

Transition State Structure in Gas Phase Thermolytic β -Elimination Processes Probed by Isotope Effect Criteria

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Abstract: The vapor-phase thermolytic β -elimination reactions of *tert*-butyl ethyl ether, *tert*-butyl-1,1- d_2 ethyl ether, and *tert*-butyl- d_9 ethyl ether have been carried out in a noncatalytic gold coil microreactor in the temperature range ca. 516–585 °C. The ethyl-deuterated substrate exhibits activation parameters which are very similar to the undeuterated. The *tert*-butyl- d_9 substrate shows enormous differences vs. the undeuterated reference; $(\Delta E_a)_D^H \approx 5.7$ kcal/mol and $A_H/A_D \approx 0.07$. These results, taken together with calculations of the dimensions of the reaction barriers, suggest a mechanism of rate-determining, linear H transfer occurring in a quantum-mechanical tunneling process completely uninfluenced by zero-point energy factors. A triangular transition state for such thermal β -elimination reactions is preferred to the previously postulated rectangular structure.

Thermolytic elimination reactions in the vapor phase have been the subject of several recent reviews.^{1,2} Where the reaction seems to be unambiguously unimolecular³ a variety of approaches, mostly kinetic, have been undertaken^{4–8} with the aim of elucidating the structure of the transition state. The stereochemistry of the alkyl halide thermolysis studied with menthyl⁹ and neomenthyl chloride,¹⁰ though subject to some ambiguities,¹¹ nonetheless appears to be a syn elimination for which a four-membered transition state has often been depicted in terms of a rectangular structure.^{5,6}

The thermal decomposition of dialkyl ethers in the gas phase has been generally regarded¹² as a radical chain process. Alkyl allyl ethers, however, have been shown^{12a} recently to undergo a cyclic, retroene decomposition via a pericyclic transition state through application of the temperature dependence of the primary kinetic deuterium isotope effect as the mechanistic criterion.¹³ A cyclic, so-called molecular process has also been claimed¹⁴ for *tert*-butyl ethyl ether thermolysis on the basis of product composition and activation parameter data. The results reported could not be reconciled with the type of radical chain mechanisms usually encountered in studies of ether thermolysis and reviewed in an earlier article.^{12a} Isobutylene and ethanol are the only products formed in the temperature range 433–484 °C in what is described as a well-seasoned, static, glass reactor system.¹⁵ A four-centered, rectangular transition state was proposed to account for these findings.¹⁴ A similar transition state has been advanced for the thermolysis of *tert*-butyl methyl ether¹⁶ and *tert*-butyl halides¹⁷ which bear structures analogous to *tert*-butyl ethyl ether.

The gas-phase thermolysis of *tert*-butyl ethyl ether has now been investigated by applying the temperature–isotope criterion of transition-state structure.¹³ Three distinct variations of the substrate structure have been studied; the reference substrate, i.e., completely undeuterated, the α -dideuterated-ethyl, and the *tert*-butyl- d_9 substrates were compared as to product composition and reaction rate as a function of temperature in the range 516–585 °C.

Experimental Section

General. All reagents and solvents were of commercial grade and were used without further purification except where noted. NMR spectra were determined using a Perkin-Elmer R-12B spectrometer at 60 MHz on carbon tetrachloride solutions with chemical shifts reported in δ (ppm) with reference to tetramethylsilane ($\delta = 0$). Mass spectra were recorded at 70 eV on a C.E.C. 21-110B double-focusing high-resolution spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard research chromatograph Model 5750 equipped with a flame ionization detector. A Varian Aerograph

series 2700 fitted with a thermal conductivity detector was utilized for the preparative scale work.

Preparation of *tert*-Butyl Ethyl Ether. The method of Norris and Rigby¹⁸ was modified as follows in order to facilitate the synthesis of small quantities of the ether. To a 50-ml, three-neck flask fitted with a distillation column of low volume, a dropping funnel, and magnetic stirring were added 10 g of water and 1.8 g of H_2SO_4 . When the solution cooled, 5.7 g (0.0039 mol) of diethyl oxalate was added and the mixture heated in an oil bath. When the bath reached ~ 70 °C, a small portion of *tert*-butyl alcohol was added. The product was distilled at a constant head temperature of 64 °C, maintained by regulation of the bath temperature and continued additions of *tert*-butyl alcohol, until a total of 2.8 g (0.038 mol) had been added. The bath temperature was then slowly raised and product collected until the distillation temperature reached 72 °C.

