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# Theoretical Secondary Kinetic Isotope Effects and the Interpretation of Transition State Geometries. 2. The Diels-Alder Reaction Transition State Geometry

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**Abstract:** Theoretical secondary deuterium and primary $^{14}C$ kinetic isotope effects have been calculated for concerted and stepwise Diels-Alder reactions of butadiene with ethylene and acrolein. Comparisons between theory and experiment on substituted cases give definitive evidence for the mechanism and transition state geometries of the Diels-Alder reactions. Five levels of ab initio theory up to MCSCF/6-31G* are used for isotope effect calculations. The isotope effects for the retro-Diels-Alder reaction of ethanoanthracene are calculated and compared directly to experiment.

## Introduction

The mechanism of the Diels-Alder reaction has attracted interest and stimulated debate since its discovery.[1,2] Theorists have studied the mechanism at all feasible levels and have debated whether the prototype Diels-Alder reaction of butadiene with ethylene has a concerted pericyclic mechanism or is a stepwise process involving a diradical intermediate.[2-5] Experimentalists have provided evidence about mechanisms from many types of experiments including kinetic isotope effect measurements.[2] There has been disagreement about whether kinetic isotope effects are sensitive enough to distinguish between concerted and stepwise mechanisms.[2,6-9]

Both experimental data and calculations indicate that the reaction of butadiene with ethylene occurs mainly by a concerted mechanism. The stepwise process with a diradical intermediate is estimated to be 3-7 kcal/mol higher in energy.[3,10] Because the concerted and stepwise-diradical mechanisms are so close in energy, there is still doubt about which mechanism occurs for each substituted case.

Calculated isotope effects were previously used in the study of the Diels-Alder reaction mechanism. Dewar compared MINDO/3 predictions to experimental results by Thornton on the retro-Diels-Alder reaction of ethanoanthracene.[11,12] Different conclusions about mechanisms were made by Thornton and by Dewar.

This paper is the second in a series addressing the interpretation of secondary deuterium kinetic isotope effects for stepwise and concerted pericyclic reaction mechanisms.[13] Isotope effects have been calculated for concerted synchronous and asynchronous mechanisms, as well as for a stepwise mechanism involving a diradical intermediate. These are compared with experimental kinetic isotope effects. We show that reaction mechanisms may easily be distinguished by comparison of experimental and theoretical secondary deuterium kinetic isotope effects.

The organization of this paper is as follows. A general introduction reviews experimental studies of isotope effects. The methodology section describes how isotope effects were calculated. Next, secondary kinetic isotope effects calculated at different theoretical levels are reported for concerted and stepwise Diels-Alder reactions of butadiene and ethylene. These are compared to experimental results for symmetrically substituted addends. Calculations on the retro-Diels-Alder reaction of ethanoanthracene are then described and compared to experiment. Results on the asynchronous Diels-Alder reaction of butadiene and acrolein are given next, and these are compared to experiment. Finally, the primary $^{14}C$ kinetic isotope effects calculated for concerted synchronous, stepwise, and asynchronous reactions are presented and compared to recent experimental data.

## Background

The Diels-Alder reaction of butadiene with ethylene is a [$_{\pi}4_s + _{\pi}2_s$] cycloaddition reaction,[14] in which two new $\sigma$-bonds are formed at the expense of two $\pi$-bonds, as shown in Figure 1. The concerted mechanism is characterized by a boat-like synchronous transition structure with $C_s$ symmetry.[3,10,15,16] Alternatively, a stepwise mechanism is possible with two bond-forming steps separated by an intermediate. Li and Houk recently completed CASSCF/6-31G* calculations on the reaction of butadiene and ethylene.[16] Single point energy calculations at the QCISD(T)/6-31G* level based on MCSCF/6-31G* optimized transition structures favor the concerted mechanism by 10 kcal/mol with respect to the stepwise mechanism.

In addition to the concerted transition structure and the diradical formation stepwise transition structure, TS-1, shown in

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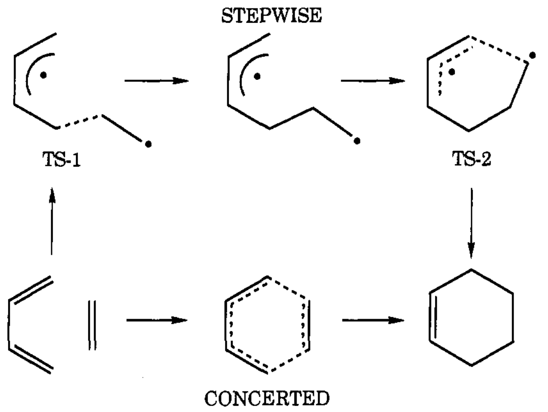


**Figure 1.** The stepwise and concerted pathways for the Diels–Alder reaction of butadiene with ethylene.

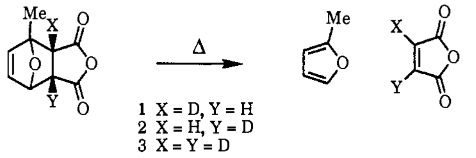
Figure 1, a diradical closure transition structure, TS-2, was located here at several levels of theory. All three transition structures were used for the calculation of isotope effects to compare to experiment. The discussion of calculated activation energies for various methods and mechanisms is presented elsewhere.[15,16]

## Secondary Kinetic Isotope Effects in Diels–Alder and Retro-Diels–Alder Reactions

When deuterium or tritium is substituted for hydrogen at the diene or dienophile terminus, a secondary kinetic isotope effect (2°-KIE) can be measured. During the course of $sp^2$ to $sp^3$ hybridization change, a C–H out-of-plane bending mode changes from a low frequency to a higher frequency.[17] This energy change causes an increase in zero-point energy along the reaction path, normally leading to an *inverse* 2°-KIE, $k_H/k_D < 1$ for forward, and a *normal* 2°-KIE, $k_H/k_D > 1$, for retro-Diels–Alder reactions. (Typical values are given later in this paper.)

## Experimental 2°-KIEs in the Diels–Alder Reaction

Experimental isotope effects in Diels–Alder reactions have been interpreted in several different ways. For example, Seltzer studied isotope effects for the retro-Diels–Alder reaction shown in eq 1.[18] Each deuterium gave an isotope effect of 1.08 ± 0.01, and the $D_2$-KIE was 1.16 ± 0.01.

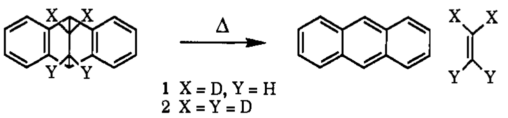


(1)

Seltzer recognized two possible interpretations of the $D_1$- and $D_2$-KIEs: they could result from either partial cleavage of both bonds in a single transition state or complete cleavage of a single bond half the time.[19] Deuterium was substituted in the methyl group to try and detect asymmetry in the bond-cleaving step. In the stepwise mechanism the methyl-$d_3$ isotope effect is expected to be larger than 1.0. The absence of such an effect led to the conclusion that the reaction is concerted.

Van Sickle measured the kinetic isotope effect in the Diels–Alder reaction of anthracene, butadiene, and cyclopentadiene with maleic anhydride.[20] The results for reaction of maleic-$d_2$ anhydride fall in the range of $k_H/k_{D_2} = 0.93$–$0.98$.

