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Isomerization of Chemically Activated Bicyclo[3.1.0]hex-2-ene and Related C_6H_8 Isomers

TIMOTHY L. ROSE, R. J. SEYSE,* and P. M. CRANE†
Department of Chemistry, Texas A&M University, College Station, Texas 77843

Abstract

Singlet methylene was reacted with cyclopentadiene to give chemically activated bicyclo[3.1.0]hex-2-ene (BCH). The rate of isomerization of BCH to 1,4-cyclohexadiene, 1,3-cyclohexadiene, *cis*-1,3,5-hexatriene, and 1-methylcyclopentadiene is compared with calculated rate constants using the RRKM theory and measured or estimated thermal Arrhenius parameters. Subsequent isomerizations of the C_6H_8 products are also measured and calculated. These include 1,4-cyclohexadiene to benzene and the reversible reactions between 1,3-cyclohexadiene, *cis*-1,3,5-hexatriene, and *trans*-1,3,5-hexatriene. The results provide new data for several of these reactions which have not been observed in thermal studies. Agreement between the observed and calculated rates using the strong collision assumption is satisfactory except for the *trans*-1,3,5-hexatriene to *cis*-1,3,5-hexatriene reaction.

Introduction

Bicyclo[3.1.0]hex-2-ene (BCH) is a member of the vinylcyclopropane class of compounds whose thermal isomerization reactions have been studied extensively [1, 2]. The thermal isomerization products of the bicyclic vinylcyclopropanes are the ring expansion products formed by cleavage of the endocyclic cyclopropyl bond. Thus bicyclo[3.1.0]pent-2-ene gives cyclopentadiene [3], BCH gives 1,3- and 1,4-cyclohexadiene [4], and bicyclo[6.1.0]-non-2-ene gives 1,4-cyclononadiene [5]. No products are observed which are attributable to exocyclic bond rupture. The exocyclic pathway is observed, however, with a higher activation energy in the thermal isomerization of saturated bicyclics such as bicyclo[3.1.0]hexane [6] and bicyclo[4.1.0]heptane [7]. Introduction of sufficient excitation energy into BCH is expected to open the exocyclic isomerization pathway. Such reactions have been observed in the photolysis of BCH derivatives in solution [8].

We have produced highly excited BCH by singlet methylene addition to cyclopentadiene. A preliminary paper dealt with the internal versus external cyclopropyl bond rupture pathways for isomerization of the excited BCH [9]. In

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* Present address: Howard County Junior College, Big Spring, Texas 79720.

† Robert A. Welch Foundation Undergraduate Scholarship Recipient.

this paper these mechanisms are discussed in more detail and the observed reaction rates compared with theoretical calculations based on the proposed transition states. We also report on the experimental and calculated rates of the following secondary isomerizations of the products produced from BCH: 1,4-cyclohexadiene to benzene and the interconversion between 1,3-cyclohexadiene, *cis*-1,3,5-hexatriene, and *trans*-1,3,5-hexatriene. A study of these isomerizations initiated by direct photolysis has been reported recently [10].

Experimental

A. *Materials*

Cyclopentadiene was prepared by cracking the commercially obtained dimer. Gas-chromatographic analysis of the cyclopentadiene starting material revealed several low-boiling impurities in the sample; however, they amounted to less than 1% and were virtually unaffected during the irradiation. A more serious problem was the slight impurities of three of the reaction products, BCH, 1-, and 2-methylcyclopentadiene. These impurities were monitored before each irradiation and subtracted from the product yields. If the total percentage of these three was above 1%, the cyclopentadiene was discarded and new material prepared. The cyclopentadiene was stored at dry ice temperatures between runs.

Diazomethane was prepared by the reaction of 60% potassium hydroxide solution with *N*,*N*′-nitrosomethylurea [11]. The diazomethane was stored in the butylphthalate matrix at liquid nitrogen temperatures and warmed up to −35°C in a Freon 113 slush to fill the reaction vessel.

Matheson extra dry grade oxygen (99.6%) was used without further purification. *Cis*- and *trans*-1,3,5-hexatriene, 1,3- and 1,4-cyclohexadiene, and benzene used for calibration of the gas-chromatography columns were obtained commercially. The 1-, 2-, and 5-methylcyclopentadiene isomers were obtained by cracking the methylcyclopentadiene dimer. Bicyclo[3.1.0]hex-2-ene was prepared according to the synthesis of Corey and Dawson [12].

B. *Apparatus*

The experimental apparatus consisted of a vacuum line, photolysis assembly, and gas chromatograph. The vacuum line was a mercury-free greaseless system employing Westeff Teflon stopcocks and reaching an ultimate vacuum $<10^{-4}$ torr. Wallace and Tiernan gauges were used to measure the pressure when filling the reaction vessel. The reaction vessel used for most of the irradiations was a cylindrical tube 2 inches in diameter with a volume of 350 cm^3. Pyrex flats were epoxied with Torrseal (Varian) on the ends of the vessel. Some experiments were also done with a 1 inch diameter 80 cm^3 cell with no significant change in the results. The vessel was attached to a cross in the vacuum line so that it could be filled, the pressure measured, and its contents monitored by the gas chromatograph without removing it from the vacuum line.

The light source was a PEK model 911 system using a 200 W high-pressure mercury lamp. The light was focused by a lens system in the housing and passed through an interference filter for 4358-Å light purchased from Industrial Optics. The filter had 40% transmission and a half-bandwidth of 100 Å. After passing through the cell, the light was monitored by an RCA 910 phototube. The aperture to the phototube was filtered with combined Corning 3-73 and 5-60 filters to block light outside the 4358-Å region. No attempt was made to monitor the absolute light intensity, but the changes in absorption during the irradiation were followed.

C. *Procedure*

The vessel was filled with the appropriate pressures of diazomethane, oxygen, and cyclopentadiene, in that order. For most runs the ratios were 0.7:1:10, respectively. For runs at pressures above 300 torr, C_3F_8 was added as an inert gas. Changes in the oxygen concentration between 7 and 15% and in diazomethane between 5 and 15% did not affect the relative yields of the products.

Five minutes after the vessel was filled and before the irradiation was begun, a small aliquot was removed and analyzed by gaschromatography. Invariably there was a small amount of bicyclo[3.1.0]hex-2-ene and 1- and 2-methylcyclopentadiene observed. These products were normally impurities in the cyclopentadiene, and their amounts were fairly time independent in the absence of the photolysis lamp, especially if the vessel had been seasoned by one run. Corrections were made for these impurities in calculating the final yields.

Irradiations were generally carried out for 3 hours. The relative product yields did not change outside the experimental error for changes in the irradiation period from ½ to 5 hours with the exception of *cis*-1,3,5-hexatriene which decreased slightly with time. As indicated by the percent conversion of cyclopentadiene to C_6H_8 products, the amount of diazomethane photolyzed during a 3-hour irradiation ranged from 3% for the high-pressure samples to nearly complete conversion at the low pressures. After the irradiation an aliquot of the sample was expanded into the evacuated gas sampling value and injected directly into the gas chromatograph.

