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Gas-Phase Kinetics and Activation Parameters for Thermal 1,5-Hydrogen Shifts Interconverting Monodeuterium-Labeled 1,3-Cyclohexadienes

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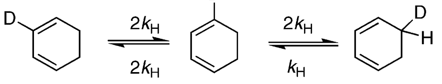
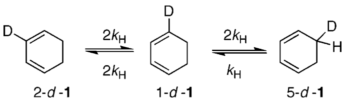


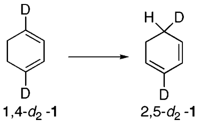
Thermal equilibrations among the three possible monodeuterium-labeled 1,3-cyclohexadienes have been followed in the gas phase at temperatures from 254 to 284 °C. The temperature-dependent rate constants for the 1,5-shift of a single hydrogen lead to the activation parameters $E_a = (40.1 \pm 0.8)$ kcal/mol, $\log A = (12.1 \pm 0.3)$, and $\Delta S^{\ddagger} = -(6.3 \pm 1.3)$ e.u. These activation parameters are reconciled with experimental values reported earlier for reactions starting with 1,4-d_2-cyclohexadiene.

Structural isomerizations through thermal 1,5-shifts of hydrogens in conjugated dienes were encountered more than 100 years ago, though it took some time for them to be recognized individually and as representatives of a specific type of reaction.[1−4] Today they are well-known as [1,5] sigmatropic rearrangements involving a suprafacial transfer of a hydrogen from one end of a pentadienyl π system to the other.[5] The stereochemistry[6] and very substantial energy of concert characteristic of these reactions[7] mark them as concerted processes, transformations that take place without the intervention of any short-lived reactive intermediate. Detailed studies of such reactions thus offer an attractive opportunity for probing into just how structure−reactivity relationships may reflect the nature of transition structures of these concerted reactions. Cyclic conjugated dienes seem well suited for kinetic and computational studies, for the structural variations they offer are related to geometrical constraints rather than to major electronic effects introduced by strongly electron-donating or -withdrawing substituents.

SCHEME 1



The 1,5-hydrogen shift reactions of monocyclic conjugated dienes such as 1,3-cyclohexadiene (**1**) give degenerate products. The reactions are detectable only with the assistance of isotopically labeled variants. An experimental activation enthalpy of $\Delta H^{\ddagger} = 40$ kcal/mol for the 1,5-hydrogen shift of 1,4-d_2-**1** was reported in 1975.[8] In 1976 in a Ph.D. thesis providing experimental details about this work, the activation enthalpy for the reaction of 1,4-d_2-**1** to give 2,5-d_2-**1** was reported to be 39 kcal/mol.[9] No other kinetic work on 1,5-hydrogen shifts shown by isotopically labeled 1,3-cyclohexadienes has appeared.



Kinetic studies of 1,5-hydrogen shifts equilibrating monodeuterium-labeled *cis*,*cis*-cyclooctadienes[10,11] and *cis*,*cis*-cycloheptadienes[12,13] have provided activation parameters necessary for comparisons with theory-derived values and for approaching better understandings of how geometrical details in transition structures impact reaction rates.[14] The present work followed the equilibrations among the three possible isotopomers of monodeuterium-labeled 1,3-cyclohexadienes.

The three monodeuterium-labeled 1,3-cyclohexadienes and the possible isomerization paths provided by 1,5-hydrogen shifts are shown in Scheme 1. The rate constant symbols in Scheme 1 reflect the path degeneracies involved and neglect possible secondary deuterium kinetic isotope effects. Two hydrogens might shift to convert 2-*d*-**1** into 1-*d*-**1**, and vice versa, or 1-*d*-**1** into 5-*d*-**1**, so on a per hydrogen shift basis the rate constants are defined as $2k_H$. Isotopomer 5-*d*-**1** can isomerize to 1-*d*-**1** through the shift of but a single hydrogen, and hence the appropriate rate constant is k_H. Were a deuterium migration to take place, 5-*d*-**1** would give another version of 5-*d*-**1** and the reaction would go undetected. A k_D shift might well occur at a kinetically competitive rate, but it would not complicate the kinetic situation at all.

