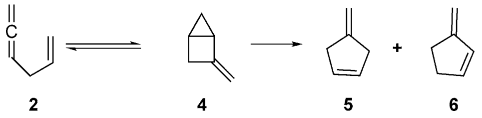


In 1988, Andrews and Baldwin[2] observed that pyrolysis of 2-methylenebicyclo[2.1.0]pentane (**4**) at 253 °C yields **2**, **5**, and **6** with the ratio of [**6**]/[**5**] = 1.4, which is consistent with Huntsman et al.'s predictions (Scheme 2). Further, they observed four major components in the reaction mixture, which are **2** (34%), **4** (11%), **5** (23%), and **6** (32%). Andrews and Baldwin predicted that the activation energy for the conversion of **4** to products was 36 kcal mol^{-1}, which was estimated by a gas chromatographic method. In a 1989 study, Roth et al.[3] determined the activation energies for the three reactions in the pyrolysis of 2-methylene bicyclo[2.1.0]pentane (Scheme 2) as 36.5 (**4** → **2**), 35.8 (**4** → **5**), and 35.8 kcal mol^{-1} (**4** → **6**).

Table 1. Huntsman's Results

temp (°C)	contact time (s)	1	2	5	6
340	62	29	65	2	3
340	130	24	62	6	8
340	150	20	50	13	17
385	62	10	22	30	38

Scheme 2. Baldwin's Mechanism



The 1-hexen-5-yne (**1**) molecule is an important species, which is a cornerstone for several interesting systems, such as the Dalacker−Hopf mechanism,[7] and Berson trimethylenemethanes (Berson-TMMs).[8−31] Our recent studies verified that the enyne **1** plays a central role in connecting the two portions of the reaction path in Berson mechanisms.[27] Further, the **1** molecule is also an prominent compound for acetylenic Cope

Received: December 22, 2011
Published: January 21, 2012

© 2012 American Chemical Society

dx.doi.org/10.1021/jo202645k | *J. Org. Chem.* 2012, 77, 2337−2344

rearrangements.[32−35] Theoretical studies on Dalacker−Hopf mechanism and Berson-TMMs will be presented in the near future. In this study, a comprehensive theoretical investigation of the thermal rearrangements of 1-hexen-5-yne, 1,2,5-hexatriene, and 2-methylenebicyclo[2.1.0]pentane is carried out employing density functional theory (DFT) and high level *ab initio* methods. The potential energy surface (PES) for the Huntsman−Baldwin system (Schemes 1 and 2) is explored to provide a theoretical account of pyrolysis experiments by Huntsman,[1] Baldwin,[2] and Roth.[3] The rate constants and product distributions are predicted using theoretical kinetic modelings.

COMPUTATIONAL METHODS

Computations in this study were mostly carried out by using the GAUSSIAN 03 (RevD.01) program[36] and the GAMESS package.[37] GAUSSIAN 03 was used for the density functional theory and coupled-cluster (CC) computations, whereas GAMESS was used for the complete active space self-consistent field (CASSCF)[38−49] and multireference second-order Møller−Plesset perturbation theory (MRMP2)[49−60] computations. For 3-dimensional chemical drawings, the CHEMVP program was used.[61]

Geometry optimizations for the closed-shell and high-spin open-shell molecules were performed with the DFT method (B3LYP functional[62,63]) using the GAUSSIAN 03 program. Vibrational frequencies were computed to characterize each stationary structure as a minimum, TS, or whatever. After locating a TS, intrinsic reaction coordinate (IRC)[64−68] computations were carried out. In order to improve the computed energies single-point frozen-core coupled-cluster singles and doubles with perturbative triples [CCSD(T)][69−77] computations were carried out at optimized DFT geometries. In all computations Pople's polarized triple-ζ split valence basis set, 6-311G(d,p), was employed.[78−80] For the biradical **3**, the geometry optimization and frequency computations were performed with the CASSCF method using the GAMESS program package. At optimized geometries, single-point frozen-core MRMP2 computations were carried out to improve the energy values.

In order to obtain a unique energy scale at CCSD(T)/6-311G(d,p) level for the biradical **3**, the vertical singlet−triplet energy differences obtained via MRMP2 computations was used with the CCSD(T) energy of the corresponding triplet states to obtain final energy of the singlet biradical. This approximation can be formalized by

$$E(^1X) = E_{\mathrm{CCSD(T)}}(^3X) + E_{\mathrm{MRMP2}}(^1X) - E_{\mathrm{MRMP2}}(^3X) \tag{1}$$

where X is a biradical and $E(^1X)$ is the final energy of species ^1X.

Among the singlet transition structures (TSs), the largest value of $\langle S^2 \rangle = 0.57$ for the TS **3**/**4**; while for all remaining TSs the value of $\langle S^2 \rangle$ is <0.50 at the B3LYP/6-311G(d,p) level. Further, when we optimized TSs with the CASSCF method and performed single-point MRMP2 computations, we did not observe significant differences from CCSD(T) predictions in relative energies. Hence, in presence of small spin-contaminations for TSs; we can still trust on single-reference methods such as DFT and CCSD(T).

Throughout this research, energies of all structures are presented relative to species **6**. Energies of all closed-shell singlets are from the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) level, while for the biradical it is computed according to eq 1. All energies reported in this paper include zero-point vibrational energy (ZPVE) corrections computed at the DFT level.

