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Kinetics of the Thermal Isomerizations of Gaseous Cycloheptene and Cyclooctene

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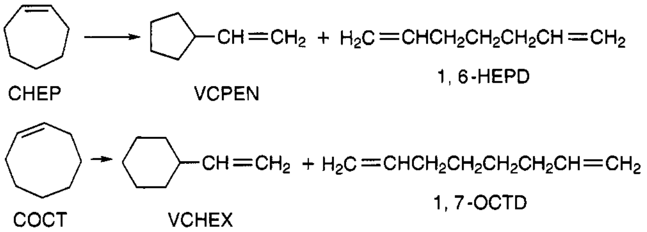
Single-pulse shock tube kinetic studies of the thermal isomerizations of gaseous cycloheptene (CHEP) and *cis*-cyclooctene (COCT), and static reactor isomerizations of COCT at lower temperatures, have revealed a mechanistic dissimilarity in the two superficially analogous cycloalkene to, α,ω-alkadiene reactions observed. At 1035−1256 K, CHEP produced mostly vinylcyclopentane, $\log_{10}(k,\mathrm{s}^{-1}) = 15.1\ (\pm\ 0.7) - 69.7\ (\pm\ 3.3) \times 10^3/4.576T$, and some 1,6-heptadiene. From COCT, heated over the range 610−1091 K, the dominant product was 1,7-octadiene, $\log_{10}(k,\ \mathrm{s}^{-1}) = 13.8\ (\pm\ 0.2) - 54.6\ (\pm\ 0.5) \times 10^3/4.576T$, with small amounts of vinylcyclohexane formed at the higher temperatures, $\log_{10}(k,\ \mathrm{s}^{-1}) = 15.2\ (\pm\ 0.3) - 64.4\ (\pm\ 1.2) \times 10^3/4.576T$. The activation energy for the COCT isomerization to 1,7-octadiene is too low to associate with formation of a diradical, but is consistent with a concerted retro-ene mechanism. The higher activation energy isomerization to vinylcyclohexane, however, passes through a diradical transition structure. In contrast, the structure of CHEP is not adaptable to a concerted retro-ene process, and both 1,6-heptadiene and vinylcyclopentane are formed through diradical-mediated reactions.

Introduction

We have been interested in the reaction rates and mechanisms of thermal isomerizations of small gaseous hydrocarbons and in the relationships between molecular structure, thermochemical barriers, and reaction mechanisms. This interest has led to studies of the interconversions of a homologous series of cycloalkenes and their related vinylcycloalkanes and linear dienes. In this report, we present the results of kinetic work on the thermal isomerizations of cycloheptene (CHEP) and *cis*-cyclooctene (COCT), two similar appearing cycloalkenes which nonetheless do not always isomerize to similar products through similar mechanistic pathways.



There have been previous thermal studies of CHEP and COCT. Crandall and Watkins[1] determined the pyrolysis products of some medium-ring olefins at relatively high temperatures, including CHEP at 800 °C and COCT at 720 °C. From CHEP were formed 55% vinylcyclopentane (VCPEN) and 14% 1,6-heptadiene (1,6-HEPD), while the pyrolysis of COCT gave 78% 1,7-octadiene (1,7-OCTD) and 14% vinylcyclohexane (VCHEX).

Brown et al.[2] studied the rates of the primary processes involved in the pyrolysis of VCPEN and VCHEX at 900−1223 K using the technique of very low-pressure pyrolysis (VLPP). Under these conditions the major primary products were the C-7 and C-8 linear dienes, 1,6-HEPD and 1,7-OCTD; the presumed mechanism involved the formation of diradicals by cleaving the C(1)−C(2) bond of the cycloalkane rings. No CHEP or COCT was detected in their study. Their reported activation energy values for the depletion of VCPEN and VCHEX were 72.6 and 73.8 kcal/mol, respectively. These are 12.2−12.4 kcal/mol lower than activation energies for the thermal decompositions of unsubstituted cyclopentane and cyclohexane,[3] a difference corresponding to the allylic resonance energy.

Doering et al.[4] reported studies of the thermal isomerization of *trans*-cyclooctene to the *cis*-isomer and 1,7-OCTD at 573−643 K and of *cis*-cyclooctene to 1,7-OCTD and VCHEX at 906−1070 K; they proposed the formation of a diradical intermediate in each of these isomerizations. No study of the kinetics of the isomerization of CHEP to VCPEN has been reported.