Gas chromatographic examination of the product indicated a mixture of three components which were identified by retention times as isobutylene, *tert*-butyl ethyl ether, and butanol. The pure ether was obtained by preparative scale gas chromatography (9.5 ft \times $\frac{3}{8}$ in. 20% SE30): NMR (CCl_4) δ 1.08 (3 H, triplet, CH_3), 1.12 (9 H, singlet, CH_3), 3.33 (2 H, quartet, CH_2); mass spectrum parent ion: 102, principal ions: 59, 87, 57, 29, 41.

Preparation of Ethanol-1,1- d_2 . To a suspension of 4 g (0.095 mol) of lithium aluminum deuteride in 200 ml of dry ether was added 33 g (0.19 mol) of *n*-octyl acetate in 75 ml of dry ether at such a rate as to maintain a slow reflux. When the addition was complete, the solution was heated at reflux for an additional 24 h. On cooling, 4 ml of water followed by 4 ml of 15% sodium hydroxide followed by 12 ml of water were added, the inorganic solids were removed by filtration, and the solution was dried over magnesium sulfate. Gross solvent was removed slowly by distillation through a 2 in. Vigreux column. The product, 9.12 g, was collected by microdistillation from 70 °C until octanol reached the head of the column. This presumed impure material was not purified further but was used directly in the preparation of ethyl-1,1- d_2 tosylate.

Preparation of Ethyl-1,1- d_2 Tosylate. The simplified method of Tipson¹⁹ was employed. Tosyl chloride (40.0 g, 0.21 mol) was dissolved in 160 ml of pyridine previously dried over barium oxide. The solution was cooled to -10 °C in an ice-salt bath and the impure ethanol-1,1- d_2 (9.1 g, ~ 0.19 mol) from the previous step was added in large portions. The temperature rose to 0 °C, then returned to -10 °C. After 30 min, 455 ml of 5 N H_2SO_4 at 0 °C was added rapidly and the temperature rose to 30 °C. Continued cooling allowed the product to crystallize at 3 °C. It was filtered off, washed with water, and dried in a vacuum desiccator. The yield was 12.0 g with a melting point 31–32 °C, in agreement with the value reported¹⁹ for the undeuterated tosylate.

Preparation of *tert*-Butyl-1,1- d_2 Ethyl Ether. A 100-ml round-bottom flask was charged with a 1 M solution of ethyl-1,1- d_2 tosylate (6.0 g, 0.03 mol) in 30 ml of *tert*-butyl alcohol and 4.6 g (0.033 mol) of potassium carbonate. The mixture was heated to reflux and stirred mechanically for 6 days. After cooling, the mixture was poured into 120 ml of water and extracted four times with 30-ml aliquots of toluene, and the combined toluene extracts were dried over magnesium

Table I. Thermolysis Rate Data for *tert*-Butyl Ethyl Ether

$T_r, ^\circ\text{C}$	$10^3/T_r, \text{K}$	C/Co	$10^3k, \text{s}^{-1}$	$\ln k$
516.66	1.2661	0.665	8.60	-4.756
516.72	1.2660	0.672	8.38	-4.782
526.40	1.2507	0.673	12.1	-4.414
526.40	1.2507	0.668	12.3	-4.396
545.62	1.2213	0.626	26.3	-3.638
545.61	1.2214	0.630	26.0	-3.650
565.21	1.1928	0.376	55.8	-2.887
565.21	1.1928	0.381	55.0	-2.901
574.49	1.1798	0.306	79.7	-2.529
574.49	1.1798	0.306	79.4	-2.533

