J. Am. Chem. Soc. **1991**, *113*, 5195-5200

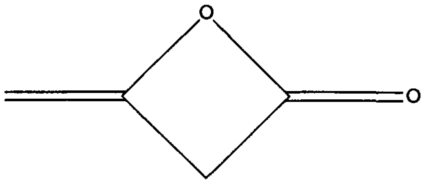
# Theoretical Investigation of the Dimerization of Ketene: Does the 2S + 2A Cycloaddition Reaction Exist?

**Edward T. Seidl* and Henry F. Schaefer III**

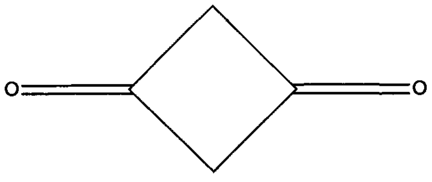
*Contribution from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602.* *Received August 6, 1990*

**Abstract:** Ab initio quantum mechanical methods have been used to study the dimerization of ketene to form diketene and 1,3-cylobutanedione. Molecular structures for reactants, products, and transition states of the above reactions have been determined at the self-consistent-field (SCF) level of theory with a double-$\zeta$ plus polarization (DZ+P) basis set. Relative energies of stationary points have been predicted at the single and double excitation configuration interaction (CISD) level of theory. At the DZ+P SCF level of theory, the formation of 1,3-cyclobutanedione is predicted to proceed through an unsymmetrical transition state and has a classical barrier height of 36 kcal/mol. The formation of diketene also proceeds through an unsymmetrical transition state and is predicted to have a barrier height of 32 kcal/mol. Inclusion of electron correlation and zero-point vibrational energy yields an estimate of 26 kcal/mol for the latter barrier. Neither transition state is consistent with the 2S + 2A cycloaddition reaction mechanism.

Since the mid-1950s it has been known that diketene, the sole product of the dimerization of ketene, has the structure **1**, rather than that of the more symmetrical 1,3-cyclobutanedione (**2**).[1]



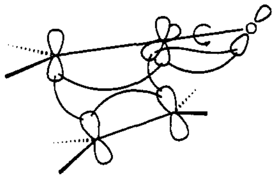
**1**



**2**

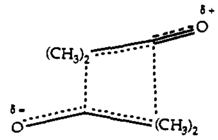
This observation has been made despite the fact that diketene is nearly isoenergetic with 1,3-cyclobutanedione.[2-4] It is also interesting to note that many substituted ketenes dimerize to form the cyclobutanedione-like structure, rather than the diketene-like one.[1] Oddly enough, given the synthetic importance of diketene, very little work has been done to elucidate the mechanism of its formation. The excellent and comprehensive review by Clemens[1] summarizes the experimental characterization of diketene and its reactions.

The dimerization of ketene does serve as an interesting test of the Woodward-Hoffmann selection rules for 2 + 2 cycloaddition reactions.[5] According to these selection rules, the 2S + 2S pathway, involving suprafacial attack on both reactants, is thermally forbidden, but the rules do allow for a 2S + 2A mode of attack, which involves suprafacial attack by one reactant and antarafacial attack by the other. The textbook example of the 2 + 2 cycloaddition reaction, the dimerization of ethylene, proceeds through a stepwise mechanism, rather than a concerted one, due to steric factors.[6] The less hindered ethylene-ketene reaction, however, is proposed as an example of a reaction which should proceed through a concerted 2S + 2A mechanism, although recent work by Bernardi et al.[7] casts some doubt on this. The even less hindered ketene dimerization reaction would seem to be the last hope for the 2S + 2A reaction. Another concerted pathway, the 2S + 2S + 2S, has been proposed for the ethylene-ketene reaction.[8] This pathway proceeds through an unsymmetrical transition state in which all three $\pi$ bonds are involved (**3**).



**3**

Experimental data concerning the mechanism of diketene formation are not abundant. In 1934 Rice and Greenberg[9] studied the kinetics of the dimerization of ketene in acetone and found it to follow a second-order rate law, indicative of an elementary bimolecular process. They also found the rate of reaction to be independent of the presence of oxygen in the reaction vessel, suggestive of a mechanism not involving a diradical intermediate. Rice and Roberts[10] then studied the pyrolysis of diketene, again concluding that the reaction does not involve a diradical intermediate. In 1968 Huisgen and Otto[11] studied the dimerization of dimethylketene to form 2,2,4,4-tetramethyl-1,3-cyclobutanedione and found second-order kinetics to be followed in this reaction as well. They conclude that the reaction does not involve a zwitterionic intermediate, but instead propose an unsymmetrical transition state of the type **4**. Finally, Chickos, Sherwood, and Jug[3] investigated the pyrolysis of isotopically labeled diketene,



**4**

---

* Robert S. Mulliken Graduate Fellow.

(1) Clemens, R. J. *Chem. Rev.* **1986**, *86*, 241.

(2) Mansson, M.; Nakasi, Y.; Sunner, S. *Acta Chem. Scand.* **1968**, *22*, 171.

(3) Chickos, J. S.; Sherwood, D. E.; Jug, K. *J. Org. Chem.* **1978**, *43*, 1146.

(4) Seidl, E. T.; Schaefer, H. F. *J. Am. Chem. Soc.* **1990**, *112*, 1943.

(5) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(6) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987.

(7) Bernardi, F.; Bottoni, A.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1990**, *112*, 2106 and references therein.

(8) (a) Zimmerman, H. E. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. I, p 77. (b) Ghosez, L.; O'Donnell, M. J. In *Pericylic Reactions*; Academic Press: New York, 1977; Vol. II, p 87.

(9) Rice, F. O.; Greenberg, J. *J. Am. Chem. Soc.* **1934**, *56*, 2132.

