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Evidence for Proton Tunneling in the Strong Base Catalyzed Elimination Reaction of β-Phenylethyl Substrates

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The TDKIE criteria have been applied to some E2 (one-step) elimination reactions. The occurrence of proton tunneling in the course of the ethoxide ion promoted eliminations of β-phenylethyl substrates in ethyl alcohol is recognized by a temperature-dependent isotope effect over an 80 °C temperature range in which $[\Delta Ea]_D{}^H \gg [\Delta Eo]_D{}^H$ and A_H/A_D values are less than $2^{1/2}$. This conclusion is supported by model calculations. A comparison of the observed temperature dependence with that calculated from the Bell theory of tunneling yields the tunnel corrections and barrier dimensions for corresponding elimination reactions.

Quantum mechanical tunneling, i.e., the ability of a particle to pass through a region of space where its total energy is less than its potential energy, has been recognized as a contribution in certain reaction mechanisms. Several reviews and discussions concerning this phenomenon have appeared in the literature. Thus, various aspects of tunneling in ordinary chemical reactions have been reviewed by Caldin[1] and Johnston.[2] Many other authors have also demonstrated the significance of tunneling in the understanding of the hydrogen bond.[3] Bell[4] showed that tunneling in proton-transfer reactions can lead to nonlinear Arrhenius plots and kinetic isotope effects larger than the "semiclassical" values based on the loss of vibrational zero-point energy in the transition state. If tunneling through the reaction barrier takes place, the true quantum mechanical rate constant is obtained by applying a correction factor, Q_{ti}, to the classical rate constant calculated with neglect of tunneling. The relation between the tunnel correction factors and the barrier (parabolic or Eckart) dimensions is useful in describing and correlating trends in barrier parameters for related reactions.

Even though there is no doubt that tunneling occurs in some chemical reactions, its experimental demonstration has been a subject of vigorous controversy. Several experiments suggest[5] that the presence of proton tunneling may be overestimated. Some recently observed examples[6] of tunneling in intramolecular H transfer are identified[7] by a temperature-dependent isotope effect in which $[\Delta Ea]_D{}^H \gg [\Delta Eo]_D{}^H$ and $A_H/A_D \ll 0.7$. The occurence of proton tunneling in the course of some E2 (single step) elimination reactions has been demonstrated by Shiner and Smith.[8] Recently, Saunders and co-workers[9,15] described a number of E2 reactions in which the Arrhenius parameters provided qualitative evidence for tunneling and fit the Bell theory expression for tunneling to the observed temperature dependence. In the case of a multistep elimination there are also some data[10] consistent with a mechanism of elimination in which the first step is reversible H tunneling through a narrow reaction barrier into the narrow potential well of a hydrogen-bonded intermediate complex. The transition state arising from this intermediate has a potential well of nearly the same dimensions as that for the initial complex of reagents.

The principal purpose of this study was to evaluate mechanistic conclusions of β-elimination reactions by application[7] of the TDKIE (temperature dependence of the kinetic (H/D) isotope effect). Its application, however, is restricted by a paucity of precise values for the Arrhenius parameters. We believe that the high precision method employed to determine isotope ratios readily yields k_H/k_D values of the necessary precision and accuracy.

A series of β-phenylethyl derivatives, the traditional substrates in β-eliminations,[11] were chosen as the models in our studies. The series comprised four different leaving groups varying in their nucleofugal properties, i.e., Br, p-$CH_3C_6H_4SO_3$, $^+S(CH_3)_2$, $^+N(CH_3)_3$. Sodium ethoxide in ethyl alcohol, which has often been used in such eliminations,[8,11a] was selected as the strong base reagent.

Results and Discussion

All reagents were prepared as described in the Experimental Section. Each reagent was subjected to the reaction in the usual manner with sodium ethoxide in ethanol at five temperatures in the range of 80 °C. Previous studies[11a,12] of the temperature dependence in this system involved a temperature range of only 0–20 °C and no more than two or three temperatures within that range. Only in Shiner and Smith's[8] case is the temperature range wide enough and populated with enough experimental points to give precise Arrhenius parameters. The magnitude of k_H/k_D at each temperature was obtained after quantitative recovery of the product, $C_6H_5CH(D){=}CH_2$, and determination of its deuterium content by means of high-precision mass spectrometry. The results are summarized in Table I. The principal observations are the striking temperature dependence of the k_H/k_D values measured for the first three leaving groups with A_H/A_D values of less than $2^{1/2}$ and $[\Delta Ea]_D{}^H > 1.15$ kcal/mol. Our data provide an empirical identification of linear H-transfer tunneling for these three substrates. For the $^+N(CH_3)_3$ group the activation parameters, $[\Delta Ea]_D{}^H = 0.93$ kcal/mol and $A_H/A_D = 0.77$, indicate[7] linear H transfer in an unsym-