Table II. Thermolysis Rate Data for *tert*-Butyl-*l,l*- d_2 Ethyl Ether

$T_r, ^\circ\text{C}$	$10^3/T_r, \text{K}$	C/Co	$10^3k, \text{s}^{-1}$	$\ln k$
516.94	1.2657	0.635	8.423	-4.778
516.95	1.2657	0.636	8.32	-4.789
526.38	1.2507	0.670	12.2	-4.403
526.38	1.2507	0.673	12.1	-4.413
545.79	1.2211	0.546	25.4	-3.627
545.78	1.2211	0.543	25.6	-3.664
565.21	1.1928	0.386	54.2	-2.914
565.22	1.1928	0.389	53.8	-2.922
575.13	1.1789	0.283	84.6	-2.470
575.14	1.1789	0.288	83.6	-2.481

sulfate. The toluene solution was distilled and all material boiling in the range 67–90 °C collected. Gas chromatographic analysis showed the distillate to be a mixture of three components which were identified as *tert*-butyl ethyl ether, butyl alcohol, and toluene by comparison with the retention times of known compounds. The product was isolated by means of preparative scale gas chromatography (5 ft \times 1/4 in. 20% DEGS). A mixture of ether so prepared with the undeuterated material synthesized previously gave only one peak under several different sets of GC conditions. NMR analysis showed complete absence of any CH₂ protons: NMR (CCl₄) δ 1.07 (3 H, singlet, CH₃), 1.12 (9 H, singlet, CH₃).

Preparation of *tert*-Butyl- d_9 Ethyl Ether. Exactly the same procedure was employed here as for the undeuterated ether with the exception that the deuterated analogues of the reactants were substituted. Thus, 11 g of D₂O and 1.9 g of D₂SO₄, prepared by the addition of D₂O to SO₃, were combined in a flask and 5.7 g (0.039 mol) of diethyl oxalate added. *tert*-Butyl- d_9 alcohol (3.2 g, 0.038 mol) was added slowly over the course of the reaction, and the product was collated as it distilled from the reaction mixture. The distillate was a mixture of three components as determined by gas chromatography. The retention times matched those for the products from the undeuterated ether synthesis. The peak corresponding to the ether was collected from the effluent of the preparative scale gas chromatograph and showed identical characteristics under various GC conditions when mixed with the undeuterated analogue. Deuterium analysis of NMR indicated the extent of deuteration to be 99% (8.91 deuterons/molecule of ether): NMR (CCl₄) δ 1.09 (3 H triplet, CH₃), 3.31 (2 H, quarter, CH₂).

Kinetics. The kinetic determinations were carried out in the gas phase using a gold coil, pulse flow reactor similar to the model described previously.^{13a,20} In continuation of our investigation of the gas-phase thermolysis of ethers, a study of the reactions of *tert*-butyl ethyl ether, *tert*-butyl-*l,l*- d_2 ethyl ether, and *tert*-butyl- d_9 ethyl ether was undertaken. In each case, the reactant ether was mixed with an unreactive internal standard (toluene) and diluted with an inert solvent (*p*-xylene) to yield a solution which contained 10% substrate by volume. Product analysis was performed on a Hewlett-Packard Model 5750 research chromatograph with flame ionization detector. Separations were effected with a 6 ft \times 1/8 in. UCW-98 chromatographic column. Peak areas were determined using a rotating disk integrator. Statistical analysis²¹ and determination of activation parameters were performed on a Burroughs 6700 computer with programs written in Fortran IV. These data are presented in Tables I, II, III, and IV.

Table III. Thermolysis Rate Data for *tert*-Butyl- d_9 Ethyl Ether

$T_r, ^\circ\text{C}$	$10^3/T_r, \text{K}$	C/Co	$10^3k, \text{s}^{-1}$	$\ln k$
536.62	1.2349	0.663	8.20	-4.804
536.63	1.2349	0.671	-7.96	-4.833
545.73	1.2212	0.623	12.0	-4.423
545.74	1.2212	0.627	11.8	-4.438
564.64	1.1936	0.435	27.5	-3.594
564.65	1.1936	0.435	27.4	-3.596
574.85	1.1793	0.493	40.0	-3.219
574.81	1.1793	0.499	39.9	-3.221
585.58	1.1645	0.411	60.6	-2.803
585.58	1.1645	0.406	-61.5	-2.788