Experimental Section

The high-temperature runs were carried out in a 2.54-cm-diameter glass single-pulse shock tube, and the lower temperature runs were carried out in a static reactor consisting of a 100-cm^3 glass cell surrounded by an aluminum furnace. Descriptions and operating procedures for both devices have been published previously.[5,6]

Materials. (a) *Cycloheptene Isomerizations.* Cycloheptene (97%), vinylcyclopentane (99%), and cyclopentene (CPEN) (99%) were obtained from Aldrich Chemical Co. The linear 1,3-, 1,4-, 1,6-, and 2,4-heptadienes, all listed at greater than 98% purity, were supplied by Wiley Organics. Cyclopentadiene (CPD) was produced by the distillation at atmospheric pressure of a 95% dicyclopentadiene sample from Aldrich; it was stored as a low-pressure vapor to prevent redimerization. Reagent grade *tert*-butyl alcohol (*t*-BuOH) from Brothers Chemical Co. wad distilled under atmospheric pressure. All these compounds were also degassed and distilled under vacuum before use.

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(b) *Cyclooctene Isomerizations.* *cis*-Cyclooctene (97%) and vinylcyclohexane (99+%) were obtained from Aldrich, 1,7-octadiene (99%) and 1,3,5-cycloheptatriene (CHT) from Wiley, and toluene (ACS grade) from Fisher Scientific Co. These were also subjected to degassing and distillation under vacuum before use. Isobutene gas (Matheson CP Grade) and nitric oxide gas (Lif-O-Gen Research Grade) were used as received.

Sample Preparation. For the shock tube work, the comparative rate method was used; in this procedure, the extent of reaction of a noninteracting reference material, either CPEN, *t*-BuOH, or CHT, was used to determine the temperature produced by the shock wave. Mixtures of CHEP plus CPEN, CHEP plus *t*-BuOH, and COCT plus CHT were prepared by the successive addition of the vapors of the needed reagents, followed by dilution with ultrahigh-purity (99.999%) Matheson argon gas into an evacuated 2- or 3-L glass bulb on a vacuum line. The pressures were measured manometrically. Dilution of the various pure reagents with argon for identification and calibration purposes was carried out in a similar manner. The mixtures were allowed to equilibrate before use for at least 3 days, although in some cases the achievement of equilibrium was accelerated by mechanical stirring.

For the static reactor runs, degassed CHEP or COCT vapor was expanded into a part of the vacuum line, diluted with excess high-purity argon, and allowed into the heated reaction cell. In some runs with COCT, nitric oxide was used instead of the argon gas.

Experimental Conditions. For the shock tube work with CHEP three mixtures were prepared, with the following compositions: (A) 0.5% CHEP + 0.44% CPEN in argon, (B) 0.77% CHEP + 0.77% *t*-BuOH in argon, and (C) 1.57% CHEP + 1.57% *t*-BuOH in argon. The pressures of the sample mixtures in the shock tube before heating varied from 80 to 110 Torr for mixture A, from 95 to 110 Torr for mixture B, and from 60 to 85 Torr for mixture C. The reaction time in the shock tube was about 800 μs for each run. The temperatures achieved in these runs had the following ranges: mixture A, 1117−1256 K; B, 1055−1155 K; and C, 1035−1181 K. Total gas pressures behind the reflected shocks were in the range 2−3 atm. To minimize the importance of further reaction of products, consumption of CHEP was kept below 50%.

For the cyclooctene work at high temperatures, 105−140-Torr samples containing 0.56% COCT and 0.71% CHT were introduced into the shock tube. The temperatures obtained from shocks at these pressures ranged from 930 to 1091 K. COCT consumption was slightly greater than 50% in the three hottest runs, but was less than 50% in all others.

For the work using the static reactor a COCT pressure of about 3−4 Torr was used and either argon or nitric oxide was used to dilute the sample. The final pressure after dilution was about 200 Torr. In one case both diluent gases were added to the COCT sample. The reaction time for all runs in the static reactor was 30 min; depletion of COCT was <50%.

