correlated with steric considerations alone. In striking contrast to these observations is the report of Cookson and Wallis[47] who have previously studied a series of para-substituted benzyl allyl ethers. These authors noted a trend of decreasing rate in the series p-$OCH_3 >$ p-H $\cong$ p-Cl $>$ p-NO_2, suggesting a reaction mechanism characterized by a negative Hammett ρ constant of significant magnitude.

Because of the implied contradictions, and because the apparatus used by Cookson and Wallis[47] was better suited for preparative work rather than kinetics, it was considered necessary to reinvestigate this question. The data obtained in this study are presented in Table XVI. Clearly, no significant rate differences are to be observed amongst the various para-substituted benzyl allyl ethers on gas-phase thermolysis. To all intents and purposes the Hammett ρ of this reaction is zero, providing full support for the conclusion reached earlier that no direct polar substituent effects are exercised in the pericyclic transition state of this retro-ene reaction.

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The Kinetic Deuterium Isotope Criterion Applied to the Thermolysis of Alkyl Allyl Ethers. II

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Abstract: Measurements of k_H/k_D as a function of the temperature of thermolysis of three different unsaturated ethers, the benzyl allyl, benzyl propargyl, and isopropyl allyl, have been carried out. The maximum theoretical isotope effect has been realized in each instance; no evidence has been found for proton tunneling. In accordance with previous application of this criterion of transition-state structure in H-transfer reactions, these results suggest fully symmetrical bond making and breaking in the activated complex of each of these typical retro-ene fragmentation processes. Earlier proposals of a completely planar transition state which have been advanced for related thermolysis reactions are also ruled out.

In a previous article,[1] studies of the thermolysis of alkyl allyl ethers were discussed in which the data gathered on product analysis, substituent effects on rate, and activation parameters were applied to elucidate the nature of this intramolecular H-transfer process. The results clearly indicated that the general reaction had a highly concerted transition state of bond making and breaking with no evidence of free radical or charge development.

The studies to be reported here were addressed to the question of whether the concerted transition state was symmetrical or otherwise. An attractive way of describing the symmetrical transition state is in terms of the bond order between hydrogen and the atoms between which it is being transferred.[2] In the instance of the thermolysis of alkyl allyl ethers, where hydrogen is transferred from carbon to carbon in a six-centered structure, the symmetrical transition state is simply that in which the bond order between hydrogen and each carbon is $^1/_2$. In this linear arrangement ($C \cdots H \cdots C$) of maximum energy content on the reaction path, the real hydrogen vibrations to carbon are immobilized and all the C–H stretching vibrational energy is lost.

This picture of the symmetrical transition state is the basis of the simplified theoretical treatments[2-6] often referred to as the three-center model of the kinetic deuterium isotope effect, which predict that under such circumstances k_H/k_D will exhibit a maximum value determined entirely by the zero-point differences of the respective C–H and C–D bonds. This analysis also anticipates that in a transition state which can be classified as either product-like or reactant-like the values of k_H/k_D will be considerably below the maximum.

Despite the expression[7-10] of numerous theoretical reservations concerning the validity of this simplified treatment of the kinetic deuterium isotope effect, it has recently been shown[11] to provide a useful criterion for the characterization of the symmetrical transition state. Thus, in cases where independent evidence can be obtained supporting the symmetrical structure of the transition state, it has been shown that $k_H/k_D = (A_H/A_D)\ \exp(\Delta E^\circ/RT)$ applies, where $A_H/A_D \cong 1.0$, and ΔE° = the zero-point energy differences of the critical bond to hydrogen and deuterium. On the other hand, any significant departure from symmetry in this linear array of the three-center model involves a very large increase in the vibrational energy of the bond to hydrogen in the transition state. Thus, contrary to the predictions of the simplified treatment of the kinetic deuterium isotope effect, in which reactant-like and

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product-like transition states are expected to have less than the maximum k_H/k_D, it is often found experimentally that the A_H/A_D is very much less than 0.5 and the activation energy can be more than twice as great as the zero-point energy difference, $\Delta E°$. Results of this nature have been correlated with the occurrence of proton tunneling.[12–16]

From a purely experimental viewpoint, then, the temperature dependence of the kinetic deuterium isotope effect becomes a relatively sensitive criterion of transition-state symmetry in reactions involving a linear transfer of hydrogen. In previous experimental tests[11] of the validity of this criterion, when the hydrogen was transferred between oxygen and carbon, it was confirmed that any serious effects arising from changes in hydridization, valence geometry, and ionic character of the bonding at the centers of the three-atom model (O···H···C) were absent.