A nonequilibrium mixture of monodeuterium-labeled cyclohexadienes was conveniently prepared through the

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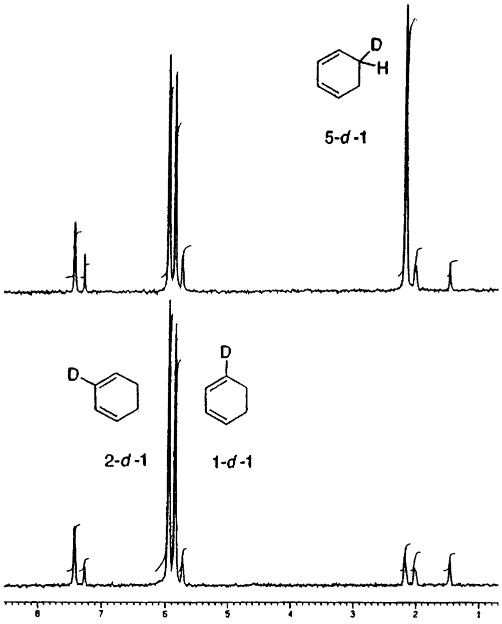

FIGURE 1. Deuterium NMR spectra for the starting mixture *d*-**1**(0) (51.8% 2-*d*-**1**, 42.7% 1-*d*-**1**, and 5.5% 5-*d*-**1**, below) and for a representative product mixture derived from gas-phase thermolysis of *d*-**1**(0) at 274.5 °C for 7200 s (above), isolated without GC purification.

SCHEME 2

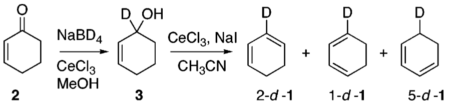

TABLE 1. Mole % Relative Concentration Data for Monodeuterium-Labeled 1,3-Cyclohexadienes as Functions of Reaction Temperature and Time

T (°C)	time (s)	2-d-**1**(t) (%)	1-d-**1**(t) (%)	5-d-**1**(t) (%)
	0	51.8	42.6	5.6
254.2	4800	45.0	37.0	18.0
	9600	43.7	30.5	25.8
	14 000	39.4	28.5	32.1
	28 800	31.7	26.9	41.3
	39 600	29.0	25.2	45.8
	50 400	26.7	25.8	47.5
264.2	2400	47.0	34.9	18.2
	4800	43.4	30.2	26.4
	7200	41.1	29.9	29.0
	10 800	34.0	27.7	38.3
	25 200	27.9	25.1	47.0
274.5	1200	47.6	34.4	18.0
	2400	43.8	30.6	25.6
	3600	38.8	29.7	31.5
	5400	35.9	26.7	37.4
	7200	31.5	25.6	42.8
	12 600	27.2	25.1	47.7
284.2	600	47.1	34.6	18.4
	1200	42.0	32.2	25.8
	1800	40.4	28.4	31.2
	2700	34.7	28.5	36.8
	3600	32.8	26.3	40.9
	6300	27.6	25.8	46.6

short synthetic sequence outlined in Scheme 2. Reduction of cyclohex-2-en-1-one (**2**) with $NaBD_4$ in the presence of $CeCl_3$ provided 1-*d*-cyclohex-2-en-1-ol (**3**),[15] which, when dehydrated with $CeCl_3$/NaI in acetonitrile,[16] afforded a mixture of monodeuterium-labeled cyclohexadienes, *d*-**1**(0), shown by careful integrations of ^2H NMR spectra at 92.1 MHz to be 51.8% 2-*d*-**1** (δ 5.95), 42.4% 1-*d*-**1** (δ 5.85), and 5.7% 5-*d*-**1** (δ 2.17) (Figure 1). The major dehydration products were those expected from 1,2- and 1,4-eliminations.