Calculation of Temperatures for the Shock Tube Runs. Reaction temperatures achieved in the shock tube were calculated from the extent of the conversion of CPEN to CPD for the CHEP−CPEN mixtures (eq 1), the conversion of *t*-BuOH to isobutene for the CHEP−*t*-BuOH mixtures (eq 2), and the conversion of CHT to toluene for the COCT−CHT mixtures (eq 3). By analysis of the shocked samples by GC the extent of conversion was determined, first-order rate constants were calculated,[7] and the Arrhenius equations given below were used to find the reaction temperatures in mixtures containing CPEN, *t*-BuOH, and CHT, respectively:

$$\mathrm{CPEN} \rightarrow \mathrm{CPD} + \mathrm{H_2}$$

$$\log_{10}(A,\ \mathrm{s^{-1}}) = 13.35;\quad E_a = 60.0\ \mathrm{kcal/mol}^{8} \qquad (1)$$

$$t\text{-BuOH} \rightarrow i\text{-}\mathrm{C_4H_8} + \mathrm{H_2O}$$

$$\log_{10}(A,\ \mathrm{s^{-1}}) = 14.60;\quad E_a = 66.2\ \mathrm{kcal/mol}^{9} \qquad (2)$$

$$\mathrm{CHT} \rightarrow \mathrm{C_6H_5CH_3}$$

$$\log_{10}(A,\ \mathrm{s^{-1}}) = 13.60;\quad E_a = 51.1\ \mathrm{kcal/mol}^{10} \qquad (3)$$

The temperatures in static reactor runs were measured with an Omega Engineering Model 650-J-D digital thermometer.

Analysis of Reactants and Products. The reactant, product, and calibration samples were analyzed on a Varian Model 1440−20 isothermal gas chromatograph, using a 3.2-mm × 3.0-m column of polypropylene glycol saturated with $\mathrm{AgNO_3}$ on 80−100 mesh Chromosorb W at temperatures of 45−55 °C. These conditions allowed good separation of all major $\mathrm{C_7}$ products from CHEP and all major $\mathrm{C_8}$ products form COCT, but some of the linear dienes which appeared as minor products were insufficiently resolved to be quantified. Likewise, lighter hydrocarbons, observed in small quantities only in the static reactor products, were not well resolved under these conditions. Concentrations of individual species were calculated from measured peak heights; calibration curves (peak height vs sample pressure) run on samples prepared from authentic reagents were highly linear.

Results and Discussion

Isomerizations of Cycloheptene. In the shock tube study of CHEP three different mixtures of CHEP with two different internal standards for the determination of temperature were used to get a wide range of reaction temperatures, 1035−1256 K. VCPEN was the dominant product throughout that temperature range. At the lowest temperatures VCPEN and 1,6-HEPD were the only products detected, and even up to about 1120 K they accounted for >90% of the products observed. At higher temperatures small amounts of other linear heptadienes (1,3-, 1,4-, and 2,4-) were detected, and at still higher temperatures a decrease in the fraction of 1,6-HEPD formed was accompanied by a corresponding increase in the fractions of the other C-7 isomers. Observed relative amounts of VCPEN and 1,6-HEPD were corrected for the small quantities of these products detected in the unshocked samples. Rate constants at different temperatures for the consumption of CHEP, k_{tot}, were determined from the ratio of CHEP concentrations before and after each shock, using the integrated form of the irreversible first-order rate equation.[7] The rate constants for the formation of VCPEN were then calculated by multiplying k_{tot} by the fraction of VCPEN present in the products of the shocked samples, based on the assumption that all major pathways for CHEP depletion are parallel unimolecular reactions. Figure 1 shows a plot of the deduced rate constants for the CHEP to VCPEN isomerization. The least-squares line gives the following activation parameters for CHEP → VCPEN:

$$\log_{10}(A,\ \mathrm{s^{-1}}) = 15.1 \pm 0.7;\quad E_a = 69.7 \pm 3.3\ \mathrm{kcal/mol} \qquad (4)$$

