

THEORETICAL STUDY OF THE THERMAL ISOMERIZATION OF FULVENE TO BENZENE

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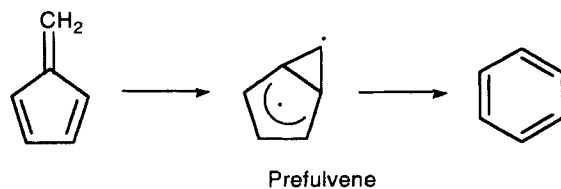
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The potential energy surface for the thermal isomerization of fulvene to benzene was studied by modified Gaussian-2 (G2M) and the bond additivity-corrected fourth-order perturbation Møller–Plesset (BAC-MP4) methods. Three isomerization pathways were investigated. One involves the intermediate prefulvene by a concerted mechanism, which has a significantly higher barrier. The second, also involving prefulvene and cyclopenta-1,3-dienylcarbene intermediates, has a barrier of $84.0 \text{ kcal mol}^{-1}$. The third, a multi-step pathway, includes bicyclo[3.1.0]hexa-1,3-diene and cyclohexadiene carbene intermediates. The activation energy of the multi-step pathway was calculated to be $74.3 \text{ kcal mol}^{-1}$, which is $7\text{--}11 \text{ kcal mol}^{-1}$ higher than the experimental value obtained by a brief very low-pressure pyrolysis (VLPP) study. RRKM calculations were performed on the multi-step pathway in order to determine the rate of isomerization. These theoretical results cast doubt on the validity of the VLPP data.

1. INTRODUCTION

Over the past few years, a significant amount of experimental and theoretical work has focused on the formation of soot in flames.^{1–10} It is well known that the rate-determining step in soot formation is the making of the first benzene ring. The isomerization of fulvene to benzene is a likely final step in the formation of the first aromatic ring in combustion.

A few mechanisms for the isomerization of fulvene to benzene have been proposed in the literature.^{6,11–13} In one mechanism, it was hypothesized that the formation of benzene from fulvene proceeded through a biradical intermediate called prefulvene:^{11–13}



This mechanism has been accepted by photochemists.

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Melius *et al.*⁶ investigated the potential energy surface of fulvene to benzene using the bond additivity corrected Møller–Plesset fourth-order perturbation (BAC-MP4) method in conjunction with the recombination of propargyl radicals, which are potential precursors of fulvene and benzene under sooting conditions. In their reaction mechanism, the isomerization occurred through two intermediates. The first was bicyclo[3.1.0]hexa-1,3-diene and the second was cyclohexadiene carbene. The activation energy they obtained was $73.2 \text{ kcal mol}^{-1}$ ($1 \text{ kcal} = 4.184 \text{ kJ}$), which is $5\text{--}9 \text{ kcal mol}^{-1}$ higher in energy than that obtained by Gaynor *et al.*⁵ in their brief very low-pressure pyrolysis (VLPP) experiments.

The purpose of this study was to use *ab initio* molecular orbital computation methods to investigate the potential energy surface of the isomerization of fulvene to benzene. The prefulvene mechanism was studied to see if this was a viable low-energy pathway for the reaction. The multi-step mechanism introduced by Melius *et al.*⁶ was also investigated using more sophisticated *ab initio* MO methods¹⁴ to determine if a different activation energy could result. RRKM calculations based on this multi-step mechanism were performed to obtain the rate constant for the isomerization reaction.

METHODS OF CALCULATION

The geometries of various isomers of C_6H_6 were fully optimized at the B3LYP/6-31G(d) level of theory.^{15,16} Vibrational frequencies were calculated at the same level for characterization of the nature of the stationary point and for zero-point corrections. The stationary points were identified as either a minimum with no imaginary frequencies or as a transition state with one imaginary frequency.

For most of the intermediates and transition-state structures, single-point energy calculations were performed using the modified Gaussian-2 method, G2M(rcc,MP2).¹⁴ It uses a series of calculations to approximate a CCSD(T)/6-311G(3df,2p) calculation. In the G2M(rcc,MP2) method, a base energy (E_{bas}) was calculated at the MP4/6-311G(d,p) level and was then modified by a number of corrections.

(a) Basis set correction:

$$\Delta E(+3df2p) = E[\text{MP2}/6-311 + \text{G}(3df,2p)] \\ - E[\text{MP2}/6-311\text{G}(d,p)]$$

(b) Coupled cluster correction:

$$\Delta E(\text{RCC}) = E[\text{RCCSD(T)}/6-31\text{G}(d,p)] \\ - E[\text{MP4}/6-31\text{G}(d,p)]$$

(c) 'Higher level' correction based on the number of α and β valence electrons:

$$\Delta E(\text{HLC}) = -4.93n_{\beta} - 0.19n_{\alpha} \text{ (in mhartree)}$$

(d) Zero-point energy correction (ZPE)

These corrections were added to E_{bas} to give the total G2M energy:

$$E[\text{G2M}(\text{rcc},\text{MP2})] \\ = E_{\text{bas}} + \Delta E(+3df2p) + \Delta E(\text{RCC}) + \Delta E(\text{HLC}) + \text{ZPE}$$

All calculations were performed using the Gaussian 92/DFT program.¹⁷

Since the reaction pathways considered in the present study involve some carbene and biradical intermediates, we have to estimate the level of accuracy which one can expect from the B3LYP and G2M methods for such structures. Carbenes are described fairly well. For instance, the B3LYP approximation gives the bond lengths and bond angles of singlet and triplet CH_2 with the deviations from experiment of less than 0.01 Å and 2°. The singlet-triplet splitting in CH_2 is calculated to be *ca* 12 and *ca* 6 kcal mol⁻¹ at the B3LYP and G2M(rcc,MP2) levels, respectively,¹⁴ vs 9 kcal mol⁻¹ in experiment. For the biradical structures, we use the unrestricted B3LYP method for the geometry optimization of the singlet state.