THEORETICAL KINETIC MODELING

The rate constant for each isomerization reaction was computed using the transition state theory (TST).[81,82] The TST rate constant is

$$k_{\mathrm{TST}} = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \tag{2}$$

where k_B is the Boltzmann constant, h is Planck's constant, $\Delta G^{\ddagger}$ is the Gibbs free energy of TS relative to reactant, R is the ideal gas constant, and T is the temperature. Then, simultaneous first-order ordinary-differential equations were solved numerically for the Huntsman−Baldwin system (Figure 1) to obtain time-dependent concentrations and hence the product distributions at a given temperature. The MATLAB 7.0.4 program package[83] was employed to solve the coupled rate equations.

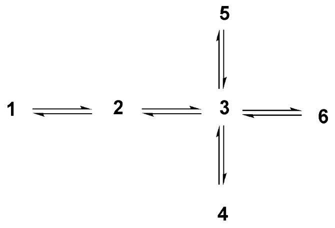


Figure 1. Mechanism considered for the kinetic simulation of the Huntsman−Baldwin system.

RESULTS AND DISCUSSION

The relative energy profile for the Huntsman−Baldwin mechanism (Scheme 1) is provided in Figure 2. Roth et al.[3] determined the activation parameters of all steps in the Huntsman−Baldwin mechanism (Scheme 1) by carrying out thermolyses experiments.[3] For the reaction **1** → **2** in the forward direction their value for the activation energy is 32.8 kcal mol^{-1}, whereas in the reverse direction it is 33.7 kcal mol^{-1} . These findings also mean that species **1** is higher in enthalpy than **2** by 0.9 kcal mol^{-1} . Even though the latter difference is within the generally accepted chemical accuracy (or error) of ±1.0 kcal mol^{-1}, it is remarkable that computations at appropriate levels can nearly reproduce the difference with the correct sign; we found 32.1 − 31.6 = 0.5 kcal mol^{-1} for it. On the other hand, the computed barrier heights, 35.3 and 35.8 kcal mol^{-1}, overestimate the experimental ones by 2.5 and 2.1 kcal mol^{-1} for the forward and reverse directions, respectively.

The interconversions among **2**, **5**, **6**, and **4** must be discussed together since the reaction paths in all of these rearrangements pass through the biradical **3**. In this species the two radical centers, being at a distance of 2.35 Å (Figure 3), should interact weakly, and we therefore expect the singlet to be close to the triplet. In order to test this hypothesis, we optimized the lowest singlet and triplet states of the biradical at the (8*e*,8*o*) CASSCF/6-311G(d,p) level. The active space consisted of two π orbitals of methelene, two π orbitals from the radical centers, and four σ orbitals of the CH_2 group lying between two radical centers. The σ orbitals of the mentioned CH_2 group were considered since structures **5** and **6** form via H-shifts. The triplet minimum was found to be lower in energy, but only by 0.5 kcal mol^{-1} at both the CASSCF and MRMP2//CASSCF levels, which differs by 2.2 kcal mol^{-1} from results in Roth et al.'s experiment.[84] Further, Sherrill et al.[85] predicted the singlet−triplet energy splitting for 1,3-cyclopentanediyl to be ~1 kcal mol^{-1} . Hence, these results confirm our expectation.

The TS **3**/**4** is involved in the *exo-endo* interconversion of **4**. Roth experimentally studied this geometric isomerization in the 5-methyl derivative of **4** and determined the activation energy for the *exo-endo* conversion as 24.5 kcal mol^{-1}, whereas for

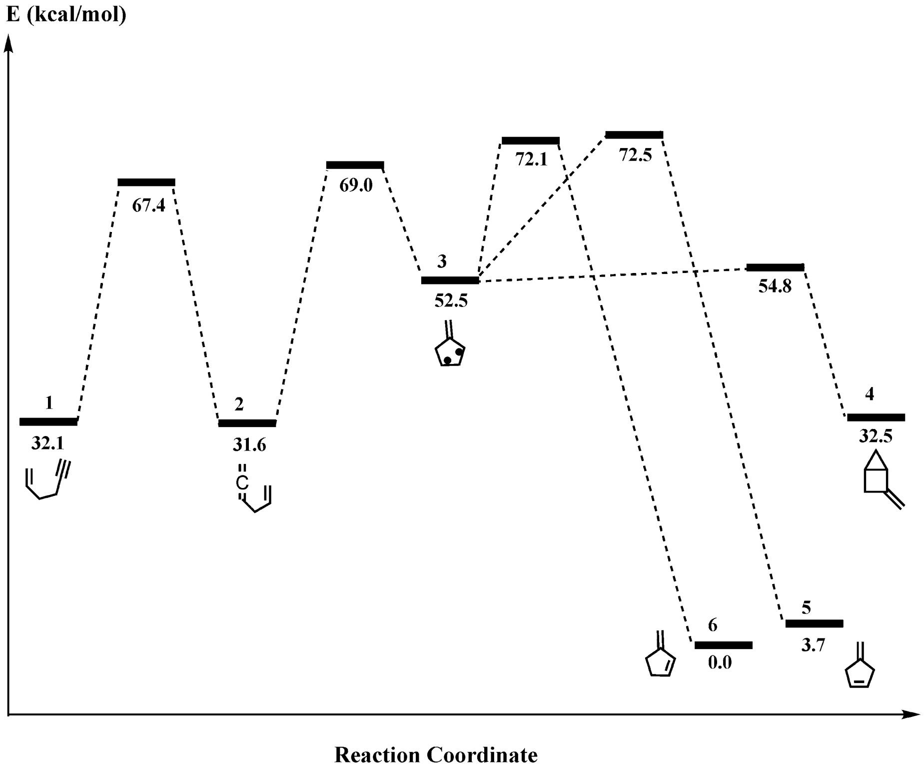


Figure 2. Computed relative energy profile for the Huntsman–Baldwin mechanism.