The corresponding values for the conversion of CHEP to all

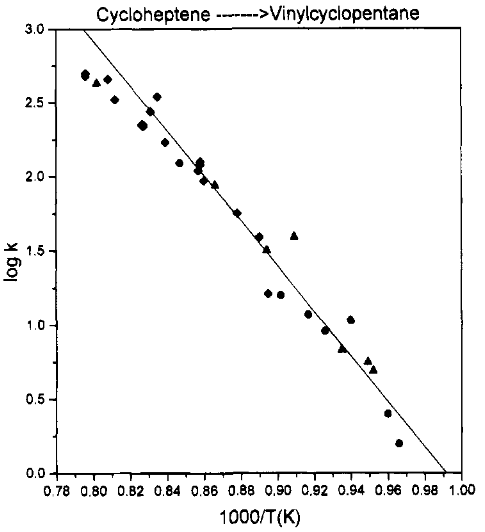

Figure 1. First-order rate constants for cycloheptene isomerization to vinylcyclopentane in the shock tube. (◆) Set A: 0.50% CHEP + 0.44% CPEN in Ar. (▲) Set B: 0.77% CHEP + 0.77% *t*-BuOH in Ar. (●) Set C: 1.57% CHEP + 1.57% *t*-BuOH in Ar.

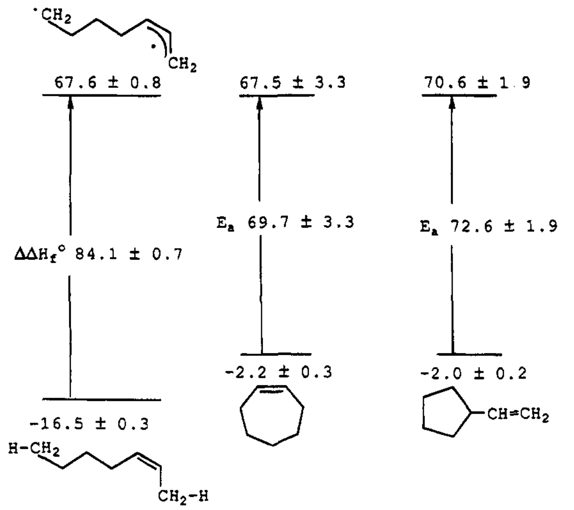

Figure 2. Three estimations of $\Delta H_f°$ for the hept-2-en-1,7-diyl diradical; see text for explanation of thermochemical values employed.

products (VCPEN and heptadienes) are

$$\log_{10}(A, \mathrm{s}^{-1}) = 15.4 \pm 0.7; \quad E_a = 69.9 \pm 3.7 \text{ kcal/mol} \qquad (5)$$

The isomerization of CHEP to VCPEN and 1,6-HEPD is thermochemically consistent with the opening of the CHEP ring to form a diradical structure, as shown in Figure 2. One estimate of the enthalpy of formation of the diradical may be derived from $\Delta H_f°$ for 2*Z*-heptene. Taking −105.1 ± 0.9 kJ/mol (−25.1 ± 0.2 kcal/mol) as the standard enthalpy of formation in the liquid phase for 2*Z*-heptene[11] and an estimated heat of vaporization,[12] a value of −16.5 ± 0.3 kcal/mol is obtained for the gas-phase enthalpy of formation of 2*Z*-heptene at 300 K. The conversion of ethane to the ethyl radical is associated with an increase of 49.0 ± 0.4 kcal/mol;[13−15] for propene to the allyl radical, the corresponding value is 35.1 ± 0.6 kcal/mol.[16] Addition of these enthalpy change values to −16.5 ± 0.3 leads to an estimated $\Delta H_f°$ value of +67.6 ± 0.8 kcal/mol for the cis diradical in the gas phase at 300 K. This value, along with the $\Delta H_f°$ of −2.2 ± 0.3 kcal/mol for cycloheptene,[11] leads to 69.8 ± 0.9 kcal/mol as the predicted minimum E_a[17] for breaking the C(3)−C(4) bond of cycloheptene to give a diradical transition structure. The observed activation energies of 69.9 ± 3.7 kcal/mol for the conversion of CHEP to all products (VCPEN and heptadienes) and 69.7 ± 3.3 kcal/mol for the conversion to VCPEN are in excellent agreement with this prediction. The new results, therefore, are consistent with previous work on cyclobutane,[18] cyclopentane,[3a,b] cyclohexane,[3c] VCPEN,[2] and VCHEX[2] in that all these molecules appear to undergo thermal isomerization via ring opening and the formation of one or more diradicals.