In the next section, we compare the UB3LYP-optimized geometry of the prefulvene biradical with the CASSCF geometry available in the literature^{13,18} and find good agreement between them. Similar comparison

is also made for some other intermediates and transition states. With regard to energetics, the G2M(rcc,MP2) method simulates a CCSD(T) calculation with a large 6-311+G(3df,2p) basis set. Recently, Lindh *et al.*¹⁹ carried out studies of the Bergman reaction and the energy splitting of the singlet *o*-, *m*- and *p*-benzynes using the CCSD(T) and the multi-reference CASPT2 methods. They concluded, for instance, that there is no significant difference between the CASPT2 and the CCSD(T) methods for the computed *ortho*-*para* energy splitting of benzyne, while *p*-benzyne is a typical biradical. Therefore, the CCSD(T) approach can provide an accurate description of biradical molecules. We have also found²⁰ that the CCSD(T) and CASPT2 methods give close energies for the intermediates and transition states of the phenoxy decomposition reaction.

RESULTS

Isomerization mechanism

Fully optimized geometries of intermediates and transition states of the C_6H_6 isomerization are given in Figure 1 and a potential energy diagram of both mechanisms in Figure 2. Table 1 lists relative energies obtained at various levels of theory.

The first isomerization mechanism investigated is the one that involved the biradical intermediate prefulvene, a bicyclic species with one electron centered on C-1 and the other delocalized about the five-carbon ring. Prefulvene has C_s symmetry and its geometry optimized at the UB3LYP level agrees well with that obtained by the CASSCF calculations.^{13,18} The differences in the bond lengths do not exceed 0.01–0.02 Å, except for the C-6–C-2 distance, where the UB3LYP value is by 0.04 Å longer than the CASSCF value. It has been debated whether prefulvene is an intermediate or a transition state.^{11–13} Oikawa *et al.*¹² used intrinsic reaction coordinate (IRC) calculations at the MINDO-3 and UHF levels and found prefulvene to be an intermediate on the PES between benzene and benzvalene. On the other hand, Palmer *et al.*¹³ found prefulvene to be a transition state at CASSCF/4-31G level of theory. They also found slightly asymmetric prefulvene intermediates that they called 'prebenzvalenes', which were only about 0.2 kcal mol⁻¹ lower in energy than prefulvene, and concluded that prefulvene was a transition state on the PES connecting two similar prebenzvalene molecules. In their PES, these prebenzvalenes move forward to form benzvalene or backward to form benzene.

At the B3LYP/6-31G(d) level we found prefulvene to be a transition state with a relative energy to fulvene of 67.6 kcal mol⁻¹. Interestingly, the CCSD(T) energy of prebenzvalene relative to fulvene, 73.7 kcal mol⁻¹, is close to its CASSCF energy, 77.9 kcal mol⁻¹.¹⁸ The optimization of both prefulvene and the prebenzvalene

Table 1. Relative energies and zero-point energy corrections of various isomers of C_6H_6

Species	ZPE ^a	E_{rel} (kcal mol ⁻¹)						
		B3LYP/ 6-31G(d)	MP2/ 6-311+G(3df,2p)	MP4/ 6-311G(d,p)	CCSD(T)/ 6-31G(d,p)	G2M (rec,MP2)	BAC-MP4 ^{b,c}	
Fulvene ^d (C_{2v}^1, A_1)	61.7	0.0	0.0	0.0	0.0	0.0	0.0	
Benzene (D_{6h}, A_g)	63.1	-34.6	-34.5	-31.9	-31.7	-30.4	-34.9	
Bicyclo[3.1.0]hexa-1,3-diene (C_1)	61.4	42.6	36.4	39.3	42.2	41.3	37.6	
Cyclohexadiene carbene (C_1)	60.3	55.5	64.4	60.4	59.4	58.4	61.5	
Benzvalene (C_1, A_1)	61.5	44.9	36.7	40.0	41.8	40.7	41.1	
Prefulvene TS ^e (C_{3v}, A_1)	58.9	67.6	84.1	68.7	73.7	75.4	—	
Cyclopenta-1,3-dienylcarbene (C_1)	59.9	79.6	79.6	77.1	80.1	77.1	78.4	
TS1 (C_1)	60.9	42.3	36.4	39.7	42.9	41.6	38.9	
TS2 (C_1)	59.9	74.3	79.4	75.0	76.1	74.3	73.2	
TS3 (C_1)	59.3	58.1	58.9	58.2	61.3	59.0	60.1	
TS4 ^f (C_1)	58.3	113.9	108.1	107.3	111.9	107.9	—	
TS5 (C_1)	59.2	73.8	64.6	67.5	70.9	67.9	—	
TS6 (C_1)	58.5	86.2	89.9	84.0	85.1	84.0	80.4	
TS7 (C_1)	59.2	83.2	78.1	79.0	83.1	78.8	—	

^a ZPE calculated at the B3LYP/6-31G(d) level.

