J. Am. Chem. Soc. **1993,** *115,* 4548–4553

Hydrogen–Deuterium Fractionation Factors for Hydrogen–sp^2 Carbon Bonds in Olefins and Allyl Radicals

Joseph J. Gajewski,* Leif P. Olson, and Kenneth J. Tupper

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received June 26, 1992

Abstract: Thermally induced 3,3-shift of *trans*-1,2-divinylcyclopropane, **1**, and *trans*-1,2-bis(2′,2′-dideuteriovinyl)-cyclopropane, 1-d_4, to cycloheptadiene has a kinetic isotope effect of 1.08 ± 0.02/D when extrapolated to 25 °C. To the extent that the transition state resembles two allyl radicals, the kinetic effect is the fractionation factor for deuterium between sp^2 allyl radical carbon and sp^2 olefinic carbon. AM1 calculations on allyl radicals reveal a similar fractionation factor. The new value for the FF of allyl radical requires a correction to previously developed linear free energy relationships for kinetic and equilibrium isotope effect in 3,3-shifts and Diels–Alder reactions. The corrections are moderate, altering the previously determined extent of bond breaking and bond making by up to 50% only when there is little bond making, but do not alter the relative extents of bond making and breaking in the large number of compounds examined.

The use of secondary deuterium kinetic isotope effects (kie) to reveal the extent of bond making and bond breaking in organic reactions in general, and pericyclic reactions in particular, relies on a comparison of the kinetic effects to equilibrium preferences for hydrogen and deuterium on the atoms of interest (EIE).[1] The comparison then takes the form of the linear free energy relationship kie = EIE^i, where i represents the extent of bond making or bond breaking, and is analogous to a Bronsted relationship for the extent of proton transfer in a general-acid-catalyzed reaction. Shiner and Hartshorn provided lists of *fractionation factors*, FFs, for the preference for deuterium on various types of carbon relative to deuterium on acetylene using the hydrogen compounds as the reference.[2] Typical values are 1.50 for the central carbon of propane and 1.214 for the terminal carbon of propene at 25 °C. If propane and 1-deuteriopropene were equilibrated, 2-deuteriopropane and propene would dominate the mixture by 1.50/1.21 = 1.23 ignoring symmetry numbers.

$$\mathrm{CH_3\text{-}CH_2\text{-}CH_3 + CHD{=}CH\text{-}CH_3 \leftrightarrow CH_3\text{-}CDH\text{-}CH_3 + CH_2{=}CH\text{-}CH_3}$$

$$K_{\mathrm{eq}} = 1.23$$

Shiner and Neumann have provided a more up to date and more extensive list of FFs.[3] The fractionation factors from Shiner's laboratory were determined from vibrational analyses of the spectra of small molecules. There should be concern as to their extrapolability to larger systems. Indeed, from some of our studies of 3,3- and 1,3-sigmatropic shifts, we would suggest that the FF of C-1 of larger olefins is more like 1.26 at 25 °C.[1]

The use of the linear free energy relationship above assumes that the only factors affecting transition states are those inherent in the overall change from initial to final state. Thus it is assumed that the sp^2 carbon of, for example, an allyl radical in a transition state is identical, that is, has the same hydrogen vibrations as an sp^2 carbon of an exomethylene group in a ground-state olefin. That this is not totally the case and the correction for the deviation is the focus of this study.

The FFs of carbons involved in unstable intermediates like cations, radicals, and carbanions represent the nature of carbon at extremes of bond breaking so the FFs of these species are particularly important in assessing transition-state structure. Often the assumption is made that the FF of these allyl centers is near that of C-1 of propene.[1] However, an ab initio study by Dupuis focused on the frequencies of allyl radical and propene as well as the 1,1,3,3-tetradeuterio and 1,1-dideuterio materials, respectively.[4a] From these an equilibrium constant can be determined and is found to be 1.07/D (frequencies scaled by 0.90) favoring deuterium on propene.[4b] This suggests that sp^2 hybridized carbon in radicals has substantially looser bonds than sp^2 carbon in olefins indicating that previous assumptions[1] might not be totally correct.

$$\mathrm{CD_2CHCD_2 + 2CH_2{=}CHCH_3 = CH_2CHCH_2 + 2CD_2{=}CHCH_3}$$

$$K = 1.07^4$$

Recently, Houk has provided ab initio theoretical support for the interpretation of kinetic isotope effects in 3,3-shifts as described above. A further calculation on the maximum isotope effect expected when sp^2 carbon of allyl radical is generated from ground-state precursors made it clear that sp^2 of allyl radical is not the same at sp^2 carbon of an olefin.[5] Indeed, the calculation suggests a fractionation factor favoring a deuterium on an olefinic carbon relative to allyl radical carbon by 1.011–1.014 at 248 °C at the UMP2/6-31G* level.

To test the predictions of ab initio theory, an experimental determination of the FF between sp^2 centers at the terminus of olefins and allylic radicals is described in this paper. Semiempirical calculations of the FF in allyl radicals were performed as a test as well.

Results

trans-1,2-Divinylcyclopropane, **1**, undergoes a 3,3-sigmatropic shift 1,4-cycloheptadiene, **2**, with log k = 12.1–31 000/2.3RT[6a] or 13.1–33 000/2.3RT.[6b] It is likely that the cis isomer is formed in the slow step of the reaction, and it rapidly undergoes the 3,3-shift. Crawford showed that the trans isomer undergoes

---

[1] Gajewski, J. J. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: New York, 1987; Vol. 7, pp 115–175.

[2] Hartshorn, S. R.; Shiner, V. J. *J. Am. Chem. Soc.* **1972,** *94,* 9002.