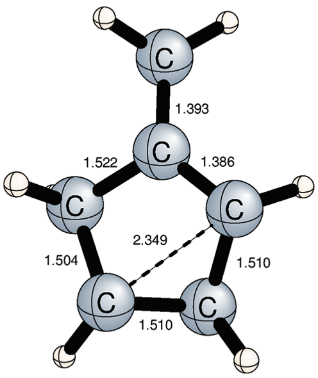


Figure 3. Selected interatomic distances (Å) for structure **3**.

the reverse process it was 23.6 kcal mol^{-1}.[3] Our result, 54.8 − 32.5 = 22.3 kcal mol^{-1} agrees reasonably well with Roth's values. Further, for the **3** → **4** reaction the computed activation barrier, 2.3 kcal mol^{-1}, is in good agreement with the experimental value of 3.1 kcal mol^{-1}, which was obtained for rearrangement of the dimethyl substituted analogue of **3** again by Roth.[3] In the same work, Roth also determined the activation energies for the three reactions **4** → **2**, **4** → **5**, and **4** → **6** as 36.5, 35.8, and 35.8 kcal mol^{-1}, respectively. According to our findings (Figure 2), the rate-determining barrier in the **4** → **2** transformation is the TS **2**/**3**. The theoretical barrier height in **4** → **2** is thus 69.0 − 32.5 = 36.5 kcal mol^{-1}, in excellent agreement with Roth.

For the rearrangements of **2** to **5** and **6**, a two-step mechanism has been proposed[1] that involves rate-determining cyclization to the 1,3-biradical **3** followed by 1,2-hydrogen migration in each of two possible directions giving the **5** and **6** molecules (Scheme 1). For the rearrangement of **2** to **3**, the reaction energy and barrier are computed as 20.9 and 37.4 kcal mol^{-1}, respectively. The computed reaction energy is consistent with Huntsman's crude estimation of 18 kcal mol^{-1}.[1] Further, for the rearrangement of **3** to **5**, the reaction energy and barrier are predicted as −48.8 and 20.0 kcal mol^{-1}, respectively, while the corresponding results are −52.5 and 19.6 kcal mol^{-1} for the conversion of **3** to **6**. The reaction energy for the second step in the cyclization of **2** is estimated to be approximately −50 kcal mol^{-1}.[1] Hence, our results, −48.8 and −52.5 kcal mol^{-1}, are again consistent with Huntsman's crude estimation of −50 kcal mol^{-1} .[1] On the other hand, Roth's measurements indicate that the barriers **3**/**5** and **3**/**6** have the same energy that is slightly lower (by 0.7 kcal mol^{-1}) than that of **2**/**3**. This means that the same barrier **2**/**3** is rate-determining in the conversions of **2** into **4**, **5**, and **6**. Again in the same work, Roth also determined the activation energies for the individual reactions **2** → **5** and **2** → **6** as 36.6 and 36.8 kcal mol^{-1}, respectively.[3] There is also the value 37.2 kcal mol^{-1} for **2** → **5** + **6**, reported by Huntsman et al.[1] We have found that the enthalpy of **4** is 0.9 kcal mol^{-1} higher than that of **2**. Assuming that our computational result is correct and combining with Roth's value for **4** → **2**, one would expect an activation energy of 36.5 + 0.9 = 37.4 kcal mol^{-1} for the reverse reaction. Furthermore, the computed barrier height is 69.0 − 31.6 = 37.6 kcal mol^{-1}, in good agreement with the expected value. It appears, therefore, that Huntsman's value of 37.2 kcal mol^{-1} is more reliable for the activation energy in **2** → **3**.

Furthermore, Black et al.[35] calculated the activation energy for the **1** → **2** reaction as 30.7 and 33.0 kcal mol^{-1} at MP2/6-31G(d)//RHF/6-31G(d) and B3LYP/6-31G(d) levels, respectively, which are also consistent with our result. The computed geometries of **1** and **2** are similar to those of Black et al.,[35] while the geometry of **1**/**2** is consistent with those reported for Cope rearrangements.[86−88] The computed geometries of **1**, **2**, **1**/**2**, **2**/**3**, **5**, **6**, **3**/**5**, **3**/**6**, **4**, and **3**/**4** are shown in Figures 4−13.

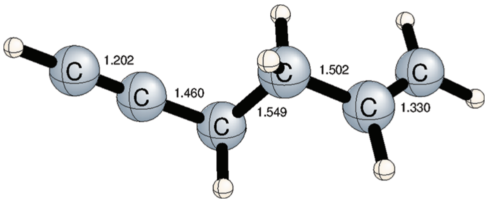


Figure 4. Selected interatomic distances (Å) for structure **1**.