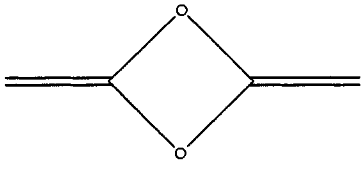
(10) Rice, F. O.; Roberts, R. *J. Am. Chem. Soc.* **1943**, *65*, 1677.

(11) Huisgen, R.; Otto, P. *J. Am. Chem. Soc.* **1968**, *90*, 5342.

0002-7863/91/1513-5195$02.50/0

concluding that the reaction is concerted. They do not speculate on the nature of the transition state, however.

Theoretical work is also scarce. Jug and Chickos,[12] performed a semiempirical study of the dimerization of ketene, predicting that the thermally forbidden 2S + 2S pathway is followed. Jug, Dwivedi, and Chickos[13] later reexamined the reaction, again using semiempirical methods, and suggested that the dimerization of ketene might be non-synchronous, yet still concerted. The only previous ab initio study is one by Fu, Decai, and Yanbo (FDY),[14] who looked at the 2S + 2S and 2S + 2A stationary points for formation of **1** and **2** as well as the 2S + 2S stationary point for formation of 2,4-dimethylene-1,3-dioxetane (**5**). Their results would lead one to predict the cyclobutanedione **2** to be the product of the dimerization of ketene.



**5**

This work will examine the transition states of the ketene plus ketene reactions to form **1** and **2**. The dioxetane **5** will be excluded as it lies some 30 kcal/mol higher in energy than **1** or **2**.[4] As such, it will be a followup of the work of FDY, but at much higher levels of theory. We hope to address the question of why **1** is experimentally favored over **2** and also shed some light on the question of whether the reaction follows a concerted 2S + 2A mechanism.

## Theoretical Approach

We first attempted to reproduce the results of FDY[14] at the SCF level using a minimum basis set.[15] Stationary points were found with use of an eigenvector following algorithm based on work by Simons and coworkers.[16] Stationary points were characterized as transition states or higher order stationary points via harmonic vibrational analyses. These analyses were accomplished with use of analytic SCF second-derivative methods.[17] We were able to find all of the structures described by FDY; however not all of the structures they call transition states are true transition states. Specifically, their 2S + 2S "transition state" for the formation of the cyclobutanedione **2** was found to have three imaginary vibrational frequencies, and their 2S + 2A transition state for the same reaction had two. Also, their 2S + 2S "transition state" for the formation of diketene **1** had two imaginary frequencies. In addition, we found a $C_1$ structure which is a true transition state for the formation of **2**.

By using the MBS-SCF structures as a starting point, geometry optimizations were performed with use of a double-$\zeta$ plus polarization (DZ+P) basis, specifically the Huzinaga[18]–Dunning[19] basis, which may be designated

C(9s5p1d/4s2p1d) O(9s5p1d/4s2p1d) H(4s1p/2s1p)

Orbital exponents for the polarization functions were $\alpha_d(\mathrm{C}) = 0.75$, $\alpha_d(\mathrm{O}) = 0.85$, and $\alpha_p(\mathrm{H}) = 0.75$. The DZ+P basis set for $C_4H_4O_2$ includes 116 contracted Gaussian basis functions.

Where possible, single point energies were determined at the DZ+P single and double excitation configuration interaction[20] (CISD) level of theory with use of the DZ+P SCF geometries. Single point CISD energies were also determined for each DZ+P stationary point with use of a basis set identical with the above DZ+P basis except for the omission of polarization functions on hydrogen (DZ+d). The effect of quadruple excitations was estimated by using Davidson's correction[21] (CISD+Q).

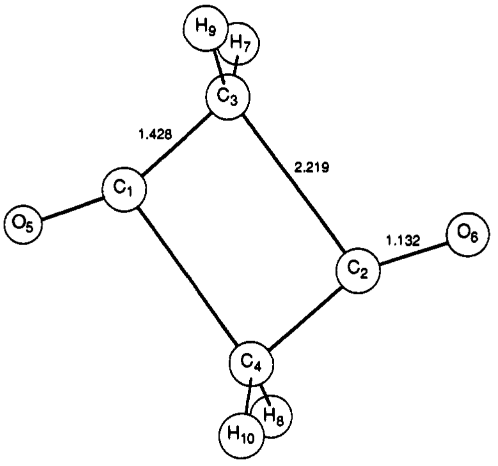


**Figure 1.** Numbering of atoms for the $C_{2h}$ (2S + 2S) stationary point (Hessian index 4) on the ketene dimerization potential energy surface leading to 1,3-cyclobutanedione. Bond distances between heavy atoms predicted at the DZ+P SCF level of theory are given in angstroms.

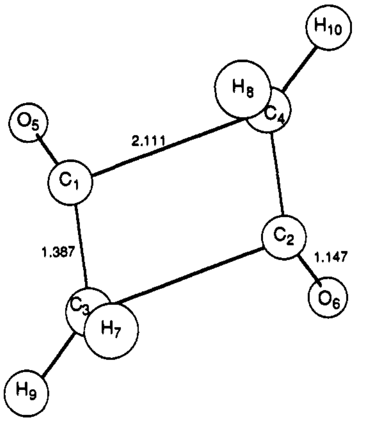


**Figure 2.** Numbering of atoms for the $C_2$ (2S + 2A) stationary point (Hessian index 2) on the ketene plus ketene reaction pathway leading to 1,3-cyclobutanedione. Bond distances between heavy atoms predicted at the DZ+P SCF level of theory are given in angstroms.

