Deuterium kinetic isotope effects on the thermal isomerizations of deuteriocyclopropane to deuterium-labeled propenes[1]

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Abstract: The gas-phase thermal isomerizations of deuteriocyclopropane to the four possible monodeuterium-labeled propenes have been followed at 435 °C. The observed distribution of products provides estimates of two deuterium kinetic isotope effects, the secondary k_H^s/k_D^s for the carbon–carbon bond cleavage leading to trimethylene diradical reactive intermediates and the primary k_H^p/k_D^p ratio for a [1,2] shift of a hydrogen or deuterium leading from the diradical to a labeled propene. The values determined are $k_H^s/k_D^s = 1.09 \pm 0.03$ and $k_H^p/k_D^p = 1.55 \pm 0.06$. The experimental k_H^s/k_D^s value found agrees well with some, but not all, earlier calculated values and conjectures.

Key words: cyclopropane, thermal rearrangement, kinetic isotope effects.

Résumé : Opérant à 435 °C, on a étudié les réactions d'isomérisation thermiques en phase gazeuse du deutérocyclopropane qui conduisent aux quatre propènes monodeutérés possibles. La distribution observée des produits permet d'évaluer deux des effets isotopiques cinétiques, l'effet isotopique secondaire k_H^s/k_D^s pour la rupture de la liaison carbone–carbone conduisant à la formation d'intermédiaires réactifs diradicalaires triméthylènes et le rapport primaire k_H^p/k_D^p pour le déplacement [1,2] d'un atome d'hydrogène ou de deutérium qui conduit du diradical à un propène marqué. Les valeurs déterminées sont $k_H^s/k_D^s = 1{,}09 \pm 0{,}03$ et $k_H^p/k_D^p = 1{,}55 \pm 0{,}06$. La valeur expérimentale trouvée pour k_H^s/k_D^s est en bon accord avec les quelques-unes des hypothèses et des valeurs calculées antérieurement, mais pas nécessairement toutes.

Mots clés : cyclopropane, réarrangement thermique, effets isotopiques cinétiques.

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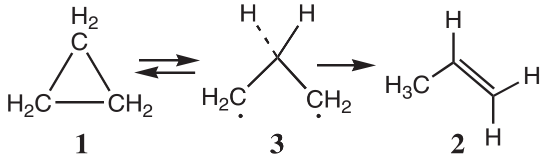
Introduction

The thermal chemistry of cyclopropane is marvelously complex relative to the small size and high symmetry of the hydrocarbon. This minimal cycloalkane (**1**) undergoes a thermal structural isomerization to propene (**2**) (1, 2). Deuterium-labeled analogs exhibit thermal stereomutations (3), which have been demonstrated to occur through both one-center and two-center epimerizations (4). The structural isomerization and the two types of stereomutations are generally held to involve transient formation of a trimethylene diradical reactive intermediate (**3**), which may revert to cyclopropane or shift a hydrogen from C2 to C1 to afford propene (5–8). The transition-state structure for the rate-determining step in this formulation leading from **3** to **2** has been characterized in several high-level theoretical calculations (9–12).



1 **3** **2**

Interpretations of experimental data providing information about rate constants for the one-center and two-center thermal epimerizations observed for the 1,2-d_2-labeled cyclopropanes depend on secondary deuterium kinetic isotope effects. The importance of k_H^s/k_D^s is easy to grasp: the C1—C2 and C1—C3 bonds of 1,2-d_2-labeled cyclopropanes might well break at different rates. A net one-center epimerization at C1 could occur through cleavage of the C1—C2 bond (rate constant k_1) or when C1—C3 breaks (rate constant k_1'). Simultaneous two-center epimerizations at C1 and C2 (rate constant k_{12}) or at C1 and C3 (rate constant k_{13}) could occur at different rates. The latter two-center event would contribute to an observable one-center epimerization at C1. All of which gets complicated. With rate constant ratios defined as $f_1 = k_1'/k_1$ and $f_{12} = k_{13}/k_{12}$, the two experimental observables, k_i (for the geometrical isomerization equilibrating *cis*- and *trans*-1,2-d_2-cyclopropane) and k_α (for racemization of nonracemic *trans*-1,2-d_2-cyclopropane), are related to the mechanistic rate constant ratio k_{12}/k_1 as in eqs. [1] and [2] (13).