Thornton and Taagepera studied the retro-Diels–Alder reaction of ethanoanthracene (eq 2) and found $k_H/K_{D_2} = 1.08$ and $k_H/k_{D_4} = 1.17$ at 220 °C.[12]

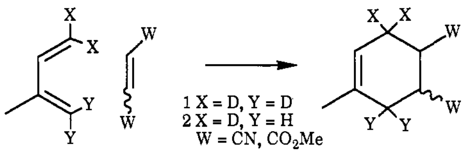


(2)

If the reaction is synchronous and concerted, then $(k_H/k_{D_2})^2 = (k_H/k_{D_4})$. That is, the isotope effects are multiplicative.[12,21] In an asynchronous or stepwise Diels–Alder reaction, the ratio will be different. If the reaction is stepwise and there is a non-zero isotope effect only at one terminus, then $k_{D_4}/k_H = 2(k_{D_2}/k_H) - 1$. That is, the isotope effects are approximately additive. Thornton and Taagepera analyzed their results in terms of both concerted and stepwise mechanistic extremes and found that their data more closely matched the multiplicative relationship, indicating that the reaction is concerted. However, this is an extremely close call, since $(1.08)^2 = 1.17$ and $2(1.08) - 1 = 1.16$.

Dewar challenged this conclusion. The MINDO/3 transition structure for the butadiene–ethylene reaction corresponds to TS-2 in Figure 1. Dewar's calculated KIE was within 2% of the experimental value, leading to the conclusion that the reaction was highly asynchronous or stepwise.[11]

Gajewski has recently studied 2°-KIEs for a variety of Diels–Alder reactions for symmetric and asymmetric dienophiles reacting with deuterated isoprene:[8]



Gajewski interpreted the experimental KIEs as indicative of concerted mechanisms. These data will be discussed later and compared with calculated isotope effects.

## Computational Methodology

Ab initio quantum mechanical calculations using the RHF, UHF, MP2, and MCSCF methods with the 3-21G and 6-31G* basis sets were employed. Vibrational analysis was carried out for each stationary point for each level of theory. This was done to verify the nature of each stationary point and to provide force constants for calculation of isotope effects. GAUSSIAN 88[22] and 90[23] were used for geometry optimizations. GAUSSIAN 90 was used to calculate force constants analytically with the 3-21G and 6-31G* basis sets. CADPAC[24] was used to determine analytically the MP2/6-31G* force constants with the exception of the concerted asynchronous reaction of butadiene with acrolein, where they were calculated numerically with GAUSSIAN 90. The MCSCF calculations were performed with GAMESS.[25]

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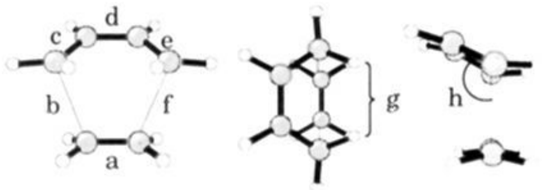
**Table 1.** Geometrical Parameters of the Concerted Transition Structure for the Diels–Alder Reaction of Butadiene with Ethylene (Distances in Å, Angles in deg)



| | RHF/ 3-21G | RHF/ 6-31G* | MP2/ 6-31G* | MCSCF/ 3-21G | MCSCF/ -31G* |
|---|---|---|---|---|---|
| *a* | 1.376 | 1.383 | 1.380 | 1.400 | 1.404 |
| *b*, *f* | **2.210** | **2.202** | **2.286** | **2.217** | **2.223** |
| *c*, *e* | 1.370 | 1.377 | 1.378 | 1.392 | 1.398 |
| *d* | 1.395 | 1.393 | 1.410 | 1.397 | 1.397 |
| *g* | 2.086 | 2.123 | 2.088 | 2.126 | 2.171 |
| *h* | 101.6 | 102.6 | 101.6 | 101.9 | 103.1 |

Geometries and corresponding force constant matrices were then used together with the QUIVER program to calculate isotope effects.[26] The QUIVER program employs the Bigeleisen and Meyer[27] formulation of the ratio of partition functions within the transition state theory approximation:[28]where $u = h\nu/kT$.

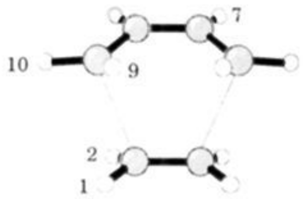
$$\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} = \frac{\nu_{\mathrm{H}}^{\ddagger}}{\nu_{\mathrm{D}}^{\ddagger}} \frac{\prod^{3N\text{-}6} \frac{u_{\mathrm{H}}}{u_{\mathrm{D}}}}{\prod^{3N^{\ddagger}\text{-}7} \frac{u_{\mathrm{H}}^{\ddagger}}{u_{\mathrm{d}}^{\ddagger}}} \frac{\prod^{3N\text{-}6} \frac{[1-\exp(-u_{\mathrm{H}})]}{[1-\exp(-u_{\mathrm{D}})]}}{\prod^{3N^{\ddagger}\text{-}7} \frac{[1-\exp(-u_{\mathrm{H}}^{\ddagger})]}{[1-\exp(-u_{\mathrm{D}}^{\ddagger})]}} \frac{\exp\left(\sum^{3N\text{-}6} \frac{(u_{\mathrm{H}}-u_{\mathrm{D}})}{2}\right)}{\exp\left(\sum^{3N^{\ddagger}\text{-}7} \frac{(u_{\mathrm{H}}^{\ddagger}-u_{\mathrm{D}}^{\ddagger})}{2}\right)}$$

QUIVER first scales the force constants according to an empirical scaling factor. In this study, scaling factors of 0.9, 0.9, and 1.0 were used for the 3-21G, 6-31G*, and MP2/6-31G* levels, respectively.[29,30] QUIVER performs the normal mode analysis for each isotopomer. The resulting harmonic frequencies are used in eq 13.

## Results and Discussion

**Butadiene and Ethylene.** The synchronous concerted and stepwise mechanisms have similar energies when computed with MCSCF techniques. The best available calculations[16] as well as experiment[2,10] indicate the activation energy of the concerted mechanism is 3–7 kcal/mol lower in energy than that for the first step of the stepwise mechanism. Although the energies of the two transition structures are similar, the geometries are fundamentally different, with one bond forming in the stepwise structure and two forming in the concerted case. In the concerted mechanism (see Table 1), there are two partially formed $\sigma$-bonds (2.2 Å) and the stabilization arising from the cyclic conjugation of 6$\pi$ electrons. In the stepwise mechanism, there is allylic stabilization of one radical center and one more fully formed bond at 1.8 Å. Although the differences in conjugation, stabilization, and bond formation fortuitously produce similar activation energies, different isotope effects are expected. Differing extents of bond formation give different force constants, and this leads to different kinetic isotope effects.