When oxygen is present in the vessel, a cloudiness appears immediately when the irradiation begins. The photometer shows the expected decrease in transmitted light intensity due to the scattering by the cloudiness. During irradiation at high pressure small droplets collect at the bottom of the vessel. These effects are not observed if either the diazomethane, the oxygen, the cyclopentadiene or the light is absent. The absolute yield of C_6 products in the oxygenated systems is about 30–50% less than in the nonoxygenated systems. Some of this loss is accounted for by the CO and CO_2 yields which have been measured. It is not known whether the rest of the decrease is due to loss of diazomethane or due to the lower light intensity because of the scattering by the fog. The relative product spectrum does not show any changes other than those attributable to triplet scavenging. Since the results presented here are based on relative yields, changes in the absolute yields will not alter the conclusions.

D. *Analysis*

The product spectrum was analyzed with a flame ionization-gas chromatograph. A $\frac{1}{8}$-inch stainless steel tandum column was used consisting of 10 ft of 5% dimethylsulfolane, 10 ft of 30% B,B′-oxydipropionitrile, and 5 ft of 10% SF-96 silicone oil. This column gave good separation of all the C_6 isomers observed as reaction products. The relative retention times from air relative to cyclopentadiene at 35°C were 1.88 (bicyclohex[3.1.0]hex-2-ene), 2.06 (2-methylcyclopentadiene), 2.30 (1-methylcyclopentadiene), 2.58 (1,3-cyclohexadiene), 2.90 (*trans*-1,3,5-hexatriene), 3.28 (*cis*-1,3,5-hexatriene), 3.85 (1,4-cyclohexadiene), and 5.15 (benzene). No attempt was made to analyze for any products having more than six carbon atoms.

There was one product formed in small yields, $<1.5\%$, which was not identified. It had the shortest retention time of any product, 1.73 on the above scale. Other C_6H_8 products which were sought but not found were 5-methylcyclopentadiene and 3-methylenecyclopentane. None of the above had retention times comparable to the unidentified compound. A possibility is 3-vinylcyclobutene, a known photoisomerization product of 1,3-cyclohexadiene [13], although its retention time would be expected to be smaller than is observed. 1,2,4-hexatriene, another known product of 1,3-cyclohexadiene photolysis [10, 14], was not sought. If its yield were $>2\%$, however, it would have been detected, and nothing was observed at its expected retention time [10].

The products were identified by comparison of their retention times with known compounds on at least two columns with different separating properties. By trapping the peaks off of one column and passing it through the other the purity was also confirmed. In addition the infrared spectra of all the products except 1,3- and 1,4-cyclohexadiene were taken and compared with the spectra in the literature. The mass spectra of the two cyclohexadiene isomer products agreed with the published spectra.

The yields of the products were determined either by electronic or disc integration of the chromatographic peaks. The relative sensitivity of the flame ionization detector for cyclopentadiene and all the C_6 products except bicyclo-[3.1.0]hex-2-ene were compared and found equal within the experimental precision.

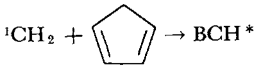
Results

A. *General Mechanism of* $^1CH_2$ + *Cyclopentadiene Reaction*

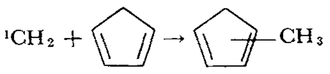
The reactions of $^1CH_2$ with cyclopentadiene have been studied over the range of 10–1400-torr total pressure. The methylene was produced by photolysis of diazomethane at 4358 Å. 10% oxygen was present in the reaction mixture to scavenge the triplet methylene produced. The products formed by the reaction were bicyclo[3.1.0]hex-2-ene (BCH), 1,4-cyclohexadiene (14CH), 1,3-cyclohexadiene (13CH), 1- and 2-methylcyclopentadiene (12MC), *cis*-1,3,5-hexatriene (CHT), *trans*-1,3,5-hexatriene (THT), and benzene (BEN). The ratio of the yields of the two methylcyclopentadiene isomers was 1.0 ± 0.1 over the entire pressure range. Failure to observe 5-methylcyclopentadiene is attributed to its rapid isomerization to the other methylcyclopentadiene isomers which is known to occur at room temperature [15].

The product spectrum can be explained by addition of $^1CH_2$ to the C=C of cyclopentadiene to give BCH*, where the asterisk indicates vibrational excitation, and insertion of $^1CH_2$ into the C—H bonds to give methylcyclopentadiene. Thus

(A)



(B)



The other C_6H_8 products observed arise from isomerization of BCH*. The mechanistic scheme is shown in Figure 1. 13CH and 14CH have been observed in the thermolysis of BCH [4] and are attributed to a mechanism involving endocyclic bond rupture of the BCH*. At the higher internal energies introduced by chemical activation, it has been proposed that BCH* undergoes exocyclic bond rupture to give CHT and 12MC as products [9]. It seems less likely that THT is formed directly from BCH* because of the "*cis*" configuration of BCH. Direct formation of the CHT isomer is possible by a mechanism involving no hydrogen migrations.

In addition to the initial isomerization of BCH*, there are a number of secondary isomerizations occurring in this system. Both 14CH [4, 16] and 13CH

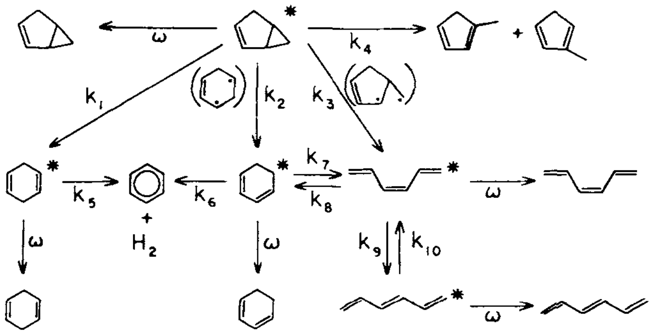


Figure 1. Reaction scheme for isomerization of chemically activated bicyclo[3.1.0]hex-2-ene and its isomerization products.

[4, 17, 18] are known to isomerize to benzene. Finally, there will be an equilibrium between 13CH and CHT [19] and between CHT and THT [18]. Since the activation energies for these secondary isomerizations are lower than those for the BCH* isomerizations, these reactions will play an important role in determining the product spectra. Table I summarizes the Arrhenius parameters which have been measured or estimated for the reactions discussed above.

No product attributable to 1,2,4-hexatriene was observed in our system. Srinivasan [23] attributed this product to reaction by an electronically excited state of 13CH and it therefore would not be expected in our system. More recent photochemical studies [10], however, have indicated that it arises from isomerization of a highly excited ground vibrational state of 13CH. In either case the yield is very small which justifies our exclusion of it in the mechanism.

In Figure 1, ω is the collisional stabilization rate constant which was calculated from the collision number [2, p. 164] estimating 5.5 Å as the diameters of all the hydrocarbons. The resulting valve is 1.28×10^7 torr^{-1}sec^{-1}. If the effect

TABLE I. Arrhenius parameters and experimental and calculated rates in chemically activated system for C_6H_8 isomerizations.