$$[1] \quad \frac{k_i}{k_\alpha} = \frac{2 + \dfrac{(2f_{12}k_{12})}{(k_1 + f_1k_1)}}{1 + \dfrac{(k_{12} + f_{12}k_{12})}{(k_1 + f_1k_1)}}$$

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$$[2] \qquad \frac{k_{12}}{k_1} = \frac{2 - \dfrac{k_i}{k_\alpha}}{\dfrac{k_i}{k_\alpha}\dfrac{(1+f_{12})}{(1+f_1)} - \dfrac{2f_{12}}{(1+f_1)}}$$

One way to simplify eq. [2] is to suppose, quite reasonably, that $f_1 \approx f_{12}$, and let $f = f_1 = f_{12}$ (13). One is left with an equation linking two observables with three unknowns (eq. [3]).

$$[3] \qquad \frac{k_{12}}{k_1} = \frac{2 - \dfrac{k_i}{k_\alpha}}{\dfrac{k_i}{k_\alpha} - \dfrac{2f}{(1+f)}}$$

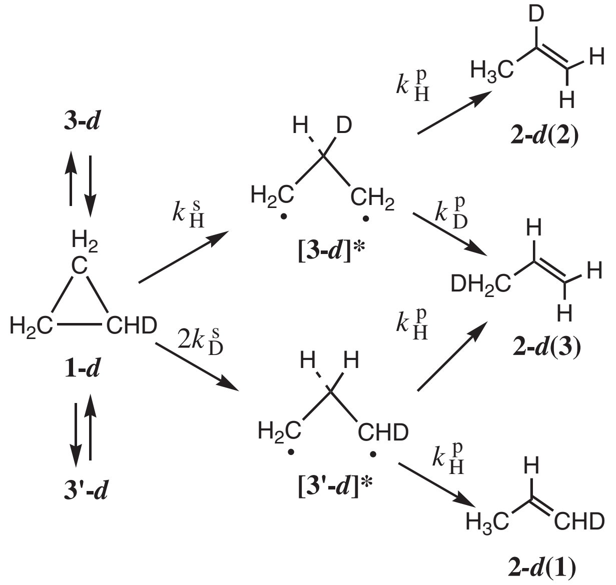
If one could estimate a reliable value of f, then k_{12}/k_1 could be derived from a reliable experimental k_i/k_α ratio. For example, if k_i/k_α were 1.07 as was reported for stereomutations of a nonracemic *trans*-1,2-d_2-cyclopropane at 422.5 °C and f were assumed to be 1.1 (4), then according to eq. [3], k_{12}/k_1 would be 42, a large number leading to the conclusion that the "double methylene rotation mechanism operates to the virtual exclusion of any other pathway" (4). Or one could view the experimental data as leading to the conclusion that double methylene rotation is favored over single methylene rotation by a factor of ≈50 (14).

Later experimental work with a nonracemic 1-^{13}C-1,2,3-d_3-cyclopropane concluded that k_{12}/k_1 is 1 ± 0.2 (15), a finding that has prompted considerable theoretical attention but no consensus on the mechanistic details of the stereomutations or on the dynamics of trimethylene diradicals.

Three groups have provided theory-based estimates of f or k_H/k_D (k_{12}) based on harmonic vibrational frequencies and various kinetic models: 1.13 and 1.12 (at 422.5 °C) (16, 17), and 1.09 (at 400 °C) (18). Other calculations have given rise to theory-based estimates of k_{12}/k_1, an undertaking sensitive to the kinetic model adopted, especially whether or not trimethylene is an intermediate to which transition-state theory may be applied, the potential energy surface used, and whether semiclassical or quantum dynamics calculations are employed. These published theory-based k_{12}/k_1 ratios are 0.94 (17), 1.18 (18), 1.35 (13), 2.2 (19), 2.3 (13), 3.5 (13), and 4.73 (18). The lower ratios are favored when transition-state theory models are applied to the transient trimethylene diradical (20); the higher ratios are calculated using dynamic models in which redistributions of vibrational energy compete poorly with momentum-preserving transits of the diradical over the potential energy surface.