**Table 2.** Secondary Deuterium Kinetic Isotope Effects for the Concerted Reaction of Butadiene with Ethylene



| | $k_{\mathrm{H}}/k_{\mathrm{D}}$ (373.15 K) | | | | |
|---|---|---|---|---|---|
| isotopomer | RHF/ 3-21G | RHF/ 6-31G* | MP2/ 6-31G* | MCSCF/ 3-21G | MCSCF/ 6-31G* |
| 1 (OUT) | 0.97 | 0.97 | 0.98 | 0.99 | 0.99 |
| 2 (IN) | 0.94 | 0.95 | 0.96 | 0.97 | 0.97 |
| 7 | 0.99 | 1.00 | 0.99 | 1.02 | 1.02 |
| 9 (IN) | 0.93 | 0.94 | 0.95 | 0.95 | 0.96 |
| 10 (OUT) | 0.98 | 0.98 | 0.99 | 0.99 | 0.98 |
| scaling | 0.90 | 0.90 | 1.00 | 0.90 | 0.90 |

**The Concerted Mechanism.** The geometry of the synchronous transition structure for the concerted Diels–Alder reaction between 1,3-butadiene and ethylene is given in Table 1 at five levels of theory. The two forming bonds, *b* and *f*, are identical by symmetry and range in length from 2.20 to 2.28 Å. The MP2/6-31G* level gives the longest forming bond distance and thus the "earliest" transition state. The MCSCF levels give geometries intermediate between the MP2 and RHF levels. The transannular, inside hydrogen–hydrogen distance *g* varies by 0.1 Å in different calculations; this has an influence on the calculated isotope effects. The forming $\sigma$-bonds have intermediate lengths in the MCSCF transition structures, but the bond lengths in the butadiene carbon framework are different from those obtained in the other calculations. The partial double bonds (a, c, d, e) average 1.37–1.41 Å. In the RHF and MP2 calculations, the 2,3-bond (d) in the diene is always longer than the 1,2-bonds or the carbon–carbon bond in the ethylene (a, c, e). In the MCSCF results all partial double bonds are the same within 0.01 Å.

The secondary KIEs calculated for the transition structures in Table 1 are given in Table 2. The 2°-KIEs for hydrogens 1, 2, 9, and 10 are all inverse as expected for sp$^2$ to sp$^3$ hybridization changes. The 2°-KIEs vary from 0.93 to 0.99 depending on position and level of theory. All computational levels agree very well with respect to the magnitudes of the isotope effects, as expected for the similar geometries. At the highest levels (MP2/6-31G* and MCSCF/6-31G*) the isotope effects are 0.95–0.97 for IN and 0.98–0.99 for OUT hydrogens. IN and OUT are the more and less crowded hydrogens, as defined in Table 2. The isotope effect at the internal position 7 is near 1.00 as expected.

Why are the isotope effects for "IN" hydrogens on both diene and dienophile more pronounced inverse values than those for "OUT" hydrogens? The larger inverse isotope effects indicate that the IN hydrogens have larger vibrational force constants than the OUT hydrogens in the transition state. In the diene, the difference between IN and OUT is about 2% at all levels calculated. The IN hydrogens on the diene are only about 2.0 Å apart (g, Table 1). Steric repulsions prevent motion and increase the out-of-plane bending force constant, resulting in a larger inverse KIE for the IN hydrogen than the OUT. Additionally, the influence of the approaching dienophile may also increase the out-of-plane bending force constant for the IN hydrogens. Both these steric effects are in addition to the normal hybridization changes taking place during bond formation. The isotope effects for OUT hydrogens are not influenced by steric effects and should depend only on the changes in hybridization.

IN hydrogens of the dienophile (commonly called *endo*) also give the larger inverse 2°-KIEs. This indicates that they too are more crowded than the OUT hydrogens, presumably due to steric interaction with the diene.

**The Stepwise Mechanism.** The stepwise addition of ethylene to *cis*-butadiene was studied by Bernardi at the MCSCF/4-31G, 4-electron/4-orbital level of theory.[31] We have recently extended

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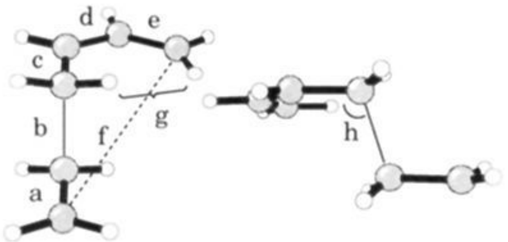
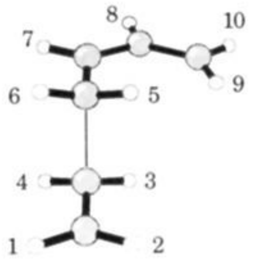
**Table 3.** Geometry of the Stepwise Transition Structure TS-1 for the Diels–Alder Reaction of Butadiene with Ethylene (Distances in Å, Angles in deg)



| | UHF/ 3-21G | UHF/ 6-31G* | MCSCF/ 3-21G | MCSCF/ 6-31G* |
|---|---|---|---|---|
| *a* | 1.408 | 1.410 | 1.434 | 1.425 |
| *b* | **2.026** | **2.037** | **1.835** | **1.869** |
| *c* | 1.426 | 1.429 | 1.440 | 1.432 |
| *d* | 1.416 | 1.419 | 1.428 | 1.436 |
| *e* | 1.374 | 1.377 | 1.362 | 1.326 |
| *f* | 4.877 | 4.965 | 4.784 | 4.844 |
| *g* | 2.277 | 2.320 | 2.293 | 2.339 |
| *h* | 106.7 | 108.0 | 108.4 | 109.3 |

**Table 4.** Secondary Deuterium Kinetic Isotope Effects for the Stepwise Diels–Alder Reaction TS-1 of Butadiene with Ethylene

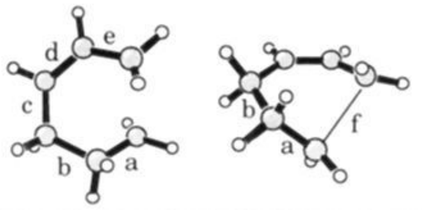


| | $k_H/k_D$ (373.15 K) | | | |
|---|---|---|---|---|
| isotopomer | UHF/ 3-21G | UHF/ 6-31G* | MCSCF/ 3-21G | MCSCF/ 6-31G* |
| 1 | 1.11 | 1.10 | 1.12 | 1.10 |
| 2 | 1.11 | 1.10 | 1.14 | 1.11 |
| 3 | 0.96 | 0.96 | 0.93 | 0.93 |
| 4 | 0.96 | 0.96 | 0.91 | 0.92 |
| 5 | 0.96 | 0.96 | 0.92 | 0.93 |
| 6 | 0.97 | 0.97 | 0.92 | 0.93 |
| 7 | 1.06 | 1.05 | 1.07 | 1.05 |
| 8 | 1.01 | 1.01 | 1.02 | 1.02 |
| 9 | 1.06 | 1.06 | 1.03 | 1.03 |
| 10 | 1.07 | 1.07 | 1.06 | 1.06 |
| scaling | 0.9 | 0.9 | 0.9 | 0.9 |

this work to the MCSCF/6-31G*, 6-electron 6-orbital (CASSCF) level.[16] The *cis-anti* transition state shown in Table 3 is TS-1 of Figure 1. Rotation about bond *b* (Table 3) leads to a *cis*-gauche boat conformation and then to ring closure. Attempts to find a *cis*-gauche boat transition state with CASSCF/6-31G* theory were unsuccessful. However, we have located a *cis*-gauche half-chair transition state with UHF theory to model transition state TS-2 of Figure 1. This transition structure resembles the half-chair of cyclohexene but is more accurately described as a sofa conformation. TS-2 was located at two lower levels of theory, Table 5. MCSCF studies have shown that TS-2 is of lower energy than TS-1,[16,31] which would make it kinetically inconsequential, but for completeness, isotope effects were calculated with TS-2 as well. TS-2 is interesting because it resembles the rate determining transition structure given by semiempirical methods for the Diels–Alder reaction and is relevant to the debate between Dewar and "the *ab initioists*" regarding the stepwise mechanism.[2]

The geometry of the *cis-anti* transition structure for the stepwise addition of ethylene to butadiene, TS-1, is given in Table 3 at four levels of theory. The structure is characterized by a forming bond length which is 0.2–0.4 Å shorter than the forming bond lengths of the concerted mechanism. In the stepwise mechanism, the MCSCF forming bond lengths are calculated to be about 0.2 Å shorter than the UHF results.