Reaction	T_{mean} (°K)	Arrhenius Parameters[a]		Ref	Chemical Activation	
		log A	E_a(kcal/mole)		$k_{exp} \times 10^{-8}$(sec^{-1})	$k_{calc} \times 10^{-8}$(sec^{-1})[b]
BCH → 14CH (k_1)	600	14.095	50.2	4	5.7 ± 0.2	5.7[c]
BCH → 13CH (k_2)	600	14.28	50.2	4	~ 15	9.7
BCH → CHT (k_3)	600	(14.6)	(57.3)	9	~ 3	3.1
BCH → 12MC (k_4)	600	(14.5)[d]	(54.1)	9	5.8 ± 1.8	5.2
14CH → BEN + H_2 (k_5)	600	12.02	42.7	4	1.6 ± 1.3	1.3[e]
	625	12.36 ± 0.13	43.8 ± 0.4	16		
13CH → BEN + H_2[f]	770	13.67	61.6	18a	not determined	
	735	13.4	59±1	18b		
→ BEN, C_6H_{10}, H_2 (k_6)	665	not first order		17		
13CH → CHT (k_7)	425	(14.4)	(44.7)	this work	~ 200	200
CHT → 13CH (k_8)	425	11.85	29.9	19	≈ 40	37[g]
CHT → THT (k_9)	600	(12.4)	(42.2)	this work	6.6 ± 0.7	4.2[g]
THT → CHT (k_{10})	615	12.65	43.3	18a	5.7 ± 1.1	12

[a] Values in parentheses are estimated using the methods of Benson and O'Neal [20–22].

[b] Transition state frequencies assigned (see Table II and text) to give agreement with A factors.

[c] Value used for normalization to determine the internal energy of BCH* at 107.7 kcal/mole. This was the basic value for $<E^*>$ used in the other calculated rates.

[d] This value has been increased by $10^{0.9}$ from the earlier estimate [9] which did not take into account sufficient loosening of the ring vibrations in the transition state.

[e] Using the E_a and A values of Benson and Shaw [16].

[f] Low-pressure pyrolysis.

[g] Assumed $\Delta H°_{f,298}$ (CHT) = 40.5 kcal/mole (see text).

of 10% oxygen ($\sigma = 3.2$ Å, 0.4 as effective an energy moderator as C_5H_6) and 6% diazomethane ($\sigma = 4.2$ Å) on ω is taken into account, the new value is 1.12×10^7 torr^{-1}sec^{-1}. Considering the approximation of the molecular diameters, however, the accuracy of ω is probably only about ±10%, and we have used a value of $1.2 \pm 0.1 \times 10^7$ torr^{-1}sec^{-1} in the following calculations of both the theoretical and experimental rate constants. The uncertainty in ω is not included in the reported precision of the experimental rates since it will not affect the relative rates or the comparison with the theoretical values.

Extraction of the experimental rate constants from the data has been divided into three sections, (1) isomerization of BCH*, (2) formation of benzene from 14CH and 13CH, and (3) interconversions between 13CH, CHT, and THT.

B. *Experimental Rates of Isomerization of BCH**

Using reactions (A) and (B), the reaction scheme in Figure 1, and the steady-state approximation, the following equation results for the total isomerization rate of BCH:

$$\text{(1)} \qquad \frac{C_6H_8}{\text{BCH}} = \frac{k_B}{k_A} + \frac{k_T}{\omega}\left(\frac{k_B}{k_A} + 1\right)$$

where C_6H_8 is the total C_6 yield minus the BCH yield and k_T is $k_1 + k_2 + k_3 + k_4$ (See Fig. 1). k_T can be obtained, therefore, from the slope and intercept of a plot of 100-BCH/BCH versus the reciprocal of the pressure (Figure 2). The values for decomposition/stabilization for the combined 1- and 2-methylcyclopentadiene yields are also shown in Figure 2. Application of the steady-state approximation to the 12MC formation leads to the equation

$$\text{(2)} \qquad \frac{\text{12MC}}{\text{BCH}} = \frac{k_B}{k_A} + \frac{1}{\omega}\left(k_4 + \frac{k_B k_T}{k_A}\right)$$

It is seen that the intercept from eq. (2) is the same as for eq. (1) as expected, since 12MC are the only C—H insertion products. Least squares analysis of the two plots leads to values for k_T and k_4 of $3.0 \pm 0.2 \times 10^9$ sec^{-1} and $5.8 \pm 1.8 \times 10^8$ sec^{-1}, respectively. The higher value reported for k_4 previously [9] resulted from incorrectly taking into account the contribution from the C—H insertion pathway.

The yield of 1,4-cyclohexadiene depends on its rate of formation from BCH* k_1 and its decomposition to benzene k_5. Use of the steady-state approximation results in an equation from which both of these rate constants can be determined,

$$\text{(3)} \qquad \frac{\text{BCH}}{\text{14CH}} = \frac{\omega}{k_1} + \frac{k_5}{k_1}$$

Figure 3(a) is a plot of the BCH/14CH ratio versus the pressure. The resulting values for the slope and intercept yield rate constants of $k_1 = 5.7 \pm 0.2 \times 10^8$

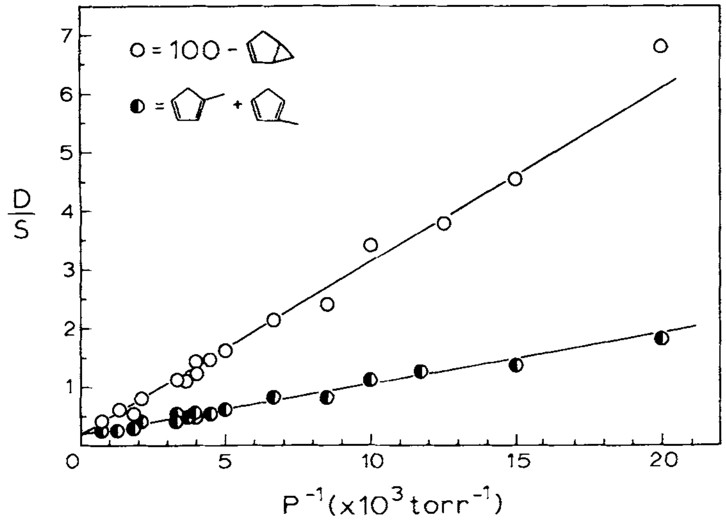


Figure 2. Plots of decomposition/stabilization (*D/S*) ratios vs. the reciprocal of total system pressure for the total isomerization of BCH*(O) and BCH* isomerization to 12MC(◐).

sec^{-1} and $k_5 = 1.6 \pm 1.3 \times 10^8$ sec^{-1}. The rate constant for k_1 is smaller than reported earlier [9], since, as will be shown, most of the benzene does not arise from 14CH as was expected from the thermal pyrolysis studies [4, 16].

Because of secondary isomerization processes k_6–k_{10}, data at pressures substantially above those in our experiments are needed to determine k_2 and k_3 individually. The sum of the rate constants should equal $k_T - (k_1 + k_4) = 1.8 \pm 0.2 \times 10^9$ sec^{-1}. At increasing pressures (300 → 1400 torr) the ratio of 13CH/CHT is increasing very rapidly, and we choose a reasonable value of 5 (see hereafter) for the ratio at infinite pressure. The rate constants are then $k_2 = 1.5 \times 10^9$ sec and $k_3 = 0.3 \times 10^9$ sec, in agreement with the rates reported earlier [9].