^b BAC-MP4 calculations performed at Sandia National Labs.

^c Theoretical $\Delta H_{f,0}^\circ = 27.38$ kcal mol⁻¹ for benzene and 57.78 kcal mol⁻¹ for fulvene by the G2M method and 21.2 and 56.2 kcal mol⁻¹, respectively, by the BAC-MP4 method. Experimental values corrected to 0 K are $\Delta H_{f,0}^\circ = 19.81$ kcal mol⁻¹ for benzene and 47.5 kcal mol⁻¹ for fulvene.²²

^d The total energies (in hartree) for fulvene are the following: B3LYP/6-31G(d), -232.19131; MP2/6-311+G(3df,2p), -231.6614; MP4/6-311G(d,p), -231.72583; CCSD(T)/6-31G(d,p), -231.52764.

^e Prefulvene and TS4 calculations were performed at the B3LYP/6-31G(d,p) level.

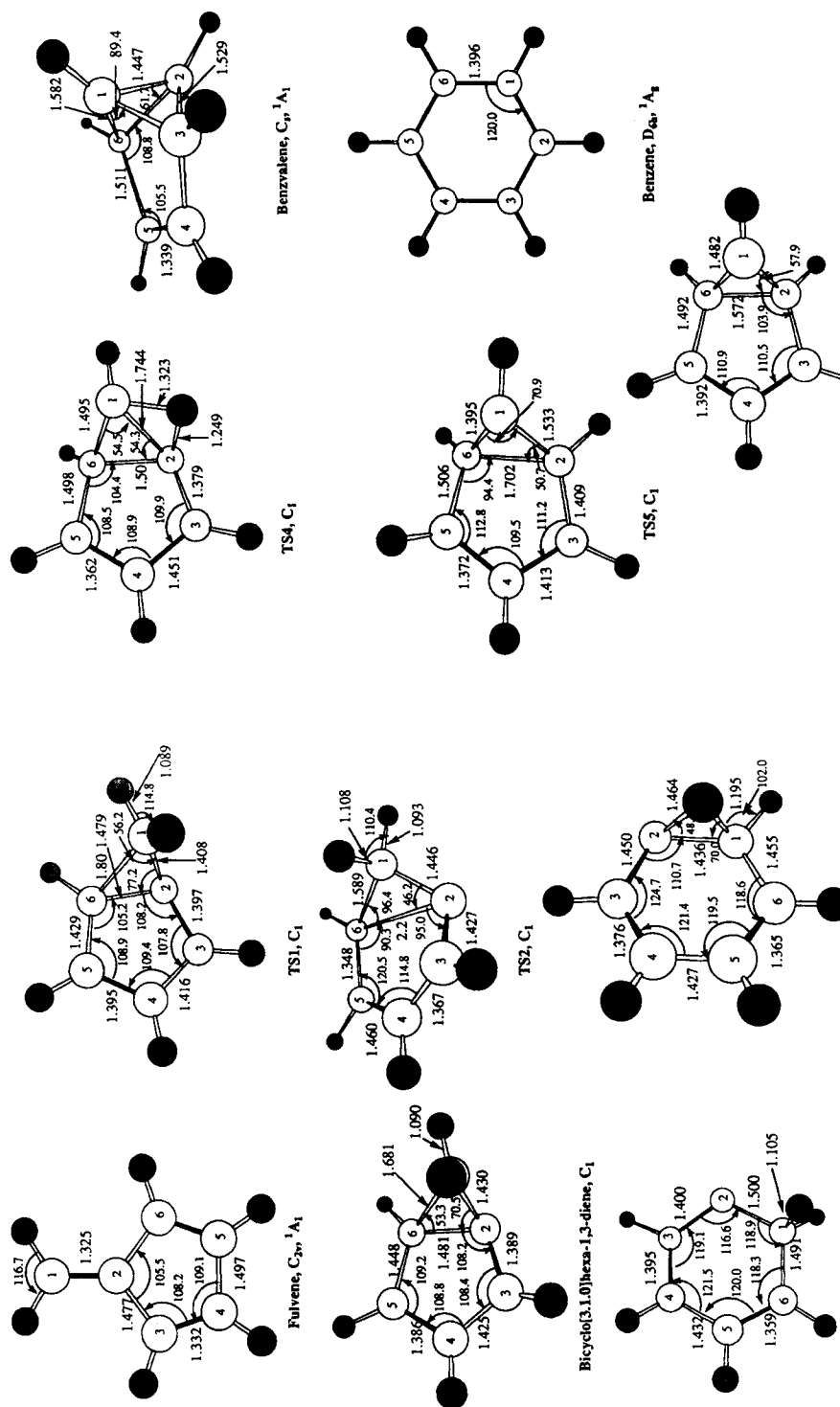


Figure 1. Calculated molecular geometries of intermediates, transition states, fulvene and benzene at the B3LYP/6-31G(d) level of theory