**Table 5.** Geometry of the Diradical Closure Transition Structure TS-2 for the Diels–Alder Reaction of Butadiene with Ethylene (Bond Lengths in Å)



| | UHF/3-21G | UHF/6-31G* |
|---|---|---|
| *a* | 1.5239 | 1.5056 |
| *b* | 1.5100 | 1.5423 |
| *c* | 1.5280 | 1.5100 |
| *d* | 1.3991 | 1.3710 |
| *e* | 1.4280 | 1.4276 |
| ***f*** | **2.4813** | **2.4417** |

The calculated KIEs for the diradical formation transition structure, TS-1, are presented in Table 4. Both inverse ($k_H/k_D < 1$) and normal ($k_H/k_D > 1$) 2°-KIEs are found in the stepwise mechanism. As in the case of the concerted mechanism, centers involving $\sigma$-bond formation exhibit inverse 2°-KIEs. The magnitude of the KIE is dependent upon the length of the forming bond for the given transition state. Thus, the UHF levels with the longer forming bond lengths exhibit a 4% inverse effect and the MCSCF levels with more advanced bond lengths both give a 7% inverse effect. The latter are presumably more reliable predictions.

Normal KIEs are calculated for hydrogens 1 and 2, which are located at the developing primary radical center, and hydrogens 7, 9, and 10, which are located at the developing allylic radical termini. The normal kinetic isotope effect occurs because the out-of-plane bending force constant of a radical center is less than that of an alkene.[32]

Isotopomers 1 and 2, Table 4, are located at the ethylene terminus, and here the largest normal KIEs of 1.10–1.11 are calculated. The allylic positions 7 and 10 have KIEs of 1.05–1.06. The inner terminal allylic hydrogen at 9 is crowded (as noted for IN hydrogens) with $k_H/k_D = 1.03$. These data indicate that the isotope effect at the primary radical center is nearly double that for the allylic centers. Both results are in good accord with experiment. Pryor and Henderson compared known frequencies for $CH_2$= and $CH_3^\bullet$ and calculated an equilibrium isotope effect of $K_H/K_D = 1.13$ per deuterium for transformation of an alkene sp$^2$ to a radical center.[33] Our results for the allyl radical terminus are also in accord with work by Baldwin and Fleming on the [2 + 2] reaction of allene with acrylonitrile.[34] They measured a $k_H/k_D = 1.06$ per deuterium for the KIE involving alkene to allyl radical change. A KIE of this magnitude is also seen in the thermolysis of appropriately deuterated *trans*-divinylcyclopropane with $k_H/k_D = 1.08$ at 25 °C.[35]

The geometry of TS-2 has one fully formed bond to the dienophile, *b*, and one partially formed bond, *f*, as tabulated in Table 5. The forming bond length is 2.44 Å at the UHF/6-31G* level of theory. There are larger differences in the optimized geometries of TS-2 at these two levels of theory than found in TS-1, and the isotope effects vary by as much as 4% between theoretical levels in TS-2 where they vary by only 1% between these levels in TS-1. The 6-31G* results are used here.

The KIEs for the diradical cyclization TS-2 are presented in Table 6. These are calculated on the assumption that TS-2 is rate determining. The results parallel those reported earlier for TS-1 except the $\sigma$-bond *b* is more fully formed, leading to larger

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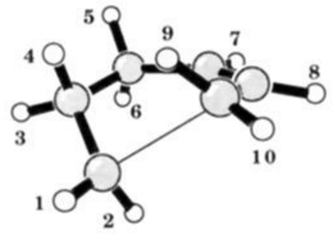
(32) Le Fevre, G. N.; Crawford, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 1019. Vukov, V.; Crawford, R. J. *Can. J. Chem.* **1975**, *53*, 1367. Pacansky, J.; Miller, M. D.; Koch, H. *J. Am. Chem. Soc.* **1991**, *113*, 317.

(33) Henderson, R. W.; Pryor, W. A. *Int. J. Chem. Kinet.* **1972**, *4*, 325.

(34) Baldwin, J. E.; Fleming, R. *Fortschr. Chem. Forsch.* **1970**, *15*, 281.

(35) Gajewski, J. J.; Olson, L. P.; Tupper, K. J. *J. Am. Chem. Soc.* **1993**, *115*, 4548. Olson, L. P. Ph.D. Dissertation, Indiana University, 1992.

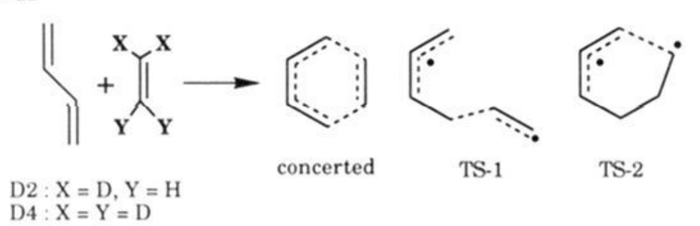
**Table 6.** Secondary Deuterium Kinetic Isotope Effects for the Reaction Involving Rate-Determining Diradical Cyclization TS-2 in the Diels–Alder Reaction of Butadiene with Ethylene



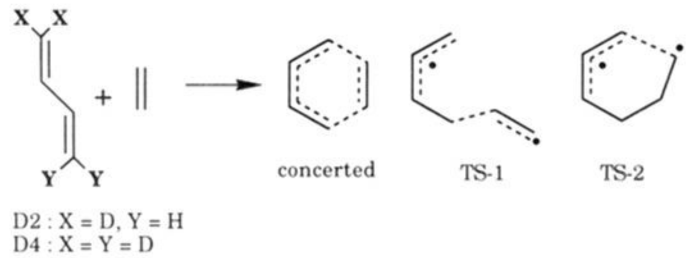
| isotopomer | $k_H/k_D$(373.15 K)<br>UHF/3-21G | UHF/6-31G* | TS-1[a] UHF/6-31G* |
|---|---|---|---|
| 1 | 1.15 | 1.12 | 1.10 |
| 2 | 1.15 | 1.10 | 1.10 |
| 3 | 0.90 | 0.90 | 0.96 |
| 4 | 0.95 | 0.95 | 0.96 |
| 5 | 0.91 | 0.92 | 0.96 |
| 6 | 0.95 | 0.95 | 0.97 |
| 7 | 1.10 | 1.06 | 1.05 |
| 8 | 1.06 | 1.04 | 1.01 |
| 9 | 1.05 | 1.04 | 1.06 |
| 10 | 1.14 | 1.11 | 1.07 |
| scaling | 0.9 | 0.9 | 0.9 |

[a] Includes KIEs for TS-1 for comparison.