C. *Experimental Rates of Formation of Benzene from the Cyclohexadiene Isomers*

The formation of benzene and hydrogen in the pyrolysis of 1,4-cyclohexadiene is a well-behaved unimolecular reaction involving 1,4-hydrogen elimination [4, 16]. Our experimental rate constants of $k_5 = 1.6 \pm 1.3 \times 10^8$ sec^{-1}, calculated above, is too slow to account for all the benzene produced. Moreover, a plot of BEN/14CH versus P^{-1} is not linear and does not pass through zero. To account for these results the formation of benzene from 13CH is included in the mechanism. Benson and Shaw [17] have reported that a chain mechanism is involved in the pyrolysis of 13CH to benzene and that the reaction order is close to $\frac{3}{2}$ in the initial stages. Although a first-order decomposition has been reported [18], the work was done at very low pressures and the measured activation

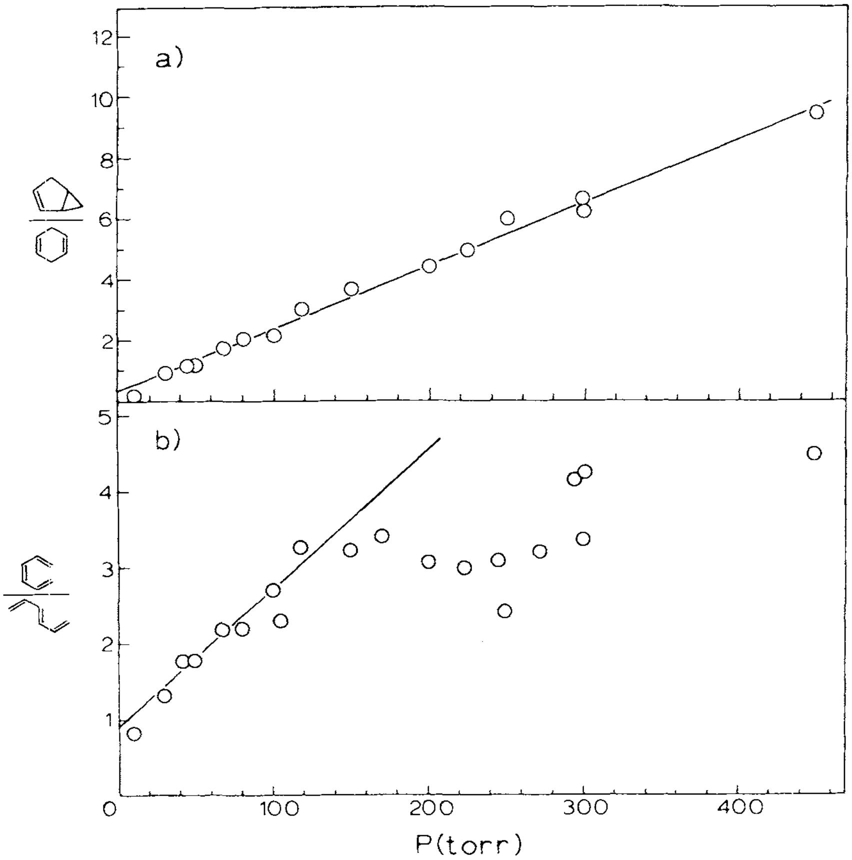


Figure 3. Plots of stabilization/decomposition rates as a function of total system pressure. (a) Ratio of BCH/14CH to determine k_1 and k_5. (b) Ratio of CHT/THT. The line drawn is the least square fit of the data below 150 torr and was used to determine k_9 and k_{10}.

energy (≈ 60 kcal/mole) is too large to expect benzene formation in our system by this pathway.

We can use the value of k_5 to determine the amount of benzene produced from 13CH. The calculated values of BEN4/14CH, where BEN4 is the amount of benzene produced from 14CH, are shown in Figure 4. The remaining benzene yield BEN3, which is attributed to formation from 13CH, can then be plotted as the BEN3/13CH ratio. Despite the large errors it is clear that the ratio does not show a first-order dependence. The data are best fit by using the $\frac{3}{2}$-order rate constant of $11.9 \pm 2.8 \times 10^7$ sec^{-1} torr$^{1/2}$. A reasonable conclusion is that cyclopentadiene is involved in the chain mechanism in a similar manner as 13CH in the pyrolysis system.

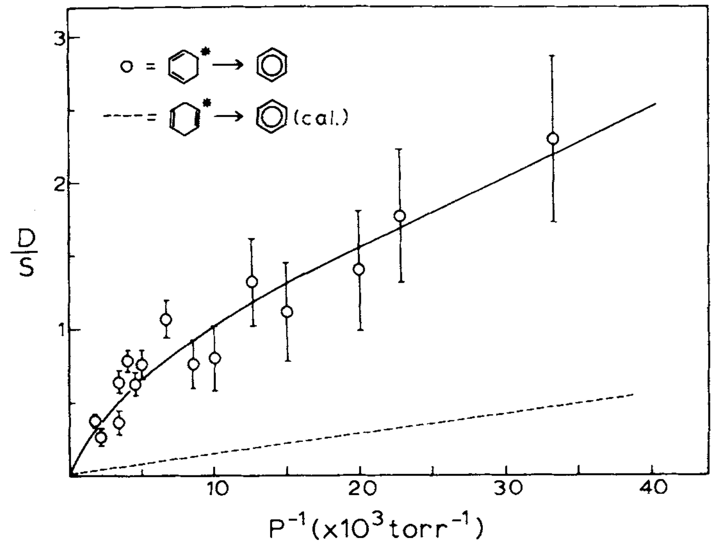


Figure 4. Plot of decomposition/stabilization (D/S) ratio vs. the reciprocal of total system pressure for the estimated yield of benzene resulting from 13CH decomposition. The dashed curve which represents the benzene production from 14CH was calculated using the experimentally obtained rate from Figure 3(a).

D. *Experimental Rates for Interconversion of 1,3-Cyclohexadiene*

Derivation of the expression to obtain k_9 and k_{10} is straightforward as long as the assumption is true that the only path of formation of the THT isomer is from CHT. This assumption requires that at infinite pressure the ratio THT/CHT should be zero. At the highest pressures obtainable in our system, the ratio was about 0.2 and decreasing, indicating that any direct formation of THT from BCH* is very small and will be disregarded in further considerations.

Application of the steady-state formalism leads to the following equation:

$$(4) \qquad \frac{\mathrm{CHT}}{\mathrm{THT}} = \frac{k_{10}}{k_9} + \frac{\omega}{k_9}$$

The plots of the ratio of *cis* to *trans* isomers versus pressure is shown in Figure 3(b). Despite the scatter in the data, it is clear that the CHT/THT ratio is not linear with pressure. The deviations from the dependence expected in eq. (4) may be due to the direct formation of THT mentioned above, or to the thermal and/or photochemical instability of CHT mentioned in the experimental section. The low-pressure data are used to calculate the values for k_9 and k_{10} since they give a reasonable intercept of about one, whereas inclusion of the higher pressure data raised the intercept to 2–3. A linear extrapolation of the points below 150 torr gives rates for k_9 and k_{10} of $6.6 \pm 0.7 \times 10^8$ sec^{-1} and $5.7 \pm 1.1 \times 10^8$ sec^{-1}, respectively.