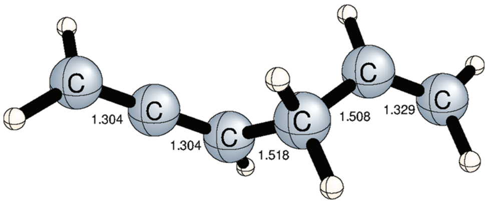


Figure 5. Selected interatomic distances (Å) for structure **2**.

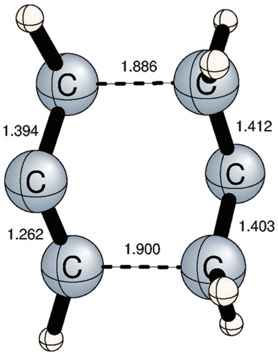


Figure 6. Selected interatomic distances (Å) for structure **1**/**2**.

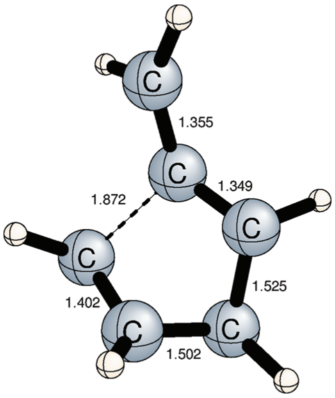


Figure 7. Selected interatomic distances (Å) for structure **2**/**3**.

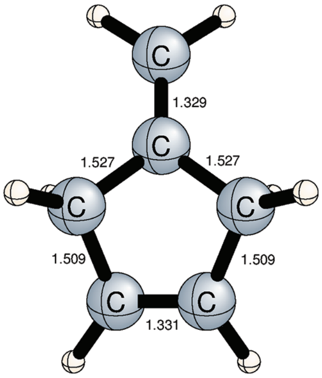


Figure 8. Selected interatomic distances (Å) for structure **5**.

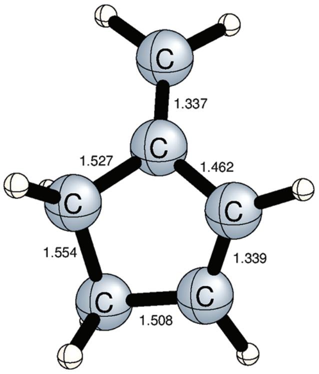


Figure 9. Selected interatomic distances (Å) for structure **6**.

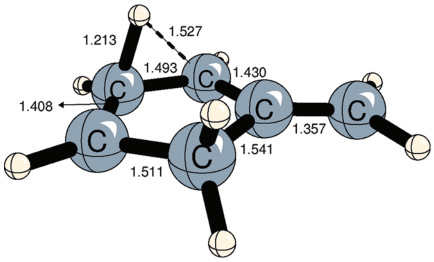


Figure 10. Selected interatomic distances (Å) for structure **3**/**5**.

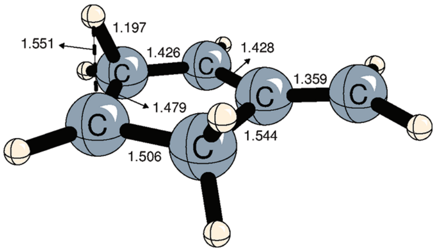


Figure 11. Selected interatomic distances (Å) for structure **3**/**6**.

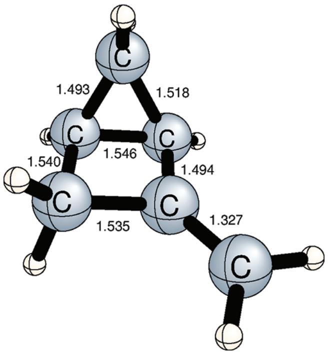


Figure 12. Selected interatomic distances (Å) for structure **4**.

Moreover, the **3** molecule has two resonance structures as shown in Figure 14. The cyclization of **3** via the second resonance hybrid will yield a cyclic molecule with bridgehead double bond. However, it is well-known that formation of such a molecule is very difficult as expressed by Bredt's rule, which states that "a double bond cannot be placed with one terminus at the bridgehead of a bridged ring system unless the rings are large enough to accommodate the double bond without

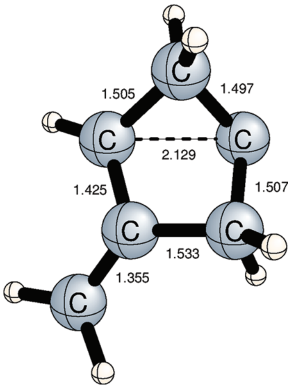
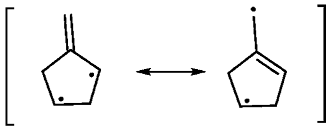


Figure 13. Selected interatomic distances (Å) for structure **3**/**4**.



3

Figure 14. Resonance structures of **3**.

excessive strain."[89,90] Indeed, a B3LYP/6-311G(d,p) optimization places the bicyclic molecule 69 kcal mol^{-1} above **4**.