**Table 7.** Secondary $D_2$- and $D_4$-KIEs for Dienophile and Diene Isotopomers in the Diels–Alder Reaction of Butadiene and Ethylene for Three Different Possible Rate Determining Transition States at 373.15 K



| level | concerted |  | TS-1 |  | TS-2 |  |
|---|---|---|---|---|---|---|
|  | $D_2$ | $D_4$ | $D_2$ | $D_4$ | $D_2$ | $D_4$ |
| MP2/6-31G* | 0.94 | 0.84 |  |  |  |  |
| MCSCF/6-31G* | 0.97 | 0.94 | 1.01 | 1.04 |  |  |



| level | concerted |  | TS-1 |  | TS-2 |  |
|---|---|---|---|---|---|---|
|  | $D_2$ | $D_4$ | $D_2$ | $D_4$ | $D_2$ | $D_4$ |
| HF/6-31G* | 0.92 | 0.85 | 1.03 | 1.06 | 1.01 | 1.01 |
| MP2/6-31G* | 0.93 | 0.87 |  |  |  |  |
| MCSCF/6-31G* | 0.94 | 0.89 | 0.98 | 0.94 |  |  |

inverse KIEs for hydrogens 3–6, and more radical character has developed at the termini, leading to larger normal KIEs for hydrogens 1, 2, 9, and 10. Steric influences discussed for the concerted mechanism also affect the relative KIEs in TS-2. For example, the inside positions 2 and 9 exhibit smaller normal KIEs than the unhindered outside positions 1 and 10.

**Comparison of Concerted and Stepwise Theoretical Results.** Most experimental studies used $D_2$ and $D_4$ substrates—either diene or dienophile—to establish mechanism. The calculated values for different mechanisms for these substrates are tabulated in Table 7.

The dienophile results are discussed first. The KIEs are all *inverse* for the concerted mechanism. The $D_2$-KIE ranges from 3 to 8% and the $D_4$ ranges from 6 to 16%. The most reliable values by MCSCF/6-31G* are 3% and 6% for $D_2$ and $D_4$, respectively. The $D_2$- and $D_4$-KIEs for TS-1 are *normal*, with values of 1% and 4% for $D_2$ and $D_4$, respectively. This is due to the large size of the normal KIE at the primary radical center formed from the dienophile. Similarly, for TS-2 the radical character at the termini of the second forming bond dominates the $D_2$- and $D_4$-KIEs. Although the magnitude of the KIEs in TS-2 is smaller than for TS-1, the $D_4$-KIEs are still normal by about 6% and opposite in direction from the concerted mechanism.

Significant differences are expected in KIEs between concerted and stepwise mechanisms. With use of the MCSCF results, the $D_4$-KIEs on the dienophile for the concerted mechanism are about 6% *inverse* and the corresponding result for TS-1 is about 4% in the *normal* direction. This difference is well within the limits of experimental precision and accuracy.

Isotope effects have usually been measured with deuterium in the less sensitive diene and not in the dienophile. The second part of Table 7 gives results for these cases. The concerted mechanism gives KIEs that are inverse and about 6% for $D_2$ and 11% for $D_4$. The $D_2$- and $D_4$-KIEs in TS-1 are inverse by 2% and 6%, respectively, at the MCSCF/6-31G* level. For TS-2, very small normal values are predicted.

Comparisons are presented below between experimental results on synchronous Diels–Alder reactions and theoretical concerted and stepwise reaction mechanisms.

**Comparison of Theoretical and Experimental 2°-KIEs for Synchronous Diels–Alder Reactions.** Experimental secondary kinetic isotope effects for Diels–Alder reactions involving symmetric or nearly symmetric dienes and symmetrically disubstituted dienophiles are given in Table 8 and compared to theoretical results for concerted and stepwise mechanisms at several indicated levels of ab initio theory. The calculations are for the butadiene–ethylene reaction.

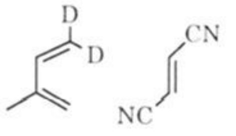
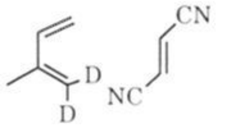
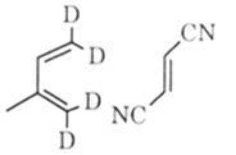
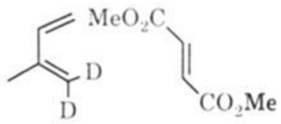
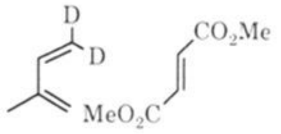
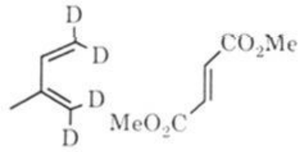
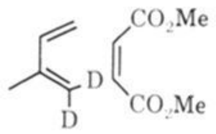
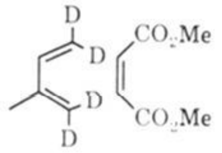
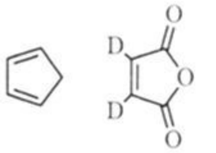
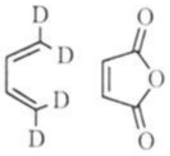
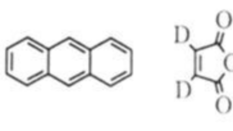
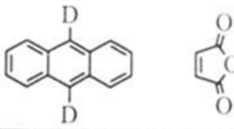
There are five Diels–Alder reactions presented in the Table with various isotopic substitutions. The first reaction involves deuterated isoprene and fumaronitrile. Experiment gives 5% and 10% $D_2$- and $D_4$-KIEs, respectively.[8] The MCSCF isotope effects for the concerted mechanism match the 5% $D_2$ result exactly and are 2% low in the prediction of the $D_4$-KIE. The stepwise mechanism varies with theoretical level and is 2% off at the MCSCF level for $D_2$ and 4% for $D_4$. The concerted mechanism is closer to the experimental results. The results for the reactions of dimethyl fumarate and dimethyl maleate are similar and provide further support for the concerted mechanism.

The reactions with maleic anhydride involve dienophile substitution and are more decisive. Experiment gives an 8% inverse KIE for the reaction of cyclopentadiene with maleic-$d_2$ anhydride.[20] The concerted mechanism matches experiment at the MCSCF level whereas the stepwise mechanism provides a 4–8% normal KIE. This clearly shows that substitution in the dienophile is better able to distinguish between mechanisms. Finally, the reaction between butadiene-$d_4$ and maleic anhydride gives a large inverse $D_4$-KIE of 0.76 which is more closely matched by the concerted results.[20] The remaining two reactions between anthracene and maleic anhydride also favor the concerted mechanism with the concerted MP2/6-31G* result matching the 7% inverse KIE while the stepwise levels register 3–6% in the normal direction. In general these comparisons favor the concerted mechanism.

It is perhaps surprising that the calculations on the unsubstituted system agree reasonably well with the experimental results for the rather highly-substituted case. As shown below, the change in degree of bond making in the transition state is quite small for symmetrical substitution.