Results and Discussion

Identical product compositions were obtained in all the cases, indicating that the influence of the isotopic label on rate did not alter the mechanistic course of reaction. Isobutylene and ethanol were identified as the primary products. No traces of acetaldehyde and/or isobutane could be detected when all the available high sensitivity, GLC techniques were applied for this purpose; the results were devoid of all possible indications that might suggest the incursion of a competing radical chain mechanism. They confirm the earlier claim that only a single, molecular mechanism of elimination occurs in a non-catalytic reactor, unlike most other dialkyl ethers.¹²

The kinetic data shown in Tables I, II, III, and IV confirm that the rate determining step involves elimination of the proton from the *tert*-butyl rather than the ethyl group. The ethyl-deuterated substrate exhibits activation parameters which are quite similar to those of the undeuterated reference. Although the activation energy and frequency factors of this substrate are slightly larger than for the reference, these magnitudes of difference ($k_H/k_D \approx 1.02$ at 555 °C) can be reconciled with an inductive, secondary deuterium isotope effect modifying the reaction basicity of the ether oxygen. The *tert*-butyl- d_9 compound by comparison shows measureable differences in its relative rate and activation parameters vs. reference: $k_H/k_D = 2.15$ at 555 °C, $[\Delta E_a]_D^H \approx 5.7$ kcal and $A_H/A_D \approx 0.07$.

The magnitudes of these values on initial inspection are certainly suggestive of a transfer of hydrogen accompanied by quantum-mechanical tunneling. However, tunneling corrections in high-temperature gas-phase reactions have not often been noted primarily because of the characteristically small size of the isotope effect at these temperatures and the consequent requirement for extraordinarily precise kinetic data. Because of these considerations, as discussed by Bell,^{22c} it behooves us to scrutinize the kinetic data for the possibility that the results arise from an artifact and are vitiated by experimental uncertainties. We are required to ask, therefore, how different is the measured temperature dependence of the isotope effect from the values of k_H/k_D to be computed exclusively on the basis of a zero-point energy determined effect (C-H stretch of ca. 3000 cm⁻¹).

It can be seen in Table V that over the full temperature range of measurements (ca. 70 °C) the change in k_H/k_D experimental values is 26%, whereas the zero-point energy determined k_H/k_D values span a range of only $\pm 3\%$ variation. That the actual experimental error is less than acceptable may be realized also in the experiences of measurement. For example, the d_9 substrate reacted too slowly at 516 °C to be measured accurately, and at 586 °C the undeuterated compound reacted too rapidly, both suggesting a very different type of temperature dependence than would be expected on the basis of the zero-point energy computed values of k_H/k_D listed in Table V. Moreover, the 26% change in $\Delta(k_H/k_D)$ is more than

Table IV. Summary of Activation Parameters for Thermolysis of Various *tert*-Butyl Ethyl Ether Substrates

	Undeuterated	Ethyl- <i>d</i> ₂	<i>tert</i> -Butyl- <i>d</i> ₉	Undeuterated (D&W) ^a
<i>E</i> _a , kcal/mol	51.6 ± 0.3	52.3 ± 0.5	57.3 ± 0.3	59.4 ± 0.4
ln <i>A</i>	28.09 ± 0.23	28.48 ± 0.41	30.79 ± 0.28	36.49 ± 0.25
<i>A</i> , s ⁻¹	1.58 ± 0.41 × 10 ¹²	2.34 ± 0.79 × 10 ¹²	2.35 ± 0.58 × 10 ¹³	7.05 ± 1.56 × 10 ¹⁵
Δ <i>S</i> [‡] , eu	-6.7 ± 0.5	-5.9 ± 0.8	-1.4 ± 0.6	10.2 ± 0.5
<i>R</i> ^b	0.9998	0.9994	0.9997	0.9999
Temp range, °C	516.66-574.49	516.94-575.14	536.62-585.58	433.0-484.2

^a Computed from rate data of Daly and Wentrup given in ref 14. ^b *R* = correlation coefficient.