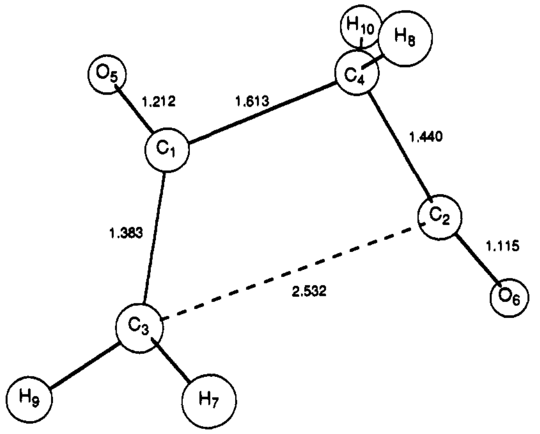


**Figure 3.** Numbering of atoms for the $C_1$ transition state on the ketene dimerization pathway leading to 1,3-cyclobutanedione. Bond distances between heavy atoms predicted at the DZ+P SCF level of theory are given in angstroms.

In the CISD wave functions the six lowest SCF molecular orbitals (corresponding to the core carbon and oxygen 1s-like functions) were frozen. Likewise, the six highest virtual orbitals were deleted from the CI procedure. Thus, the largest DZ+P CISD wave function, that for the $C_s$ stationary point for the formation of **1**, included 515 657 configura-

---

(12) Jug, K.; Chickos, J. *Theor. Chim. Acta* **1975**, *40*, 207.

(13) Jug, K.; Dwivedi, C. P. D.; Chickos, J. S. *Theor. Chim. Acta* **1978**, *49*, 249.

(14) Fu, X. Y.; Decai, F.; Yanbo, D. *J. Mol. Struct.* **1988**, *167*, 349.

(15) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(16) (a) Simons, J.; Jorgensen, P.; Taylor, H.; Ozment, J. *J. Phys. Chem.* **1983**, *87*, 2745. (b) Banerjee, A.; Adams, N.; Simons, J.; Shepard, R.; *J. Phys. Chem.* **1985**, *89*, 52.

(17) Saxe, P.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1982**, *77*, 5647.

(18) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(19) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(20) Brooks, B. R.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *70*, 5092.

(21) Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; D. Reidel: Dordrecht, Holland, 1974.

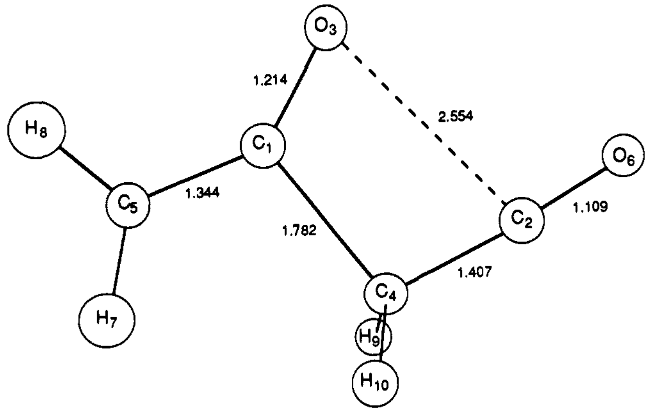


**Figure 4.** Numbering of atoms for the $C_s$ stationary point (Hessian Index 2) on the pathway leading from two ketene molecules to diketene. Bond distances between heavy atoms predicted at the DZ+P SCF level of theory are given in angstroms.

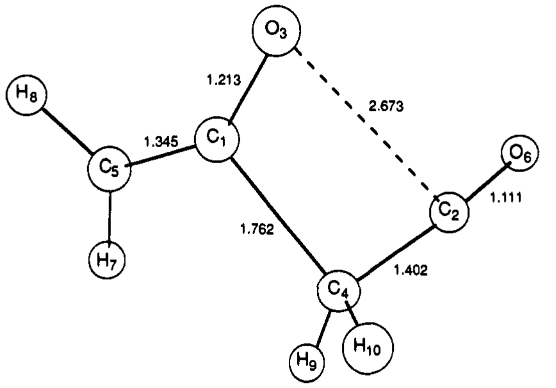


**Figure 5.** Numbering of atoms for the $C_1$ transition state on the reaction pathway connecting ketene plus ketene to diketene. Bond distances between heavy atoms predicted at the DZ+P SCF level of theory are given in angstroms.

tions, while the largest DZ+d CISD wave function, that for the $C_1$ transition state for the formation of **1**, included 741 153 configurations. Single point energies were also determined for several stationary points at the DZ+d single and double excitation coupled cluster[22] (CCSD) level of theory. As with the CISD wave functions, the six lowest and six highest molecular orbitals were frozen. The largest DZ+d CCSD wave function, that for the $C_s$ stationary point for the formation of **1**, included 387 393 configurations. Finally, within the harmonic approximation, the zero-point vibrational energies (ZPVE) of the ketene molecule and each stationary point were evaluated at the DZ+P SCF level. A ZPVE correction for each barrier was determined with use of the formula

$$\Delta\text{ZPVE} = \text{ZPVE(stationary point)} - 2\text{ZPVE(ketene monomer)} \tag{6}$$

## Results

The geometries of the stationary points found for the dimerization of ketene to form **1** and **2** are summarized in Tables I and II and Figures 1–5. In Table III are listed the absolute energies of the DZ+P stationary points, their energies relative to two separated ketene molecules, and ZPVE corrections for each barrier. Values of the imaginary vibrational frequencies for each stationary point are also listed in Table III. Table IV lists the absolute and relative energies for each stationary point obtained by using the DZ+d basis set.

**A. The 1,3-Cyclobutanedione Pathway.** Three stationary points were found for the reaction to form **2** at the DZ+P SCF level. These are a $C_{2h}$ structure corresponding to the 2S + 2S pathway, a $C_2$ structure corresponding to the 2S + 2A pathway, and a $C_1$ structure. The $C_{2h}$ and the $C_2$ structures are not true transition states, the former having four imaginary vibrational frequencies and the latter having two. The $C_1$ structure is a true transition state, having only one imaginary frequency. This structure would appear to be the saddle point connecting **2** with the reactants; no minima were found when this structure was allowed to relax other than **2**.