The complete rate expression for the ratio of 13CH to CHT is

$$\frac{\text{13CH}}{\text{CHT}} = \frac{k_2(\omega + k_8 + k_9)(\omega + k_{10}) + k_3k_8(\omega + k_{10}) - k_2k_{10}k_9}{(\omega + k_{10})(k_3(\omega + k_6 + k_7) + k_2k_7)} \tag{5}$$

which is entirely untractable at intermediate pressure ranges where all terms must be taken into account. If we assume (1) that at low pressures terms with ω^2 and k_6 can be neglected and (2) k_3 is considerably smaller than k_2, then the RHS of eq. (5) can be simplified to give

$$\frac{\text{13CH}}{\text{CHT}} \approx \frac{k_8}{k_7} + \frac{\omega k_2(k_9 + k_{10})}{k_7[(\omega + k_{10})(k_2 + k_3)]} \tag{6}$$

The intercept of the data at zero pressure, therefore, will give the ratio of k_8/k_7. Our experimental ratio, extrapolated to zero pressure, is 0.21 ± 0.02 so that k_7 is about five times faster than k_8. Although an exact determination of k_7 and k_8 is not possible from this treatment, some idea of the magnitude of these rates can be obtained. If the values of $k_2/k_3 = 5$ and ω at 100 torr are used in eq. (5), the value obtained for $k_7 \approx 30 \times 10^9$ sec^{-1}, which is an upper limit because of the assumptions made above. Even with its large uncertainty, it is clear that the magnitude of k_7 is very large as expected from its Arrhenius parameters (see Table I). The result indicates why the observed yields of CHT are so large, even though the rate of formation from BCH* is probably quite small.

Table I lists the derived experimental rates from k_1 to k_{10}. The only reported values to which our high-energy isomerizations can be compared are those reported for k_7–k_{10} by Orchard [10] based on photochemical results. The rates were determined by RRKM calculations fitted to photochemical data. At an excitation energy of THT of 106 kcal/mole, his rates are about twenty times smaller than ours. However, the ratios of rates in the two studies are within experimental error. The difference in absolute values is attributed to use of a cascade quenching model in the photochemical work, whereas we have assumed a strong collision model. The poorest agreement is between the k_9/k_{10} ratios and probably reflects the experimental problems mentioned previously. (See also RRKM calculation of k_{10} discussed below). It is interesting to note that Orchard's results also showed the greatest internal inconsistency for the THT isomer [10].

We now wish to compare our experimental rates with those calculated by the RRKM theory using transition states which give agreement with the Arrhenius parameters taken from pyrolysis studies or estimated by thermochemical kinetic methods (see Table I). This method of comparison has been successfully used in other chemically activated hydrocarbon systems [24].

Theoretical Rate Calculations

The theoretical rate constants were calculated based on the RRKM formalism using the following equation [2, p. 75]:

$$k_a(E^*) = L^{+} \frac{Q_1^{+}}{Q_1^{*}} \frac{\Sigma P(E_{vr}^{+})}{hN^*(E^*)} \tag{7}$$

where L^+ is the reaction path degeneracy and Q_1^+/Q_1^* the ratio of the partition functions for the adiabatic rotations in the activated complex (A^+) and the chemically activated molecule (A^*), respectively. $\Sigma P(E_{vr}^+)$ is the sum quantum states of A^+ at all energies up to and including E^+, the total nonfixed energy in the active degree of freedom of the activated complex. $N^*(E^*)$ is the density of quantum states of A^* at energy E^*. For these calculations it is assumed that the energy spread in E^* can be neglected. Evaluation of the sum and density of states was done using the approximation of Hoare and Ruijgrok [25].

An estimation of the average internal excitation of BCH* was made using the following equation:

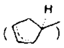
$$-\langle E^* \rangle = \Delta H_{r,298} - E^*(CH_2) + RT - (E_T - E_0)_{vib} \tag{8}$$

where $\Delta H_{r,298}$ is the heat of reaction in eq. (A), $E^*(CH_2)$ the excess energy carried by methylene, and $(E_T - E_0)$ is the vibrational energy difference for the BCH molecule at 298 and 0°K. The RT term arises from the conversion of enthalpy to energy and inclusion of the overall stoichiometry change in the reaction from two to one moles. From the previous work of Taylor and Simmons [26,27] the value for $\Delta H^\circ_{f,0}(CH_2) + E^*(CH_2)$ was taken as 112.6 kcal/mole and reduced to 112.5 kcal/mole at 298°K. $\Delta H^\circ_{f,298}(C_5H_6)$ and $\Delta H^\circ_{f,298}$(BCH) were taken as 31.8 [28] and 37.6 [21] kcal/mole, respectively. Finally from the estimated frequencies for BCH (Table II), the last term in eq. (8) is 1.0 kcal/mole. The resulting value of $\langle E^* \rangle$ is 107.1 kcal/mole with an estimated precision of ± 2–3 kcal/mole. As will be seen this agrees very well with the value of 107.7 kcal/mole arrived at from the RRKM calculation for isomerization of BCH* to 14CH. This latter value will be used in the RRKM calculations since it gives the best fit to the experimental rate and is well within the estimated precision for the $\langle E^* \rangle$ value calculated above from thermodynamic considerations.

A. *Isomerization of BCH**

Since the thermal Arrhenius parameters for k_1 and the experimental determination of that rate were most straightforward, the isomerization of BCH* to 14CH was chosen as the normalizing reaction. The frequencies of the BCH molecule given in Table II were estimated from group frequencies [20, 22] and from assigned frequencies from the cyclopentene [29], cyclohexene [30], and cyclopentadiene [31] molecules. Selection of the frequencies for the transition state leading to 14CH were guided by the calculations of O'Neal and Benson [21] for

TABLE II. Vibrational parameters for bicyclo[3.1.0]hex-2-ene and the activated complexes leading to the C_6H_8 isomers.

Motion	BCH Molecule	14CH complex (H)	CHT complex ()	1MCP complex ()
stretches				
C-H	3000(8)	3000(8)	3000(8)	3000(8)
C=C	1625	1300	1625	1300
C-C	1000(6)	1300, 1000(4), 550	1300, 1000(3), 675, 350	1300, 1000(4), 700
bends				
CH_2(def)	1425(2)	1425(2)	1425(2)	1425(2)
CH_2(rock)	1325(2)	1325(2)	1325, 1150	1325(2)
C=C-H C-C-H in plane	1300(4)	1300, 800(3)	1200(4)	1200(3), r.c.
CH_2(twist)	1200(2)	1200, r.c.	1200, 1000	1200(2)
C=C-H C-C-H out plane	900(4)	900, 800(3)	800(4)	900, 800(3)
CH_2(wag)	900(2)	900(2)	900(2)	900(2)
ring def.				
C-C in plane	550(5)	550(5)[a]	550, 400, 225(2), r.c.	550(2), 400, 225(2)
$\log_{10}$ A(600°K)		14.1[a]	14.6	14.5

[a] Lowering one of these ring deformations to 325 cm^{-1} raises the A factor to $10^{14.28}$ as observed for formation of 13CH in the pyrolysis of BCH.

this reaction and adjusted to give the experimental thermal A factor. The ratio of the partition functions for the adiabatic rotations is assumed to be 1 and the reaction path degeneracy is 1. Varying the energy of BCH* with the activation energy fixed at the pyrolysis value of 50.2 kcal/mole gave agreement between the experimental and calculated rates at a value of $\langle E^* \rangle = 107.7$ kcal/mole.

The calculated rates of isomerization of BCH* to the other C_6H_8 isomers as a function of activation energy are shown in Figure 5. The value of $\langle E^* \rangle$ has been fixed at 107.7 kcal/mole. The frequencies of the activated complexes are given in Table II and have been selected to agree with observed or estimated thermal A factors. As with 14CH, we have used values of 1 for both Q_1^+/Q_1^* and the reaction path degeneracy.