The ^2H NMR spectra in Figure 1 demonstrate that the thermal 1,5-hydrogen shifts take place without appreciable complications from other reactions. The absorptions other than those associated with isotopomers 2-*d*-**1**, 1-*d*-**1**, and 5-*d*-**1** present in *d*-**1**(0) and in product mixtures are readily assigned. The small signals at δ 5.74 and 2.02 are due to 1-*d*-1,4-cyclohexadiene and 3-*d*-1,4-cyclohexadiene, respectively, minor side-products from the dehydration of **3**. The signal at δ 1.46 derives from naturally abundant deuterium in cyclohexane, the bath gas. The peaks at δ 7.42 ppm and 7.26 stem from benzene-d_1, a synthetic side-product, and naturally abundant $CDCl_3$ in the $CHCl_3$ employed as the NMR solvent.

Gas-phase thermal isomerizations were run using a static reactor; product mixtures from each run were analyzed by ^2H NMR spectroscopy, as in the example at the top of Figure 1. The relative concentrations of isotopomers 2-*d*-**1**, 1-*d*-**1**, and 5-*d*-**1** as functions of temperature and reaction time are summarized in Table 1.

The set of linear first-order differential equations appropriate to the kinetic situation summarized in Scheme 1 may be solved exactly to provide functions of 2-*d*-**1**(t), 1-*d*-**1**(t), and 5-*d*-**1**(t), which depend on a single rate constant ($k = k_H$) for the 1,5-shift of a single hydrogen and the initial relative concentrations 2-*d*-**1**(0), 1-*d*-**1**(0), and 5-*d*-**1**(0).[17] For the experimentally determined set of initial concentrations relevant here, the three functions may be calculated readily with the aid of a linear algebra package[18] (eqs 1−3).

$$2\text{-}d\text{-}\mathbf{1}(t) = 25.0 + 31.74\ \exp(-1.438kt) - 4.94\ \exp(-5.562kt) \quad (1)$$

$$1\text{-}d\text{-}\mathbf{1}(t) = 25.0 + 8.90\ \exp(-1.438kt) + 8.80\ \exp(-5.562kt) \quad (2)$$

$$5\text{-}d\text{-}\mathbf{1}(t) = 50.0 - 40.64\ \exp(-1.438kt) - 3.86\ \exp(-5.562k\mathrm{t}) \quad (3)$$

The data points gathered in Table 1 may be fit with theory-based values calculated using a least-squares best-fit program and a single-variable parameter ($k = k_H$). The temperature-dependent values of k found through these calculations for 5-*d*-**1**(t), the concentration showing the largest dynamic range, are summarized in Table 2. A representative plot of observed time-dependent mole percent relative concentrations, C_i(obs), and the calculated functions is provided in Figure 2 for isomerizations at 284.2 °C. The average absolute value of C_i(obs) − C_i(cal) for the 69 kinetic points in Table 1 having $t > 0$ was 0.7%. The estimated uncertainties in the rate

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TABLE 2. Rate Constants for the 1,5-Shift of a Single Hydrogen in 1,3-Cyclohexadiene

T (°C)	rate constant k
254.2	$(3.94 \pm 0.12) \times 10^{-5}\ \mathrm{s}^{-1}$
264.2	$(7.54 \pm 0.23) \times 10^{-5}\ \mathrm{s}^{-1}$
274.5	$(1.56 \pm 0.05) \times 10^{-4}\ \mathrm{s}^{-1}$
284.2	$(3.00 \pm 0.09) \times 10^{-4}\ \mathrm{s}^{-1}$

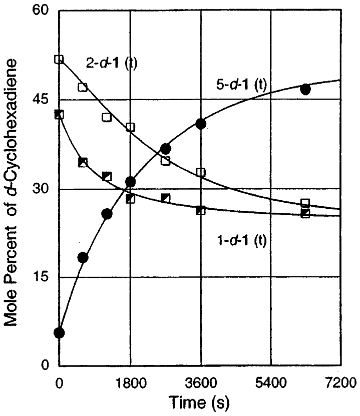

FIGURE 2. Mol % concentrations of 2-*d*-**1**(*t*), 1-*d*-**1**(*t*), and 5-*d*-**1**(*t*) as functions of time at 284.2 °C. The functions are given in eqs 1−3, and $k = (3.00 \pm 0.09) \times 10^{-4}\ \mathrm{s}^{-1}$.