The values of calculated k_H/k_D (k_{12}) ratios depend on the accuracy of theory-derived transition structures and vibrational frequencies, the broad potential energy surface on which the trimethylene diradical lives its brief existence, and whether explicit consideration of torsional potentials may be appropriate; the calculated values may not be correct. Other reasonable values might be more accurate (13). If the ratio f is uncertain within the range 0.8–1.1, and if k_i/k_α were 1.07, then corresponding values of k_{12}/k_1 would be in the range from 5 to 42 (13). Or if f were 0.8 and k_i/k_α were indeed 1.07 then k_{12}/k_1 would be 5, a value close to one theory-based estimate (18). The k_{12}/k_1 ratio is obviously a sensitive function of the value of f. But the k_{12}/k_1 ratio is also a sensitive function of the experimental value of k_i/k_α (eq. [3]).

Fig. 1. Isomerization paths from **1-*d*** to four monodeuteriopropenes.



There have been no *experimentally* estimated values of the secondary deuterium kinetic isotope effect associated with homolytic thermal cleavage of a cyclopropane C—C bond, and no attempts yet published to face the more exacting challenge of measuring the k_H^s/k_D^s ratios for k_1 and k_{12} for the stereomutations of appropriate isotopically labeled cyclopropanes. The present work describes experiments leading to two deuterium kinetic isotope effects of import to thermal cyclopropane-to-propene isomerizations, the secondary k_H^s/k_D^s ratio for C—C bond cleavage and the primary k_H^p/k_D^p effect on [1,2] shifts leading from a deuterium-labeled trimethylene diradical to labeled propenes.

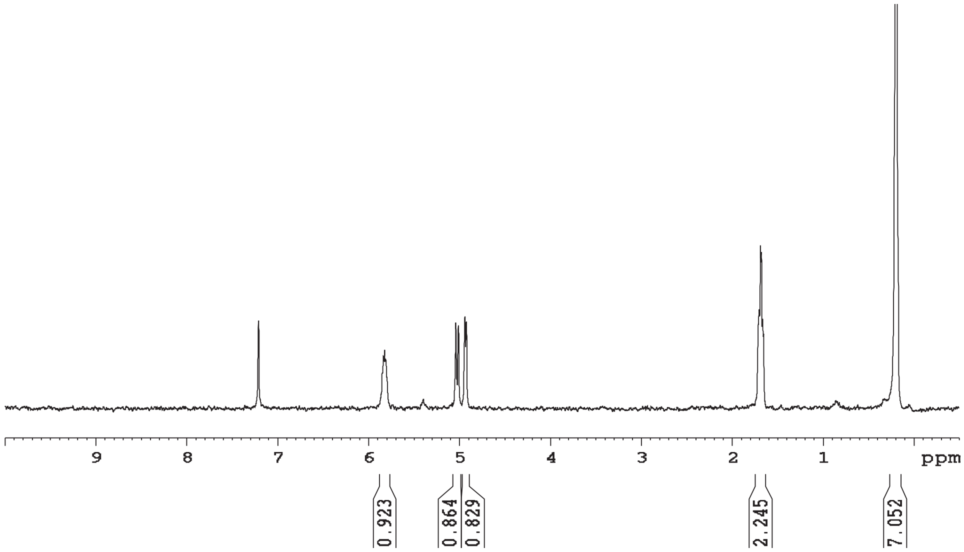
Results and discussion

Deuteriocyclopropane (**1-*d***) was identified as a labeled cyclopropane suitable for gaining an experimental value for the secondary k_H^s/k_D^s effect on the C—C cleavage of cyclopropane. It is easily made and presents no complications related to stereomutations: all one-center and two-center epimerizations for this molecule are unobservable. The isomerizations of **1-*d*** could lead to four monodeuterium-labeled propenes, as diagrammed in Fig. 1. The E- and Z-isomers of **2-*d*(1)** are not shown explicitly.

The model depicted in Fig. 1 recognizes that the lifetime of trimethylene diradicals, about 120 fs (20), is too short for significant intramolecular redistributions of vibrational energy under the gas-phase reaction conditions. Trimethylene diradicals **3-*d*** and **3′-*d***, which lack sufficient vibrational energy to give propenes, revert to **1-*d***. Related trimethylene diradicals with additional isotopic labeling could give rise to stereoisomeric cyclopropanes but not related propenes.