The calculated rates of formation of 1MC and CHT are in good agreement with the experimental rates at the expected activation energies. For 13CH, however, the calculated rate constant at the thermal activation energy of 50.2 kcal/mole is only two thirds of our experimental value. It appears therefore that the thermal E_a may be a little high or the A factor low, although our calculated and observed rate differences were probably not outside the combined uncertainties of the values.

B. *Formation of Benzene from 1,4-Cyclohexadiene*

The elimination of hydrogen from 14CH has been confirmed as a 1,4 elimination reaction in agreement with the Woodward–Hoffmann rules. There are three

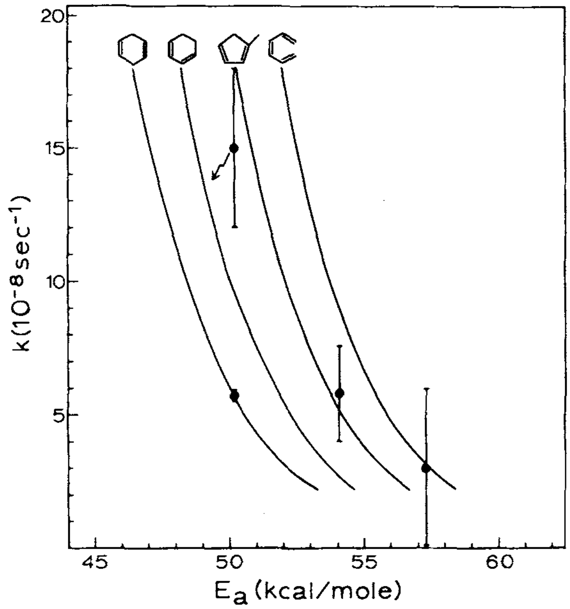


Figure 5. Results of RRKM calculations of the isomerization rates of BCH* to the four C_6H_8 isomers as a function of activation energy E_a. The frequencies of the transition states are given in Table II and the internal of energy of BCH is taken as 107.7 kcal/mole. The experimental rates are plotted at the observed or estimated activation energies for the isomerization (see Table I).

reported values for the Arrhenius parameters [4, 16, 32] with *A* factor ranges from $10^{11.96}$ to $10^{12.36}$ and activation energies from 42.5 to 43.8 kcal/mole. It was hoped that the present results might help pin down these ranges. Unfortunately, our experimental rate has a very appreciable error. Nonetheless, a RRKM calculation was carried out using the reported infrared frequencies for 14CH [33]. The *A* factor for the reaction indicates that the transition state is quite tight with $\Delta S^{+} \approx -5$ or -6 e.u. [16]. Most of the loss in entropy is attributed to the stiffening of the ring vibrations, especially the low-frequency pucker at 108 cm^{-1} [33b]. For our calculations the three lowest ring vibrations were raised to 550 cm^{-1}, the standard tight ring vibration [22]. The other changes we attributed to the CH_2 deformations. Four of them were changed to typical C—C—H bonds, two at 1150 cm^{-1} and two at 830 cm^{-1}. Of the remaining four, one was removed as the reaction coordinate and the other three taken to be equal and adjusted to give the observed *A* factor of Benson and Shaw. The three frequencies were given the value of 1600 cm^{-1}, which can be considered as the equivalent entropy contribution for two C—C···H bends and an H···H stretching. No account was taken of any change in the rotation partition functions since neither the sophistication of the calculation nor the precision of the data seemed to warrant it. The excitation energy of the 14CH* was set at 119 kcal/mole, which is the value of $\langle E^* \rangle$ for BCH* plus the differences in enthalpy of the two C_6H_8 molecules.

The resulting rate from the calculation using the activation energy of 43.8 kcal/mole [16] was 1.3×10^8 sec^{-1} in very satisfactory agreement with the experimental rate of $1.8 \pm 1.6 \times 10^8$ sec^{-1}. The effect of changes in the Arrhenius parameter was tested by increasing the three ring vibrations to 750 cm^{-1}. With the A value now reduced to $10^{12.03}$ and the activation energy lowered to 42.7 kcal/mole [4], the resulting rate was 0.8×10^8 sec^{-1}. This result is farther from our experimental value, and the still lower A factor and activation energy of Swinehart would be even less satisfactory. We favor, therefore, the values of Benson and Shaw.

C. *Isomerization of 1,3-Cyclohexadiene and Cis-1,3,5-Hexatriene*

Because of the difficulty in obtaining the experimental rates in the interconversion of 13CH, CHT, and THT, the calculated rates are particularly helpful in understanding the resulting product spectrum. The thermal ring closing of CHT to 13CH has been studied by Lewis and Steiner [19]. The very low activation energy for the process makes the reaction very rapid at moderate temperatures. The reverse reaction can be estimated from the ring closing activation energy and the differences in the $\Delta H^\circ_{f,425}$ for CHT and 13CH, taken as 1.1 kcal/mole [20, 35]. It should be pointed out, however, that some recent work has indicated that $\Delta H^\circ_{f,298}$(CHT) is about 2.5 kcal/mole higher than the *trans* isomer [10, 18, 36].

The fundamental vibrations assigned from the Ramen and infrared spectra of 13CH [37] and CHT [38] have been used with some modification of the latter. The skeletal bends reported by Lippincott and Kenney [38] at 243 cm^{-1} and 264 cm^{-1} have been deleted leaving skeletal bends at 479, 393, 357, 331, and 167 cm^{-1}. The remaining two vibrations are assigned as hindered rotations and presumably would appear at frequencies below the measured range.

The moments of inertia were calculated assuming that CHT has the same band lengths at THT [39]. The resulting reduced moments for the internal rotations were 18.2×10^{-40} g·cm^2/molec. For the excited molecule the rotors were considered free and the entropy contribution calculated using Benson's tables [20]. The product of the principal moments of inertia was 1.82×10^{-113} g^3·cm^6/molec for CHT compared with 3.88×10^{-113} g^3·cm^6/molec for 13CH [40].

The transition state for the isomerization is assumed to be nonplanar [19] and to have frequencies close to that of 13CH. The ring opening reaction coordinate is assigned to the low out-of-plane bending frequency of 13CH at 201 cm^{-1}. For the ring closing reaction, the reaction coordinate is the movement of the coupled internal rotations. The transition state has the low-frequency C—C stretch of 13CH at 850 cm^{-1} lowered to 675 ($C \overset{\cdot}{—} C$). The frequencies of the skeletal bends are adjusted to give the experimentally observed A factor for the ring closing. The resulting frequencies, 4 at 240 cm^{-1} and 1 at 150 cm^{-1}, correspond to values of roughly half the ring bending vibrations of 13CH as is expected for a loosened ring system. $\langle E^* \rangle$ for CHT is about 105 kcal/mole and for 13CH about 119.5 kcal/mole.

The results of the RRKM calculations are shown in Figure 6. The rate is plotted as a function of internal energy of the activated molecule. At the expected internal energies the calculated rate of 13CH → CHT is about 20×10^9 sec^{-1} and for CHT → 13CH about 3.7×10^9 sec^{-1}. The ratio of the rates, 5.4:1, is in fairly good agreement with the experimental ratio and the absolute magnitudes, particularly ½ for the ring opening, is extremely fast as was suggested by the experimental results.