Table V. Comparison of Isotope Effects with Values Computed on Zero-Point Energy Basis

Temp, °C	<i>k</i> _H / <i>k</i> _D (Arrh) ^a	<i>k</i> _H / <i>k</i> _D (ZPE) ^b
516	2.55	2.08
546	2.23	2.03
565	2.06	1.99
575	1.98	1.98
586	1.89	1.96

^a Values picked off the Arrhenius line delineated by data in Tables I through IV. ^b Values computed on the basis of an exclusively zero-point energy determined isotope effect.

a factor of six greater and, therefore, readily distinguishable from the *d*₂ substrate data: Δ(*k*_H/*k*_D) ≈ 4%. It can be regarded as a contradiction of the argument² that the magnitude of *k*_H/*k*_D in thermal β-elimination processes⁸ should be interpreted as a secondary deuterium isotope effect in an E1 (like) mechanism.

Moreover, both the size and the temperature-dependent character of the isotope effect would seem to rule out the rectangular transition state of concerted bond making and breaking proposed earlier.¹⁴ This conclusion can be inferred on the basis of the analysis²² of the isotope effect size with the bonding angle in a nonlinear complex. Furthermore, for ordinary nonpericyclic reactions which may involve a bent, nonlinear transition state of H transfer, it has been experimentally demonstrated^{23,24} that *k*_H/*k*_D will be both small and relatively temperature independent, in contrast to the observations made in these studies.

In fact, the large value of (Δ*E*_a)_D^H, the small value of *A*_H/*A*_D, and the large, temperature-dependent *k*_H/*k*_D ratios can be associated with the presence of a linear transition state accompanied by quantum-mechanical tunneling, in keeping with the previously defined experimental criteria.²⁵ These values are to be compared, for example, with those reported by Lewis and co-workers²⁶ in the oxidation of triphenylmethane dyes, by Kwart and Nickle^{13b} for the Cr(VI) oxidation of alcohols, and by Caldin and Mateo²⁷ for the proton-transfer reactions between 4-nitrophenylnitromethane and various bases. All of these processes have been explained by invoking quantum-mechanical tunneling in a process of linear H transfer.

As a further test of the occurrence of tunneling in the process under study, the experimental data were subjected to analysis by the equations of Bell²⁸ after the method of Caldin.²⁹ In this procedure, Bell's tunneling correction factor, *Q* = *k*_{QM}/*k*_{class}, is substituted into the Arrhenius equation for the classical reaction giving

$$k_{QM} = Q A_{class} \exp(-E_{class}/RT)$$

where *k*_{QM}, the rate constant for proton transfer accompanied by quantum-mechanical tunneling is expressed in terms of a quantum correction, *Q*, to the Arrhenius parameters, *E*_{class} and *A*_{class}, for the same process treated by classical mechanics, i.e.,

Table VI. Barrier Calculation Data Where -1.2 ≤ (*E*^D_{class} - *E*^H_{class}) ≤ 1.2

<i>T</i> , °C	ln (<i>k</i> _H / <i>k</i> _D) _{Arrh}	ln (<i>k</i> _H / <i>k</i> _D) _{QM}	Difference	% difference
536	0.838	0.840	0.002	0.23
545	0.799	0.798	-0.001	-0.17
555	0.757	0.755	-0.002	-0.30
565	0.716	0.716	-0.000	-0.05
574	0.679	0.683	0.004	0.64

$$E_{class}^H = 57.7 \text{ kcal} \quad E_{class}^D = 57.4 \text{ kcal} \quad a = 0.394 \text{ \AA}$$

Sum of the squares of the deviations at the five temperatures

$$= \sum (\bar{X} - X_i)^2 = 2.98 \times 10^{-5}$$

excluding the wave nature of the reacting species and concerned only with zero-point energy differences. The isotopic rate constant ratio is then

$$\ln (k_H/k_D)_{QM} = \frac{E_{class}^D - E_{class}^H}{RT} + \ln (Q_H/Q_D)$$

where it is assumed that secondary isotope effects are negligible (or have been corrected for) and that both the preexponential factor for classical behavior and the barrier width, 2*a*, are the same for hydrogen and deuterium transfer.