The fractions of trimethylene diradicals having sufficient thermal energy to proceed to propene products would be proportional to $k_H^s/(k_H^s + 2k_D^s)$ for [**3-*d***]* and $2k_D^s/(k_H^s + 2k_D^s)$ for [**3′-*d***]*. The second isotopomer [**3′-*d***]* would be favored, for two CHD—CH$_2$ bonds of **1-*d*** could be broken.

Fig. 2. ^{2}H NMR spectrum at 92.1 MHz of propene-*d* isomers from the thermal rearrangement of **1-*d*** for 12.5 h at 435 °C.



Diradical [**3-*d***]* could react with rate constant k^{p}_{H} to yield **2-*d*(2)**, and with rate constant k^{p}_{D} to afford **2-*d*(3)**. The second energized trimethylene diradical ([**3′-*d***]*) could react further through $k^{p}{}_{H}$ to give **2-*d*(3)** and through k^{p}_{H} in the other direction to provide a mixture of both isomers of **2-*d*(1)**.

All four rate constants for hydrogen shifts in Fig. 1 (k^{s}_{H}, k^{p}_{H} leading to **2-*d*(2)**, k^{p}_{H} leading to **2-*d*(3)**, and k^{p}_{H} leading to **2-*d*(1)**) might be conditioned by secondary k_{H}/k_{D} effects. The possible β-secondary k_{H}/k_{D} contribution to the k^{s}_{H}/k^{s}_{D} ratio will be considered further when comparisons with theory-predicted k^{s}_{H}/k^{s}_{D} values are made. Possible secondary effects for the [1,2] shifts associated with rate constants k^{p}_{H} for reactions of [**3-*d***]* or [**3′-*d***]* were neglected. The k^{p}_{H}/k^{p}_{D} ratio was assumed to be largely determined by the primary [1,2] shifts of H vs. D.

Given the model of Fig. 1, the relative concentrations of deuterium-labeled propenes in product mixtures would be as expressed in the proportional relationships shown in eqs. [4]–[6].

[4] $$\mathbf{2\text{-}}\boldsymbol{d}\mathbf{(1)} \propto 2k^{p}_{H}k^{s}_{D}/(k^{s}_{H} + 2k^{s}_{D})$$

[5] $$\mathbf{2\text{-}}\boldsymbol{d}\mathbf{(2)} \propto k^{p}_{H}k^{s}_{H}/(k^{s}_{H} + 2k^{s}_{D})$$

[6] $$\mathbf{2\text{-}}\boldsymbol{d}\mathbf{(3)} \propto (k^{s}_{H}k^{p}_{D} + 2k^{s}_{D}k^{p}_{H})/(k^{s}_{H} + 2k^{s}_{D})$$

These proportionalities may be expressed more conveniently by dividing the right-hand sides of each of these three expressions by $k^{s}_{D}k^{p}_{D}/(k^{s}_{H} + 2k^{s}_{D})$ (eqs. [7]–[9]).

[7] $$\mathbf{2\text{-}}\boldsymbol{d}\mathbf{(1)} \propto 2k^{p}_{H}/k^{p}_{D}$$

[8] $$\mathbf{2\text{-}}\boldsymbol{d}\mathbf{(2)} \propto (k^{s}_{H}/k^{s}_{D}) \times (k^{p}_{H}/k^{p}_{D})$$

[9] $$\mathbf{2\text{-}}\boldsymbol{d}\mathbf{(3)} \propto k^{s}_{H}/k^{s}_{D} + 2k^{p}_{H}/k^{p}_{D}$$

The product mixtures from a series of five gas-phase thermal rearrangements of **1-*d*** at 435 °C with cyclopentane as the bath gas were analyzed by ^{2}H NMR in nine independent integrations. A representative spectrum of a product mixture is shown in Fig. 2. The ^{2}H NMR resonance signals are as expected (21), with the distinct vicinal $^{3}J_{H\text{-}D}$ coupling constants for the E- and Z-isomers of **2-*d*(1)** in clear evidence. Unreacted **1-*d*** is evident as a doublet centered at 0.22 ppm, with $^{2}J_{H\text{-}D} = 0.95$ Hz.