The thermolysis of alkyl allyl ethers presents the opportunity to apply this criterion to a cyclic, concerted transition state of much simpler symmetry character, since the hydrogen in transit in the activated complex is passing between nearly identical atoms in the three-center model, C···H···C. In addition, recent calculations based[2] on a more elaborate five-center model suggest that in this system the neglect of bending vibrations in the transition state produces no significant difference in the magnitude of k_H/k_D. Conversely, it can be expected that any significant departure from linearity of hydrogen transfer or any element of asymmetry in the timing of bond making and bond breaking in the activated complex would produce an increase in C–H vibrational energy compared to the ground state of either reactants or products and would result in very considerable abnormality of k_H/k_D and its temperature dependence.

Experimental Section

Synthesis of Substrates. Deuterioisopropyl Allyl Ether. This compound was prepared by the method of Skrabal[17] by the same procedure used for the undeuterated ether,[1] after first obtaining isopropyl alcohol-*O-d* from the reaction of acetone with sodium in amyl alcohol-*O*-d.

α,α-Dideuteriobenzyl Allyl Ether. This compound was synthesized from α,α,β-trideuteriobenzyl alcohol and allyl bromide in 80% yield by the Williamson method, bp 45° (1 mm). It was 98–99% deuterated in the benzyl position as determined by nmr integration: nmr (CCl_4) δ 3.88 (d with allylic fine splitting, 2, J = 5 Hz, OCH_2CH), 4.40 (0.03, $PhCH_2$), 5.12 (complex m, 2, $CH{=}CH_2$), 5.82 (complex m, 1, $CH{=}CH_2$) 7.22 (s, 5, aromatic); ir (neat) 2180 and 2070 (C–D), 1650 (C=C), 1090 (C—O—C), 985 and 920 ($CH{=}CH_2$), 735 and 695 (monosubst benzene), C–D stretch 2062 cm^{-1}; Perkin-Elmer Model 180; mass spectrum (70 eV) *m/e* (rel intensity) 150 (1), 108 (6), 106 (12), 95 (5), 94 (66), 93 (100), 92 (6), 81 (10), 67 (5), 66 (5), 41 (5), 39 (4).

α,α-Dideuteriobenzyl Propargyl Ether. This compound was synthesized from α,α,β-trideuteriobenzyl alcohol and propargyl bromide in 50% yield by the Williamson method: bp 43° (0.4 mm); nmr (CCl_4) δ 2.33 (t, 1. J = 2.5 Hz, $C{\equiv}CH$), 4.01 (d, 2, J = 2.5 Hz, OCH_2 $C{\equiv}C$, 4.50 (0.03, $PhCH_2O$), 7.25 (s, 5, aromatic); ir (neat) 3300 (H—C≡C), 2180 and 2070 (C—D), 2120 (HC≡C), 1070 (C—O—C), 720 and 695 cm^{-1} (monosubst benzene); mass spectrum (70 eV) *m/e* (rel intensity) 148 (8), 117 (15), 116 (53), 108 (11), 105 (25), 94 (73), 93 (100), 92 (14), 91 (12), 81 (54), 80 (11), 79 (28), 78 (18), 77 (28), 67 (16), 66 (18), 53 (13), 52 (15), 51 (32), 49 (17), 41 (14), 40 (22), 39 (54), 38 (18),

α,α,β-Trideuteriobenzyl Alcohol. A solution of ethyl benzoate (17 g, 0.11 mol, Eastman) in 40 ml of dry ether was added dropwise to a stirred suspension of lithium aluminum deuteride-d_4 (99% D) (3.0 g, 0.29 mol % D, Stohler) in 100 ml of ether at such a rate as to maintain reflux. The mixture was refluxed for an additional 30 min and cooled to 0°, and then 3 g of D_2O, 3 g of 15% NaOD in D_2O, and 9 g of D_2O were added successively. The slurry was filtered and the solids were washed with ether. The combined etherial solution was dried ($MgSO_4$), concentrated, and distilled, giving 11 g (89%) of **1a**, bp 50–53° (0.7 mm). This alcohol was used to prepare the deuterated benzyl allyl and benzyl propargyl ethers: nmr (CCl_4) δ 1.17 (s, aromatic); ir (neat), spectrum lacked carbonyl at 1720 and hydroxyl at *ca.* 3300 and was similar to spectrum of proteobenzyl alcohol, 2400 cm^{-1} (O–D).