**Table I.** Selected Geometrical Parameters (angstroms and degrees) for the Product 1,3-Cyclobutanedione Ground State and Three Different Stationary Points for the Ketene Dimerization Optimized at the DZ+P SCF Level of Theory

| | ground state | $C_{2h}$ (2S + 2S) | $C_2$ (2S + 2A) | $C_1$ |
|---|---|---|---|---|
| $r_e(C_3–H_7)$ | 1.086 | 1.087 | 1.074 | 1.079 |
| $r_e(C_4–H_8)$ | 1.086 | 1.087 | 1.074 | 1.083 |
| $r_e(C_3–H_9)$ | 1.086 | 1.087 | 1.080 | 1.077 |
| $r_e(C_4–H_{10})$ | 1.086 | 1.087 | 1.080 | 1.083 |
| $\theta_e(C_4–C_1–C_3)$ | 93.2 | 92.3 | 88.1 | 107.9 |
| $\theta_e(C_3–C_2–C_4)$ | 93.2 | 92.3 | 88.1 | 69.1 |
| $\theta_e(C_1–C_3–C_2)$ | 86.8 | 87.7 | 78.0 | 63.8 |
| $\theta_e(C_2–C_4–C_1)$ | 86.8 | 87.7 | 78.0 | 96.8 |
| $\theta_e(C_3–C_1–O_5)$ | 133.4 | 158.3 | 152.8 | 135.6 |
| $\theta_e(C_4–C_2–O_6)$ | 133.4 | 158.3 | 152.8 | 170.4 |
| $\theta_e(C_4–C_1–O_5)$ | 133.4 | 109.4 | 117.2 | 115.7 |
| $\theta_e(C_3–C_2–O_6)$ | 133.4 | 109.4 | 117.2 | 120.4 |
| $\theta_e(C_1–C_3–H_7)$ | 114.8 | 118.3 | 117.4 | 119.6 |
| $\theta_e(C_2–C_4–H_8)$ | 114.8 | 118.3 | 117.4 | 109.3 |
| $\theta_e(C_1–C_3–H_9)$ | 114.8 | 118.3 | 114.6 | 119.8 |
| $\theta_e(C_2–C_4–H_{10})$ | 114.8 | 118.3 | 114.6 | 109.3 |
| $\omega_e(C_3–C_1–C_4–C_2)$ | 0.0 | 0.0 | 49.2 | 53.4 |
| $\omega_e(C_1–C_4–C_2–C_3)$ | 0.0 | 0.0 | −29.9 | −26.5 |
| $\omega_e(C_4–C_2–C_3–C_1)$ | 0.0 | 0.0 | 49.2 | 35.2 |
| $\omega_e(C_2–C_3–C_1–C_4)$ | 0.0 | 0.0 | −29.9 | −30.4 |

**Table II.** Selected Geometrical Parameters (angstroms and degrees) for the Product Diketene Ground State and Two Different Stationary Points for the Ketene plus Ketene Addition Optimized at the DZ+P SCF Level of Theory

| | ground state | $C_s$ | $C_1$ |
|---|---|---|---|
| $r_e(C_5–H_7)$ | 1.075 | 1.073 | 1.072 |
| $r_e(C_5–H_8)$ | 1.076 | 1.077 | 1.077 |
| $r_e(C_4–H_9)$ | 1.083 | 1.083 | 1.082 |
| $r_e(C_4–H_{10})$ | 1.083 | 1.083 | 1.082 |
| $\theta_e(O_3–C_1–C_4)$ | 92.3 | 111.5 | 108.5 |
| $\theta_e(C_1–C_4–C_2)$ | 81.9 | 102.9 | 99.9 |
| $\theta_e(C_4–C_2–O_3)$ | 93.1 | 71.6 | 64.9 |
| $\theta_e(C_2–O_3–C_1)$ | 92.7 | 73.9 | 65.4 |
| $\theta_e(O_3–C_1–C_5)$ | 127.5 | 141.2 | 141.7 |
| $\theta_e(C_4–C_1–C_5)$ | 140.2 | 107.3 | 109.8 |
| $\theta_e(C_4–C_2–O_6)$ | 138.7 | 184.6 | 174.6 |
| $\theta_e(O_3–C_2–O_6)$ | 128.2 | 103.8 | 111.6 |
| $\theta_e(C_1–C_5–H_7)$ | 119.8 | 122.3 | 122.4 |
| $\theta_e(C_1–C_5–H_8)$ | 120.9 | 118.0 | 117.9 |
| $\theta_e(H_7–C_5–H_8)$ | 119.3 | 119.7 | 119.6 |
| $\theta_e(C_2–C_4–H_9)$ | 114.4 | 108.9 | 109.7 |
| $\theta_e(C_2–C_4–H_{10})$ | 114.4 | 108.9 | 110.0 |
| $\omega_e(O_3–C_1–C_4–C_2)$ | 0.0 | 0.0 | −55.7 |
| $\omega_e(C_1–C_4–C_2–O_3)$ | 0.0 | 0.0 | 23.1 |
| $\omega_e(C_4–C_2–O_3–C_1)$ | 0.0 | 0.0 | −38.1 |
| $\omega_e(C_2–O_3–C_1–C_4)$ | 0.0 | 0.0 | 28.0 |

As can be seen in Table I, the transition state is highly unsymmetrical. In particular, note the difference in the lengths of $C_1$–$C_4$ and $C_2$–$C_3$, which in the $C_{2h}$ and $C_2$ structures are (of necessity) equal. This large difference suggests that the dimerization reaction is non-synchronous, with formation of the $C_1$–$C_4$ bond and partial breakage of the $C_1$–$C_3$ and $C_2$–$C_4$ double bonds, followed by formation of $C_2$–$C_3$. Since no minima were found other than the product cyclobutanedione, the reaction is concluded to be concerted rather than stepwise.