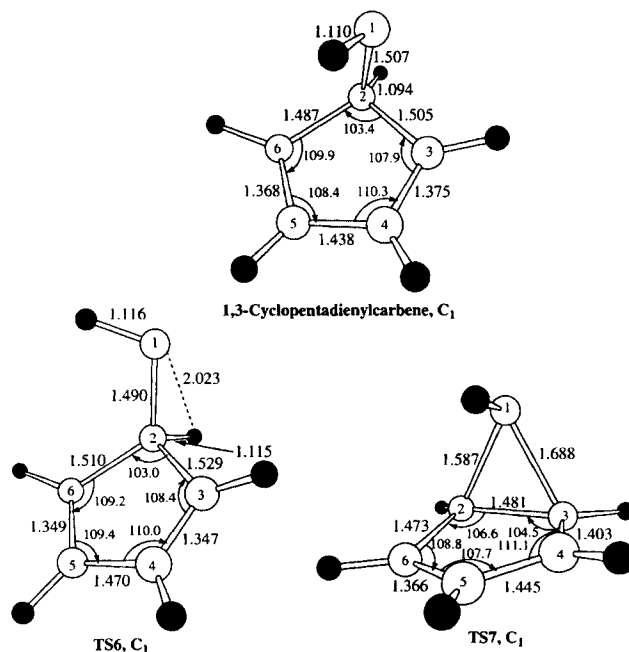


Figure 1. (Continued from previous page).

structures of Palmer *et al.*¹³ leads to benzvalene and we therefore deduced that these prebenzvalene intermediates do not exist at this level of theory. Based on these results, we concluded that prefulvene serves as a transition state for the degenerate benzvalene rearrangement with an energy barrier of 22.7 and 34.7 kcal mol⁻¹ at the B3LYP and G2M(rcc,MP2) levels, respectively. The potential energy surface is extremely flat in the vicinity of prefulvene. According to the results of the CASSCF calculation of Palmer *et al.*,¹³ prefulvene, prebenzvalene and the transition states between prebenzvalene and benzvalene as well as prebenzvalene and benzene all lie within the energy range of 0.2 kcal mol⁻¹. Therefore, the existence of prefulvene or prebenzvalene as local minima is not critical for the thermal isomerization of fulvene to benzene.

We have investigated two mechanisms that contain benzvalene as an intermediate. Benzvalene is a symmetrical species with a relative energy of 40.7 kcal mol⁻¹ higher than fulvene. In this molecule, C-1 is bound to C-2, C-3 and C-6 at distances of 1.447, 1.582 and 1.582 Å, respectively.

We first considered a one-step mechanism to form benzvalene from fulvene via TS4 with an energy barrier of 107 kcal mol⁻¹ at the G2M(rcc,MP2) level. Benzvalene is formed through TS4 by having the C-1 of fulvene twisting above the plane of the five-carbon ring by 103°. The C-1—C-2 bond is lengthened from 1.325 Å in fulvene to 1.744 Å in TS4 and then shortened to 1.477 Å

in benzvalene and a new bond between C-1 and C-6 of length 1.495 Å is formed. Also in TS4, an H-atom migration from C-1 to C-2 occurs simultaneously.

In the second step of the isomerization, benzvalene is converted into benzene through TS5, where the C-1—C-3 bond of benzvalene is broken as C-1 starts to move back into the plane of the five-carbon ring. The C-2—C-6 bond of 1.529 Å is lengthened to 1.702 Å in TS5 and finally broken to form benzene. The last step has an energy barrier of 67.9 kcal mol⁻¹ relative to fulvene.

An alternative path to forming benzvalene involves the cyclopenta-1,3-dienyl carbene and prefulvene species, as recently suggested by Dreyer and Klessinger.¹⁸ In the first step, a 1,2-hydrogen shift takes place in fulvene to form cyclopenta-1,3-dienylcarbene via TS6. The carbene lies 77.1 kcal mol⁻¹ higher than fulvene at the G2M(rcc,MP2) level, which can be compared with 76.7 kcal mol⁻¹ obtained at the CASSCF/6-31+G(d,p) level.¹⁸ Since the rearrangement is highly endothermic, TS6 has a very late character; its geometry is close to that of carbene. Connections of TS6 to fulvene and cyclopenta-1,3-dienylcarbene are confirmed by the IRC calculations. At the G2M(rcc,MP2) level, the barrier for the hydrogen shift is 84.0 kcal mol⁻¹ relative to fulvene and 6.9 kcal mol⁻¹ relative to the carbene. In the next step, a new C-2—C-3 bond is formed via TS7, and the barrier is 78.8 kcal mol⁻¹ with respect to fulvene. The system finds itself in the vicinity of prefulvene and relaxes to benzvalene. The overall mechanism is described as