The effect of the $\Delta H°_{f,298}$(CHT) can also be seen. The higher value has only a slight effect on the ring closing reaction due to a decrease in the internal energy of CHT*. The effect on the ring opening rate, however, is more pronounced since the activation energy would be increased by 1.5 kcal/mole. The resulting rate would be reduced to about 14×10^9 sec^{-1} giving a ratio of 3.8:1 which is slightly smaller than the experimental values. These two calculations bracket the experimental value and neither is outside the experimental uncertainty. It should be pointed out in anticipation of the following calculation, however, that for these secondary isomerizations the internal energies of the activated molecules

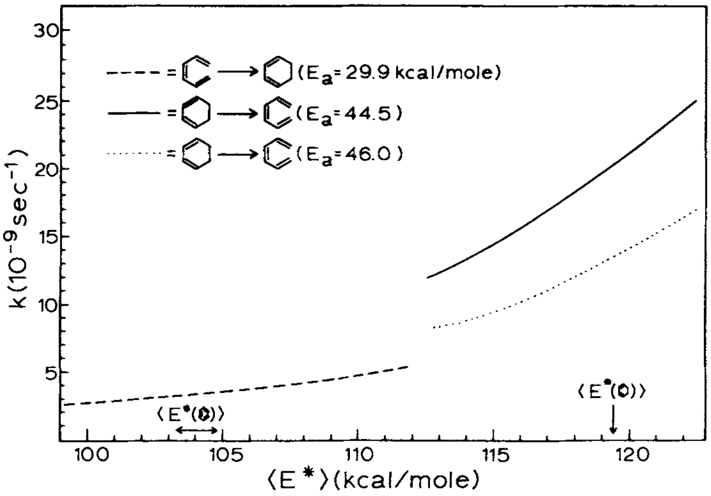


Figure 6. Results of RRKM calculations of k_7 and k_8 for the 13CH $\underset{k_8}{\overset{k_7}{\rightleftharpoons}}$ CHT isomerization as a function of internal energy. The experimental rates are $k_7 \approx 20 \times 10^9$ sec^{-1} and $k_8 \approx 4 \times 10^9$ sec^{-1}. The range in $\langle E^*$(⌬)$\rangle$ and the two E_a values for k_7 are the result of the uncertainty in $\Delta H_f°$ (CHT).

thus far considered are evidently in the right range and have not been degraded significantly by collisions.

D. *Geometric Isomerization of 1,3,5-Hexatriene*

The Arrhenius parameters for thermal isomerization of THT to CHT has been reported recently by Orchard and Thrush [18a]. The activation energy for the reverse reaction will be lower by the difference in the heats of formation of the two isomers at the isomerization temperature of 600°K. As mentioned above, there is some question concerning the value of this difference, but from the 13CH results we prefer the smaller value of 1.1 kcal/mole.

The frequency assignment for the CHT isomer has already been discussed. For the THT isomer, the frequencies of Lippincott and Kenney were used, except that the out-of-plane CH torsion was lowered from 758 to 589 cm^{-1} and a skeletal bend at 157 cm^{-1} was used on the basis of Traetteberg's work [41]. The remaining two out-of-plane skeletal bends were taken as the internal rotations with a moment of inertia of 16.6×10^{-40} $\mathrm{g \cdot cm^2/molec}$ calculated from the geometry of the *trans* molecule [39]. The product of the principal moments of inertia is 1.38×10^{-113} $\mathrm{g^3 \cdot cm^6/molec}$.

For the THT → CHT isomerization the skeletal frequency at 157 cm^{-1} was assigned as the reaction coordinate. The torsional frequencies at 658 cm^{-1} and 589 cm^{-1} were halved to 310 cm^{-1} for the expected $3e^-$ torsions in the transition state. The $3e^-$ torsions resulting from the tightening of the hindered rotors were assigned values of 160 cm^{-1} to obtain the experimental A factor when combined with the reaction path degeneracy of 2. With these frequencies for the transition state, the resulting A factor at 600°K for the CHT → THT reaction is $10^{12.4}$, slightly less than $10^{12.6}$ for the reverse reaction.

The results of the RRKM calculations for the CHT and THT conversion rates are shown in Figure 7. The rates are plotted as a function of internal energy. At the expected $\langle E^* \rangle$ value for CHT, the calculated rate is 4.2×10^8 sec^{-1} which is slightly lower than the experimental rate of $6.6 \pm 0.6 \times 10^8$ sec^{-1}. The values for the THT → CHT isomerization at the expected internal energy of 105.9 kcal/mole is over a factor of 2 too high compared with the experimental rate. It is difficult to see how any changes in the transition state frequencies which would be consistent with the thermal A factor could lower the rate significantly, indicating that the average internal energy may be in error. Agreement between the observed and calculated experimental rates is obtained at an internal energy of about 98 kcal/mole. Some of the THT energy may have been degraded by collisions, a reasonable hypothesis since this product is the last of a series of unimolecular isomerizations.

The assignment of the lowest bending mode in the CHT molecule has a decided effect on the A factor and the rate of the CHT → THT reaction. If the lowest frequency is raised from 167 cm^{-1} to 264 cm^{-1} on the grounds that the

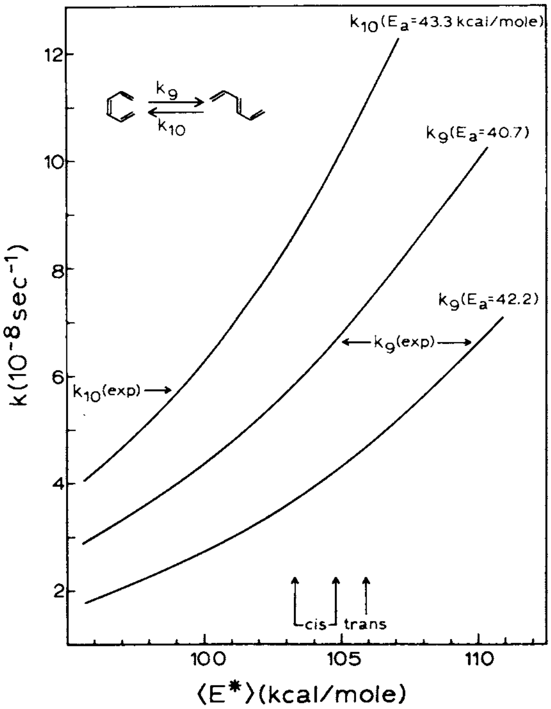


Figure 7. Results of RRKM calculation for CHT ⇄ THT isomerization as a function of internal energy. As in Figure 6 the range in ⟨E^*⟩ for CHT and in the activation energy for k_9 is a result of the uncertainty in $\Delta H_f°$ (CHT).

torsional frequency of *cis* isomers is generally about 100 cm^{-1} greater than that of the *trans* isomer [20], then the A factors for the geometric isomerization are equal and the rate for CHT → THT increases to about 8×10^8 sec^{-1}. While the agreement is as good as with the 167 cm^{-1} vibration, use of the 264-cm^{-1} frequency in the 13CH → CHT reaction discussed earlier leads to a rate constant for k_7 of 12×10^9 sec^{-1} and a ratio of 3.2:1, which is unacceptably far from the measured ratio of 4.7:1. The reported results, therefore, use 167 cm^{-1} as the torsional frequency of central double bond in the CHT molecule.

Discussion

The reaction of singlet methylene with cyclopentadiene to give highly excited bicyclo[3.1.0]hex-2-ene begins a series of unimolecular isomerizations complicated by consecutive and reversible processes. We have used a combination of the experimental rates, Arrhenius parameters obtained from pyrolysis data and thermochemical estimates, and the RRKM formalism to develop a consistent kinetic mechanism for the C_6H_8 system. The results have pointed out some of the strengths and weaknesses of the chemical activation method.