**The Retro-Diels–Alder Reaction.** The calculated KIEs for the retro-Diels–Alder reaction of cyclohexene are given in Table 9. The dienophile $D_2$ and $D_4$-KIEs for the concerted and stepwise retro-Diels–Alder reaction are all normal in magnitude. The stepwise mechanisms give $D_2$-KIEs that are about 10% larger than the concerted mechanism. The MCSCF/6-31G* level is

**Table 8.** Comparison of Experimental and Theoretical Kinetic Isotope Effects for Diels–Alder Reactions of Nearly Symmetrical Addends

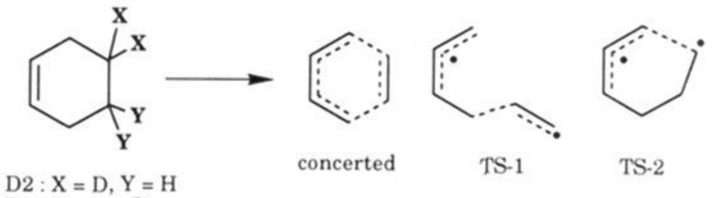
| compound | T(K) | expt. | concerted MP2/ 6-31G* (MCSCF/ 6-31G*) | TS-1 UHF/ 6-31G* (MCSCF/ 6-31G*) |
|---|---|---|---|---|
|  | 373 | 0.95[a] | 0.93<br>(0.95) | 1.02<br>(0.97) |
|  | 373 | 0.95[a] | 0.93<br>(0.95) | 1.02<br>(0.97) |
|  | 373 | 0.90[a] | 0.87<br>(0.90) | 1.06<br>(0.94) |
|  | 373 | 0.92[a] | 0.93<br>(0.95) | 1.02<br>(0.97) |
|  | 373 | 0.93[a] | 0.93<br>(0.95) | 1.02<br>(0.97) |
|  | 373 | 0.85[a] | 0.87<br>(0.90) | 1.06<br>(0.94) |
|  | 373 | 0.92[a] | 0.93<br>(0.95) | 1.02<br>(0.97) |
|  | 373 | 0.87[a] | 0.87<br>(0.90) | 1.06<br>(0.94) |
|  | 298 | 0.92[b] | 0.89<br>(0.92) | 1.08<br>(1.04) |
|  | 298 | 0.76[b] | 0.81<br>(0.85) | 1.07<br>(0.92) |
|  | 373 | 0.93[b] | 0.93<br>(0.95) | 1.06<br>(1.03) |
|  | 373 | 0.91[b] | 0.97<br>(0.97) | 1.04<br>(0.99) |

[a] References 6–8. [b] Reference 20.

available for the concerted and TS-1 stationary points; there is a 14% difference between the $D_2$-KIEs and an 8% difference in the $D_4$-KIEs. Thus, the concerted and stepwise mechanisms should still be distinguishable as in the forward Diels–Alder reaction.

The ab initio derived KIEs for TS-2 are quite different from those obtained by Dewar with the semiempirical MINDO/3 level.[10] Ab initio results on TS-2 give $D_2$- and D4-KIEs that are 3% and 10% larger than the MINDO/3 results, respectively. The experimental results for the retro-Diels–Alder reaction in ethanoanthracene[12] are included at the bottom of Table 9 together with ab initio results for the same reaction and the MCSCF results for the cyclohexene cycloreversion. The concerted transition state for the ethanoanthracene retro-Diels–Alder reaction was located at the RHF/3-21G level. The transition structure has $C_{2v}$ symmetry and is given in Table 10. The breaking bond distance in the transition state is found at 2.232 Å. This distance is very close to that found for the concerted reaction of butadiene with ethylene at the same level of theory (2.210 Å), Table 1. This is remarkable when one considers that the activation enthalpies for cycloreversion are $\Delta H^{\ddagger} = 49.1$ kcal/mol in ethanoanthracene and ~66 kcal/mol in cyclohexene. The heats of reaction should also vary to a larger extent, but the transition states stay relatively constant. We have recently reported on the

**Table 9.** Secondary Deuterium KIEs for the Retro-Diels–Alder Reation[a]



D2 : X = D, Y = H
D4 : X = Y = D

| level | concerted $D_2$ | concerted $D_4$ | TS-1 $D_2$ | TS-1 $D_4$ | TS-2 $D_2$ | TS-2 $D_4$ |
|---|---|---|---|---|---|---|
| MCSCF/6-31G* | 1.09 | 1.20 | 1.23 | 1.28 | | |
| MP2/6-31G* | 1.10 | 1.21 | | | | |
| HF/6-31G* | 1.06 | 1.12 | 1.16 | 1.35 | 1.14 | 1.31 |
| MINDO/3[b] | | | | | 1.10 | 1.22 |

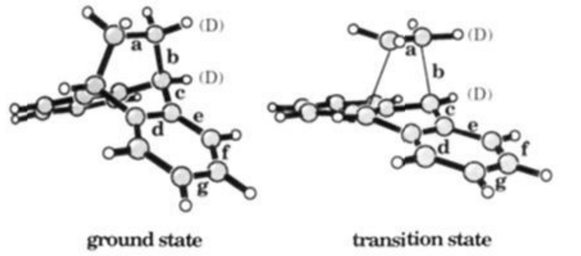
D2 : X = D, Y = H
D4 : X = Y = D

Ethanoanthracene

| level | $k_H/k_{D_2}$[d] | $k_H/k_{D_4}$[d] |
|---|---|---|
| MCSCF/6-31G* (cyclohexene) concerted | 1.09 | 1.20 |
| RHF/3-21G (ethanoanthracene) concerted | 1.08 | 1.16 |
| exp (220 °C)[c] | 1.08 | 1.17 |

[a] Isotope effects are given for the dienophile component at 473.15 K. [b] Reference 11. [c] Reference 12. [d] T (473.15 K).

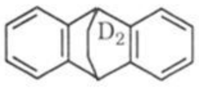
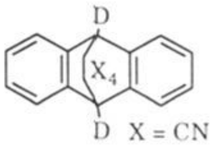
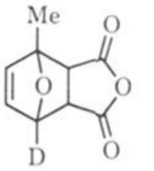
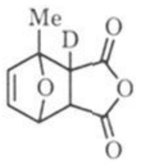
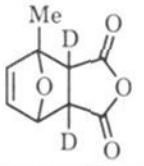
**Table 10.** RHF/3-21G Geometries and Isotope Effects for the Retro-Diels–Alder Reaction of Ethanoanthracene



| bond | distance (Å) ground state | distance (Å) transition state |
|---|---|---|
| *a* | 1.561 | 1.375 |
| *b* | 1.561 | 2.232 |
| *c* | 1.517 | 1.423 |
| *d* | 1.392 | 1.401 |
| *e* | 1.377 | 1.414 |
| *f* | 1.390 | 1.360 |
| *g* | 1.381 | 1.412 |

| isotopomer | $k_H/k_D$ (473.15 K) |
|---|---|
| $D_1$-dienophile | 1.04 |
| $D_1$-diene | 1.04 |

**Table 11.** Comparison of Experimental and Theoretical Kinetic Isotope Effects for Retro-Diels–Alder Reactions

| compound | T(K) | expt. | concerted<br>RHF/ 3-21G (MCSCF/ 6-31G*) | TS-1<br>UHF/ 3-21G (MCSCF/ 6-31G*) |
|---|---|---|---|---|
|  | 323 | 1.17[a] | 1.17<br>(1.20) | 1.36<br>(1.25) |
|  | 323 | 1.36[a] | 1.36<br>(1.38) | 1.90<br>(1.64) |
|  | 323 | 1.17[b] | 1.18<br>(1.14) | 1.12<br>(1.16) |
| compound | T(K) | expt. | MP2/ 6-31G* (MCSCF/ 6-31G*) | UHF/ 6-31G* (MCSCF/ 6-31G*) |
|  | 323 | 1.08[c] | 1.10<br>(1.06) | 1.11<br>(1.08) |
|  | 323 | 1.09[c] | 1.09<br>(1.08) | 1.16<br>(1.14) |
|  | 323 | 1.16[c] | 1.19<br>(1.17) | 1.34<br>(1.29) |

[a] Reference 12. [b] Reference 36. [c] References 18 and 19.