One can see from Table III that there is a sizable barrier at the DZ+P SCF level of theory to the 2S + 2S reaction of 67.7 kcal/mol. The DZ+P SCF barrier to the 2S + 2A reaction is much lower at 46.8 kcal/mol, and the analogous barrier to the reaction involving the $C_1$ transition state is the lowest at 35.8 kcal/mol. When using the DZ+P CISD single point energies of the $C_{2h}$ (2S + 2S) and $C_2$ (2S + 2A) structures, their respective

---

[22] (a) Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *86*, 2881. (b) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1988**, *89*, 7382.

**Table III.** Absolute Energies (hartrees), Barrier Heights,[a] and Zero-Point Vibrational Energy Corrections (kcal/mol) for Dimerization Reactions, Together with Imaginary Vibrational Frequencies ($cm^{-1}$) determined for stationary points

| | absolute energy | | | barrier heights | | | | |
|---|---|---|---|---|---|---|---|---|
| | SCF | CISD | CISD+Q | SCF | CISD | CISD+Q | ZPVE correction | imaginary freq |
| | | | | 1,3-Cyclobutanedione | | | | |
| ground state | −303.556 19 | −304.286 52 | −304.406 03 | | | | 5.8 | |
| $C_{2h}$ (2S + 2S) | −303.405 48 | −304.137 38 | −304.260 40 | 67.7 | 60.7 | 58.1 | −3.9 | 940i, 605i, 258i, 149i |
| $C_2$ (2S + 2A) | −303.438 71 | −304.178 07 | −304.302 65 | 46.8 | 35.2 | 31.6 | 2.1 | 791i, 333i |
| $C_1$ | −303.456 23 | | | 35.8 | | | 3.5 | 322i |
| | | | | Diketene | | | | |
| ground state | −303.553 35 | −304.285 40 | −304.404 83 | | | | 6.8 | |
| $C_s$ | −303.458 54 | −304.190 02 | −304.311 32 | 34.4 | 27.7 | 26.1 | 2.4 | 435i, 75i |
| $C_1$ | −303.461 81 | | | 32.3 | | | 2.8 | 350i |

[a] Energy of two separated ketene molecules: −303.513 34 (SCF), −304.234 15 (CISD), −304.352 94 hartrees (CISD+Q).

**Table IV.** Absolute Energies (hartrees) and Barrier Heights[a] (kcal/mol) for Dimerization Reactions Determined at the DZ+d Level

| | absolute energy | | | | barrier heights | | | |
|---|---|---|---|---|---|---|---|---|
| | SCF | CISD | CISD+Q | CCSD | SCF | CISD | CISD+Q | CCSD |
| | | | 1,3-Cyclobutanedione | | | | | |
| ground state | −303.548 79 | −304.259 00 | −304.373 92 | −304.413 09 | | | | |
| $C_{2h}$ (2S + 2S) | −303.397 04 | −304.108 58 | −304.226 97 | −304.269 43 | 67.6 | 61.1 | 58.6 | 57.3 |
| $C_2$ (2S + 2A) | −303.430 36 | −304.149 44 | −304.269 38 | −304.311 37 | 46.7 | 35.4 | 31.9 | 31.0 |
| $C_1$ | −303.448 22 | −304.162 27 | −304.279 75 | | 35.5 | 27.4 | 25.4 | |
| | | | Diketene | | | | | |
| ground state | −303.545 91 | −304.257 62 | −304.372 39 | −304.411 50 | | | | |
| $C_s$ | −303.450 50 | −304.161 76 | −304.278 45 | −304.319 89 | 34.0 | 27.7 | 26.2 | 25.6 |
| $C_1$ | −303.453 90 | −304.166 04 | −304.282 96 | | 31.9 | 25.0 | 23.4 | |

[a] Energy of two separated ketene molecules: −303.504 73 (SCF), −304.205 92 (CISD), −304.320 28 (CISD+Q), −304.360 72 hartrees (CCSD).

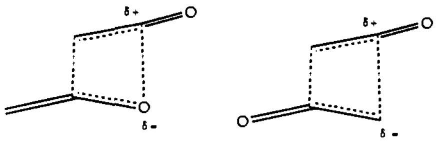
barriers are lowered by 7 and 12 kcal/mol. These barriers are reduced further at the CISD+Q level to 58.1 and 31.6 kcal/mol. As can be seen in Table IV, these values change little when the DZ+d basis is used. Thus from the DZ+d values, we estimate the DZ+P CISD+Q barrier for the $C_1$ transition state to be approximately 25 kcal/mol. Inclusion of the DZ+P SCF ZPVE correction yields a final estimate of 28 kcal/mol for the true barrier to the $C_1$ transition state.

**B. The Diketene Pathway.** Two stationary points were found for this reaction at the DZ+P SCF level. A $C_s$ structure with two imaginary frequencies and a $C_1$ structure having one. Since diketene is of lower symmetry than the dione, and no geometrical constraints were used in the search for stationary points other than those imposed by symmetry, no stationary points corresponding to the 2S + 2S or 2S + 2A reactions were found. As shown in Table II, the $C_s$ stationary point is similar to the $C_1$ transition state when only comparing bond lengths. Both indicate partial bond breakage and formation as in the cyclobutanedione case. As with the above dione, no minima were found other than the product diketene. We again infer this to be a non-synchronous, concerted reaction.