The intensities of the various ^{2}H NMR absorptions were determined without broadband proton decoupling so as to obviate possible NOE effects. For all but one integration, the pulse delay was 50 s; for the last 20 h run, the delay was 10 s. No significant differences in relative intensities at different reaction times were noted (Table 1), and no appreciable complications from secondary reactions were evident. Two minor absorptions (at 5.4 and 0.9 ppm) were contributed by unidentified side products (Fig. 2).

The relative ^{2}H NMR integral intensities of Z- and E-isomers of **2-*d*(1)** were 17.2 ± 0.46% and 17.3 ± 0.39%, respectively, equal within experimental uncertainties. The relative intensities for **2-*d*** isomers and for unreacted **1-*d*** as a function of reaction time showed a simple exponential decay of starting material corresponding to a rate constant for isomerzations of 1.13×10^{-5} s^{-1}. The high-pressure rate constant for rearrangement of unlabeled cyclopropane at 435 °C may be calculated from the activation parameters reported by Chambers and Kistiakowsky (22), $\log_{10} A = 15.17$, E_{a} 65.0 kcal/mol (1 cal = 4.184 J): it is 1.29×10^{-5} s^{-1}, just slightly larger than the rate constant derived here. The difference may be ascribed to a combination of two factors: the pressure in the kinetic bulb during thermal reactions with cyclopentane present as a bath gas (113 to 114 torr, 1 torr = 133.322 4 Pa), is less than would be required to give kinetic behavior at the high-pressure limit, and deuterium kinetic isotope effects could lower the rate of isomerization moderately.

The experimental data summarized in Table 1 and the relationships shown in eqs. [7]–[9] lead easily to values for the two deuterium isotope effects involved, k^{s}_{H}/k^{s}_{D} for cleaving a cyclopropane C—C bond and k^{p}_{H}/k^{p}_{D} for shifting a hydrogen or deuterium from C2 to C1 in the trimethylene diradical **3-*d***. The three expressions (eqs. [7]–[9]) are just proportionalities; they can be used to formulate two independent equations with two unknowns. From eqs. [7] and [8], eq. [10] follows, and $k^{s}_{H}/k^{s}_{D} = 2 \times 18.8/34.6 = 1.09$.

Table 1. Relative intensities of ^{2}H NMR absorptions for propene-*d* products from thermal isomerizations of deuteriocyclopropane at 435 °C.

Time (h)	**2-*d*(2)** (%) (5.87 ppm)	**2-*d*(1)** (Z and E) (%) (5.07 and 4.98 ppm)	**2-*d*(3)** (%) (1.64 ppm)
7.5	18.6	34.7	46.7
10	18.9	35.4	45.7
10	18.8	35.2	46.0
12.5	19.7	34.5	45.8
12.5	19.0	34.8	46.2
5	18.0	33.3	48.7
20	18.9	33.9	47.2
20	18.4	34.4	47.2
20	18.5	35.3	46.2
Average	18.8	34.6	46.6
Standard deviation	0.4	0.6	0.8
Relative error	1.9	1.7	1.7

$$[10]\qquad [\mathbf{2}\text{-}\boldsymbol{d}(\mathbf{1})]/[\mathbf{2}\text{-}\boldsymbol{d}(\mathbf{2})] = 2/(k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}})$$

An equation may be constructed from eqs. [8] and [9] with but a single unknown, the primary kinetic isotope effect rate-constant ratio, $k_{\mathrm{H}}^{\mathrm{p}}/k_{\mathrm{D}}^{\mathrm{p}}$ (eq. [11]).

$$[11]\qquad [\mathbf{2}\text{-}\boldsymbol{d}(\mathbf{3})]/[\mathbf{2}\text{-}\boldsymbol{d}(\mathbf{2})] = (k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}} + 2k_{\mathrm{H}}^{\mathrm{p}}/k_{\mathrm{D}}^{\mathrm{p}})/[(k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}}) \times (k_{\mathrm{H}}^{\mathrm{p}}/k_{\mathrm{D}}^{\mathrm{p}})]$$