As was reported earlier [9], the high-energy isomerization of BCH results in two products, 12MC and CHT, which were not observed in the pyrolysis of BCH. Both of these products presumedly arise by exocyclic bond rupture of the cyclopropyl ring of BCH and are reactions with higher activation energies than the endocyclic mechanisms leading to 13CH and 14CH. Although the experimental rate of formation of CHT k_3 was not explicitly determined, the estimated rate of 3×10^8 sec^{-1} is in good agreement with the calculated rate using the RRKM theory and the previously estimated Arrhenius parameters [9]. On the other hand, the RRKM calculations for the rate of formation of 13CH indicated that the experimental rate should be reduced from 1.5 to 1.0×10^{-8} sec^{-1}. The concomitant increase in k_3 to 8×10^{-8} sec^{-1} would imply that the activation energy for k_3 be reduced from 57.3 to 54.5 kcal/mole (see Fig. 5). The resulting ratio for k_3/k_2 of 1.25 would not give as good an agreement with the experimental ratio of 13CH/CHT, but is probably within the reasonable limits.

Any CHT formed in the pyrolysis system would be immediately converted to 13CH, so that the thermal Arrhenius parameters for 13CH could be the result of the two reactions. With the lower value of the activation energy for the formation of CHT, the ratio of 13CH to CHT formed at the highest pyrolysis temperature is 15 : 1. Calculation of a new set of Arrhenius parameters for 13CH after subtracting out the contribution to the yield from the CHT pathway yields values of $A = 10^{14.17}$ and $E_a = 49.9$ kcal/mole. The changes in the values from those reported are slight but in the direction of a priori estimates which would predict the A factors for 14CH and 13CH to be very similar [21] and the 13CH isomer having a lower activation energy [4]. Indeed, at the higher energies of our experiment, the experimental ratio of k_2/k_1 seems to be higher than the 1.5 value reported over the whole temperature range of the pyrolysis experiment.

The formation of methylcyclopentadiene from BCH* in our system is more difficult to rationalize with the pyrolysis results. Using our new Arrhenius parameters for 12MC, this product would account for about 4% of the decomposition of BCH at the pyrolysis temperatures. Since the yield is divided equally between the 1- and 2-methylcyclopentadiene isomers, it is possible that these small qualities were not noticed as stated in [4]. If the isomerization rate of BCH is corrected for the formation of 12MC, the Arrhenius parameters for the isomerization to the cyclohexadiene isomers become $A = 10^{14.41}$ and $E_a = 50.0$ kcal/mole, changes which are well within the error limits of the published pyrolysis work.

It was pointed out in the results section that the excitation energy of BCH* calculated from thermodynamic data agreed quite well with the value obtained from the RRKM calculation for 14CH. If, however, the Arrhenius parameters for 14CH are corrected to take care of 12MC production as discussed in the preceding paragraph, the activation energy would be lowered by 0.2 kcal/mole and the A factor reduced by $10^{0.1}$ with the effect on the RRKM calculations of raising the $\langle E^* \rangle$ value for BCH* $\rightarrow$ 14CH to about 109 kcal/mole. If it is assumed that the heats of formation of the compounds used in eq. (8) are correct, then this higher energy value is attributable to more energy being brought into the activated complex by the methylene, a reasonable conclusion since conjugated double bond systems have shown a higher reactivity toward methylene than alkane or alkene systems [42, 43].

The formation of benzene in the chemically activated BCH system could not be explained simply on the basis of decomposition of 14CH as was the case for the pyrolysis system. 13CH is known to thermally decompose to benzene by a complex radical mechanism [17]. The major experimental observations supporting this mechanism were the nonequal yields of hydrogen and benzene, formation of cyclohexene, and yield dependence on NO radical scavenging. Although it was stated in the results section that the decomposition versus stabilization plot (see Fig. 4) was not linear as expected from the thermal studies, no product analogous to cyclohexene was observed even in the unscavenged systems. Unfortunately the hydrogen yield was not measured in our analyses.

It is interesting to note that photochemical studies of 13CH have shown that the excited molecule decomposes to give benzene and hydrogen in equal yields [10, 23]. The postulated mechanism for the reaction, which has recently been questioned [44], is internal conversion from the excited singlet state formed in the photolysis. The resulting high vibrational level of the singlet ground state then decomposes. The excitation energy of this excited state is expected to be on the order of 100–120 kcal/mole, the same range as produced in our system. It is quite possible, therefore, that both a unimolecular process and the more complex radical mechanism is operative in our system, the latter being more important at the higher pressures.

If the data in Figure 4 between 100 and 30 torr are assumed to be linear, a rate of 6×10^8 sec^{-1} is obtained for the unimolecular decomposition of 13CH to benzene. This rate would be a factor of 3 faster than that for benzene formation from 14CH. Direct concerted 1,4 elimination of H_2 from 14CH is allowed by the Woodward-Hoffmann rules [45], whereas loss of the *cis*-hydrogens is forbidden from the ground state of 13CH. Orchard and Thrush's unimolecular isomerization of 13CH to benzene through BCH [18] has too high an activation energy to be a significant process in our system. The fast unimolecular rate of benzene formation from 13CH, therefore, would be most consistent with decomposition of an electronically excited state which may be a triplet state [44]. While this is an interesting conclusion, the fact that no electronic excitation as a result of methylene reactions has been reported, mediates against it.[1] Additional work on the product analysis, effect of triplet quenchers, and yields in the low-pressure region may answer the questions concerning benzene production from 13CH.

The ring closing reaction of CHT to 13CH has been analyzed previously in some detail [19]. The reverse reaction has not been observed thermally. Our

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[1] See, however, Izania and coworkers [46] for a discussion of electronic excitation from recoil tritium reactions.

estimated Arrhenius parameters and RRKM calculation give a rate which is consistent with the experimental data, although k_7 could not be explicitly derived from the data. The very high rates for k_7 and k_8 point out an important aspect of chemical activation work which must be kept in mind for complex systems. At the high energies involved, reversible reactions become important which can be neglected at lower thermal temperatures. For example, a plot of 13CH/BCH versus P^{-1} gives a straight line corresponding to a rate for k_2 of 5×10^8 sec^{-1}. A similar plot for CHT is also linear leading to a rate for k_3 of 1.3×10^9 sec^{-1} and a ratio of k_2/k_3 of 0.38. As was seen in the results section, however, the actual ratio of k_2/k_3 is on the order of 3–5. Thus the same high energy which has permitted us to observe new channels of BCH isomerization has also introduced several complicating reactions and made it impossible to completely sort out the rate constants from data taken at reasonably accessible pressures.

The biggest discrepancy between the theoretical rate and the experimental value was for the THT → CHT reaction. Since the Arrhenius parameters and frequencies of THT were available, the RRKM model should give good results. The only way of resolving the differences in rates is to lower the excitation energy of the THT isomer. The implication, therefore, is that for this last product in a series of reversible, consecutive reactions there has been a lowering of the average energy by deactivating collisions. The energy loss of about 6 kcal/mole agrees very well with the average energy loss in collisions of C_6H_8 isomers derived from the photochemical study [10]. This substantial change in the internal energy shows the limit to the number of consecutive reactions initiated by a single chemical activation reaction which can be analyzed by the simple strong collision assumption.

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