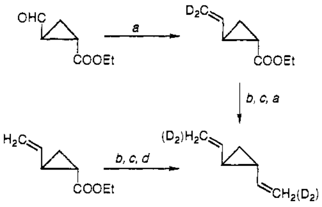
[3] Shiner, V. J.; Neumann, T. E. *Z. Naturforsch., A: Phys. Sci.* **1989,** *44,* 337.

[4] (a) Takada, T.; Dupuis, M. *J. Am. Chem. Soc.* **1983,** *105,* 1713. (b) Bigeleisen, J.; Mayer, M. *J. Chem. Phys.* **1947,** *15,* 261. Wolfsberg, M.; Stern, M. J. *Pure Appl. Chem.* **1964,** *8,* 225.

[5] Houk, K. N.; Gustafson, S. M.; Black, K. A. *J. Am. Chem. Soc.* **1992,** *114,* 8565.

0002-7863/93/1515-4548$04.00/0

Scheme I[a]



1 (or 1-d_4)

[a] (a) $Ph_3P{=}CD_2$, DMSO-d_6; (b) $LiAlH_4$, Et_2O; (c) Cro_3/3,5-dimethylpyrazole, CH_2Cl_2; (d) $Ph_3P{=}CH_2$, DMSO.

Table I. Two Point Rate Constants from Simultaneous Pyrolyses of **1** and **1**-d_4 at the Temperatures Indicated[a]

temp (°C)	k^H (**1**)	$k^{D}4$ (**1**-d_4)	$k^H/k^{D}4$	calc[b]	calc[c]
100.	0.0109	0.00854	1.27	1.17	1.215
140.	0.635	0.556	1.14	1.15	1.18
144.	0.827	0.666	1.24	1.14	1.18
157.	4.68	4.05	1.16	1.13	1.17
159.	4.14	3.52	1.18	1.13	1.17
159.	5.09	4.32	1.18	1.13	1.17
173.	13.9	11.9	1.17	1.12	1.15
180.	27.6	23.4	1.18	1.12	1.15
182.	35.2	31.0	1.13	1.12	1.15
190.	59.9	51.1	1.17	1.11	1.14
191	56.4	48.9	1.16	1.11	1.14

[a] Rate constants are $k(/s) \times 10^{-5}$; temperature control is to ±2 °C. [b] From frequencies of ref 4 scaled by 0.9; gives 1.07/D at 25 °C. [c] From frequencies of ref 4 unscaled; gives 1.08/D at 25 °C.

racemization 2.4 times faster than rearrangement suggesting that homolytic ring opening occurs to give a biradical species which undergoes rotation around previously restricted ring bonds then recloses either to the enantiomer or to the cis isomer.[6b] Thus, a determination of the kinetic isotope effect for the conversion of *trans*-1,2-bis-(2′,2′-dideuteriovinyl)cyclopropane, **1**-d_4, to cycloheptadiene should be closely related to the equilibrium constant between olefinic sp² carbon and allylic radical sp² carbon provided that the biradical intermediate does not reside in a deep potential energy well.

trans-1,2-Divinylcyclopropane, **1**, and its tetradeuterioisomer were synthesized by well-known procedures (Scheme I).[7] The thermal rearrangement of each proceeded to **2** as reported. In order to examine the kinetic isotope effects, two tubes containing **1** and **1**-d_4 were pyrolyzed simultaneously to a certain percent reaction in an oil bath held to roughly the temperature indicated in Table I. The analyses were conducted by GC with the injector and detector at 140 °C and a column temperature of 70 °C. The kinetic isotope effect at each temperature is shown in Table I along with the calculated FF based on scaled and unscaled frequencies of ref 4a.

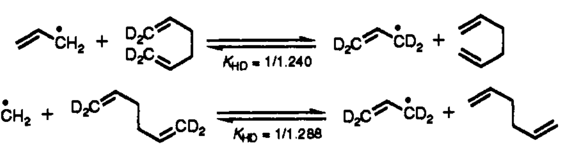
The AM1 program[8] was employed to obtain harmonic vibrational frequencies of propane, 2-deuteriopropane, propene, and *trans*-1-deuteriopropene to determine the equilibrium constant at 248 and 25 °C for the reaction

$$CH_3\text{-}CH_2\text{-}CH_3 + CHD{=}CH\text{-}CH_3 \rightarrow CH_3\text{-}CDH\text{-}CH_3 + CH_2{=}CH\text{-}CH_3$$

The values are 1.054 and 1.165, respectively. The vibrational frequencies were used without weighting in the Bigeleisen equation (ignoring symmetry) expressed as a vibrational product after application of the Teller–Redlich rule.[4b]

AM1 was also used to determine the frequencies of allyl radical as well as the 1,1,3,3-tetradeuterio species and 1,5-hexadiene and 1,1,6,6-tetradeuterio-1,5-hexadiene to determine the FFs relative to olefinic carbon. Both extended and gauche conformations of the diene were used. The tetradeuterio substitution was employed to reduce complications from symmetry destruction. The results are given in Table II.