constants (taken to be $\pm 2\sigma_k$) ranged from 3.0 to 3.2%. These temperatures and rate constants provide a good linear Arrhenius correlation of $\log(k) = \log(k)$ versus $1/T$ (K) having slope and intercept of -8.754×10^3 and +12.12, respectively. The activation parameters are $E_a = (40.1 \pm 0.8)$ kcal/mol and $\log A = (12.1 \pm 0.3)$, with estimated uncertainties in E_a and $\log A$ calculated according to O'Neal and Benson.[19] A nonlinear least-squares exponential fit of the Arrhenius equation gave $E_a = 39.7$ kcal/mol and $\log A = 12.0$, values well within the estimated uncertainties. Calculation of $\Delta S^‡$ using $A = eT(k/T)\exp(\Delta S^‡/R)$ and taking T to be 542 K gave $\Delta S^‡ = -(6.3 \pm 1.3)$ cal K^{-1} mol^{-1} (e.u.). An Erying plot of $\log(k/T)$ versus $1/T$ led to $\Delta S^‡ = -6.4$ e.u.

This experimental value for the activation energy of a 1,5-hydrogen shift in 1,3-cyclohexadiene, 40.1 kcal/mol, is slightly less than $E_a = 41.2$ kcal/mol, a value one may calculate from $\Delta H^‡ = 40$ kcal/mol at 315 °C reported in 1975,[8] since $E_a = \Delta H^‡ + RT$. It is identical with the E_a value recorded in de Dobbelaere's dissertation, 40 ± 1 kcal/mol.[9]

The experimental details for the kinetic study of 1,5-hydrogen shifts shown by 1,4-d_2-**1** have never appeared in a journal article, but they can be found in the Ph.D. dissertation of de Dobbelaere,[9] a thesis concerned primarily with applications of semiempirical quantum-chemical methods to define transition structures and activation parameters for 1,5-hydrogen shifts in cyclopentadiene, 1,3-cyclohexadiene, and 1,3,5-cycloheptatriene.[8,20] The experimental work expended in synthesizing 1,4-d_2-**1** and in following thermal isomerizations as functions of temperature is described in less than two pages of text, an Arrhenius plot, and a table of the parameters obtained from that plot.[920]

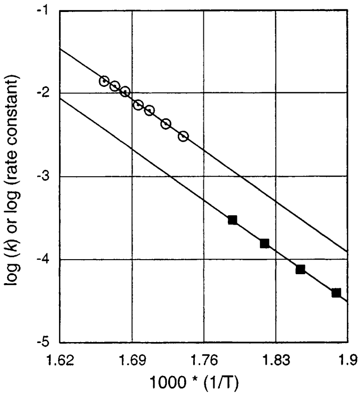

FIGURE 3. Arrhenius plots for 1,5-hydrogen shifts starting with 1,4-d_2-**1** (upper line)[9] and with the *d*-**1**(0) mixture of monodeuterium-labeled 1,3-cyclohexadienes (51.8% 2-*d*-**1**, 42.4% 1-*d*-**1**, 5.7% 5-*d*-**1**; lower line, rate constant $k = k_H$).

The required sample of 1,4-d_2-**1** was prepared following a route reported by Franzus.[21] 1,4-Cyclohexanedione was reduced with LiAlH$_4$; the diols obtained were treated with TsCl to provide 1,4-d_2-1,4-di(tosyloxy)cyclohexanes, and the ditosylates were heated with NaOH in *n*-propyl alcohol to give 1,4-d_2-**1**.[21] Preparative GC provided 1,4-d_2-**1** free of 1,4-d_2-cyclohexa-1,4-diene, a synthetic byproduct.[9]

The 1,4-d_2-**1** was isomerized 303 to 330 °C using a 9.15 mL micro flow reactor 186.5 cm in length.[22,23] Residence times varied from 5 to 60 s. For each temperature and residence time, 10 injections of 2.5 μL gave product mixtures that were collected together at −60 °C, dissolved in CDCl$_3$, and analyzed by ^{1}H NMR using a 60 MHz instrument. Five to eight spectra from each product mixture were recorded, and the integrated intensities were averaged. The NMR absorptions at δ 6.0 for olefinic protons and at δ 2.2 for the allylic hydrogens were digitized and integrated by computer methods.[9]