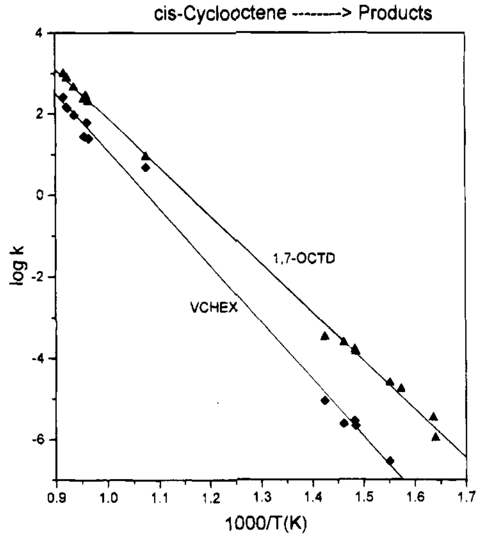

Figure 3. First-order rate constants for the isomerization of *cis*-cyclooctene to 1,7-octadiene (▲) and to vinylcyclohexane (◆), in the shock tube and the static reactor.

In their study of the primary processes involved in the pyrolysis of VCPEN using the VLPP technique, Brown et al.[2] found that VCPEN was primarily converted to 1,6-HEPD and 1,3-HEPD, and thence to propene plus 1,4-pentadiene. Under these conditions the VCPEN ring was assumed to open to give a diradical responsible for the formation of these heptadienes. The activation energy for reactant decay was determined to be 72.6 ± 1.9 kcal/mol, 12.2 kcal/mol lower than that determined for the decay of cyclopentane.[3] From the enthalpy of formation of VCPEN, −2.0 ± 0.2 kcal/mol,[19] an increase of 72.6 ± 1.9 kcal/mol would place the $\Delta H_f°$ estimation for the diradical structure, presumably some mixture of cis and trans forms, at 70.6 ± 1.9 kcal/mol, a value completely consistent with the other two estimates shown in Figure 2.

Whereas the isomerizations of VCPEN at high temperatures lead mainly to linear heptadienes and no detectable CHEP,[2] heating the CHEP produces both VCPEN and heptadienes. This suggests that the diradicals obtained in these two cases are of different geometries, cis and trans. From CHEP the *cis*-hept-2-en-1,7-diyl diradical may be formed, which may give VCPEN or 1,6-HEPD through a hydrogen transfer from C(6) to C(3). But VCPEN could well give *trans*-hept-2-en-1,7-diyl preferentially and thus produce linear dienes. The isomerization and decomposition of vinylcyclobutane similarly involve cis and trans versions of hex-2-en-1,6-diyl.[18]

Isomerizations of *cis*-Cyclooctene. The isomerization of COCT was carried out both at low temperatures (610−702 K) in the static reactor and at higher temperatures (930−1091 K) in the shock tube. While most substrate samples were diluted with argon, five of the eight low-temperature runs were carried out by using nitric oxide as the diluent gas. Under all these experimental conditions the main product was 1,7-OCTD, accounting for 80−95% of the products in 12 of the 16 runs. The other major product, VCHEX, was undetectable up to 636 K but increased with increasing temperature and represented

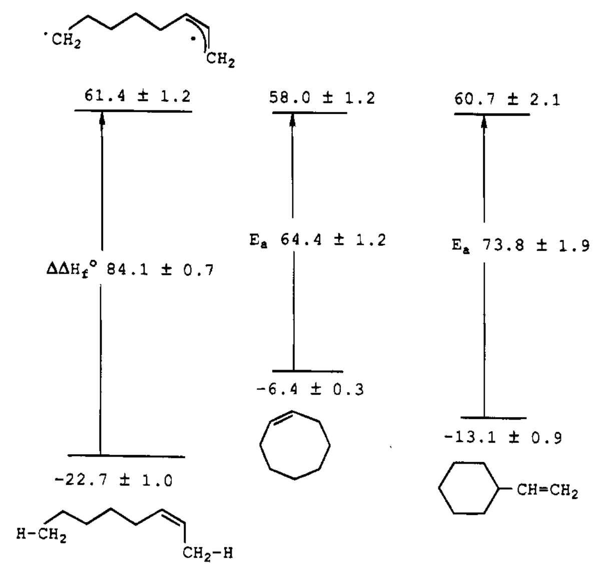

Figure 4. Three estimations of $\Delta H_f°$ for the oct-2-en-1,8-diyl diradical; see text for explanation of thermochemical values employed.