Table II. AM1 Calculated Fractionation Factors (25 °C)



Discussion

Fractionation Factor for Allyl Radical. Initially, kinetic data for conversion of **1** to **2** was gathered only at 159 °C where $k^H/k^{D_4} = 1.18$ was found. Extrapolation of this value to 25 °C assuming similar A factors for H and D gives 1.275 or 1.06/D, a value that cannot be ignored in any analysis of reactions involving homolysis of C–C bonds. Concern that the temperature dependence was more complex and that more experiments especially at lower temperatures were necessary, a temperature study was initiated even recognizing that only a small change might be observed over the usual 40 °C temperature range. This concern prompted inclusion of kinetic points at 100 °C where the half-life approached 3 months and at 191 °C where the half-life is less than 0.5 h. Even though the temperature control for the pyrolyses of **1** and **1**-d_4 was suboptimal by the usual standards for accurate determination of Arrhenius parameters, the enormous temperature range used allowed accurate determination, with low standard deviations of $\log k(\mathbf{1}) = 12.42(0.337) - 33183(667)/2.303RT$ ($r = 0.998$) and of $\log k(\mathbf{1}\text{-}d_4) = 12.52(0.352) - 33519(697)/2.303RT$ ($r = 0.998$) using an unweighted least squares analysis. This shows that the reaction has kinetic behavior nearly identical to that previously reported.[6]

The difference in activation parameters gives an equation for the temperature dependence of the isotope effect namely $\log k^H/k^{D_4} = -0.1 + 326/2.303RT$. This allows calculation of $k^H/k^D = 1.083$ per deuterium at 25 °C. Alternatively, the temperature dependence of the kinetic isotope effects gives $\log k^H/k^{D_4} = -0.088(0.053) + 316(105)/2.303RT$ ($r = 0.709$) or 1.085 per deuterium at 25 °C. While great accuracy and precision cannot be claimed for the calculated value at room temperature, its value is probably greater than 1.06 and less than 1.10 per deuterium. Concern that the temperature dependence of the isotope effect might not have been sufficiently established by the data should be examined in light of the expected equilibrium isotope effect at each temperature predicted by the Bigeleisen equation from the ab initio calculations with and without scaling of the frequencies (Table I).[4] Clearly the unscaled frequencies provide a better match to experiment. It should be recognized that the change in observed isotope effect from 100 to 191 °C is only a factor of 1.07. Considering that secondary isotope effects determined by GC under similar circumstances are good to ±2%, the experimental data appear to reproduce the temperature dependence expected.

As a point of comparison of the isotope effects, Crawford found that *trans*-1,2-bis(2′,2′-dideuteriovinyl)oxirane, **3**-d_4, gave the 3,3-shift product, dihydroxepin, with $k^H/k^{D_4} = 1.16$ at 150 °C.[9] A companion study of the effect of the terminal deuterium on the racemization of optically active starting material gave an isotope effect of 1.084 and a kinetic effect of 1.11 on the formation of a 1,3-shift product-all at 150 °C. Thus, substantial isotope effects accompany conversion of terminal olefinic sp² carbon to allyl radical sp² carbon.

---

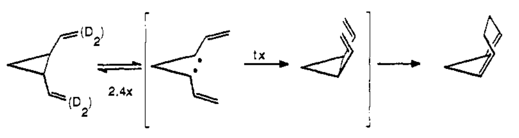
(6) (a) Vogel, E. *Angew. Chem.* **1960**, *72*, 4. Vogel, E.; Ott, K.-H.; Gajek, K. *Justus Liebigs Ann. Chim.* **1961**, *644*, 172. (b) Arai, M.; Crawford, R. J. *Can. J. Chem.* **1972**, *50*, 2158.

(7) Brown, J. M.; Golding, B. T.; Stofko, J. J., Jr. *J. Chem. Soc., PII* **1978**, 436.

(8) Dewar, M. J. S.; Merz, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 5146.

(9) Vukov, V.; Crawford, R. J. *Can. J. Chem.* **1975**, *53*, 1367.

Scheme II



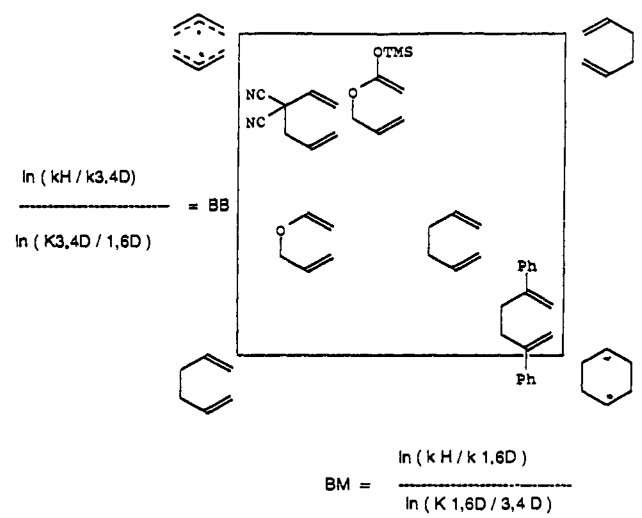
The value of the kinetic isotope effect for the 3,3-shift of **1** is probably close to the value for equilibration of deuterium between sp^2 terminal olefinic carbon and allyl radical terminal carbon as argued in the introduction. Since the 3,3-shift of *cis*-1,2-divinylcyclopropanes is fast even at room temperature, the rate determining step for the reaction is either ring opening to a diradical which undergoes the 3,3-shift or geometric isomerization to the cis isomer. Ring opening of the trans isomer cannot be rate determining since formation of enantiomerized trans material occurs 2.4 times faster than the 3,3-shift unless the enantiomerization is a separate pathway, perhaps a concerted double rotation reaction. However, it is most likely that a biradical is formed by homolytic cleavage of the C-1, C-2 bond and that species gives the cis isomer in the rate determining step for the 3,3-shift. Further, this species must closely resemble the transition state for formation of the cis isomer judging by reasonable estimates of its heat of formation relative to starting material: i.e., using 82 kcal/mol for the BDE of a tertiary–tertiary bond, 27 kcal/mol for the strain which is relieved on ring opening, 12.5(2) kcal/mol for the allyl radical resonance energy, and the biradical species should be about 30(4) kcal/mol above starting material. Thus the biradical resembles closely the transition state for reaction which is 33 kcal/mol above the starting material (Scheme II).