The values of *E*^H_{class}, *E*^D_{class}, and *a* are all unknown and are tested by an iterative trial and error process until good agreement, found by minimizing the sum of the squares of the deviations, is obtained at all temperatures between the generated values (*k*_H/*k*_D)_{QM} and the values (*k*_H/*k*_D)_{Arrh} calculated from the experimental Arrhenius plots. In addition, the following conditions were required of a good fit: (a) *E*^H_{obsd}/*E*^H_{class} < 1; (b) *E*^D_{obsd}/*E*^D_{class} < 1; (c) 0 ≤ (*E*^D_{class} - *E*^H_{class}) ≤ 1.2 kcal/mol; and (d) all points must be reproduced with a precision greater than 1%. To facilitate the evaluation of broad ranges of the unknowns, the actual curve fitting was performed with the aid of a Burroughs 6700 computer for which Fortran IV programs were written.

For a first approximation of the barrier dimensions, it was assumed that no enthalpy change occurred in the reaction (Δ*H*^o = 0), i.e., the barrier was considered as being symmetric, and only the first term of the tunnel correction factor was used. It can be demonstrated that these simplifications do not affect the degree of fit but will limit the accuracy of *E*^H_{class} and *E*^D_{class} in some cases.

Attempts to obtain a fit were unprofitable. No solution could be found which was better than 3%. The nature of the line generated by the attempted fit, however, suggested that the *E*^D_{class} - *E*^H_{class} term was too large. To remedy this, the required condition *c* was modified to allow negative values, as follows: -1.2 ≤ (*E*^D_{class} - *E*^H_{class}) ≤ 1.2 kcal. Good agreement between the experimental data and those derived from Bell's equations was then obtained as shown in Table VI.

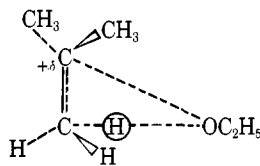


Figure 1. Proposed transition state for the thermal fragmentation reaction of *tert*-butyl ethyl ether.

The fact that the classical barrier height is greater for hydrogen transfer than for deuterium transfer indicates that the primary isotope influence is accompanied by a simultaneous and considerably smaller secondary one which has been neglected in the calculation and which has the effect of slightly lowering the energy barrier of the deuterium reaction. A review³⁰ of all the possible consequences of β secondary, deuterium isotope substitution suggested that only an inductive influence could yield the inverse effect required to account for the lowered barrier.

The difficulty in measuring the magnitude of such an inductive effect hitherto has been considered³⁰ to arise from the fact that it frequently competes with and is over-shadowed by the hyperconjugative effect. It has also been shown³¹ that only where hyperconjugation is prevented from occurring can the inductive effect be seen. Moreover, Streitwieser estimates³² from Hammett data that replacing CH_3 by CH_2D should result in a 2% reduction in the rate of acetolysis of $\text{CH}_3\text{CH}(\text{R})\text{OTS}$.

A β deuterium isotope effect of $k_{\text{H}}/k_{\text{D}} = 0.98$ per deuterium would be approximately equal to 0.834 for the substrate containing nine deuterium atoms. An inductive effect of identical magnitude has also been demonstrated³¹ for cases where hyperconjugation is sterically inhibited.

Treatment of the original data to correct for an inductive secondary β deuterium isotope effect of this size prior to applying an analysis by Bell's equations,²⁸ including the revised condition c, now gave a very good fit (Table VII).

Since the actual barrier is not symmetrical, $\Delta H^\circ = 17.7$ kcal/mol at 555 °C,³³ the final barrier dimensions were determined using the form of Bell's equations for an unsymmetrical barrier. For added precision, the first four terms of Q were included in the calculation. The values obtained are given in Table VIII, and the Arrhenius parameters and barrier dimensions are summarized in Table IX.