Results and Discussion

The zero-point energy differences of interest were checked by high precision infrared measurements on benzyl allyl ether. A $(\Delta E°)_{H-D}$ value of 1.145 kcal/mol was calculated from stretching frequencies of 2850 cm^{-1} for the C–H and 2062 cm^{-1} for the C–D bonds. This is in excellent agreement with the "normal" value of 1.15 kcal/mol, and indicates no abnormalities in the vibrational ground states of the substrate.

Three typical substrates with deuterium substituted for hydrogen at the critical locations were thermolyzed in the gas phase and their reactivities determined as a function of temperature by means of the apparatus previously described.[18] The data obtained in this manner were reduced by the techniques previously employed[1] to calculate the activation parameters characteristic of each of the deutero substrates for comparison with the corresponding proteo references. The most extensive measurements of rate as a function of temperature were made with both the deuterated benzyl allyl ether [$CH_2{=}CHCH_2OCD_2C_6H_5$] and benzyl propargyl ether [$CH{\equiv}CCH_2OCD_2C_6H_5$]. More limited measurements were carried out with isopropyl allyl ether in which nearly total deuteration of the isopropyl function had been accomplished, *i.e.*, $CH_2{=}CHCH_2OCD(CD_3)_2$. Tables I and II summarize the rate data obtained in each of these cases. Each table also expresses the rate law governing the temperature

Table I. Gas-Phase Thermolysis of α,α'-Dideuteriobenzyl Allyl Ether. Rates and Activation Parameters

$k = 4.06 \times 10^{12} \exp(-42{,}300/RT)$ sec^{-1}
$\Delta E^{\ddagger} = 42.3 \pm 0.1$ kcal/mol
$\text{Ln } A = 26.73 \pm 0.10$
$\text{Log } A = 11.61 \pm 0.04$
$\Delta A^{\ddagger} = -9.2 \pm 0.2$ eu
Correlation coeff = 0.999

Table II. Gas-Phase Thermolysis of α,α'-Dideuteriobenzyl Propargyl Ether. Rates and Activation Parameters

$k = 1.02 \times 10^{12} \exp(-42{,}000/RT)$ sec^{-1}
$\Delta E^{\ddagger} = 42.0 \pm 0.1$ kcal/mol
$\text{Ln } A = 27.65 \pm 0.08$
$\text{Log } A = 12.01 \pm 0.04$
$\Delta S^{\ddagger} = 7.4 \pm 0.2$ eu
Correlation coeff = 0.999

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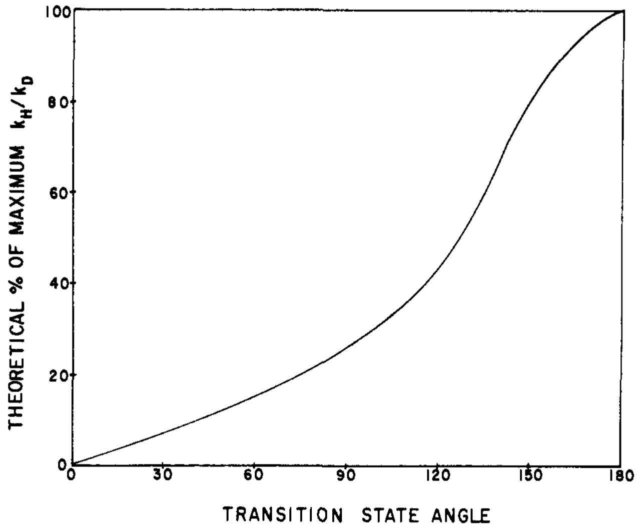

Figure 1. Effect of the transfer angle on the isotope effect.

dependence of the rate and the activation parameters of reaction computed therefrom.