AM1 Calculation the Allyl Radical Fractionation Factor. Interestingly, the AM1 calculation of the equilibrium isotope effect expected for the terminal olefinic sp^2 carbon in the anti conformation of 1,5-hexadiene to allyl radical sp^2 carbon is 1.065/D at 25 °C. The quality of this type of calculation was assessed by comparison of the calculated equilibrium constant for the 1-deuteriopropene plus propene to 2-deuteriopropane plus propene reaction to the equilibration of various terminal olefin sp^2 deuterium containing materials with saturated methylene containing deuterium molecules.[1] The calculated value of 1.165 per deuterium at 25 °C is in excellent agreement with that extrapolated from ref 1. On the other hand AM1 underestimated the equilibrium isotope effect in the 1,1,6,6-tetradeuterio-1,5-hexadiene to 3,3,4,4-tetradeuterio-1,5-hexadiene equilibrium by roughly 40%.

The origin of the isotope effect observed in the 3,3-shift of **1** and the AM1 and ab initio[4] calculated values appears to be looser out-of-plane bends in the allyl radical.

Previous Relationship between kie and EIE. Previous analyses of Cope and Claisen rearrangements focused on bond making and bond breaking processes whose kinetic isotope effects might be compared with measured equilibrium fractionation of deuterium between sp^3 and sp^2 carbon in starting material and product using the linear free energy relationship; kie = EIE^i as illustrated in the More O'Ferrall–Jencks (MOFJ) diagram of Scheme III.[1] In the case of Cope rearrangements of 1,5-hexadienes with substitution on C-2 and/or C-5, the allylic carbons, C-3 and C-4, are interchanged with the terminal methylene carbons, C-1 and C-6, so that the fractionation factors or equilibrium isotope effects for comparison of the bond making and bond breaking kies are the same. Further, in this case the extent of bond making and bond breaking are related as $i_{\mathrm{BM}} + (1 - i_{\mathrm{BB}}) = 1$, i.e., the average transition state lies along the diagonal of Scheme III which connects the 2-allyl radical extreme with the 1,4-diyl extreme. However, the kies at the bond making and bond breaking sites are unrelated if unsymmetrical 1,5-hexadienes are studied with the Claisen rearrangement being a particularly important example. Here the equilibrium isotope effect at the bond making site involves conversion of sp^2 olefinic methylene carbon to an sp^3 aliphatic methylene carbon. And, the equilibrium isotope effect at the bond breaking site involves conversion of sp^3 aliphatic carbon which is attached to oxygen to an sp^2 olefinic methylene carbon.

Scheme III



Ramifications of the Current Results. As indicated above, the linear free energy relationship, kie = EIE^i, has been assumed to be appropriate for the comparison of kies to EIEs on the expectation that the factors affecting transition-state vibrations are the same as those affecting ground states. Thus the equilibrium fractionation factors are assumed to represent the maximum possible kinetic isotope effect at that site. However, if the terminal allyl radical C–H bonds are looser than terminal olefinic C–H bonds giving rise to an equilibrium isotope effect of 1.08/D favoring olefinic sp^2 C–D bonds, then the maximum expected for bond breaking kinetic isotope effects must include this factor. In all of the previously examined 3,3-shifts this amounts to an increase of roughly 50% in the maximum value expected when deuterium is on the sp^3 carbon which becomes an sp^2 carbon of an allylic radical. This gives a corresponding reduction (up to $^1/_3$) in the extent of bond breaking estimated for the 3,3-shifts previously examined depending on the extent of bond making.

The most economical description of the relationship between the bond breaking kie and the fractionation factors is given in eq 1 where $K_{\mathrm{sp^2D/allylD}}$ is the fractionation factor for two deuteriums between olefinic sp^2 carbon and allyl radical terminal carbon, i.e., the square root of the value determined in the experiments above for pyrolysis of **1**-d_4. The relationship of eq 1 is the simplest correction possible for the fractionation factor recognizing that the more bond making that occurs, the smaller is the "allyl radical CH loosening correction" necessary for characterization of bond breaking. The "allyl radical CH loosening correction" should be zero when the transition state has 100% bond making which is the case when the transition state resembles cyclohexane-1,4-diyl or when the transition state resembles product, hence the exponent, 1-BM, on this correction in eq 1. Equation 2, which is eq 1 rearranged, represents the new relationship between the kinetic and equilibrium isotope effects on the bond breaking site.

$$\mathrm{BB} = \frac{\ln k^{\mathrm{H}}/k_{3,4\mathrm{D}}}{\ln (K_{3,4\mathrm{D}/1,6\mathrm{D}}(K_{\mathrm{sp^2D/allylD}})^{1-\mathrm{BM}})} \qquad (1)$$

$$k^{\mathrm{H}}/k_{3,4\mathrm{D}} = (K_{3,4\mathrm{D}/1,6\mathrm{D}})^{\mathrm{BB}}(K_{\mathrm{sp^2D/allylD}})^{\mathrm{BB}(1-\mathrm{BM})} \qquad (2)$$

When deuterium is on the terminal sp^2 olefinic center which becomes a saturated carbon, the maximum bond making kinetic isotope effect expected is also affected by the increase in the bond breaking effect. Thus transition states with little bond making and a large amount of bond breaking can have a normal kinetic isotope effect at the terminal methylene position due to the allyl radical–olefinic carbon fractionation factor which is in the opposite direction from the bond making isotope effect. However, transition states with only a small amount of bond breaking have but a small contribution of the allyl radical–olefinic carbon fractionation factor which would then have inverse kinetic isotope effects. One way of allowing a comparison between kinetic and equilibrium isotope effects here is to scale both by the "allyl radical CH loosening factor" so that the extent of bond making ranges from 0 to 1.0. But, to accurately model the extent of bond making the scaling factor must be a function of the extent of bond breaking hence the exponent BB in eq 3 which appears to be the simplest expression for bond making given the coupling to bond breaking. Equation 4, which is eq 3 rearranged, represents the new relationship between kinetic and equilibrium effects at the bond making sites.