Any proposed mechanism, therefore, must take into account the following: (a) linear or nearly linear transfer of H, (b) reaction retardation by increased oxygen basicity stemming from α deuteration in the ethyl moiety, (c) reaction accelerated by an electron releasing inductive effect in the deuterated *tert*-butyl moiety. All of these imperatives can be accommodated by a considerable amount of C-O bond extension preceding the actual H transfer in order to fulfill the geometric requirement for linear H transfer. Substitution of deuterium in the ethyl group makes C-O bond elongation more difficult, whereas the inductive effect of the *tert*-butyl- d_9 group facilitates it. Such C-O bond extension is accompanied by change in hybridization at the central carbon in the *tert*-butyl group from tetrahedral sp^3 to planar sp^2 , thus bringing the methyl groups closer to the oxygen. In the course of realizing a sufficient degree of C-O bond elongation, corresponding to an energy input of some 51.6 kcal/mol vs. the bond dissociation energy of 80.8 kcal/mol,^{34,35} the oxygen atom can attain coplanarity with one of the nine identical C-H bonds and H transfer occurs with formation of the double bond. Because of the relatively high (73.8 kcal/mol) and extremely narrow (0.830 Å) construction of the classical energy barrier associated with this process, the transfer is characterized by a large tunneling correction. Hydrogen tunnels at a point 30% below the top of the barrier and deuterium, 22% below. Figure 1 is

Table VII. Barrier Calculation Data Including Correction for Inverse β Isotope Effect

$T, ^\circ\text{C}$	$\ln (k_{\text{H}}/k_{\text{D}})_{\text{corr}}$	$\ln (k_{\text{H}}/k_{\text{D}})_{\text{QM}}$	Difference	% difference
536	1.020	1.026	0.006	0.55
545	0.981	0.981	0.000	0.01
555	0.938	0.936	-0.002	-0.23
565	0.897	0.895	-0.002	-0.27
574	0.861	0.860	-0.001	-0.09
$E_{\text{class}}^{\text{H}} = 63.8$ kcal		$E_{\text{class}}^{\text{D}} = 63.8$ kcal	$a = 0.414$ Å	
Sum of the squares of the deviations at the five temperatures				
$= \sum (\bar{X} - X_i)^2 = 4.21 \times 10^{-5}$				

Table VIII. Barrier Calculation Data for Unsymmetrical Barrier

$T, ^\circ\text{C}$	$\ln (k_{\text{H}}/k_{\text{D}})_{\text{corr}}$	$\ln (k_{\text{H}}/k_{\text{D}})_{\text{QM}}$	Difference	% difference
536	1.020	1.025	0.005	0.50
545	0.981	0.981	-0.000	-0.03
555	0.938	0.936	-0.002	-0.27
565	0.897	0.894	-0.003	-0.31
574	0.861	0.860	-0.001	-0.12
$E_{\text{class}}^{\text{H}} = 73.8$ kcal		$E_{\text{class}}^{\text{D}} = 73.8$ kcal	$a = 0.415$ Å	
Sum of the squares of the deviations at the five temperatures				
$= \sum (\bar{X} - X_i)^2 = 4.15 \times 10^{-5}$				

Table IX. Summary of Arrhenius Parameters and Barrier Dimensions

$A_{\text{H}}/A_{\text{D}}$	0.067
$E_{\text{obsd}}^{\text{D}} - E_{\text{obsd}}^{\text{H}}$	5.7 kcal/mol
$E_{\text{class}}^{\text{H}}$	73.8 kcal/mol
$E_{\text{class}}^{\text{D}}$	73.8 kcal/mol
$E_{\text{obsd}}^{\text{H}}/E_{\text{class}}^{\text{H}}$	0.699
$E_{\text{obsd}}^{\text{D}}/E_{\text{class}}^{\text{D}}$	0.776
Barrier width	0.830 Å

offered as a diagrammatic representation of the transition state.