Our results for the kinetic simulation of Huntsman−Baldwin mechanisms (Schemes 1 and 2) are provided in Tables 2 and 3, and Figures 15−17. Relative free energies used as input in the calculations are reported in Tables 4 and 5. For the Huntsman mechanism our predictions are in good agreement with experiment.[1] All results at 340 and 385 °C with various reaction times are in accord with experiment. However, when initial molecule is chosen as **4** at 253 °C, our estimated product fractions are at variance with the Andrews-Baldwin experiment.[2] They did not indicate a specific reaction time; nevertheless, the main aspects of the mechanism can be understood by analyzing time-dependent concentrations presented in Figure 17. We calculate that (Figure 17), on thermolysis of **4**, species **1** and **2** are major products at a reaction time of 1000 s at 253 °C, while **5** and **6** are still minor ones. However, Andrews and Baldwin[2] observed **2**, **5**, and **6** as major products, and did not observe species **1**.

Table 2. Product Distribution for the Huntsman Mechanism at 340 °C

reaction time (s)	molecule	% (computed)	% (expt)[a]
62	**1**	35.1	29
	2	55.6	65
	4	0.4	0
	5	3.3	2
	6	5.6	3
130	**1**	31.5	24
	2	49.8	62
	4	0.4	0
	5	6.9	6
	6	11.5	8
150	**1**	30.5	20
	2	48.2	50
	4	0.4	0
	5	7.8	13
	6	13.1	17

Table 3. Product Distribution for the Huntsman Mechanism at 385 °C

reaction time (s)	molecule	% (computed)	% (expt)[a]
62	**1**	15.4	10
	2	23.5	22
	4	0.2	0
	5	23.0	30
	6	37.9	38

[a] Reference 5.

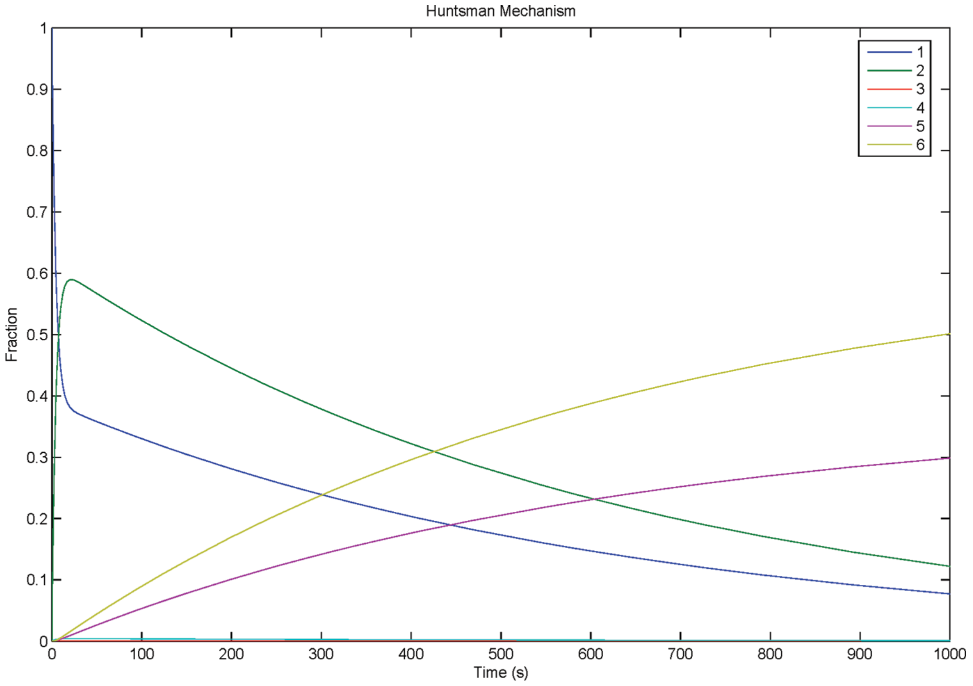


Figure 15. Time-dependent fractions for the Huntsman mechanism at 340 °C temperature (initial molecule is **1**).

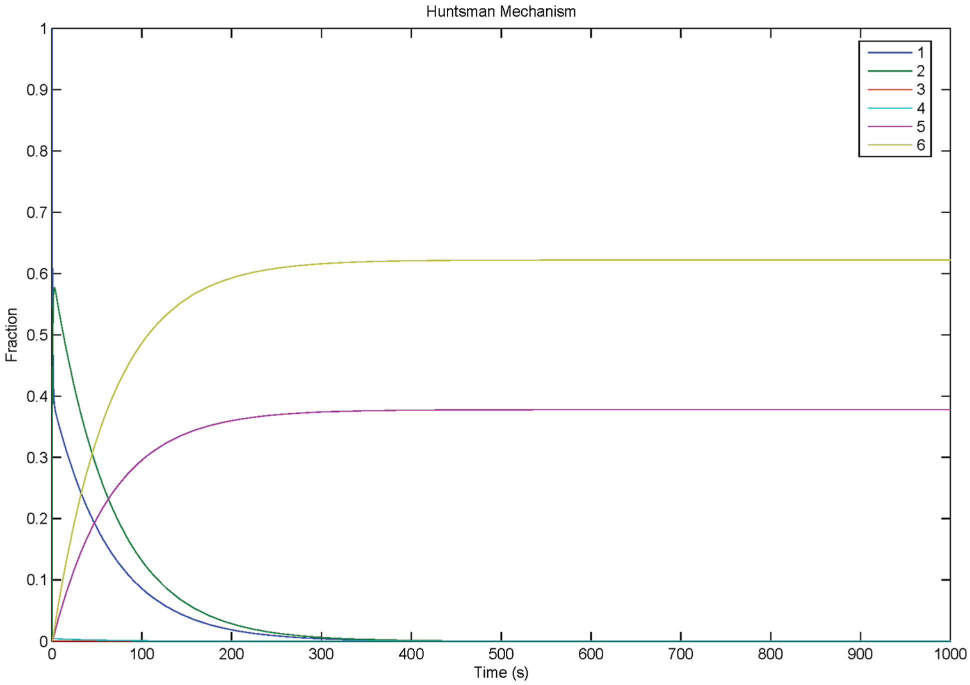


Figure 16. Time-dependent fractions for the Huntsman mechanism at 385 °C temperature (initial molecule is **1**).