$$\mathrm{BM} = \frac{\ln((k^{\mathrm{H}}/k_{1,6\mathrm{D}})/(K_{\mathrm{sp^2D/allylD}})^{\mathrm{BB}})}{\ln((K_{1,6\mathrm{D}/3,4\mathrm{D}})/(K_{\mathrm{sp^2D/allylD}})^{\mathrm{BB}})} = \frac{\ln(k^{\mathrm{H}}/k_{1,6\mathrm{D}}) - \mathrm{BB}\ln(K_{\mathrm{sp^2D/allylD}})}{\ln(K_{1,6\mathrm{D}/3,4\mathrm{D}}) - \mathrm{BB}\ln(K_{\mathrm{sp^2D/allylD}})} \quad (3)$$

$$k^{\mathrm{H}}/k_{1,6\mathrm{D}} = (K_{1,6\mathrm{D}/3,4\mathrm{D}})^{\mathrm{BM}}(K_{\mathrm{sp^2D/allylD}})^{\mathrm{BB}(1-\mathrm{BM})} \quad (4)$$

In any one case, the determination of the extent of bond breaking and making must be done by substituting the appropriate rate and equilibrium ratios into eqs 1 and 3 and then solving for BB and BM simultaneously.

Equations 1–4 are more complicated than the original linear free energy equations used to characterize these reactions but resemble the original zeroth-order linear free energy relationship of Scheme III for more central transition states (with more bond making) and provide the same relative positions for all transition states. Thus previously published results with transition states having less than 50% bond breaking, i.e., the parent 1,5-diene systems with radical stabilizing groups at C-2 and C-5, need little correction, but the transition states for the Evans' oxyanionic Cope rearrangement in THF,[10] the Ireland Claisen rearrangement,[11] the aromatic Claisen rearrangement,[12] the 3,3-dicyano-1,5-hexadiene studied originally by the Zagreb (Croatia) group,[13] and the *cis*-1,2-divinylcyclobutane and cyclopropane rearrangements[14] should be recognized as having more bond making and less bond breaking than previously estimated using the original linear free energy relationship.

More O'Ferrall–Jencks Diagrams Incorporating Eqs 1 and 3. Recently, Houk has suggested that the MOF-J diagram appropriate to 3,3-shifts based on the standard linear free energy relationship, kie = EIE^i, be altered as a result of the finding by ab initio theory that allylic CH bonds are "looser" than olefinic CH bonds.[5] Houk's modification takes the form of extending the bond making coordinate in the negative direction (to the left of zero in Scheme III) to account for kinetic isotope effects resulting from transition states with little bond making (see Figure 11 of ref 5). Equations 1 and 3 give rise to a more complicated modification of the MOF-J diagrams which at the same time retain the symmetry and apparent orthogonality of the bond making and breaking coordinates. Thus, it is possible to plot lines of constant C3,4 and of constant C1,6 kinetic isotope effects (isokies) ranging from unity to the maximum value *in units relative to the maximum expected isotope effect* within a square whose coordinates are still the extent of bond breaking and making coordinates from zero to unity.[15] This is shown in Scheme IV where what is plotted within the diagram are ten contour lines of relative kies from unity to the maximum values as a function of the values of BB and BM necessary to reproduce the constant kinetic isotope effects. The dotted lines within Scheme IV depict the limits of the original linear free energy relationship represented by Scheme III. Thus, for a given bond breaking kinetic isotope effect, the calculated BB will lie along one of the more or less horizontal contours, and, for a given bond making kinetic isotope effect, the calculated BM will lie along one of the more or less vertical contours. At the intersection of the two contour lines is the transition-state structure located relative to the bond breaking and bond making extremes and relative to starting material and product.

Characterization of Diels–Alder Reactions. The finding that deuterium on the allyl radical carbon is less stable than on the sp^2 olefinic carbon alters the characterization of transition states in the Diels–Alder reaction where deuterium substitution on the terminal carbons of isoprene were used to assess the extent of bond making in the reaction with acrylonitrile and vinylidene cyanide. Here, no bond making at the isotopic site accompanied by complete bond making at the other terminal carbon should lead to a normal isotope effect instead of but a small inverse effect.[16] The correction must be in the form of a scaling factor just as with the BM coordinate in the 3,3-shift (eqs 3 and 4). The correction suggests that previous observations of no kinetic isotope effect at the olefinic carbon which would form a bond to the α carbon of acrylonitrile and vinylidene cyanide should be interpreted in terms of a small amount (ca. 20%) of bond making (Scheme V).

Summary

The moderately large normal secondary deuterium kinetic isotope effect at the terminal positions of *trans*-1,2-divinylcyclopropane when undergoing ring opening ($k^{\mathrm{H}}/k^{\mathrm{D}_2}$ = 1.16 at 25 °C) requires reevaluation of the maximum kinetic isotope expected at the terminal and allylic positions upon conversion of a ground-state olefin to an allyl radical by cleavage of an allylic bond. Since the maximum effect expected for two deuteriums in the conversion of an aliphatic methylene to a terminal olefinic methylene is ca. 1.36 at 25 °C, and now the maximum effect expected for two deuteriums in the conversion of a terminal olefinic methylene to an allyl radical is 1.16, the maximum normal kinetic isotope effect in the conversion of an aliphatic methylene to an allylic radical is 1.42 for two deuteriums. However, in pericyclic reactions where olefinic and aliphatic methylene carbons are interconverted via transition states with partial allylic radical character, the maximum expected isotope effect at the bond breaking and bond making sites is a function of the extent of bond making and bond breaking, respectively, i.e., the extent of formation of allyl radical character. Previously characterized pericyclic transition states with small inverse kies at the bond making site and a large normal kie at the bond breaking site are now recognized as having more bond making than was suggested on the basis of just the aliphatic methylene to olefinic methylene fractionation factor.