Rearranging eq. [11] to express $k_{\mathrm{H}}^{\mathrm{p}}/k_{\mathrm{D}}^{\mathrm{p}}$ as a function of knowns gives eq. [12], which leads at once to the solution $k_{\mathrm{H}}^{\mathrm{p}}/k_{\mathrm{D}}^{\mathrm{p}} = 1.55$.

$$[12]\qquad k_{\mathrm{H}}^{\mathrm{p}}/k_{\mathrm{D}}^{\mathrm{p}} = (k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}})/\{(k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}}) \times [\mathbf{2}\text{-}\boldsymbol{d}(\mathbf{3})]/[\mathbf{2}\text{-}\boldsymbol{d}(\mathbf{2})] - 2\}$$

When the experimental uncertainties in the integrated NMR absorption intensities are taken into account, the two isotope effects and error estimates are $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}} = 1.09 \pm 0.03$ and $k_{\mathrm{H}}^{\mathrm{p}}/k_{\mathrm{D}}^{\mathrm{p}} = 1.55 \pm 0.06$.

How significantly would these estimates be altered if a minor contribution to the overall isomerization from a different path, one involving a direct rate-determining isomerization of **1-*d*** to a monodeuterium-labeled singlet 1-propylidene reactive intermediate, followed by a very rapid [1,2]-hydrogen or [1,2]-deuterium shift (12)? Were this hypothetical path a contributor, there would be some bias favoring the formation of **2-*d*(2)** at the expense of the other three propene-*d* isotopomers. Primary kinetic isotope effects could be involved at two stages, during formation of a propylene-*d* intermediate or during a [1,2] shift. But a contribution of as much as 10% by such a path would not lead to significant changes in the estimated values for $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}}$ (1.09 ± 0.03) and $k_{\mathrm{H}}^{\mathrm{p}}/k_{\mathrm{D}}^{\mathrm{p}}$ (1.55 ± 0.06). Were the primary $k_{\mathrm{H}}/k_{\mathrm{D}}$ effects on the cyclopropane to 1-propylene to propene route equal to 1.6, and the secondary effect 1.09 once again, the changes in the calculated distributions of **2-*d*** isomers would lead to calculated $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}}$ and $k_{\mathrm{H}}^{\mathrm{p}}/k_{\mathrm{D}}^{\mathrm{p}}$ values of 1.11 and 1.63, estimates very close to the values based on taking the trimethylene diradical intermediate mechanistic model to be the only path. A minor contribution from the 1-propylidene route would not influence the two kinetic isotope effect estimations significantly (23).

The kinetic model adopted and the experimental observations of the present work define $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}}$ as the ratio of rate constants leading from **1-*d*** to [**3-*d***]* and from **1-*d*** to [**3′-*d***]*. The value obtained for $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}}$ (1.09 ± 0.03) is a composite of α and β effects. The α effect influences the cleavage leading to **3′-*d*** and the β effect influences the cleavage leading to **3-*d***, each relative to the rate constant for cleaving one C—C bond in unlabeled cyclopropane. Thus, $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}}$ is a ratio of one rate constant modified by a β secondary effect divided by one conditioned by an α effect.

Direct comparisons with the theory-derived values for k_{13} vs. k_{12} rate constants in 1,2-d_2-cyclopropanes previously cited, 1.13 and 1.12 (at 422.5 °C) (16, 17) and 1.09 (at 400 °C) (18), are appropriate, for k_{13} in conditioned by the product of one α and one β effect, while k_{12} is conditioned by the product of two α effects. The k_{13}/k_{12} ratio, the *f* factor, is equivalent to the present $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}}$ ratio. Thus, the experimental value 1.09 ± 0.03 is completely consistent with the value assumed in 1975 (4) and with the several subsequent theory-derived values (16–18).

The hypothetical $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}} = 0.8$ value may successfully serve as a device for reinterpreting one reported $k_{\mathrm{i}}/k_{\alpha}$ value for 1,2-d_2-cyclopropanes (1.07) as consistent with $k_{12}/k_1 \approx 5$, a ratio found in one theory-based model for the stereomutations (18). With $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}} = 0.8$, the earlier conclusion (4) that $k_{12}/k_1 \approx 42$ could be abandoned, while the experimentally reported (4) rate constant ratio ($k_{\mathrm{i}}/k_{\alpha} = 1.07$) could remain unquestioned. The present experimental value ($k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}} = 1.09 \pm 0.03$) makes the hypothetical $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}} = 0.8$ value seem unlikely. The discrepancies in the literature as to the k_{12}/k_1 ratio for cyclopropane stereomutations may hinge more plausibly on problems associated with experimental determinations of k_{i} and k_{α} values than in different judgments on the $k_{\mathrm{H}}^{\mathrm{s}}/k_{\mathrm{D}}^{\mathrm{s}}$ ratio (15*e*).