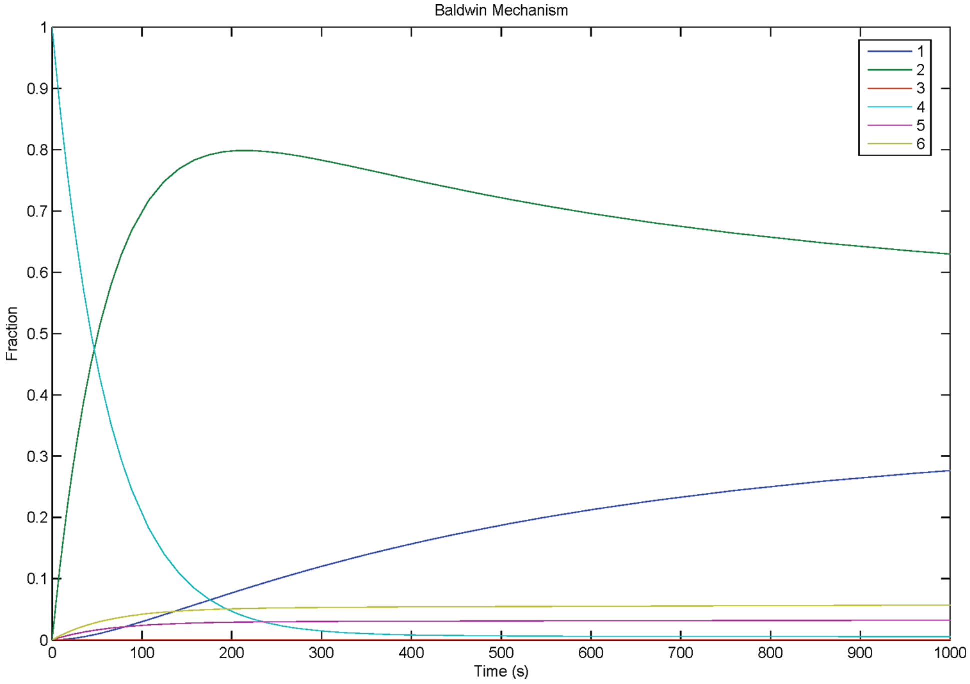


Figure 17. Time-dependent fractions for the Baldwin mechanism at 253 °C temperature (initial molecule is **4**).

Table 4. Relative Free Energies (kcal mol^{-1}) of the Minima in the Huntsman–Baldwin Mechanism with Respect to 6 at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) Level[a]

minimum	*G* (253 °C)	*G* (340 °C)	*G* (385 °C)
1	29.38	28.66	28.28
2	28.81	28.08	27.70
3	52.42	52.25	52.15
4	33.71	33.91	34.02
5	3.71	3.71	3.71
6	0.00	0.00	0.00

[a] Energy of the biradical **3** is computed according to eq 1.

Table 5. Relative Free Energies (kcal mol^{-1}) of the TSs in the Huntsman–Baldwin Mechanism with Respect to 6 at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) Level

TS	*G* (253 °C)	*G* (340 °C)	*G* (385 °C)
1/2	67.81	67.80	67.80
2/3	69.51	69.52	69.53
3/4	55.68	55.83	55.90
3/5	73.10	73.13	73.14
3/6	72.51	72.50	72.48

CONCLUSIONS

In this research, thermal rearrangements of 1-hexen-5-yne and several other isomers connected to it by chemical reaction pathways were investigated employing the highest level of theory available within our computational facilities. The relevant portions of the lowest-energy, singlet-spin potential energy surface of the C_6H_8 chemical systems were explored in order to determine the reaction energies and activation parameters accurately, with the ultimate objective of providing a theoretical account of pyrolysis experiments by Huntsman,[1] Baldwin,[2] and Roth[3] on the target system. For this purpose, a combination of DFT, CASSCF, MRMP2, and CCSD(T) methods were-employed, all with the triple-split valence 6-311G(d,p) basis set. Stationary points of closed-shell species (minima and TSs) were located at the DFT level, while CASSCF was used for the open-shell singlets (biradicals). Dynamical correlation was included by single-point CCSD(T) calculations for the former and by MRMP2 for the latter species. ZPVE corrections were all at the DFT level.

The rate constants and product distributions were calculated using theoretical kinetic modelings. The rate constant for each isomerization reaction was computed using the transition state theory (TST). The simultaneous first-order ordinary-differential equations were solved numerically for the Huntsman–Baldwin system (Figure 1) to obtain time-dependent concentrations and hence the product distributions at a given temperature.