Both the $C_s$ and the $C_1$ reaction pathways have lower barriers at the DZ+P SCF level than the $C_1$ reaction for formation of **2**. These barriers are 34.4 and 32.3 kcal/mol respectively. As with **2** adding electron correlation reduces the barrier, and using the DZ+d CISD+Q results given in Table IV, one can estiamte a value of 23 kcal/mol for the DZ+P CISD+Q barrier to this reaction. Inclusion of the DZ+P SCF ZPVE correction yields a final estimate of 26 kcal/mol for this barrier. The experimental activation energy for diketene formation in the gas phase[3] of 31 kcal/mol seems a bit high in this light. Some caution is called for, however. While including electron correlation effects decreases the barrier for the reaction leading to diketene by some 9 kcal/mol, the same is not true for the reverse reaction. We predict the barrier for the dissociation of diketene to two ketenes to be 57.7 kcal/mol at the DZ+d SCF level of theory. This barrier is reduced to 56.1 kcal/mol at the DZ+d CISD+Q level of theory. Inclusion of a ZPVE correction obtained from the DZ+P SCF results gives a final estimate of 52 kcal/mol for the barrier to this reaction, compared to a value of 53 kcal/mol from experiment.[3] Further, we predict the dimerization of ketene to have a $\Delta E$ of −25.1 kcal/mol at the DZ+P SCF level of theory and a $\Delta E$ of −32.6 kcal/mol at the DZ+P CISD+Q level. Inclusion of ZPVE yields a final estimate of −26 kcal/mol, in good agreement with the experimental heat of reaction, −23 kcal/mol.[2]

## Discussion

Why does the dimerization of ketene yield diketene rather than the nearly isoenergetic 1,3-cyclobutanedione? The trivial answer is that the activation energy for the formation of diketene is lower (at the DZ+P SCF level). But why is this? The simplest explanation is that the HOMO and LUMO of ketene are the C–C $\pi$ and the C–O $\pi^*$ MO's respectively. Clearly, a concerted 2 + 2 reaction involving these MO's would yield diketene. Another explanation could be that, given the partial charge separation in the transition states for the two reactions, the negative charge would be more stable on the oxygen than on the less electronegative $CH_2$ group (**7**). The question of why substituted ketenes yield the dione structure is somewhat more complex. However, this experimental finding is clearly consistent with the present theoretical prediction that the barrier heights to **1** and **2** are comparable. The nature of the reaction changes with various substituents, e.g. concerted for methyl substituents, while the evidence seems to point to stepwise mechanisms for substituents bearing electron-withdrawing substituents.[23] In the case of the dimethylketene dimerization, the transition state to formation of the dione now has some tertiary carbanion character, i.e. it will be stabilized by the polarizable methyl groups, so it will be favored over the transition state to form the substituted diketene. Presumably, better electron withdrawing substituents will better stabilize the transition state, eventually leading to a zwitterionic intermediate.



**7**

Does the 2S + 2A cycloaddition reaction mechanism exist? If one defines the 2S + 2A as a synchronous concerted pathway, the answer to this question would seem to be no. The $C_1$ transition

---

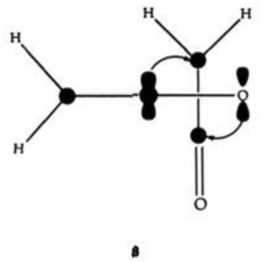
(23) Moore, H. W.; Wilbur, D. S. *J. Am. Chem. Soc.* **1978**, *100*, 6523 and references therein.

state for formation of the cyclobutanedione **2** is predicted here to lie 11 kcal/mol below the 2S + 2A stationary point (Hessian index 2), and no analogous stationary point is found on the diketene surface. The transition state for ketene dimerization clearly indicates a non-synchronous reaction with partial formation of the $C_1$–$C_4$ bond and partial breakage of the $C_1$–$O_3$ and $C_2$–$C_4$ double bonds being followed by formation of the $C_2$–$O_3$ bond. However, the dimerization of ketene does appear to be a concerted reaction, but rather than following a 2S + 2A path, the transition state for the reaction seems consistent with the 2S + 2S + 2S reaction discussed in our introduction.

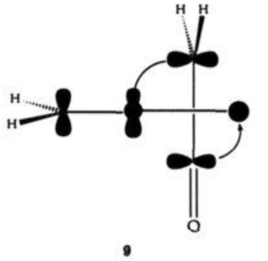
Our interpretation of the ab initio transition state is not the only one possible. In their original paper Woodward and Hoffmann[5] make no mention of synchronicity as a criterion for a 2S + 2A pathway. Thus one can make the argument that *any* concerted 2 + 2 cycloaddition involving a nonplanar transition state is a 2S + 2A reaction. We do not feel this interpretation is correct, however. The Woodward–Hoffmann rules are based on the conservation of orbital symmetry. In their discussion of the 2S + 2A cycloaddition reaction involving two ethylenes, they stipulate that a $C_2$ axis along the line connecting the bisectors of the C–C double bonds must be preserved throughout the reaction. This $C_2$ axis can only be preserved if there exist planes containing the carbon atoms of the ethylene molecules which are parallel to each other and perpendicular to the $C_2$ axis. This parallel approach implies that the reaction would be synchronous.

In the case of ketene dimerization, one would expect a 2S + 2A transition state to have an approximate $C_2$ axis, i.e. the $C_1$–$C_4$ and $C_2$–$O_3$ bonds would need to be nearly equal in length. In our transition state, however, these bonds differ by nearly an angstrom; clearly there is no approximate $C_2$ axis. Bernardi et al.,[7] in their studies of the ketene–ethylene cycloaddition, also rule out a 2S + 2A type mechanism due to the non-synchronous nature of the transition state. In this they echo Zimmerman,[8a] who distinguishes between two alternative views of the ketene–ethylene reaction: one being the 2S + 2A pathway and the other being a concerted reaction which occurs in two distinct stages, which we have already introduced as the 2S + 2S + 2S.