20.7% of the products at the highest temperature of 1091 K. For the static reactor runs, some propene and 1,4-pentadiene plus very small amounts of two products believed to be other octadienes were also detected. The presence of nitric oxide as the diluent gas did not affect the identity or the distribution of products. Thus, the reaction was apparently homogeneous and unimolecular, involving no significant radical–radical or radical–molecule interactions.

Rate constants for the disappearance of COCT, k_{tot}, were calculated at various temperatures from the ratio of COCT concentrations in a substrate sample before and after being heated in the shock tube or in the static reactor, using the integrated rate equation for irreversible first-order consumption of the reactant.[7] Rate constants for the formation of 1,7-OCTD and for VCHEX were then determined by multiplying k_{tot} by the fraction of the 1,7-OCTD and of VCHEX, respectively, in product samples. Figure 3 shows the plots of log k values vs the reciprocal of temperature. Linear least-squares calculations give the following Arrhenius parameters:

$$\text{COCT} \rightarrow \text{1,7-OCTD}$$

$$\log_{10}(A, \text{s}^{-1}) = 13.8 \pm 0.2; \quad E_a = 54.6 \pm 0.5 \text{ kcal/mol} \qquad (6)$$

$$\text{COCT} \rightarrow \text{VCHEX}$$

$$\log_{10}(A, \text{s}^{-1}) = 15.2 \pm 0.3; \quad E_a = 64.4 \pm 1.2 \text{ kcal/mol} \qquad (7)$$

The estimated $\Delta H_f°$ for the formation of the diradical from the opening of the COCT ring, from calculations similar to those for the CHEP ring-opening, is 67.8 ± 1.2 kcal/mol, as shown in Figure 4. This may be compared with our experimental activation energy of 64.4 ± 1.2 kcal/mol for COCT → VCHEX. The listed uncertainties in experimentally determined E_a values represent only one standard deviation in the linear least-squares calculation; at the 95% confidence limit, the calculated $\Delta H_f°$ and experimental E_a values are not significantly different.

From their study of the pyrolysis of VCHEX, Brown et al.[2] reported an activation energy of 73.8 ± 1.9 kcal/mol. They proposed that VCHEX ($\Delta H_f°$ −13.1 ± 0.9 kcal/mol)[19] was first converted to 1,7-OCTD (and 1,3-OCTD) via a diradical mechanism, with subsequent breakdown into propene and 1,4-pentadiene. This is an energetically feasible mechanism as the reported activation energy equals the energy required for breaking a C–C bond in VCHEX to produce the diradical (ca. 74.5 kcal/mol; see Figure 4). The value for the activation energy is again just 12.4 kcal/mol less than the corresponding value for the reaction involving the disappearance of cyclohexane,[3] the difference expected due to the allylic resonance stabilization of the diradical formed from VCHEX.

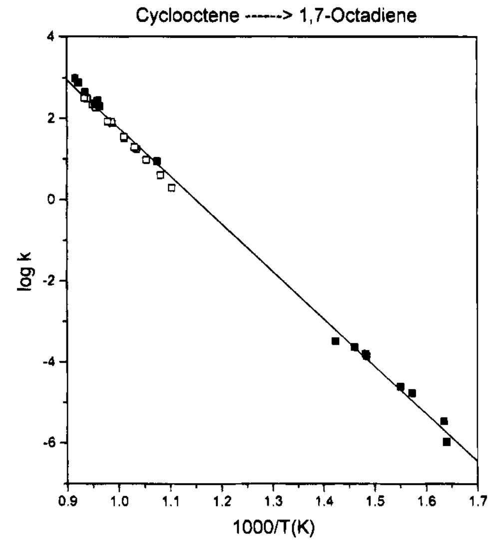

Figure 5. Comparison of rate constants for isomerization of *cis*-cyclooctene to 1,7-octadiene. (■) Present study. (□) Work of Doering et al.[4]