A comparison of the pertinent data for each of the substrate pairs (proteo *vs.* deutero) is presented in Table III. Clearly, the maximum "theoretical" isotope effect has been realized in each instance, in that the activation energy differences of 1.1 ± 0.14 kcal/mol for each of the benzyl ethers and 1.3 for the isopropyl ether is, within experimental error, equivalent to the magnitude of the zero-point energy difference, 1.15 kcal/mol. Furthermore, the activation entropy differences in each case, 0.3 ± 0.2 eu, while not precisely the zero value anticipated by the idealized model, are different from zero by magnitudes within the range of potential error in the measured values, as given by the standard deviations.

Table III. Comparison of Kinetic Data for Proteo[a] and Deutero Substrates

	Log A	$\Delta E^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta(\Delta E^{\ddagger})$	$\Delta(\Delta S^{\ddagger})$	A_H/A_D
			Benzyl Allyl Ether			
Proteo	11.53	41.2	−9.5			
Deutero	11.61	42.3	−9.2	1.1 ± 0.14	−0.3 ± 0.17	0.8
			Benzyl Propargyl Ether			
Proteo	11.92	40.9	−7.7			
Deutero	12.01	42.0	−7.4	1.1 ± 0.14	−0.3 ± 0.2	0.8
			Isopropyl Allyl Ether			
Proteo	11.34	41.3	−10.5			
Deutero	11.56	42.6	−9.5	1.3 ± 0.8	−1.0 ± 0.8	0.6

[a] From data reported in ref 1.

The largest deviations which can be noted in Table III are to be found in the case of the isopropyl ether where deuterium existed in the methyl groups as well as at the critical carbon. It may well be that this magnitude of $\Delta(\Delta S^{\ddagger})_{H-D}$ of about 1 eu and the slight increase of the $\Delta(\Delta E^{\ddagger})_{H-D}$ over the "theoretical" maximum are a reflection of a possible α (secondary) deuterium isotope effect superimposed on the primary isotope criterion under examination. In no case, however, can the results be interpreted as other than the experimental realization of the primary kinetic deuterium isotope criterion confirming a symmetrically structured transition state for the thermolysis of benzyl allyl, benzyl propargyl, and alkyl allyl ethers in general. No evidence of proton tunneling,[16] a frequent consequence of increased vibrational energy of the proton in an asymmetric transition state, can be perceived, since $A_H \cong A_D$ and $\Delta(\Delta E^{\ddagger}) = \Delta(\Delta E^{\circ})_{H-D}$. Finally, some notice must be taken to earlier work by Cookson and Wallis[19] on the thermolysis of benzhydryl allyl ether. These authors have reported that deuteration of the critical benzhydryl carbon produces little or no change in rate. In view of the data under consideration here, any failure to detect an isotope effect may be attributed to the use of a somewhat crude and insensitive kinetic technique.

Further Considerations of Transition-State Structure. The pericyclic transition state[20] of a retro-ene reaction appears to be consistent with the information gleaned by application of the kinetic deuterium isotope criterion in one important respect. The hydrogen transfer must occur in a linear or nearly linear arrangement of the three-atom model. The influence of possible deviations from a C–H–C angle of 180° can be estimated from the model calculations of More O'Ferrall[2] whose data have been applied in constructing the curve in Figure 1. It can be perceived that a small deviation from linearity (say, from 180 to 150°) can account for lowering of the predicted isotope effect to 80% of its (linear) value. It has already been pointed[2,21] out that a bent transition state construction deviating the angle of H-transfer much below 150° involves consequences that lead to an entirely altered temperature dependence of the primary kinetic isotope effect.

The proposal of a completely planar transition state such as has been made for the related thermolysis of esters[22] must be rejected on this basis. Such a transition state construction necessarily involves a 120° (C–H–C) angle for which a temperature independent kinetic isotope effect has been both predicted and observed.[2,21] It must also be recalled that a planar transition state of alkyl allyl ether thermolysis is not in accord with the various substituent influences (or their absence) which were noted in prior investigations.[1]

The earlier work[11] has shown that the thermolysis of β-hydroxyolefins may also be characterized as a retro-ene reaction possessing a fully symmetrical transition state. Nonetheless, Viola[23] has proposed a chair-like transition-state geometry for this related reaction. In the alkyl allyl ether thermolysis this would correspond to positions 1, 2, 4, and 5 (in structure I) lying in a common plane, with position 3 above this plane and position 6 (the hydrogen in transit) beneath. This proposal must be rejected, however, since it entails an acute C–H–C angle which would be at variance with the observed temperature dependence of the primary deuterium isotope effect.