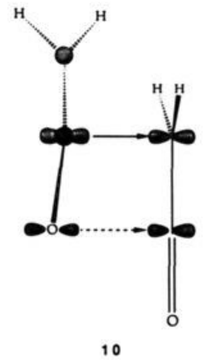
Finally, further inspection of the geometry of addition shows that it cannot be a 2S + 2A reaction. Two geometries are possible in this case for a 2S + 2A transition state: one in which all four hydrogens lie in parallel planes (**8**) and one in which they lie in planes perpendicular to a common plane (**9**). In our transition state, however (shown schematically in **10**), one set of hydrogens lies (more or less) in the plane of the paper, while the others lie in a plane perpendicular to the plane of the paper.



**8**



**9**



**10**

Table V. Values of $C_0$ and $T_1$ at the DZ+d and DZ+P CISD and CCSD Levels of Theory

| | DZ+d | | DZ+P | |
|---|---|---|---|---|
| | $C_0$ | $T_1$ | $C_0$ | $T_1$ |
| | 1,3-Cyclobutanedione | | | |
| ground state | 0.9155 | 0.0155 | 0.9145 | 0.0156 |
| $C_{2h}$ (2S + 2S) | 0.9130 | 0.0188 | 0.9121 | |
| $C_2$ (2S + 2A) | 0.9128 | 0.0188 | 0.9119 | |
| $C_1$ | 0.9140 | | | |
| | Diketene | | | |
| ground state | 0.9158 | 0.0153 | 0.9148 | 0.0152 |
| $C_s$ | 0.9143 | 0.0202 | 0.9133 | |
| $C_1$ | 0.9142 | | | |

A few words are merited at this point concerning the multiconfigurational nature of the stationary points considered here. Bernardi and co-workers, in their studies of 2 + 2 cycloaddition reactions, use MCSCF methods with small basis sets.[7,24] They state, however, that "this computational approach is not expected to provide an accurate treatment of the energetics of the reaction, which will probably require dynamic correlation and large basis sets". In this study, we have opted for larger basis sets, rather than a multiple configuration approach. In the 1990 paper of Bernardi et al.,[7] the energetics of the ethylene–ketene reaction proved to be sensitive to the choice of basis set. At the MBS MCSCF level of theory, they find a transition state corresponding to the formation of the first C–C bond to lie 18.7 kcal/mol above a gauche intermediate, but at the 4-31G level this barrier is reduced to 0.4 kcal/mol. At neither level of theory could they find a transition state linking the gauche intermediate with the product cyclobutanone. The importance of electron correlation is demonstrated by Wang and Houk[25] in their study of the ketene plus ethylene reaction. At the 6-31G* SCF level of theory they predict the activation energy of this reaction to be 46.6 kcal/mol, but at the 6-31G* MP2 level, the activation energy is reduced to 26.7 kcal/mol. Indeed, as stated above, our results are qualitatively different using the larger DZ+P basis set, thus we would be loath to undertake any type of post Hartree–Fock treatment of the problem with a small basis set. Further, our single point CISD calculations would seem to indicate that we are describing the ground states and stationary points equally well with a single configuration. For the cyclobutanedione reaction, $C_0$ for the ground state was 0.9145 at the DZ+P CISD level, compared to values of 0.9121 for the $C_{2h}$ structure and 0.9119 for the $C_2$ structure. Similarly, diketene has a $C_0$ of 0.9148, while for the $C_s$ stationary point this coefficient is 0.9133.

It has been shown, however, that $C_0$ from CISD theory is not a truly reliable test of the multiconfigurational nature of a wave function.[26] Instead, it is more illustrative to use the $T_1$ diagnostic obtained from the CCSD method, defined as the norm the single-excitation coupled cluster amplitudes divided by the square root of the number of active electrons.[27] It has been proposed that a $T_1 \geq 0.025$ is an indication that non-dynamical correlation effects are very important.[26] Table V lists values of $C_0$ and $T_1$ determined with the DZ+d and DZ+P basis sets. As can be seen, while the $C_0$ values of the stationary points are not much different from those of the ground-state structures, the $T_1$ values vary greatly. It appears that the stationary points for the reaction leading to **2** are adequately described with a single reference wave function, although the $T_1$ values for the reaction leading to diketene are on the borderline. While this is no guarantee that other configurations are unimportant, it does indicate that at the very least these reactions are not pathological. Also, our results are conceptually consistent with those of Bernardi et al. and Wang and Houk for the reaction of ethylene with ketene, at least in as

---

(24) Bernardi, F.; Bottoni, A.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1985**, *107*, 2260.

(25) Wang, X.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 1754.

(26) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F. *Theor. Chim. Acta* **1989**, *75*, 81.

(27) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199.

far as all predict the respective reactions to be non-synchronous and concerted.

### Concluding Remarks

We have reported a comprehensive theoretical study of the cycloaddition reactions of ketene leading to the products diketene and 1,3-cyclobutanedione. Our results indicate that diketene should be the major product of the reaction of two ketenes, in agreement with experiment. Our predictions as to the energetics of these reactions are also in reasonable agreement with experiment.

**Acknowledgment.** This research was supported by the U.S. National Science Foundation, Grant No. CHE-8718469. All computations were carried out with the PSI suite of programs distributed by PSITECH, Inc., Watkinsville, Georgia.