The computational results herein on the target system fully support the mechanism experimentally studied by Huntsman,[1] Baldwin,[2] and Roth[3] (Schemes 1 and 2). In particular, we have verified that the reaction paths from **1** and **4** to **2**, **5**, and **6** all go through the biradical species **3**. Roth had measured the activation parameters for both the forward and reverse directions in each step in this mechanism. Our computed energy values (reaction energies and activation parameters) are in agreement with Roth's experiments and the product distributions of Huntsman's experiments at 340 and 385 °C with various reaction times. However, our estimated product fractions are at variance with the Andrews–Baldwin experiment. We calculate that, on thermolysis of **4**, species **1** and **2** are major products at a reaction time of 1000 s at 253 °C, and **5** and **6** are minor ones.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates, total energies, and ZPVE values for all stationary structures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ugur.bozkaya@atauni.edu.tr; ilker@metu.edu.tr.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the Academic Staff Development Program, ÖYP-1624. U.B. thanks the Scientific and Technological Research Council of Turkey (TÜBİTAK) for supporting his scientific studies at the Middle East Technical University, BİDEB-2211.

REFERENCES

(1) Huntsman, W. D. In *The Chemistry of Ketenes, Allenes and Related Compounds, Part 2*; Patai, S., Ed.; John Wiley & Sons: New York, 1972; pp 521–667.

(2) Andrews, G. D.; Baldwin, J. E. *J. Org. Chem.* **1988**, *53*, 4624.

(3) Roth, W. R.; Bauer, F.; Braun, K.; Offerhaus, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1056.

(4) Huntsman, W. D.; Dykstra, K. A. Unpublished results; Dykstra, K. A. Ph.D. Dissertation, Ohio University, 1972.

(5) Huntsman, W. D.; Boer, J. A. D.; Woosley, M. H. *J. Am. Chem. Soc.* **1966**, *88*, 5846.

(6) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*, 2nd ed.; Academic Press: New York, 2004; pp 114–116.

(7) Dalacker, V.; Hopf, H. *Tetrahedron Lett.* **1974**, 15.

(8) Chesick, J. P. *J. Am. Chem. Soc.* **1962**, *85*, 2720.

(9) Schaefer, H. F.; Yarkony, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 3754.

(10) Goddard, W. A.; Davis, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 303.

(11) Goddard, W. A.; Davis, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 4242.

(12) Dixon, D. A.; Foster, R.; Halgren, T. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 1359.

(13) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1977**, *99*, 2053.

(14) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(15) Schaefer, H. F.; Pitzer, R. M.; Hood, D. M. *J. Am. Chem. Soc.* **1978**, *100*, 2227.

(16) Schaefer, H. F.; Pitzer, R. M. *J. Am. Chem. Soc.* **1978**, *100*, 8009.

(17) Dixon, D. A.; Dunning, T. H.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878.

(18) Auster, S. B.; Pitzer, R. M.; Platz, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 3812.

(19) Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 967.

(20) Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783.

(21) Borden, W. T.; Du, P. *J. Am. Chem. Soc.* **1987**, *109*, 5330.

(22) Skancke, A.; Schaad, L. J.; Hess, B. D. *J. Am. Chem. Soc.* **1988**, *110*, 5315.

(23) Schaefer, H. F.; Ma, B. *Chem. Phys.* **1996**, *207*, 201.

(24) Davidson, E. R.; Gajewski, J. J.; Shook, C. A.; Cohe, T. *J. Am. Chem. Soc.* **1995**, *117*, 8495.

(25) Cramer, C. J.; Smith, B. A. *J. Phys. Chem.* **1996**, *100*, 9664.

(26) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.

(27) Mazur, M. R.; Potter, S. E.; Pinhas, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 6823.

(28) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2217.

(29) Rule, M.; Mondo, J. A.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2209.

(30) Salinaro, R. F.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2228.

(31) Berson, J. A. *Acc. Chem. Res.* **1997**, *30*, 238.

(32) Owens, K. A.; Berson, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5973.

(33) Parziale, P. A.; Berson, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 4595.

(34) Houk, K. N.; Beno, B. R.; Nendel, M.; Black, K.; Yoo, H. Y.; Wilsey, S.; Lee, J. K. *J. Mol. Struct.(THEOCHEM)* **1997**, *398*, 169.

(35) Black, K. A.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 5622.

(36) Frisch, M. J.et al. *Gaussian 03*; Gaussian, Inc.: Wallingford, CT, 2004.

(37) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(38) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*; McGraw-Hill: New York, 1989; pp 258–260.

(39) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic Structure Theory*; John Wiley & Sons: New York, 2000; pp 598–647.

(40) Shepard, R. *Adv. Chem. Phys.* **1987**, *69*, 63.

(41) Olsen, J.; Yeager, D. L.; Jørgensen, P. *Adv. Chem. Phys.* **1983**, *54*, 1.

(42) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399.

(43) Shepard, R.; Shavitt, I.; Simons, J. *J. Chem. Phys.* **1982**, *76*, 543.

(44) Dalgaard, E.; Jørgensen, P. *J. Chem. Phys.* **1978**, *69*, 3833.

(45) Dalgaard, E. *Chem. Phys. Lett.* **1979**, *65*, 559.

(46) Yeager, D. L.; Jørgensen, P. *J. Chem. Phys.* **1979**, *71*, 755.