---

(10) Gajewski, J. J.; Gee, K. R. *J. Am. Chem. Soc.* **1991**, *113*, 968.

(11) Gajewski, J. J.; Emrani, J. *J. Am. Chem. Soc.* **1984**, *106*, 5733.

(12) McMichael, K. D.; Korver, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 2746. Kupczyk-Subotkowska, L.; Saunders, W. H., Jr.; Shine, H. J. *J. Am. Chem. Soc.* **1988**, *110*, 7153. Kupczyk-Subotkowska, L.; Subotkowski, W.; Saunders, W. H., Jr.; Shine, H. J. *J. Am. Chem. Soc.* **1992**, *114*, 3441.

(13) Humski, K.; Malojcić, R.; Borcić, S.; Sunko, D. E. *J. Am. Chem. Soc.* **1970**, *92*, 6534.

(14) Gajewski, J. J.; Hawkins, C. M.; Jimenez, J. L. *J. Org. Chem.* **1990**, *55*, 674.

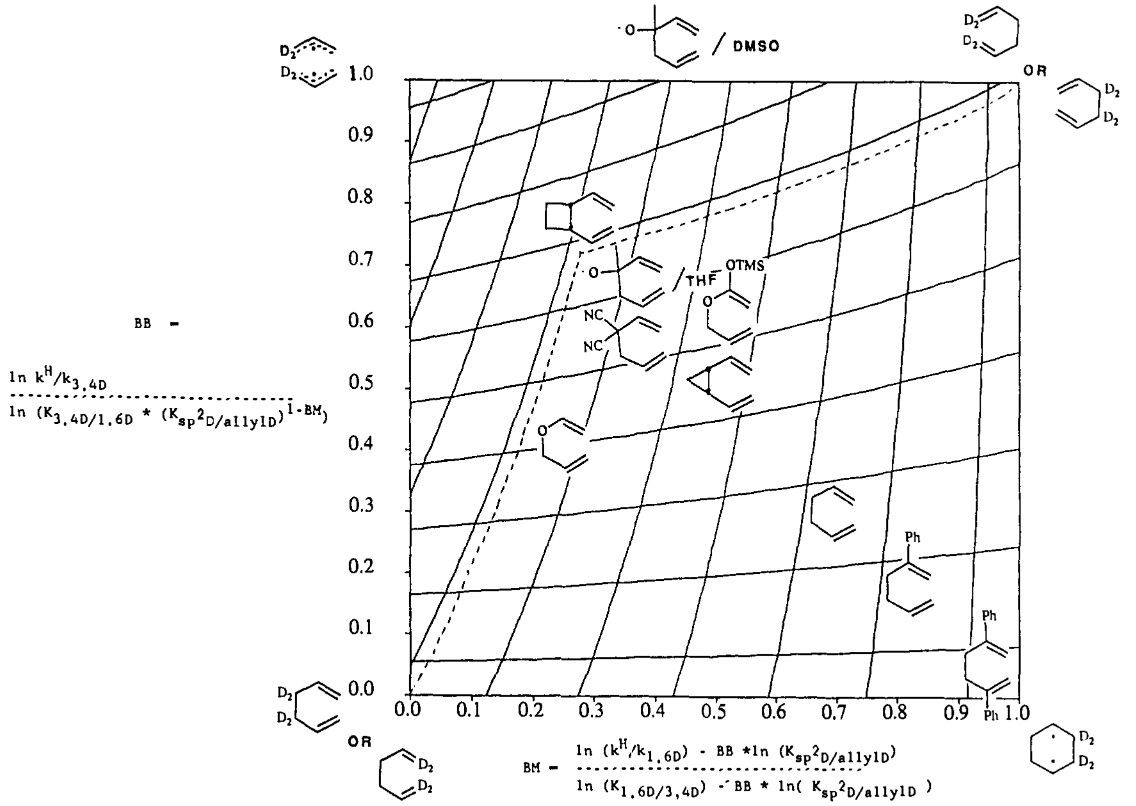
(15) Sims, L. B.; Lewis, D. E. In Isotopes in Organic Chemistry; Buncel, E., Lee, C. C., Eds.; Elsevier: New York, 1984; Vol. 6, pp 161–259.

(16) Gajewski, J. J.; Peterson, K. B.; Kagel, J. R.; Huang, Y. C. *J. Am. Chem. Soc.* **1989**, *111*, 9078.

(17) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.

(18) Core, E. J.; Fleet, G. W. J. *Tetrahedron Lett.* **1973**, *45*, 4499.

Scheme IV



Experimental Section

NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300 MHz for proton and at 75 MHz for carbon. Mass spectra were obtained on a Hewlett-Packard 5980 GC/MS system with an HP 5971 mass-selective detector. Infrared spectra were recorded on a Mattson 4020 Galaxy Series FT-IR spectrometer. Analytical gas chromatography was done on a Varian 3700 GC equipped with a 60-m × 0.25-mm (I.D.) DB-5 capillary column and flame ionization detection, connected to a Varian Model 4270 electronic integrator. Preparative gas chromatography of the final products was performed on a Varian 2700 GC using a 10′ × 1/4″ packed column (OV-17, 25% on Chromosorb P).

