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A Rotational Kinetic Isotope Effect in the Cyclopropylallene to 3-Methylenecyclopentene Thermal Rearrangement

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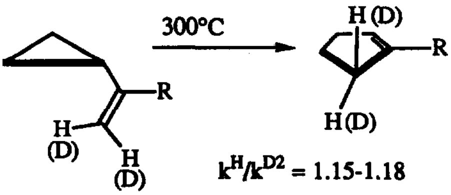
Abstract: The deuterium kinetic isotope effect at the exo-methylene carbon of allenyl-cyclopropane in its thermal 1,3-sigmatropic shift to 3-methylenecyclopentene was found to be 1.15/D_2 at 311.5°C. This is a striking example of a rotational effect.

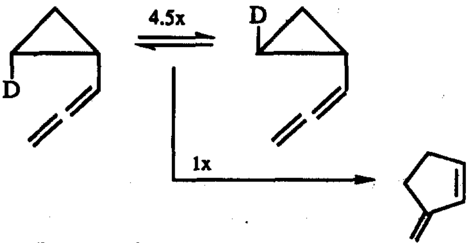
α-Secondary deuterium kinetic isotope effects usually result from reactions involving changes in the number of ligands attached to carbon and/or changes in electronegativity of substitutents. Generally, changes in bending frequencies which determine changes in zero point energy, are most important since deuterium generally lowers frequencies involving hydrogen motion by 0.707.[1] Shiner has tabulated the preference for deuterium on various types of carbon relative to that on acetylene at 25°C based on analysis of the vibrational spectra and application of the Bigeliesen equation.[2] These preferences allow prediction of isotope equilibria and even of kinetic isotope effects provided that the reaction coordinate vibration does not involve much hydrogen motion.[2] Indeed, it is possible to compare kinetic isotope effects with equilibrium isotope effects to determine the extent of changes in bonding.[3] However, occasionally secondary deuterium kinetic isotope effects are inverted relative to expectations based on equilibrium considerations. This occurs most notably when rotation of a methylene group is required in the reaction as first noted independently by both Crawford and Dolbier[4] and subsequently in our laboratory.[5] Such effects have also been noted by Caldwell in the thermal geometric isomerization of a *trans*-cyclohexene[6] and by Chickos and ourselves in the thermal vinylcyclopropane to cyclopentene rearrangement (Scheme 1).[7]



Scheme 1.

Equilibrium considerations would suggest that deuterium on the exomethylene carbon of vinylcyclopropane would promote its rearrangement to cyclopentene (olefin bending frequencies are low relative to alkyl methylene hydrogen scissoring frequencies so deuterium in the product will lower the zero point energy more than deuterium in the reactant). However, the exomethylene deuteriums slow the reaction by 15-18% at temperatures around 300°C. Since rotation of the exomethylene is required in this reaction, the observation is consistent with the previous citations and in the same direction. This "rotational" effect has been attributed to the conversion of an exomethylene rotational mode in the reactant to a reaction coordinate motion in the transition state so that the difference in zero point energies between the H and D compounds is lost in the transition state.[4,5] Therefore the hydrogen compound reacts faster. A similar argument based on semiempirical MO calculations was provided subsequently in ref. 6. Recently, Perrin questioned both the experimental and theoretical origin of rotational effects in alkene geometric isomerizations.[8] Further, it was found that there was little evidence for a deuterium effect in the rotation about an amide bond although the effect for N-deuterioformamide is 1.16 ±0.1 at 25°C. However, Perrin argues that a low frequency out of plane vibration is excited in the transition state to give rise to this isotope effect. Since examples of rotational deuterium kinetic isotope effects do not abound, reactions which display such an effect are welcome. One involving rotation about an allene moiety is described below.

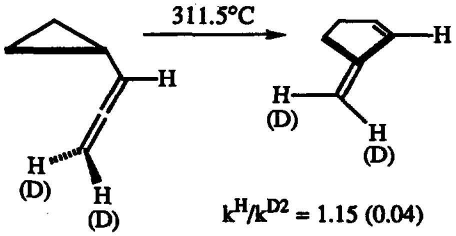
Dewar reported the thermal rearrangement of 1-methyl-1-cyclopropylallene to 2-methyl-3-methylenecyclopentene with log k (sec^{-1})=12.8-41,500/2.3RT.[9] Roth examined the rearrangement of cyclopropylallene itself to 3-methylenecyclopentene over a larger temperature range than Dewar's and found log k (sec^{-1})=14.08 -50,200/2.3RT.[10] Further, Roth found that *cis*-2-deuterio-1-allenylcyclopropane undergoes *cis* to *trans* isomerization roughly 4.5 times faster than the 1,3-shift (Scheme 2). The similarity of the activation parameters to the vinylcyclopropane rearrangement suggests a similar pathway. The vinylcyclopropane rearrangement proceeds with suprafacial-inversion stereochemistry which is consistent with orbital symmetry control, and as noted above has a substantial normal secondary deuterium kinetic isotope effect at the terminal methylene.[7]



Scheme 2.

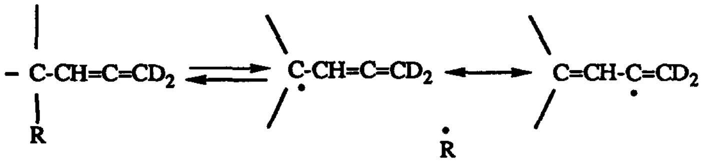
3',3'-Dideuterio-1-cyclopropylallene was prepared by a modification of the procedure described by Roth[10] using the Skattebol[11] allene route which involves addition of dibromocarbene to vinylcyclopropane followed by reaction with methyl lithium in diethylether at -40°C. The vinylcyclopropane used was prepared from cyclopropanecarboxaldehyde and triphenyl-dideuteriomethylene phosphorane giving material with 97% of two deuteriums by nmr.

After gc purification protio and 3',3'-dideuteriocyclopropylallene were pyrolyzed separately in a well-conditioned 2-liter bulb held at 311.5°C. Capillary gc analysis of the reaction products followed careful removal of the pyrolysate from the bulb, including exclusion of air.[10] At longer reaction times methylcyclopentadienes were formed from the primary product as was reported by Roth. The kinetics revealed that $k^{H}=2.44(0.09) \times 10^{-5}$ sec^{-1}, and $k^{D}2 = 2.12 (0.02) \times 10^{-5}$ sec^{-1} where the errors are calculated from the combined data of 6-7 runs for each compound, it is worthwhile noting that the rate constants are consistent with Roth's data, Thus $k^{H}/k^{D}2 =$ 1.15 (0.04) at 311.5°C (Scheme 3). Since there must be a ninety degree (90°) rotation of the exo-methylene of the allene to give the exo-methylene of the primary product, the isotope effect is consistent with the previous work.



Scheme 3.

An alternative origin of the kinetic isotope effect is a fraction factor difference between deuterium on exomethylene carbon of an allene and on an exo-methylene carbon of a 1-methyleneallyl radical (Scheme 4).



Scheme 4.

However, submission of unscaled PM3 and AM1 calculated frequencies for the deuterated and undeuterated molecules to the Bigeleisen equation reveals but a small preference for deuterium on the allene compared to the methylene-allyl radical (1.024 ave. for two deuteriums at the reaction temperature).[12] Thus the isotope effect would appear to be a rotational one.

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12. We thank Nancy L. Brichford for this result. At 25°C the preference in 1.075 for two deuteriums (average of 1.084 [PM3] and 1.066 [AM1]).

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