**Registry No. 1**, 674-82-8; **2**, 15506-53-3; ketene, 463-51-4.

---

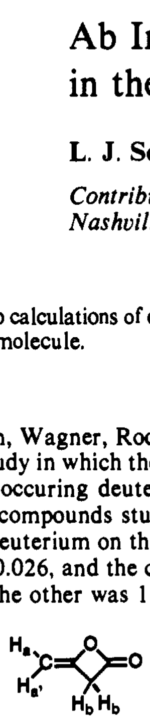
# Ab Initio Calculation of Secondary Deuterium Isotope Ratios in the Formation of Diketene

**L. J. Schaad,* I. Gutman,[†] B. A. Hess, Jr.,* and Jiani Hu**

*Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235.* *Received October 11, 1990*

**Abstract:** Ab initio calculations of deuterium isotope ratios in the formation of diketene agree with natural deuterium abundances reported for this molecule.

In 1986, Pascal, Baum, Wagner, Rodgers, and Huang[1] published a careful NMR study in which they were able to measure differences in naturally occuring deuterium concentrations in various positions of the compounds studied. In particular for diketene **1**, the ratio of deuterium on the exo methylene to that in the ring was 0.975 ± 0.026, and the concentration in the one exo position relative to the other was 1.040 ± 0.025.



**1**

We report here ab initio calculations of deuterium isotope ratios in the formation of diketene from ketene. Calculated isotope ratios resulting from both secondary kinetic and equilibrium control are reported over the temperature range 100–600 K. Results are consistent with Pascal's observations.

### Computations

Energy calculations, geometry optimizations, and vibrational frequency calculations were done by using the Cambridge University CADPAC program[2] on an SCS 40 computer. The built-in STO-3G, 3-21G, and 6-31G* basis sets were used in RHF calculations on ketene, diketene, the transition structure for the formation of diketene, and the diketene isomers cyclobutane-1,2-dione and cyclobutane-1,3-dione.

Moments of inertia and vibrational frequencies from CADPAC were used to calculate partition functions in the rigid-rotor–harmonic-oscillator approximation. These in turn gave rate and equilibrium constants for the required isotopomers.

### Structures

Optimized RHF/6-31G* structures are shown in Figures 1 and 2 with energies in the STO-3G, 3-21G, and 6-31G* bases given in Table I. These structures agree with those of Seidl and Schaefer,[3,4] who give leading references into the literature of diketene and who discuss the interesting problem of why ketene dimerizes to diketene rather than to cyclobutane-1,3-dione. Harmonic vibrational frequencies were computed for all optimized species, and as expected all were real except for a single imaginary frequency of the transition structure.

**Table I.** Energies (au) of Optimized Structures

| | STO-3G | 3-21G | 6-31G* |
|---|---|---|---|
| ketene | −149.726 105 | −150.876 526 | −151.724 672 |
| diketene | −299.575 309 | −301.779 262 | −303.487 380 |
| diketene transition structure | −299.381 164 | −301.690 107 | −303.394 561 |
| cyclobutane-1,2-dione | −299.579 483 | −301.777 479 | −303.482 226 |
| cyclobutane-1,3-dione | −299.579 960 | −301.782 977 | −303.489 561 |

**Table II.** Optimized RHF/6-31G* Geometry of the Transition Structure for the Formation of Diketene from Ketene

| bond lengths (Å) | | bond angles (deg) | | dihedral angles (deg)[a] | |
|---|---|---|---|---|---|
| $O_1C_2$ | 1.223 | $O_1C_2C_3$ | 140.8 | $O_1C_2C_3H_4$ | −3.5 |
| $C_2C_3$ | 1.338 | $O_1C_2C_8$ | 107.5 | $O_1C_2C_3H_5$ | 178.6 |
| $C_2C_8$ | 1.711 | $C_2C_3H_4$ | 118.7 | $O_1C_2C_8C_6$ | −48.2 |
| $C_3H_4$ | 1.073 | $C_2C_3H_5$ | 122.3 | $O_7C_6C_8C_2$ | −52.2 |
| $C_3H_5$ | 1.073 | $C_2C_8C_6$ | 99.0 | $O_7C_6C_8H_9$ | 74.5 |
| $C_6O_7$ | 1.107 | $C_6C_8H_9$ | 109.9 | $O_7C_6C_8H_{10}$ | −160.7 |
| $C_6C_8$ | 1.413 | $C_6C_8H_{10}$ | 109.0 | $C_8C_2C_3H_4$ | 177.0 |
| $C_8H_9$ | 1.081 | $O_7C_6C_8$ | 175.6 | | |
| $C_8H_{10}$ | 1.081 | | | | |

[a] The dihedral angle conventions of the CADPAC program are used. See Figure 2a,c for numbering.

Two ORTEP views of the transition structure for ketene dimerization are shown in Figure 2b,c. This structure agrees well with Seidl and Schaefer's result.[4] The reaction is far from synchronous, with the $C_2$–$C_8$ bond formation being more advanced than the $C_6$–$O_1$. This is in spite of the fact that this CO bond is shorter (1.358 Å) than the CC bond (1.508 Å) in the product. It may not be useful to force too close an analogy between this [2 + 2] cycloaddition and the related reaction of ethylene plus ethylene, since the double bonds involved in the ketene have fewer substituents and therefore lack most of the stereochemical consequences of the ethylene prototype. Further, the three-center

---

[†] Permanent Address: Faculty of Science, University of Kragujevac, P.O. Box 60, 34000 Kragujevac, Yugoslavia.

(1) Pascal, R. A., Jr.; Baum, M. W.; Wagner, C. K.; Rodgers, L. R.; Huang, D.-S. *J. Am. Chem. Soc.* **1986**, *108*, 6477.

(2) Amos, R. D.; Rice, J. E. *CADPAC: The Cambridge Analytic Derivatives Package*, Issue 4.0, Cambridge, 1987.

(3) Seidl, E. T.; Schaefer, H. F. *J. Am. Chem. Soc.* **1990**, *112*, 1493.

(4) Seidl, E. T.; Schaefer, H. F. preceding paper in this issue.

0002-7863/91/1513-5200$02.50/0