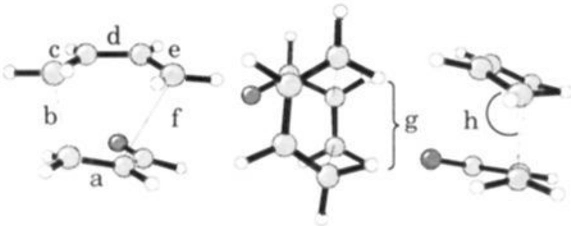
similarities of hydrocarbon pericyclic reaction transition structures regardless of $\Delta H_{\mathrm{rxn}}$.[15]

The calculated $D_2$- and $D_4$-KIE results fall within 1% of the experimental values, providing strong evidence in favor of the concerted mechanism. Thornton and Taagepera gave $D_2$- and $D_4$-KIEs of 1.17 and 1.36 respectively, at 323 K and 1.08 and 1.17, respectively, at 473 K.[12] The 473 K results are used in Table 9 to allow comparison with Dewar's MINDO/3 result. The 323 K results are used in Table 11 where experiment and theory are compared for three different retro-Diels–Alder reactions.

Three other retro-Diels–Alder reactions are compared to theory in Table 11. In the substituted ethanoanthracene cases the RHF/3-21G results are derived from the ethanoanthracene transition state and the UHF/2-21G results are for TS-1. The agreement between experiment and concerted RHF/3-21G results is excellent. The stepwise mechanism gives KIEs that are more than double the experimental values. The results for tetracyanoethanoanthracene are within 1% for the concerted mechanism, whereas the stepwise result is smaller than the experiment by 5%.[36]

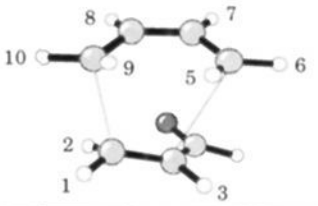
The remaining comparisons are for the retro-Diels–Alder reactions of the adduct of 1-methylfuran and maleic anhydride.[18,19] Deuterium in the 4-position of the furan gives an 8% normal KIE. Both concerted and stepwise results agree with experiment in this example. However, deuterium in the dienophile gives different results for the two mechanisms, and the calculated values for the concerted mechanism agree best with experiment. The agreement between experiment and the concerted mechanism is within 2%, and the stepwise mechanism deviates by 5–7% in the $D_2$ and 13–18% in the $D_4$ results.

**Table 12.** Geometry of the Concerted Transition Structure of the Diels–Alder Reaction of Butadiene with Acrolein (Distances in Å, Angles in deg)



|  | RHF/3-21G | RHF/6-31G* | MP2/6-31G* |
|---|---|---|---|
| *a* | 1.382 | 1.392 | 1.382 |
| *b* | **2.088** | **2.053** | **2.141** |
| *c* | 1.377 | 1.386 | 1.383 |
| *d* | 1.394 | 1.394 | 1.416 |
| *e* | 1.364 | 1.370 | 1.368 |
| *f* | **2.353** | **2.392** | **2.588** |
| ***b–f*** | (0.27) | (0.33) | (0.45) |
| *g* | 2.1 | 2.1 | 2.1 |
| *h* | 103.3 | 104.5 | 104.8 |

**Table 13.** Secondary Deuterium Kinetic Isotope Effects for the Concerted Reaction of Butadiene with Acrolein



|  | $k_H/k_D$ (373.15 K) |  |  |
|---|---|---|---|
| isotopomer | RHF/3-21G | RHF/6-31G* | MP2/6-31G* |
| 1 (OUT) | 0.96 | 0.96 | 0.96 |
| 2 (IN) | 0.91 | 0.92 | 0.92 |
| 3 (OUT) | 0.97 | 0.98 | 1.00 |
| 5 (IN) | 0.93 | 0.94 | 0.97 |
| 6 (OUT) | 0.99 | 0.98 | 1.01 |
| 7 | 0.98 | 0.98 | 0.98 |
| 8 | 0.99 | 0.99 | 1.00 |
| 9 (IN) | 0.92 | 0.93 | 0.93 |
| 10 (OUT) | 0.96 | 0.95 | 0.95 |

The calculated isotope effects for the concerted Diels–Alder reaction agree more closely with experiment than those obtained for a stepwise mechanism in retro-Diels–Alder reaction as well as forward Diels–Alder reactions.

**Diels–Alder Reactions of Unsymmetrical Addends.** The concerted asynchronous transition structure for the Diels–Alder reaction of butadiene and acrolein has been located at the RHF/3-21G, RHF/6-31G*, and MP2/6-31G* levels of theory. These are summarized in Table 12. The endo *s-cis* transition structure is lowest in energy,[37,38] and is the one used here for isotope effect calculations.

Geometrical features of special note are the forming bond lengths, *b* and *f*. The effect of larger basis sets and the inclusion of correlation energy corrections increases not only the absolute value of the forming bond distances but also the difference between the forming σ-bond lengths, (*b–f*). At the MP2/6-31G* level the asynchronicity is 0.45 Å. The other bond lengths in the transition structure do not vary significantly with level of theory.

The KIEs calculated for this reaction are given in Table 13. As before, the IN hydrogens have larger inverse isotope effects than the OUT hydrogens. Of more significance, the isotope effects at the more fully-formed σ-bond are significantly larger inverse

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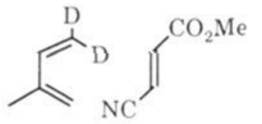
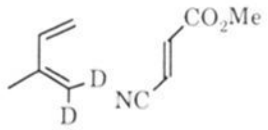
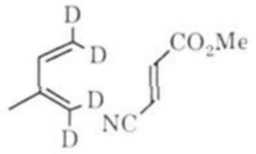
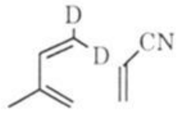
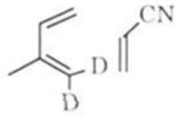
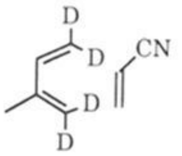
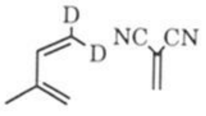
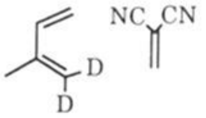
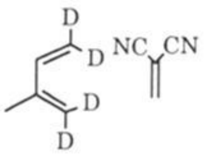
(36) Brown, P.; Cookson, R. C. *Tetrahedron* **1965**, *21*, 1973.

(37) Loncharich, R. J.; Brown, F. K.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 1129.

(38) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127.