The kinetic data led to the parameters $\Delta E^‡ = 40 \pm 1$ kcal/mol, $\Delta H^‡$ 39 ± 1 kcal/mol, $\Delta S^‡ - 4 \pm 2$ e.u., $\Delta G^‡$ 41.0 ± 0.5 kcal/mol, and $\log A' = 12.7 \pm 0.4$.[9] When the present Arrhenius plot and de Dobbelaere's are compared, the identical slopes and very distinct intercepts are vividly apparent (Figure 3). Yet the apparent conflict between the two experimental studies could be misleading. While the experimental details provided in the dissertation[9] did not include specifications of measured NMR integration intensity ratios for product mixtures or residence times for kinetic runs or derived rate constants at specific temperatures or a definition of the rate constant used for the Arrhenius plot, one can nevertheless plausibly infer the cause of the apparent discrepancy and demonstrate a fine agreement between the two kinetic investigations.

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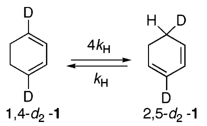
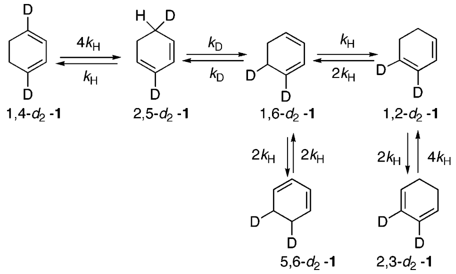
SCHEME 3



SCHEME 4



The kinetic scheme for interconversion of 1,4-d_2-**1** and 2,5-d_2-**1** given in Scheme 3 will serve well as long as there is no significant participation of deuterium shifts. Were they to intrude, the kinetic situation outlined in Scheme 4 would be relevant, and the challenges posed by data reduction requirements would be substantially more difficult.

The ratio of absorption intensities for allylic to vinyl hydrogens at 1,4-d_2-**1** is 2:1, and for 2,5-d_2-**1** it is 1:1. The reversible interconversion of 1,4-d_2-**1** and 2,5-d_2-**1** starting from 1,4-d_2-**1** at 100 mol % would be governed by a single-exponential function when expressed as in eq 4, if $k_H \gg k_D$ so that k_D may be neglected.

$$1.25 \times [1,4\text{-}d_2\text{-}\mathbf{1}(t)] - 25 = [1,4\text{-}d_2\text{-}\mathbf{1}(0)] \exp(-5kt) \tag{4}$$

The rate constant for the observable first-order decay would be the sum of the forward and reverse rate constants in Scheme 3. As the reaction progressed toward equilibrium (20% 1,4-d_2-**1**, 80% 2,5-d_2-**1**) the allylic:vinyl ratio of NMR intensities would progress from 2 toward 1.14. At any reaction time, the mole fraction of 1,4-d_2-**1** would be equal to 3 $(r - 1)/(r + 1)$, where r is the observable ratio of these NMR intensities.

For a 60 s kinetic run at 330 °C, the instance of maximum conversion of starting material, the rate constant calculated from the Arrhenius parameters (1.6×10^{-2} s^{-1}) would correspond to about 1.4 half-lives, or a reduction of 1,4-d_2-**1** from 100 to 51% of the mixture or of r from 2 to 1.4. The kinetic runs thus were restricted to relatively low conversions so as to avoid complications from k_D shifts which, at high conversion factors, might have been problematic.

The rate constants used in the Arrhenius plot (Figure 3) for reactions starting from 1,4-d_2-**1** may have been for the exponential approach to the equilibrium proportions of the two isomers and thus been equal to 5k_H (Scheme 3; eq 4). Then, $\log A' = (12.7 \pm 0.4)$[9] should be equal to $(\log 5 + \log A) = 0.7 + (12.1 \pm 0.3)$, which is indeed the case. The apparent inconsistency of Figure 3 is most probably just a consequence of different definitions of rate constant. This reading of the kinetic analysis leads to an agreement in E_a and log A values secured in Eindhoven and at Syracuse that could hardly be better.