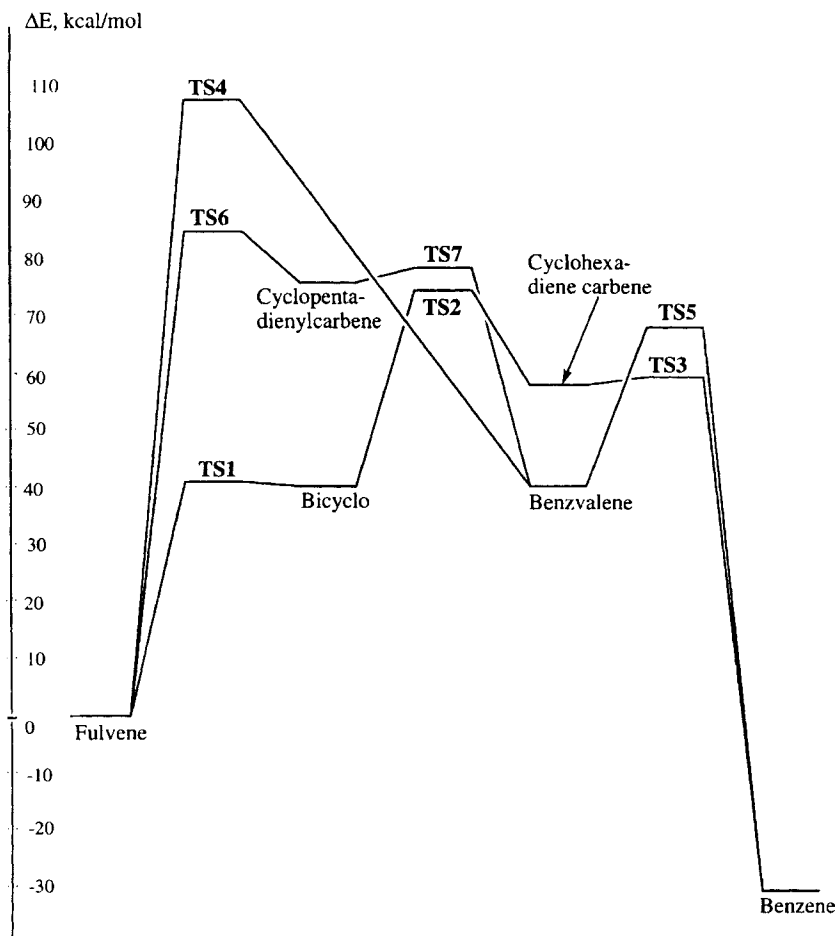


Figure 2. Profile of the potential energy surface for fulvene to benzene isomerization. All energies were calculated at the G2M level of theory

follows: fulvene \rightarrow **TS6** \rightarrow cyclopenta-1,3-dienyl carbene \rightarrow **TS7** \rightarrow (prefulvene) \rightarrow benzvalene \rightarrow **TS5** \rightarrow benzene. The highest barrier, $84.0 \text{ kcal mol}^{-1}$, is calculated for **TS6**. This is about $17\text{--}21 \text{ kcal mol}^{-1}$ greater than the experimental value.⁵

CASSCF-optimized geometries of **TS4** and **TS5** can be found in the literature. Dreyer and Klessinger¹⁸ assigned **TS4** as a transition state for the prefulvene–isofulvene (bicyclo[3.1.0]hexa-1,3-diene) isomerization. In general, their CASSCF geometry agrees well with our B3LYP geometry, except for the C-1–C-2 and C-2–H_r distances which are $0.11\text{--}0.14 \text{ \AA}$ shorter at the B3LYP level. It is known that the CASSCF approach tends to overestimate some bond lengths. A higher level geometry optimization, using the CCSD(T) method, would be needed in order to obtain more accurate geometry of **TS4**. However, all the calculations consistently show that the energy of **TS4** is very high, 121.3 , 113.9 , 111.9 , and $107.9 \text{ kcal mol}^{-1}$ at

the CASSCF/6-31+G(d,p),¹⁸ B3LYP/6-31G(d), CCSD(T)/6-31G(d,p) and G2M (rcc,MP2) levels of theory, respectively, relative to fulvene. With regard to the connection of **TS4**, at the B3LYP level prefulvene evolves into benzvalene and, as shown below, isofulvene or bicyclo[3.1.0]hexa-1,3-diene is a very shallow minimum separated from fulvene by a barrier in less than 1 kcal mol^{-1} . Therefore, we connect **TS4** with benzvalene and fulvene directly, which is confirmed by the IRC calculations. The geometry of **TS5** was reported by Palmer *et al.*¹³ and the differences in the bond lengths optimized in their CASSCF/4-31G and our B3LYP/6-31G(d) approximations do not exceed $0.03\text{--}0.04 \text{ \AA}$.