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Table I. Temperature Dependence of the Kinetic Isotope Effect (TDKIE) in the Strong Base Catalyzed Elimination Reaction in the Series

$$C_6H_5CHDCH_2X \xrightarrow[C_2H_5OH(-HX)]{C_2H_5ONa} [C_6H_5CH{=}CH_2 + C_6H_5CD{=}CH_2]^a$$

X	temp, °C ± 0.05 °C	$(k_H/k_D)_{corr}$[b]	$[\Delta Ea]_D{}^H$,[e] kcal/mol	A_H/A_D
Br	20.00	7.933 ± 0.009	1.569 ± 0.009	0.536 ± 0.009
	40.00	6.693 ± 0.006		
	60.00	5.726 ± 0.005		
	80.00	4.998 ± 0.005		
	100.00	4.468 ± 0.006		
p-$CH_3C_6H_4SO_3$	20.00	6.015 ± 0.005	1.531 ± 0.005	0.431 ± 0.004
	40.00	5.053 ± 0.005		
	60.00	4.340 ± 0.003		
	80.00	3.815 ± 0.006		
	100.00	3.431 ± 0.009		
$^+S(CH_3)_2$	0.00	6.988 ± 0.031	1.626 ± 0.091	0.342 ± 0.012
	20.00	5.480 ± 0.025		
	40.00	4.574 ± 0.022		
	60.00	3.950 ± 0.050		
	80.00	3.550 ± 0.040		
$^+N(CH_3)_3$	20.00	3.766 ± 0.002	0.93 ± 0.01	0.77 ± 0.01
	40.00	3.449 ± 0.002		
	60.00	3.094 ± 0.004		
	80.00	2.869 ± 0.006		
	100.00	2.695 ± 0.008		

[a] Analysis of the deuterium content of the styrene mixture was carried out by mass spectrometric procedures previously described.[7] The parent peaks of the products analyzed were scanned 15 000 times per sample to yield a mean value of the M_{104}/M_{105} amu ratio. [b] Mass spectral corrections and calculations of the isotope effect were carried out as described in the Appendix. [c] All of the data were fitted to the Arrhenius equation by a linear regression program. The correlation coefficients were close to unity (i.e., 0.9999, 0.9997, 0.9970, 0.9945, respectively).

Table II. Calculations of Reaction Barrier Parameters for the Temperature Dependence of the Isotope Effects[a]

no.[b]	temp, °C ± 0.05 °C	$\ln (k_H/k_D)^e$ quantum mechanical	difference[c] to $\ln (k_H/k_D)_{Arrh}$[d] (abs value)	$E_{class}{}^H$, kcal/mol	$E_{class}{}^H$, kcal/mol	barrier width, Å	
						proton	deuterium
1	20.00	2.0760	0.0050	19.64 ± 0.01	20.55 ± 0.01	1.558 ± 0.001	1.594 ± 0.001
	40.00	1.8916	0.0094				
	60.00	1.7402	0.0048				
	80.00	1.6129	0.0039				
	100.00	1.5039	0.0069				
2	20.00	1.8052	0.0109	21.46 ± 0.01	22.13 ± 0.01	1.500 ± 0.001	1.523 ± 0.001
	40.00	1.6147	0.0054				
	60.00	1.4651	0.0029				
	80.00	1.3433	0.0043				
	100.00	1.2415	0.0085				
3	0.00	1.9492	0.0050	24.14 ± 0.01	24.75 ± 0.01	1.592 ± 0.001	1.602 ± 0.001
	20.00	1.7009	0.0002				
	40.00	1.5173	0.0030				
	60.00	1.3737	0.0000				
	80.00	1.2571	0.0097				

[a] Sum of the squares of the deviations = $\sum (x - x_i)^2$ was 2.01×10^{-4}, 2.47×10^{-4}, and 1.28×10^{-4}, respectively. [b] 1, Br; 2, p-$CH_3C_6H_4SO_3$; 3, $^+S(CH_3)_2$ (the same series as in Table I). [c] The uncertainty of $\ln (k_H/k_D)QM$ according to the error analysis is about 2%. [d] $\ln (k_H/k_D)_{Arrh}$ is the experimental result from Table I.

metrical transition state with a broad barrier.

The Arrhenius parameters in Table I give clear evidence for tunnel effects[4a] even though the isotope effects do not show the large values previously found to be characteristic for tunneling.[13] In order to evaluate the magnitudes of the tunnel effects we have calculated the barrier dimensions required to account for the isotope effects in three of the leaving groups, with the aid of Bell's equations. As in the previous work,[13b,14] the tunnel corrections were estimated utilizing the following expressions:

$$k_{QM} = Q_t A_{class} \exp(-E_{class}/RT) \tag{1}$$

where k_{QM}, the rate constant for proton transfer accompanied by quantum mechanical tunneling, is expressed in terms of quantum mechanical correction, Q_t, to the Arrhenius parameters for the same process treated by classical mechanics (i.e., excluding the wave nature of the species). The isotopic rate constant ratio is given then by

$$\ln (k_H/k_D)QM = (E^D{}_{class} - E^H{}_{class})RT + \ln (Q_{tH}/Q_{td}) \tag{2}$$

$$Q_t = \frac{k_{QM}}{k_{class}} = 0.5u_t/\sin(0.5u_t) - u_t \exp(E_i/kT)\left(\frac{y}{2-u_t} - \frac{y^2}{4-u_t} + \frac{y^3}{6-u_t} - \ldots\right) \tag{3}$$

$$y = \exp(-2\pi E_i/h\nu_t) \tag{4}$$

$$u_t = h\nu_t/kT = (h/kT)(E^{1/2}/\pi a_i(2m)^{1/2}),\ \mathrm{i} = \mathrm{H, D} \tag{5}$$

