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Diastereotopically Distinct Secondary Deuterium Kinetic Isotope Effects on the Thermal Isomerization of Vinylcyclopropane to Cyclopentene

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Abstract: The (2'-deuterioethenyl)cyclopropanes isomerize to 3-deuteriocyclopentene at 341 °C with k_H/k_D = 1.08 and 1.15 for the Z and E isomers, respectively. These normal effects are consistent with 2Z-penten-1,5-diyl diradical transition structures for the isomerization.

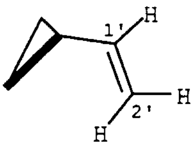
Thermochemical considerations appear to favor diradical mediated formulations for vinylcyclopropane to cyclopentene isomerizations[1] and yet mechanistic understandings of this reaction have not been definitive, for the stereochemistry of the isomerization and high level theoretical calculations of transition structures have not yet been reported.

Another approach to mechanistic insight is afforded by secondary deuterium kinetic isotope effect studies, especially when experimental and modern theoretical estimates of k_H/k_D rate constant ratios may be compared. For the isomerization of vinylcyclopropane to cyclopentene, possibly the simplest known hydrocarbon [1,3] sigmatropic shift, this objective remains elusive, for the experimental work is incomplete and no theory-based calculated k_H/k_D ratios are available. Thus the substantial normal intermolecular effect reported in 1984 by Chickos for the 2',2'-d_2 system, $k_H/k_D = 1.17 \pm 0.02$ at 338 °C,[2] has yet to be rationalized in detail. Qualitatively, this important preliminary observation suggested that there is no appreciable bond making at C(2') in the transition state, for the α-secondary isotope effect is not inverse; rather, the effect was interpreted in terms of a two-step path involving a stabilized diradical intermediate.[3] Similar k_H/k_D effects have been observed for other vinylcyclopropane to cyclopentene isomerizations.[4]

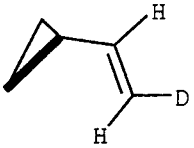
A comparable effect has been noted in the thermal stereomutation of *trans*-1,2-divinylcyclopropane to the cis isomer; kinetic runs with unlabeled and d_4-labeled systems revealed an isotope effect of 1.08 ± 0.02 (extrapolated to 25 °C) per deuterium at C(2') of a vinyl substituent.[5] Here again, the mechanism most probably involves a diradical transition structure: the sum of ΔH_f^o estimated for *trans*-divinylcyclopropane[6] and E_a for the isomerization,[7] (48.3 + 32.1) = 80.4 kcal/mol, is very nearly equal to an estimated ΔH_f^o for the 2*E*,5*E*-heptadien-1,7-diyl diradical, 79.3 kcal/mol.[8]

Mechanistic and stereochemical interests in the vinylcyclopropane to cyclopentene isomerization[9] and in diasteretopically specific secondary deuterium kinetic isotope effects[10] prompted the present work; it has found that deuterium substitution in the two distinct C(2') positions of vinylcyclopropane results in quite different k_H/k_D values.

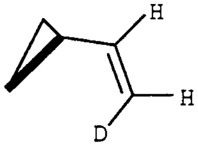
Vinylcyclopropane (**1**) was prepared from acetylcyclopropane;[11] reduction of ethynylcyclopropane[12] with Dibal-H, followed by D_2O, afforded ***E*-1-d** (C(2')H, 5.05 ppm, d, J = 17 Hz); reaction of deuterioethynylcyclopropane with Dibal-H, followed by H_2O, provided ***Z*-1-d** (C(2')H, 4.83 ppm, d, J = 10.3 Hz); and the 2',2'-d_2 analog **1-d₂** was prepared similarly (C_5H_5D + Dibal-H, then D_2O).[13] Reductions of ethynylcyclopropyl systems with Dibal-H are known to take place with very high regioselectivity and stereoselectivity.[13] The sample of **1-d₂** appeared to be at least 97% deuterium labeled at the two C(2') positions (Figure 1).