The alternative mechanism to benzvalene studied in this paper is the multiple step pathway proposed by Melius *et al.*⁶ Calculations for it were performed at the G2M(rcc,MP2) level of theory.¹⁴ The first step of the mechanism is the formation of bicyclo[3.1.0]hexa-1,3-

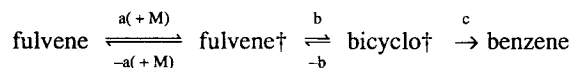
diene or isofulvene. The structure of this intermediate consists of a five-carbon ring with a three-carbon ring fused to it at an angle of 125.2° and has a relative energy to fulvene of $41.3 \text{ kcal mol}^{-1}$. This bicyclic intermediate is formed from **TS1**, where the CH_2 group of fulvene has twisted and risen 126.6° above the plane of the cyclopentadiene group. The C-1—C-2 bond is elongated from 1.325 \AA in fulvene to 1.408 \AA in **TS1** and is further lengthened to 1.430 \AA in bicyclo[3.1.0]hexa-1,3-diene. Also in **TS1**, a new carbon—carbon bond of 1.800 \AA is formed between C-1 and C-6 and is shortened to 1.681 \AA in the bicyclo intermediate. The geometries of **TS1** and bicyclo[3.1.0]hexa-1,3-diene, calculated at the B3LYP level, are similar to those obtained by Dreyer and Klessinger¹⁸ at the CASSCF level. The structure of **TS1** is similar to that of bicyclo[3.1.0]hexa-1,3-diene and, therefore, the energy of **TS1** is only $0.3 \text{ kcal mol}^{-1}$ higher than that of the intermediate. The second step of the isomerization involves the formation of cyclohexadiene carbene. This intermediate, with a relative energy of $61.6 \text{ kcal mol}^{-1}$ to fulvene, is a puckered six-carbon ring with a lone pair of electrons on C-2. Cyclohexadiene carbene is formed via **TS2**, where the C-2—C-6 bond is lengthened from 1.481 \AA in bicyclo[3.1.0]hexa-1,3-diene to 2.200 \AA in **TS5** and later broken in cyclohexadiene carbene. The angle between the fused rings in **TS2** is 116.3° , about 9° smaller than in bicyclo[3.1.0]hexa-1,3-diene, showing that the three-carbon ring is moving back into the plane of the five-carbon ring. This step of the reaction has the highest energy barrier ($74.3 \text{ kcal mol}^{-1}$). The final step of the reaction is a hydrogen migration from C-1 to C-2 to form benzene, which occurs through **TS3** with an energy barrier of $59.0 \text{ kcal mol}^{-1}$.

Our results, obtained by the G2M(rcc,MP2) method, were similar to those obtained by Melius *et al.*⁶ Their highest barrier ($73.2 \text{ kcal mol}^{-1}$) was $1.1 \text{ kcal mol}^{-1}$ lower in energy than the highest barrier we obtained by the G2M method. Therefore, our more sophisticated

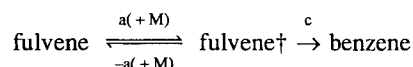
methods of calculation did not find a significantly different activation energy for the isomerization reaction.

RRKM calculations

RRKM calculations were performed on the isomerization mechanism occurring by the lower energy path in order to compare our G2M(rcc,MP2) results with the kinetic parameters gathered through VLPP experiments. The calculations were carried out for two cases, one with the bicyclo[3.1.0]hexa-1,3-diene intermediate:



and the other without the intermediate:



In the above reaction schemes, \ddagger represents vibrational excitation by collision with the third body, M. All relevant equations for RRKM calculations have been derived previously.^{20,21} All parameters used in these calculations are given in Table 2. Energies used were calculated at the G2M(rcc,MP2) level of theory and all frequencies and moments of inertia at B3LYP/6-31G(d). Rate constants for both pathways were calculated over the temperature range $1000\text{--}1200 \text{ K}$ at 760 and 10^{-6} Torr . Figure 3(A) shows an Arrhenius plot of the results at 760 Torr , corresponding to the high-pressure, first-order limit of the reaction. Both the multi-step and single-step mechanisms have the same rate at 760 Torr . The Arrhenius parameters obtained from a linear fit of the plot were $A_\infty = 2.6 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_\infty = 75.1 \text{ kcal mol}^{-1}$. This activation energy is consistent with that calculated by both the BAC-MP4 and G2M(rcc,MP2) methods but is $6\text{--}11 \text{ kcal mol}^{-1}$ higher than the experimental value.⁵ Figure 3(B) shows

Table 2. Molecular and transition state parameters used for RRKM calculations

Species or transition states	E_{rel} (kcal mol ⁻¹)	I_a, I_b, I_c (amu)	ν_1 (cm ⁻¹)	
Fulvene	0.0	220.145	208.6	338.0
		474.900	491.2	643.5
		695.045	676.9	694.5
			781.7	800.9
			804.6	913.5
			925.4	939.2
			958.0	972.3
			1007.9	1116.2
			1118.4	1268.2
			1351.8	1388.5
			1476.5	1553.7
			1638.7	1720.0
			3163.9	3220.0
			3230.4	3245.1
			3248.6	3253.9

Table 2 (continued)