The present kinetic data for COCT → VCHEX and 1,7-OCTD compare reasonably well with results of a study of the isomerizations of cis and trans isomers of cyclooctene recently reported by Doering and co-workers.[4] For COCT → VCHEX at 903–1073 K in a shock tube, they found E_a = 61.7 ± 0.6 kcal/mol, and for COCT → 1,7-OCTD, they deduced E_a = 58.8 ± 0.6 kcal/mol. We again note that the listed uncertainties in experimental E_a values should be doubled for 95% confidence limits. This factor, plus small systematic errors in determination of the reacting gas temperatures in either or both studies, probably accounts for the difference between their values and the present ones. Plotting the data of Doering et al. together with our data from Figure 3 shows the data points to be well mixed, as shown in Figure 5, and leads to a least-squares activation energy of 53.8 ± 0.5 kcal/mol for the combined data sets for the COCT → 1,7-OCTD reaction.

The three mutually consistent estimations of $\Delta H_f°$ for an oct-2-en-1,8-diyl diradical structure portrayed in Figure 4 place it at 60 ± 3 kcal/mol. The $\Delta H_f°$ for the transition structure for the reaction leading from COCT ($\Delta H_f°$ −6.4 kcal/mol) to 1,7-OCTD with an activation energy of 54.6 ± 0.5 kcal/mol is about 48.2 ± 0.6 kcal/mol, *some 12 kcal/mol lower than the* $\Delta H_f°$ *value estimated theoretically and experimentally* (Figure 4) *for the oct-2-en-1,8-diyl diradical.* It is thus apparent that the formation of 1,7-octadiene from *cis*-cyclooctene cannot involve or require diradical formation. A faster alternative process is available here, one that was not accessible to cycloheptene, namely, a unimolecular concerted retro-ene reaction involving transfer of a hydrogen from C(5) to C(1) with simultaneous cleavage of the C(3)–C(4) bond and formation of a new double bond between C(2) and C(3). The facile occurrence of this process in COCT, but not in CHEP, is suggested by comparing molecular models of the two molecules. However, the important consideration here is not the bond distances in unexcited molecules at their potential minima; rather, it is the distances of closest approach of atoms in highly vibrationally excited molecules as they near the transition states of the various competing reaction paths. Interestingly, the prototypical retro-ene reaction of 1-pentene to give ethene and propene was studied by Brown et al.[2] in their VLPP work; they reported a very similar activation energy, 56.9 ± 2.4 kcal/mol. The cyclooctan-1,4-diyl diradical, a hypothetical intermediate for the reaction of COCT to 1,7-OCTD, can also be ruled out, since the transition-state energy for the isomerization of *trans*-cyclooctene to 1,7-OCTD lies some 15 kcal/mol lower than the estimated ΔH_f° of that diradical.

Conclusions

In this study of the reactions of gaseous *cis*-cyclooctene at temperatures between 610 and 1091 K, 1,7-octadiene and vinylcyclohexane were found to be the primary products. It is most likely that the formation of 1,7-octadiene followed a concerted retro-ene reaction path, whereas vinylcyclohexane came by way of a diradical formed by breaking a C(3)−C(4) bond of *cis*-cyclooctene. For the latter process, the difference between the experimental activation energy (64.4 ± 1.2 kcal/mol) and the theoretical value (67.8 ± 1.2) seems too small to serve as a basis for claiming that the 1,3-carbon shift converting *cis*-cyclooctene to vinylcyclohexane occurs in a concerted fashion and thus with a significant energy of concert. At the 95% confidence limits, the difference vanishes.

The structure of *cis*-cyclooctene is sufficiently flexible for the retro-ene reaction leading to 1,7-octadiene to occur in a concerted fashion, but formation of vinylcyclohexane follows a diradical-mediated path. In contrast, the structure of cycloheptene is less flexible and it cannot accommodate the geometric requirements of a concerted retro-ene path leading to 1,6-heptadiene. Both that product and vinylcyclopentane are produced by way of diradical transition structures. One may expect that stereochemical studies with substituted systems will demonstrate the high degree of stereoselectivity expected for orbital-symmetry-allowed and concerted isomerizations of *cis*-cyclooctenes to 1,7-octadienes and substantial loss of stereochemical definition in reactions converting *cis*-cyclooctenes to vinylcyclohexanes and cycloheptenes to vinylcyclopentanes and to 1,6-heptadienes.

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