**Table 14.** Comparison of Experimental and Theoretical Kinetic Isotope Effects for Diels–Alder Reactions of Unsymmetrical Addends[a]

| | | | concerted | TS-1 |
|---|---|---|---|---|
| reactants | T (K) | expt. | MP2/ 6-31G* | UHF/ 6-31G* |
|  | 298 | 0.88 | 0.84 | 0.90 |
|  | 298 | 0.92 | 0.97 | 1.18 |
|  | 298 | 0.81 | 0.81 | 1.07 |
|  | 373 | 0.91<br>0.99 | 0.88<br>0.98 | 0.93<br>1.13 |
|  | 373 | 0.98<br>0.88 | 0.98<br>0.88 | 1.13<br>0.93 |
|  | 373 | 0.89<br>0.89 | 0.87 | 1.06 |
|  | 298 | 0.79<br>1.02 | 0.84<br>0.97 | 0.90<br>1.18 |
|  | 298 | 0.98<br>0.78 | 0.97<br>0.84 | 1.18<br>0.90 |
|  | 298 | 0.78<br>0.79 | 0.81 | 1.07 |

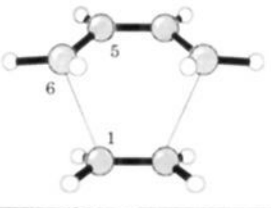
[a] Reference 12.

values than those at the less fully-formed bond. The former are 4–8% inverse, while the latter are from 3% inverse to 1% normal and are essentially negligible.

The Diels–Alder reactions of unsymmetrical addends studied by Gajewski and co-workers are compared to theoretical $D_2$- and $D_4$-KIEs for the reaction of butadiene and acrolein in Table 14. The concerted column is derived from calculations on butadiene and acrolein. The stepwise column is from TS-1 calculated for butadiene plus ethylene. This provides a model to estimate what the isotope effects would be if the reaction were stepwise, since we have not studied butadiene and acrolein at the MCSCF level to find a potential diradical intermediate. For some reactions two isotope effects are given which correspond to results from different regioisomers.

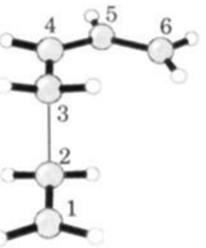
The results from the stepwise mechanism (TS-1) vary widely from experiment in most cases, while the theoretical results on the reaction of butadiene and acrolein agree rather well with experiment in every case. Gajewski concluded that these asynchronous Diels–Alder reactions are concerted by comparison to maximum KIEs predicted by fractionation factors.[7,8] This conclusion is supported here by direct comparison with the asynchronous Diels–Alder reaction of butadiene and acrolein.

**Table 15.** $^{14}C$ Primary Kinetic Isotope Effects for the Concerted Reaction of Butadiene with Ethylene



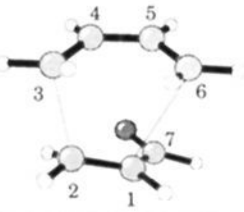
| | $k_{^{12}C}/k_{^{14}C}$ (373.15 K) | | | | |
|---|---|---|---|---|---|
| isotopomer | RHF/ 3-21G | RHF/ 6-31G* | MP2/ 6-31G* | MCSCF/ 3-21G | MCSCF/ 6-31G* |
| 1 | 1.035 | 1.035 | 1.033 | 1.047 | 1.046 |
| 5 | 1.007 | 1.009 | 1.003 | 1.019 | 1.035 |
| 6 | 1.029 | 1.029 | 1.027 | 1.037 | 1.039 |
| scaling | 0.90 | 0.90 | 1.00 | 0.90 | 0.90 |

**Table 16.** $^{14}C$ Primary Kinetic Isotope Effects for the Stepwise Reaction of Butadiene with Ethylene



| | $k_{^{12}C}/k_{^{14}C}$ (373.15 K) | | | |
|---|---|---|---|---|
| isotopomer | UHF/ 3-21G | UHF/ 6-31G* | MCSCF/ 3-21G | MCSCF/ 6-31G* |
| 1 | 1.039 | 1.036 | 1.042 | 1.037 |
| 2 | 1.078 | 1.077 | 1.075 | 1.070 |
| 3 | 1.074 | 1.071 | 1.068 | 1.064 |
| 4 | 1.033 | 1.032 | 1.041 | 1.038 |
| 5 | 1.029 | 1.031 | 1.028 | 1.027 |
| 6 | 1.029 | 1.029 | 1.025 | 1.023 |
| scaling | 0.90 | 0.90 | 1.00 | 0.90 |

**Table 17.** $^{14}C$ Primary Kinetic Isotope Effects for the Concerted Reaction of Butadiene with Acrolein



| | $k_{^{12}C}/k_{^{14}C}$ (373.15 K) | | |
|---|---|---|---|
| isotopomer | RHF/3-21G | RHF/6-31G* | MP2/6-31G* |
| 1 | 1.026 | 1.028 | 1.015 |
| 2 | 1.041 | 1.044 | 1.045 |
| 3 | 1.037 | 1.038 | 1.042 |
| 4 | 1.007 | 1.010 | 1.005 |
| 5 | 1.004 | 1.009 | 1.002 |
| 6 | 1.024 | 1.023 | 1.015 |
| 7 | 0.999 | 1.002 | 1.000 |
| scaling | 0.90 | 0.90 | 1.00 |

**Primary Heavy Atom Kinetic Isotope Effects.** Table 15 presents the primary $^{14}C$ kinetic isotope effects calculated for the concerted Diels–Alder reaction of butadiene with ethylene. Calculations for the stepwise mechanism are given in Table 16. Table 17 presents the $^{14}C$-KIEs for the reaction of butadiene and acrolein.

The use of heavy atom kinetic isotope effects in the study of the Diels–Alder reaction is limited to three cases in the literature. In a dissertation study by C. B. Warren, $^{13}C$ KIEs were reported in the retro-Diels–Alder reaction for the adduct of 1,2-dicyanoacetylene and cyclopentadiene.[40] The conclusion was made

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(39) Ropp, G. A.; Raaen, V. F.; Weinberger, A. J. *J. Am. Chem. Soc.* **1953**, *75*, 3694.

that the reaction is stepwise. Ropp studied the reaction of [2-$^{14}$C]-1-nitro-2-phenylethylene with 2,3-dimethylbutadiene.[39] No rate effect was observed, and it was concluded that the reaction was stepwise although no isotope effect was given for the *b*-position. Shine has reinvestigated this reaction with [1-$^{14}$C]- and [2-$^{14}$C]-1-nitro-2-phenylethylene.[40] Isotope effects are found to be similar at both reacting termini, suggesting that the reaction is concerted. The experimental data are 1.0438 and 1.0474, respectively. These results are in reasonable accord with the prediction given in Table 15 of 1.046 for the synchronous concerted Diels–Alder reaction but deviate from the values of 1.015 and 1.045 predicted for the asynchronous acrolein reaction.

## Summary

The kinetic isotope effects for the Diels–Alder reaction of butadiene and ethylene and the cycloreversion of cyclohexene have been calculated at several levels of theory for both concerted and stepwise mechanisms. The two pathways are predicted to have very different secondary deuterium kinetic isotope effects. The concerted mechanism gives a good account of the experimental isotope effects. These results support a concerted and synchronous reaction between butadiene and ethylene.

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(40) Warren, C. B. Thesis, Diss. Abstr. 31/03B, 1188, 1970.

(41) Kupczyk-Subotkowska, L.; Shine, H. J. *J. Am. Chem. Soc.* **1993**, *115*, 5296.