Bicyclo[3.1.0]hexa-1,3-diene	41.3	236.916	266.4	312.6
		392.723	541.7	608.6
		560.069	743.7	770.3
			780.5	826.5
			860.2	924.5
			927.9	1013.6
			1020.6	1054.8
			1090.5	1109.9
			1122.7	1149.3
			1278.9	1354.0
			1438.1	1467.5
			1533.2	1580.9
			3103.5	3184.8
			3200.7	3210.6
			3220.4	3229.3
Benzene	-30.4	317.344	413.2	416.0
		317.344	622.9	623.0
		634.689	691.9	717.4
			862.2	863.1
			966.6	968.4
			1009.2	1020.0
			1070.4	1070.5
			1187.5	1209.8
			1357.6	1387.8
			1532.2	1533.0
			1656.7	1657.1
			3175.1	3184.4
			3185.1	3200.2
			3200.7	3211.1
		TS1	41.6	237.646
399.772	607.1			744.3
572.165	748.2			762.5
	818.8			848.4
	886.5			922.1
	1008.3			1011.4
	1041.8			1089.7
	1110.7			1129.5
	1176.1			1288.4
	1357.3			1454.3
	1463.5			1531.3
	1588.8			3107.8
	3191.6			3206.1
	3223.3			3235.9
	3243.8			
TS2	74.3	293.238	284.9	388.8
		352.391	511.3	570.9
		601.339	686.2	695.0
			765.5	840.3
			879.8	955.8
			973.7	1007.7
			1071.7	1106.8
			1134.6	1165.6
			1236.4	1266.8
			1389.0	1426.9
			1502.3	1553.8
			1656.8	2923.1
			3105.0	3184.1
			3190.3	3212.4
			3221.6	

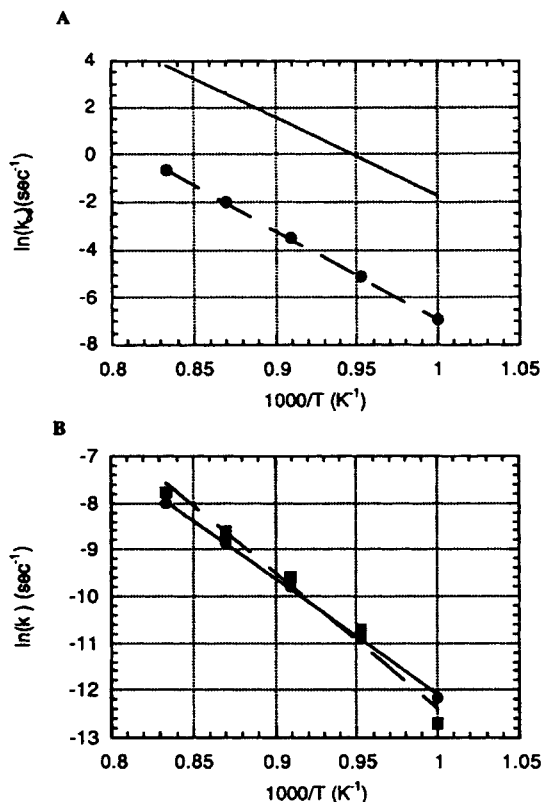


Figure 3. Arrhenius plot of the calculated first-order rate constant for the isomerization of fulvene to benzene at (A) 760 and (B) 10^{-6} Torr. Squares represent the result from the single-step calculation and circles that from the multi-step calculation. The solid line in (A) is a plot of the first-order rate constant given by Gaynor *et al.*⁵

an Arrhenius plot of the results at 10^{-6} Torr. At low pressures, the rates of the two pathways are slightly different. The Arrhenius parameters were $A_0 = 2.7 \times 10^{19} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_0 = 49.3 \text{ kcal mol}^{-1}$ for the multi-step case and $A_0 = 9.5 \times 10^{17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_0 = 57.5 \text{ kcal mol}^{-1}$ for the single-step case. Pressure effects at 1050 and 1150 K were also investigated and the results are shown in Figure 4(A) and (B). As can be seen, both mechanisms have the same reaction rates at high pressures but the multi-step reaction becomes slower than the single step reaction at low pressures.

CONCLUSIONS

From the *ab initio* calculations of the potential energy surface of fulvene to benzene, it was found that the multi-step pathway derived by Melius *et al.*⁶ was the lowest energy pathway to benzene with a barrier of *ca*

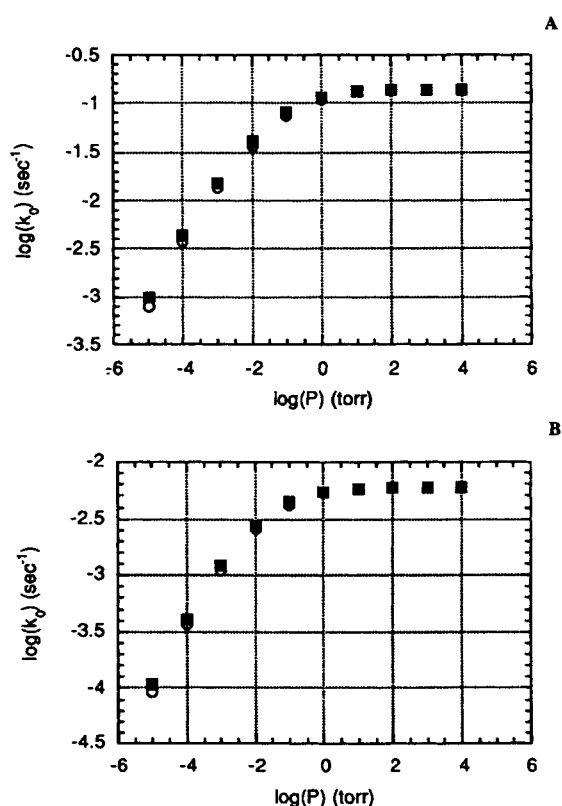


Figure 4. Pressure dependence of reaction rate at (A) 1050 and (B) 1150 K. Squares represent the result from the single-step calculation and circles that from the multi-step calculation