Ethyl *trans*-2-(2′,2′-Dideuteriovinyl)cyclopropanecarboxylate. Ethyl 2-formyl cyclopropanecarboxylate (Aldrich, "predominantly trans", 4.0 g, 28 mmol) in 10 mL of DMSO-d_6 was added at room temperature to a solution of (dideuteriomethylene)triphenylphosphorane (28 mmol; prepared according to literature procedures[17]) in 20 mL of DMSO-d_6. Stirring for 45 min was followed by pouring the reaction mixture into 150 mL of ice water, and extraction occurred with 3 × 75 mL portions of pentane. The combined extracts were washed with 100 mL of water, dried (Na_2SO_4), concentrated, and distilled (75–80 °C/8 Torr) to give 3.52 g (21 mmol, 75% yield) of product, which was a 74:12:14 mixture of desired product, its cis isomer, and starting material by ^{1}H NMR and GC. Deuterium incorporation at the terminal vinyl position was 93%: ^{1}H NMR ($CDCl_3$) δ 5.41 (br d, J = 3 Hz, 1 H), 5.06 (d, J = 17 Hz, 0.07 H), 4.89 (d, J = 10 Hz, 0.07 H), 1.45 (m, 2 H), 0.86 (t, J = 8 Hz, 2 H).

***trans*-2-Vinylcyclopropanemethanol.**[7] Ethyl *trans*-2-vinylcyclopropanecarboxylate[7] (3.6 g, 25 mmol) in 10 mL of ethyl ether was added to a solution of $LiAlH_4$ (1.0 g, 25 mmol) in 25 mL of ethyl ether at 0 °C. The mixture was stirred for 1 h at room temperature and then carefully quenched at 0 °C with 1 mL of water, 1.5 mL of 10% aqueous NaOH, and 3 mL of water. Filtration, drying ($MgSO_4$), and concentration, followed by distillation (57–58 °C/8 Torr), gave 2.2 g (22 mmol, 90% yield) of product: ^{1}H NMR ($CDCl_3$) δ 5.45 (ddd, J = 16, 12, and 5 Hz, 1 H), 5.05 (dd, J = 12 and 2 Hz, 1 H), 4.90 (s, 1 H), 4.84 (dd, J = 12 and 2 Hz, 1 H), 3.43 (d, J = 7 Hz, 2 H), 1.34 (septet, J = 4 Hz, 1 H), 1.10 (m, 1 H), 0.65 (m, 2 H).

***trans*-2-(2′,2′-Dideuteriovinyl)cyclopropanemethanol.** Ethyl *trans*-2-(2′,2′-dideuteriovinyl)cyclopropanecarboxylate (3.0 g, 21 mmol) was reduced and worked up in the same way as for the nondeuterated compound to obtain 1.1 g (11 mmol, 52% yield) of product, containing 15% cis isomer by GC and ^{1}H NMR: ^{1}H NMR ($CDCl_3$) δ 5.40 (br d, J = 3 Hz, 1 H), 5.05 (d, J = 16 Hz, 0.07 H), 4.89 (d, J = 12 Hz, 0.07 H), 3.52 (br d, J = 2 Hz, 2 H), 1.59 (s, 1 H), 1.45 (m, 1 H), 0.70 (m, 2 H).

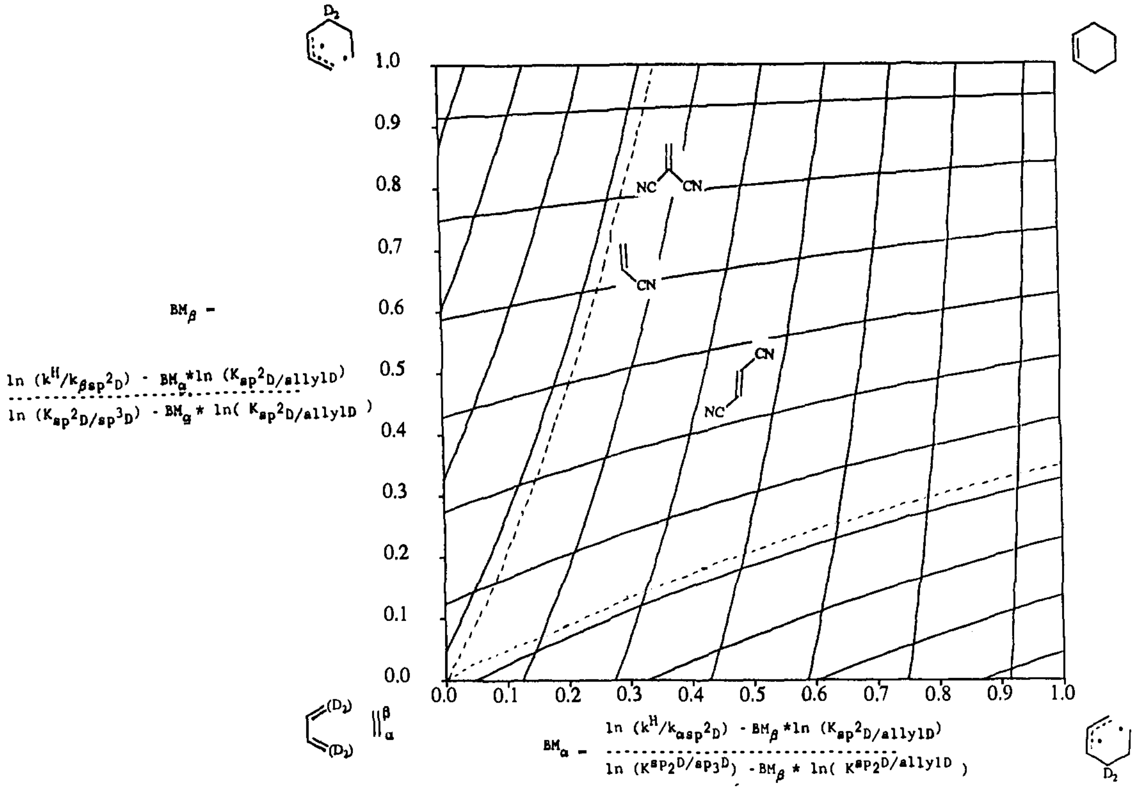
***trans*-2-Vinylcyclopropanecarboxaldehyde.**[7] *trans*-2-Vinylcyclopropanemethanol (2.0 g, 20 mmol) was added to a solution of 60 mmol of CrO_3–3,5-dimethylpyrazole complex[18] in 40 mL of CH_2Cl_2 at room temperature and stirred for 30 min. Then 500 mL of pentane was added to precipitate the complex, the mixture was filtered, and the filtrate was carefully concentrated. Distillation (bulb-to-bulb) at 70 °C gave 1.6 g (16 mmol, 81% yield) of product: ^{1}H NMR ($CDCl_3$) δ 9.16 (d, J = 5 Hz, 1 H), 5.42 (ddd, J = 17, 10, and 8 Hz, 1 H), 5.20 (dd, J = 17 and 1 Hz, 1 H), 5.05 (dd, J = 10 and 1 Hz, 1 H), 2.12 (m, 1 H), 1.92 (m, 1 H), 1.51 (m, 1 H), 1.19 (m, 1 H).