(47) Werner, H.-J. *Adv. Chem. Phys.* **1987**, *69*, 1.

(48) Chaban, G.; Schmidt, M. W.; Gordon, M. S. *Theor. Chem. Acc.* **1997**, *97*, 88.

(49) Shepard, R. In *Modern Electronic Structure Theory, Part I*, 1st ed.;Yarkony, D. R., Ed.; Advanced Series in Physical Chemistry Vol. 2; World Scientific Publishing Company: London, 1995; pp 345−458.

(50) Sherrill, C. D.; Schaefer, H. F. In *Advances in Quantum Chemistry*; Löwdin, P.-O., Ed.; Academic Press: New York, 1999; Vol. *34*, pp 143−269.

(51) Shavitt, I.; Bartlett, R. J. *Many-Body Methods in Chemistry and Physics*; Cambridge Press: New York, 2009; pp 185−250.

(52) Hoffmann, M. R. In *Modern Electronic Structure Theory Part II*; Yarkony, D. R., Ed.; Advanced Series in Physical Chemistry Vol. 2; World Scientific Publishing Company: London, 1995; pp 1166−1190.

(53) Andersson, K.; Malmqvist, P.-A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483.

(54) Andersson, K.; Malmqvist, P.-A.; Roos, B. O. *J. Chem. Phys.* **1990**, *96*, 1218.

(55) Andersson, K.; Roos, B. O. In *Modern Electronic Structure Theory Part II*; Yarkony, D. R., Ed.; Advanced Series in Physical Chemistry Vol. 2; World Scientific Publishing Company: London, 1995; pp 55−109.

(56) Roos, B. O. In *Theory and Applications of Computational Chemistry: The First Forty Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G., Eds.; Elsevier: Amsterdam, 2005; pp 725−764.

(57) Hirao, K. *Chem. Phys. Lett.* **1992**, *190*, 374.

(58) Hirao, K. *Chem. Phys. Lett.* **1992**, *196*, 397.

(59) Hirao, K. *Int. J. Quant. Chem. S.* **1992**, *26*, 517.

(60) Hirao, K. *Chem. Phys. Lett.* **1993**, *201*, 59.

(61) cheMVP is free, open-source software designed to make clean, simple molecule drawings suitable for publications and presentations. The program is written in C++, using the QT library and some icons from the SVG icons project by A. Simmonett (andysim@ccc.uga.edu) and J. M. Turney (jturney@ccc.uga.edu), Center for Computational Quantum Chemistry (CCQC), University of Geoergia (USA) , 2008.

(62) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(63) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(64) Ishida, K.; Morokuma, K.; Komornicki, A. *J. Chem. Phys.* **1977**, *66*, 2153.

(65) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(66) Hratchian, H. P.; Schlegel, H. B. *J. Chem. Phys.* **2004**, *120*, 9918.

(67) Hratchian, H. P.; Schlegel, H. B. In *Theory and Applications of Computational Chemistry: The First 40 Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G., Eds.; Elsevier: Amsterdam, 2005; pp 195−249.

(68) Hratchian, H. P.; Schlegel, H. B. *J. Chem. Theory Comput.* **2005**, *1*, 61.

(69) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(70) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697.

(71) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(72) Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *86*, 2881.

(73) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1988**, *89*, 7382.

(74) Scuseria, G. E.; Schaefer, H. F. *J. Chem. Phys.* **1989**, *90*, 3700.

(75) Crawford, T. D.; Schaefer, H. F. *Rev. Comp. Chem.* **2000**, *14*, 33.

(76) Bartlett, R. J. In *Modern Electronic Structure Theory Part II*; Yarkony, D. R., Ed.; Advanced Series in Physical Chemistry Vol. 2; World Scientific Publishing Company: London, 1995; pp 1047−1131.

(77) Bartlett, R. J.; Musial, M. *Rev. Mod. Phys.* **2007**, *79*, 291.

(78) Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acc.* **1973**, *28*, 213.

(79) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(80) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(81) Holbrook, K. A.; Pilling, M. J.; Robertson, S. H. *Unimolecular Reactions*, 2nd ed.; John Wiley & Sons: New York, 1996; pp 39−77.

(82) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*, 2nd ed.; Prentice Hall: New Jersey, 1999; pp 287−382.

(83) MATLAB 7.0.4, The Language of Technical Computing, The MathWorks Inc., 2005.

(84) Roth, W. R.; Bauer, F.; Breuckmann, R. *Chem. Ber.* **1991**, *124*, 2041.

(85) Sherrill, C. D.; Seidl, E. T.; Schaefer, H. F. *J. Phys. Chem.* **1992**, *96*, 3712.

(86) Özkan, I.; Zora, M. *J. Org. Chem.* **2003**, *68*, 9635.

(87) Zora, M.; Özkan, I. *J. Mol. Struct.(THEOCHEM)* **2003**, *625*, 251.

(88) Zora, M.; Özkan, I.; Dansman, M. F. *J. Mol. Struct. (THEOCHEM)* **2003**, *636*, 9.

(89) Bredt, J.; Thout, H.; Schnitz, J. *Liebigs Ann.* **1924**, *437*, 1.

(90) IUPAC. *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"); compiled by McNaught, A. D. Wilkinson, A.; Blackwell Scientific Publications: Oxford, 1997.