74 kcal mol⁻¹. It was also determined that the prefulvene molecule is a transition state and does not play a role in the isomerization but serves as a transition state for the degenerate benzvalene rearrangement. Two isomerization mechanisms including benzvalene were also studied. A concerted mechanism with direct formation of benzvalene from fulvene via TS4 has a barrier about 40 kcal mol⁻¹ higher than the experimental value and would not be significant in benzene formation. In the second mechanism, benzvalene is formed from fulvene in two steps via the cyclopenta-1,3-dienylcarbene intermediate and the highest barrier is 84.0 kcal mol⁻¹. For the thermal isomerization, this mechanism still cannot compete with the multi-step¹⁸ pathway involving bicyclo[3.1.0]hexa-1,3-diene. However, it was suggested to be important for the photochemical benzene-fulvene isomerization because the S_0 and S_1 surfaces of C_6H_6 cross in the vicinity of prefulvene which isomerizes to fulvene via cyclopenta-1,3-dienylcarbene. RRKM calculations were performed based on the G2M(rcc,MP2) parameters of the multi-step mechanism with the bicyclo[3.1.0]hexa-1,3-diene

intermediate. The reaction was found to have an activation energy of 75 kcal mol⁻¹, which was close to the 0 K barriers determined by G2M(rcc,MP2) and BAC-MP4 methods. This activation energy was 7–11 kcal mol⁻¹ higher than that obtained by Gaynor *et al.*,⁵ using the very low-pressure pyrolysis method with molecular–surface collision as a means of thermal activation. This large discrepancy suggests that the fulvene to benzene isomerization may be sensitive to surface effect, which usually lowers the values of activation energy. More experimental rate measurements need to be carried out on the isomerization reaction under high-pressure conditions so as to minimize the catalytic effect of surfaces. Additionally, more sophisticated multi-reference CI calculations for the critical TS2 might be useful in order to reconcile theory and experiment.

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REFERENCES

1. U. Alkemade and K. H. Homann, *Zeit. Phys. Chem. N. F.* **161**, 19 (1989).
2. M. Frenklach, D. W. Clary, W. C. Gardiner and S. E. Stein, in *Twentieth Symposium (International) on Combustion*, pp. 887–901. Combustion Institute (1984).
3. M. Frenklach, D. W. Clary, W. C. Gardiner and S. E. Stein, in *Twenty-First Symposium (International) on Combustion*, p. 1067. Combustion Institute (1986).
4. J. A. Miller, R. J. Keen and C. W. Westbrook, *Annu. Rev. Phys. Chem.* **41**, 345 (1990).
5. B. J. Gaynor, R. G. Gilbert, K. D. King and P. J. Harman, *Aust. J. Chem.* **34**, 449 (1981).
6. C. F. Melius, J. A. Miller and E. M. Evleth, *Twenty-Fourth Symposium (International) on Combustion*, pp. 621–628. Combustion Institute (1992).
7. J. A. Miller and C. F. Melius, *Combust. Flame* **91**, 21 (1992).
8. S. E. Stein, J. A. Walker, M. M. Suryan and A. Fahr, in *Twenty-Third Symposium (International) on Combustion*, pp. 85–90. Combustion Institute (1990).
9. P. R. Westmoreland, A. M. Dean, J. B. Howard and J. P. Longwell, *J. Phys. Chem.* **93**, 8171 (1989).
10. C. H. Wu and R. D. Kern, *J. Phys. Chem.* **91**, 6291 (1987).
11. I. Jano and Y. Mori, *Chem. Phys. Lett.* **2**, 185 (1968).
12. S. Oikawa, M. Tsuda, Y. Okamura and T. Urabe, *J. Am. Chem. Soc.* **106**, 6751 (1984).
13. I. J. Palmer, I. N. Ragazos, F. Bernardi, M. Oilvucci and M. A. Robb, *J. Am. Chem. Soc.* **115**, 673 (1993).
14. A. M. Mebel, K. Morokuma and M. C. Lin, *J. Chem. Phys.* **103**, 7414 (1995).
15. A. D. Becke, *J. Chem. Phys.* **96**, 2155 (1992); **97**, 9173 (1992); **98**, 5648 (1993).
16. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
17. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, J. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart and J. A. Pople, *Gaussian 92*. Gaussian, Pittsburgh, PA (1992).
18. J. Dreyer and M. Klessinger, *Chem. Eur. J.* **2**, 335 (1996).
19. R. Lindh, T. J. Lee, A. Bernhardsson, B. J. Persson, and G. Karlstrom, *J. Am. Chem. Soc.* **117**, 7186 (1995).
20. R. Liu, K. Morokuma, A. M. Mebel and M. C. Lin, *J. Phys. Chem.* **100**, 9314 (1996).
21. M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.* **94**, 64 (1968).
22. N. C. Baird, *Mol. Phys.* **18**, 39 (1970).