***trans*-2-(2′,2′-Dideuteriovinyl)cyclopropanecarboxaldehyde.** *trans*-2-(2′,2′-Dideuteriovinyl)cyclopropanemethanol (1.1 g, 11 mmol) was oxidized and worked up in the same manner as for the nondeuterated compound, to obtain 0.47 g (4.8 mmol, 44% yield) of product, containing 12% cis isomer by GC and ^{1}H NMR: ^{1}H NMR ($CDCl_3$) δ 9.16 (d, J = 5 Hz, 1 H), 5.42 (br d, J = 8 Hz, 1 H), 5.20 (d, J = 17 Hz, 0.07 H), 5.05 (d, J = 10 Hz, 0.07 H), 2.12 (m, 1 H), 1.92 (m, 1 H), 1.51 (m, 1 H), 1.19 (m, 1 H).

***trans*-1,2-Divinylcyclopropane.**[7] *trans*-2-Vinylcyclopropanecarboxaldehyde (0.75 g, 8 mmol) in 3 mL of DMSO was added to a solution of methylenetriphenylphosphorane[17] (15 mmol) in 15 mL of DMSO at room temperature. After 30 min of stirring, the volatile products were evacuated into a cold trap (−78 °C), giving 0.61 g (6.4 mmol, 81% yield) of product. An analytical sample was GC-purified to >99.5% purity as determined by capillary GC: ^{1}H NMR ($CDCl_3$) δ 5.41 (m, 2 H), 5.06 (dd, J = 17 and 2 Hz, 2 H), 4.89 (dd, J = 10 and 2 Hz, 2 H), 1.45 (m, 2 H), 0.86 (t, J = 8 Hz, 2 H); MS (m^+/e) 94.

***trans*-1,2-Bis(2′,2′-dideuteriovinyl)cyclopropane.** *trans*-(2′,2′-Dideuteriovinyl)cyclopropanecarboxaldehyde (0.47 g, 4.8 mmol) in 1.5 mL of DMSO-d_6 was added to a stirred solution of (dideuteriomethylene)triphenylphosphorane (9.6 mmol) in 9 mL of DMSO-d_6 at room temperature. After 30 min, the volatile products were evacuated into a cold trap (−78 °C), giving 0.35 g of material, which was 60% desired product and 10% 6,6,7,7-tetradeuterio-1,4-cycloheptadiene in addition to other volatile impurities; thus 50% yield of divinylcyclopropanes was obtained. This material showed, after GC purification, 92% deuterium incorporation by ^{1}H NMR. The parent ion in the mass spectrum could

Scheme V



be observed, but fragmentation was too great for mass spectral determination of deuterium incorporation: ^{1}H NMR (CDCl$_3$) δ 5.41 (br d, J = 9 Hz, 2 H), 5.06 (d, J = 17 Hz, 0.16 H), 4.89 (d, J = 10 Hz, 0.16 H), 1.45 (m, 2 H), 0.86 (t, J = 8 Hz, 2 H); MS (m^+/e) 98.

Pyrolysis and Kinetics. Pyrolyses were carried out in a well-stirred, insulated oil bath with temperature control to ±2 °C, or in one case refluxing water was used as the constant temperature bath. Samples of GC-purified divinylcyclopropanes (5 μL) were vacuum-sealed in 10 cm × 6 mm Pyrex tubes after three freeze–pump–thaw degassing cycles. Deuterated and nondeuterated samples in separate tubes were placed into and removed from the pyrolysis bath in parallel, after 0.5–2 half-lives of rearrangement in most cases. Then the tubes were cooled to −78 °C at one end to condense the pyrolysate, the tubes were opened, and 0.5 mL of pentane was added to the tubes to dilute the pyrolysate for GC analysis. The response factor of the GC detector was assumed to be unity for starting material and product. Injector and detector temperatures were low (140 °C) as well as the column temperature (70 °C) to minimize error due to rearrangement during gas chromatography.

Fine temperature control for the pyrolysis bath was not used since small temperature variations should have only a negligible contribution to error in determination of the desired quantity, namely the *ratio* of rate constants at a given temperature.

Product Analysis. Samples of both divinylcyclopropanes were pyrolyzed to nearly complete conversion (2 h at 200 °C), at which time analytical GC and ^{1}H NMR data analysis showed that rearrangement had occurred to form 1,4-cycloheptadiene or 6,6,7,7-tetradeuterio-1,4-cycloheptadiene, exclusively.

Acknowledgment. We thank the National Science Foundation for support of this work. K.J.T. also thanks the Quantum Chemistry Program Exchange for support.