Experimental section

Deuteriocyclopropane

To an oven-dried, heavy-walled tube fitted with a stopcock and provided with an argon atmosphere and a tiny stirring bar was added, in turn, AIBN (0.10 g, 0.61 mmol), Bu_3SnD (2.0 g, 1.8 mL, 6.8 mmol), and cyclopropyl bromide (0.39 g, 3.2 mmol). The stopcock was closed and the reaction tube was heated at 85 °C for 5 h. The reaction mixture was then cooled to room temperature; the stopcock was opened to allow the volatile materials in the product mixture to be collected in an evacuated glass coil cooled in liquid nitrogen. The deuterium-labeled cyclopropane product was purified and isolated by preparative gas chromatography (15*c*) using a modified Varian Aerograph A90-P3 instrument and a 0.63 cm × 3.7 m 20% SE-30 60/80 mesh Chromosorb W HMDS column.

Thermal isomerizations

The glass collection vessel containing the preparative GC purified **1-*d*** was connected to a glass adapter containing 3 Å molecular sieves; the adapter led to a vacuum line. The sample was cooled with liquid nitrogen and the helium present was removed from the collection vessel and the vacuum line. The cooling bath was removed to allow the gas to volatilize and fill the vacuum line. The pressure of gas in the line was noted, and the **1-*d*** sample was condensed in a small cold finger in the vacuum line close to the kinetic bulb with liquid nitrogen and a small Dewar. The pressure remaining in the line was noted, and a stopcock was closed to isolate the condensed **1-*d***. The difference in the two pressures recorded and the volume of the line defined the amount of **1-*d*** that had been condensed. The **1-*d*** remaining in the line was removed. Cyclopentane (anhydrous, Aldrich, Milwaukee, Wisconsin) in a glass coil was degassed 3 times using a freeze–thaw routine, allowed to warm, and admitted to the vacuum line. The pressure in the line was noted, the cyclopentane was condensed into the small cold finger containing the **1-*d*** sample, the stopcock was closed to isolate the condensed hydrocarbons, and the pressure in the line from the remaining cyclopentane was noted. The two pressure readings provided a measure of the amount of cyclopentane that had been condensed. The cyclopentane remaining in the line was pumped off.

The condensed mixture of **1-*d*** and cyclopentane was allowed to expand into an evacuated 280 mL kinetic bulb over a 2 min period by appropriate manipulations of stopcocks and warming the cold finger with hot water. The kinetic bulb was closed, the small amount of reactant and cyclopentane remaining between the cold finger and the cut-off stopcock atop the kinetic bulb was determined manometrically and then evacuated from the vacuum line.

When the designated time for a thermal isomerization had elapsed, the reaction mixture was quickly transferred from the kinetic bulb and collected in an evacuated u-tube immersed in liquid nitrogen. Subsequently the product mixture was transferred from the u-tube to a degassed NMR tube containing $CHCl_3$ and immersed in liquid nitrogen; the tube was sealed and the product mixture was analyzed by ^2H NMR spectroscopy at 92.1 MHz.

Thermal runs over 7.5, 10, 12.5, and 20 h used from 8.7 to 9.2 mg of **1-*d*** and 42 to 43 mg of cyclopentane; pressures in the kinetic bulb were 113 to 114 torr. The single run over 15 h employed 8.3 mg of **1-*d*** and no cyclopentane; the pressure was only 24 torr. The isomerization for this run was notably slower, but the distribution of **2-*d*** products was consistent with the distributions observed in other product mixtures (Table 1). The conversion vs. time data used to calculate the rate constant $1.29 \times 10^{-5}\ s^{-1}$ for the **1-*d*** to **2-*d*** isomerizations did not include the run in which cyclopentane was not present.

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