Considerations Pertaining to the Character of the Thermolytic Elimination Transition State. Maccoll and Thomas,⁴ on the basis of substituent rate effects observed in thermolysis of a series of substituted alkyl bromides, concluded that vapor-phase β -elimination reactions had a quasi-heterolytic character, with strong elongation and polarization of the $\text{C}^{+\delta}-\text{X}^{-\delta}$ bond. Subsequently, Maccoll⁵ elaborated this to an ion pair description which was later modified by Benson and Bose⁶ to a semi-ion pair model. For example, α -methoxylation of ethyl chloride³⁶⁻³⁸ greatly accelerates the elimination rate but α carboxylation³⁹ diminishes it. This suggests little or no $\text{C}_{\beta}-\text{H}$ bond polarization.

Such proposals have been disputed by the results of Blades et al.,⁸ who identified an intramolecular primary deuterium isotope effect in ethyl chloride thermolysis. These data seemed to suggest that the breaking of the C-H bond must be an important aspect of the rate-determining step, contrary to the lack of rate influence by an α carboxyl function. However, Saunders and Cockerill² have argued that a large proportion of the $k_{\text{H}}/k_{\text{D}}$ value could be correlated with the occurrence of a secondary, β -deuterium isotope effect at the temperatures of measurement.

Such disparate deductions and interpretations are apparently reconciled by the transition state structure proposed in Figure 1. Thus, it can be estimated from the results supporting this picture that the C–X bond is about 60% advanced toward full bond-breaking when the β hydrogen tunnels through from a point along the reaction hill representing about 30% less than half bond-breaking. Moreover, the results appear to indicate that an inverse, inductive, secondary isotope effect may be involved rather than the normal hyperconjugative secondary isotope effect suggested² to account for the measurements of Blades.⁸ The absence of a hyperconjugative influence may possibly be a consequence of the transition-state geometry; the β hydrogens, other than the one suffering linear H transfer in the planar (triangular) transition state, cannot achieve the coplanarity necessary to conjugate with charge developing at $C_{\alpha}^{+\delta}$.

Clearly, the earlier concept^{5,6,14} of a rectangularly structured transition state may need some review in the light of all these results. The observed tunnel correction attending linear or nearly linear H transfer, and the negative entropy of activation in uncatalyzed, thermolytic β eliminations studied previously are consistent with the cyclic structure of Figure 1, but probably not in keeping with any kind of rectangular configuration. Furthermore, since the barrier calculations show that $E_{\text{class}}^{\text{H}} = E_{\text{class}}^{\text{D}}$, zero-point energy differences appear to play no part in determining $k_{\text{H}}/k_{\text{D}}$ and the tunnel correction is the controlling factor.

The possibility of a 2S + 2S pericyclic mode for similar reactions has been considered in ab initio molecular orbital calculations.⁴⁰ Such an approach,⁴¹ however, perhaps may be invalidated through failure to take into consideration the possibility of tunneling in the H-transfer process.

Finally, it may be deduced from the differences in activation parameters observed for thermolysis under various conditions (cf. data listed in Table IV), that the character of the reaction is sensitive to the nature of the reactor surface. Thermolysis in the well-seasoned reactor of Daly and Wentrup at some 100 °C lower temperature than the gold coil microreactor seems to pass through a transition state of considerably greater carbonium ion (E1) character, judging from the higher E_{a} and the large positive entropy computed from their rate data. Apparently, the pure gold surfaces of the microreactor afford a negative entropy of activation, in line with expectation for a cyclic concerted process, and lower reaction rates than reported for the well-seasoned reactor. All this would suggest that even under seemingly pure vapor-phase reaction conditions a "wall factor" could be involved in all so-called molecular mechanisms of thermolysis, including the present studies of the thermolysis of *tert*-butyl ethyl ether in the gold-coil microreactor. The previously studied thermolysis reactions of alkyl allyl ethers and various ester derivatives,^{12a,13a,c} which can be regarded as established pericyclic processes, manifested only a zero-point energy determined isotope effect without any indication of a measureable tunnel correction. The tunnel

correction determined for *tert*-butyl ethyl ether may be significant if only by comparison with the absence of this effect in thermolytic retroene reactions^{12a,13a,c} previously studied under the same reactor conditions and wall-factor characteristics.

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