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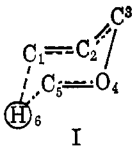

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Viola and coworkers[23] have also proposed a completely planar transition state for the related thermolysis of β-hydroxyacetylenes. This reaction has also been previously shown[11] to have a symmetrical transition state by application of the full kinetic deuterium isotope criterion. It bears the same resemblance to β-hydroxyolefin thermolysis as has been identified here for the analogous reactions of benzyl allyl and benzyl propargyl ethers. The postulation[23] of two different transition states for β-hydroxyolefin and β-hydroxyacetylene thermolysis implies that the observed similarity of the activation parameters of these reactions is purely coincidental. It has been demonstrated in a previous article[1] that the near identity of activation parameters of benzyl allyl and benzyl propargyl ether thermolysis is not believed to be a mere coincidence.

A further reason for rejecting this as a coincidence of transition-state properties is based on the evidence afforded through application of the full kinetic deuterium isotope criterion. The identity of the isotope effect dependence on temperature, taken together with the striking similarity of activation parameters for allylic and propargylic ether (as well as for β-hydroxyolefins and β-hydroxyacetylene), thermolysis constitutes the most persuasive argument favoring a commonly structured transition state for all of these reactions. The constraint imposed by the ground-state geometry of the acetylenic bonding is clearly of no decisive consequence in the transition state of the retro-ene reaction.[1,20,24] This can be seen by comparing the ground state C–C–C distances (2.67 Å in acetylenes *vs.* 2.46 Å in olefins) and noting that the bending of the C–C–C framework in acetylenes requires surprisingly little energy (0.3 kcal for a 6° bend[23,25]). Thus, it is a matter of high likelihood that in a transition state some 40 kcal/mol above ground acetylenic substrates can assume the same geometry as their olefinic analogs. The considerations discussed above provide a reasonable (experimental) basis for the conclusion that this likelihood is realized in a number of reactions possessing a cyclic, symmetrical, transition state. Figure 2 appears to be an attractive way of portraying the molecular orbitals involved in such pericyclic processes of bond making and breaking.

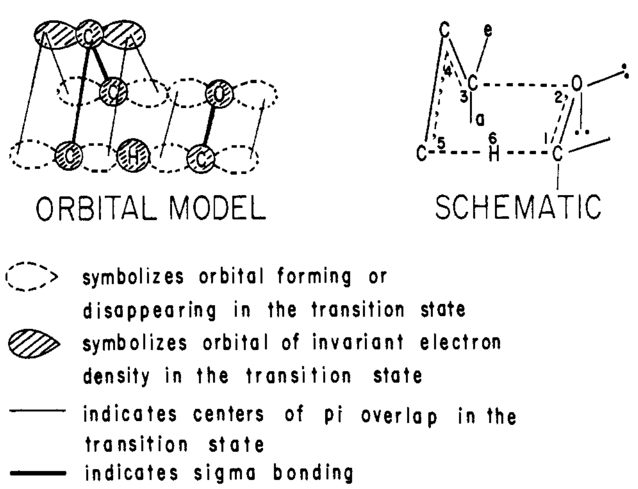

Figure 2. Transition state structure.

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Ground States of Molecules. XXIV.[1] MINDO/2 Study of Some Reactions of Cyclopropylidene[2]

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Abstract: MINDO/2 calculations are reported for the rearrangements of singlet cyclopropylidene (carbenacyclopropane) to allene and to cyclopropene and for its addition to ethylene. The results account well for its observed behavior.

The reactions of atomic carbon with olefins have been studied in some detail by Skell and Engel.[5] In the case of singlet carbon, the product first formed is a singlet state of a cyclopropylidene (**1**). If the reacting carbon atom is in the excited ^1S singlet state, the cyclopropylidene rearranges immediately to an allene (**2**). If, however, it is in the lowest (^1D) singlet state, the cyclopropylidene does not rearrange in this way. In-

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