Comparisons between calculated[14] and experimentally determined E_a values for hydrogen shifts in cyclic dienes show reasonable agreements (Table 3). The agreement for cyclohexadiene, the main concern of the present work, is the best of this limited set. Further experimental and theoretical work on degenerate thermal 1,5-hydrogen shifts in these and related cyclic dienes should serve to uncover or rule out possible variations in contributions from tunneling as functions of geometries of transition structures.

TABLE 3. Experimental and Calculated E_a Values (in kcal/mol) for 1,5-Hydrogen Shifts in Cyclic 1,3-Dienes

diene	E_a (exptl)	E_a(calcd)^a	ΔE_a(calcd − exptl)
1,3-cyclohexadiene	40.1	41.9	1.8
1,3-cycloheptadiene	27.5^b	33.7	6.2
cis-1,3-cyclooctadiene	29.0^c	32.2	3.2

^{a} Ref 14. ^{b} Ref 13. ^{c} Ref 11.

Experimental Section

1-Deuterio-2-cyclohexenol (3).[15] To a solution of cyclohexenone (3.84 g, 0.04 mol) and $CeCl_3 \cdot 7H_2O$ (14.92 g, 0.04 mol) in 20 mL of MeOH was added $NaBD_4$ (1.68 g, 0.04 mol) over a 10 min period. The reaction mixture was stirred for 3 h at room temperature and then quenched with H_2O (20 mL) and extracted with pentane (5 × 15 mL). The combined organic extracts were washed with H_2O (20 mL) and dried over Na_2SO_4. Filtration and concentration by patient fractional distillation at atmospheric pressure gave 3.84 g (97% yield) of **3** as a slightly yellow oil. ^{1}H NMR δ 1.6−2.1 (m, 6H), 5.7 (d, 1H), 5.8 (m, 1H).

Monodeuterio-1,3-cyclohexadiene (2-*d*-1, 1-*d*-1, 5-*d*-1).[16] To a stirred solution of **3** (2.54 g, 0.026 mol) and $CeCl_3$ (14.54 g, 0.039 mol) in acetonitrile (20 mL) was added NaI (1.95 g, 0.039 mol). The reaction mixture was heated to reflux for 5 h and then cooled, diluted with pentane (10 mL), and quenched with 0.5 N HCl (10 mL). The layers were separated, and the aqueous layer was extracted with pentane (3 × 10 mL). The combined organic material was washed with aq $NaHCO_3$ (10 mL) and brine (10 mL) and dried over Na_2SO_4. Filtration, concentration, and microspinning band column distillation at atmospheric pressure gave a mixture of 2-*d*-**1**, 1-*d*-**1**, and 5-*d*-**1** contaminated with several minor impurities (see Figure 1). ^{1}H NMR δ 1.7−2.0 (m, 6H), 5.73 (d, 1H), 5.81−5.87 (m, 1H). ^{2}H NMR δ 7.41 (s), 5.93 (s) (51.8% 2-*d*-**1**), 5.84 (s) (42.4% 1-*d*-**1**), 5.72 (d), 2.16 (s) (5.7% 5-*d*-**1**).

Thermal Isomerizations of *d*-1(0).[24] The mixture of monodeuterium-labeled 1,3-cyclohexadienes *d*-**1**(0) (51.8% 2-*d*-**1**, 42.7% 1-*d*-**1**, and 5.5% 5-*d*-**1**) (0.278 g, 3.5 mmol) was diluted 1:15 by volume with cyclohexane. A 150 μL portion of this dilute solution containing *d*-**1**(0) (0.112 g, 1.4 mmol) was injected into an evacuated 300 mL kinetic bulb stabilized to ± 0.1 °C and allowed to react for a defined time (Table 1). The product mixture and cyclohexane bath gas were actively transferred to a U tube and trapped in liquid nitrogen. The trapped hydrocarbons were then warmed and passively transferred on a vacuum line into an evacuated NMR tube containing degassed chloroform cooled in liquid nitrogen. The NMR tube was sealed off, and a ^{2}H NMR spectrum was recorded (see Figure 2).

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