1



***E*-1-d**



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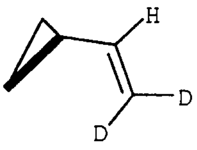

1-d₂

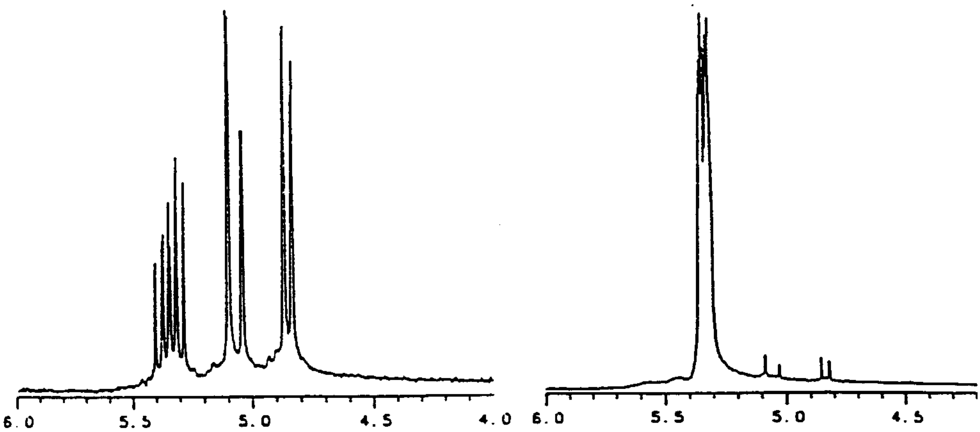

Figure 1. The vinyl ^1H NMR absorption region for **1** (left) and for **1-d₂** (right).

All four vinylcyclopropanes were purified by preparative gas chromatography on an SE-30 column and isomerized in a static gas-phase reactor at pressures of 485-500 torr at 341.2 ± 0.3 °C; the reactions were followed by capillary GC analyses; each 7-point kinetic run extended over more than 3 half-lives; and non-linear least-squares calculations[14] gave the first-order rate constants and k_H/k_D ratios shown in Table I.

Table I. First-Order Rate Constants and k_H/k_D Ratios for Gas Phase Isomerizations of Vinylcyclopropane and Deuterium Labeled Analogs to Cyclopentenes at 341.2 °C

Vinylcyclopropane	k_i (x 10^{-5} s^{-1})	k_H/k_D
1	8.29 ± 0.14	
***Z*-1-d**	7.67 ± 0.31	1.08 ± 0.05
***E*-1-d**	7.21 ± 0.18	1.15 ± 0.03
1-d$_2$	6.86 ± 0.16	1.21 ± 0.03

There is fair agreement between the product of the k_H/k_D ratios for ***E*-1-d** and ***Z*-1-d** and the measured k_H/k_D for **1-d$_2$**; the latter is not significantly larger than the value reported by Chickos,[2] especially considering possible differences in deuterium incorporation in the **1-d$_2$** samples employed.

The two hydrogens at C(2') of the vinyl group in **1**, and at C(1) of the 2*Z*-penten-1,5-diyl diradical, are diastereotopic, and there is no particular reason for deuterium substitution at one or the other position to cause the same k_H/k_D effect; not all nominally sp^2-hybridized C-H bonds of ground state or transition state structures are identical. The sense of the inequality is suggestive: with formation of an allylic radical moiety in a transition structure the H-C(2') bonds might well experience some modest changes in hydridization and more importantly, perhaps, the C(1')-C(2') bond would be expected to lengthen:[15] the anticipated increase from 1.33 to 1.39 Å would reduce eclipsing interactions between H-C(1') and *E*-H-C(2'), and, to a lesser degree, between C(1)-C(1') and *Z*-H-C(2'). These unequal reductions in steric congestion in transition structures should lead to normal k_H/k_D values as observed.

When reliable theoretical calculations become available for vinylcyclopropane and the C_5H_8 open-shell transition structures probably involved in this isomerization it should be possible to associate these diastereotopically distinct k_H/k_D effects with understandable force constant and frequency characteristics of the species involved. In the meantime, the case for diradical transition structures is somewhat augmented, and one may recognize that more information is potentially available in such isotope effects than previously appreciated.

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