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Table III. Fits to the Bell Equation of the Temperature Dependent Kinetic Isotope Effects in Elimination Reactions[a]

No.[a]	Q_{tH}/Q_{tD}[b]	$(k_H/k_D)s$[c]	Q_{tH}	$E_{class}{}^D - E_{class}{}^H$, kcal/mol
1	1.672 ± 0.009	4.77 ± 0.003	2.529 ± 0.009	0.91 ± 0.01
2	1.925 ± 0.011	3.16 ± 0.04	3.165 ± 0.010	0.67 ± 0.01
3	1.923 ± 0.010	2.85 ± 0.04	3.158 ± 0.011	0.61 ± 0.01

[a] See footnote *b* to Table II. [b] temperature, 20 °C. [c] Semiclassical isotope effect, $(k_H/k_D)/(Q_{tH}/Q_{tD})$.

At temperatures in the range of 20–100 °C, $y \exp(E/kT) \ll 1$, and the correction factor simplifies to

$$Q_t = 0.5u_t/\sin(0.5u_t) \tag{6}$$

The values of $E^H{}_{class}$, $E^D{}_{class}$, A_H, and A_D were obtained by an iterative trial-and-error process until good agreement (found by minimizing the sum of the squares of the deviations) was obtained at all temperatures between the generated values $(k_H/k_D)_{QM}$ and the values (k_H/k_D) Arrh. calculated for the experimental Arrhenius plots. Tunneling frequencies (ν_t) for both isotopic species were calculated assuming $m_H = 1$ and $m_D = 2$ amu. From the calculations of Kaldor and Saunders[15] we know that increasing m_H to 1.5 and m_D to 2.5 changes the tunnel corrections by less than 10%. The following conditions were required of a good fit: the curvature of the inverted parabola at its vertex, $-2E_i/a_i{}^2$ and the difference in barrier heights, $E^D - E^H$, were constant during the entire approximation process; $E_a{}^i$(ref 16)$/E_{class}{}^i < 1$; and all points had to be reproduced with a precision greater than 1%. To enable the evaluation of broad ranges of the unknowns, the actual curve fittings were performed with the aid of a DEC 10 computer. The values of the parameters of eq 1–6 which give the best fits are listed in Table II. The uncertainties of calculated values were computed by using a standard method for error analysis. The Q_{tH}/Q_{tD} values at 20 °C range from 1.672 ± 0.009 to 1.925 ± 0.011 (Table III). The tunnel corrections are not large, and there is no significant trend in Q_{tH}/Q_{tD} over the range of the nucleofugal properties of the Br, $CH_3C_6H_4SO_3$, and $^+S(CH_3)_2$ leaving groups. In our studies, the tunnel and the semiclassical effects make almost equal contributions to the observed isotope effects. In our cases, the barrier value at the point of tunneling implies tunneling across a barrier of narrower width for p-$CH_3C_6H_4SO_3$ than for the $^+S(CH_3)_2$ group. In presenting these data, we are aware that the one-dimensional parabolic barrier is probably an oversimplification and calculations of barrier dimensions from A_H/A_D data may be an artifactual approach since the relation to real barriers has never been definitely shown.

Finally, we take note of the fact the data in Table I indicate that in the E2 (one step) elimination, the tunneling may be identified by the TDKIE criteria. To be used for detection of tunneling, this criterion depends upon accurate measurement of k_H/k_D as a function of temperature without an accurate knowledge of k_H and k_D separately.

Experimental Section

General Methods. Reagents and solvents were of commercial grade and were usually purified before use. Ethyl alcohol was dried according to the method described by Smith.[17] Sodium ethoxide solutions were prepared from sodium metal cleaned under hexane and rinsed in hexane and ethanol. Diglyme and boron trifluoride etherate were purified as previously described.[18] Sodium borodeuteride from Aldrich (98 atom%) was utilized without purification.

2-Phenylethanol-*2-d*$_1$ was synthesized via the deuterioboration–oxidation method described previously by H. C. Brown and co-workers.[18,19] The hindered hydroborating agent, bis(3-methyl-2-butyl)borane-*d*, directed the entering boron atom to the terminal position in 98–99% distribution in our experiments and also in those of Brown.[19] Analysis of the product by ^1H NMR showed complete monodeuteration within the usual precision of the 60 MHz instrument. NMR ($CDCl_3$) δ 7.20 (5 H, s, aromatic protons), 3.72 (2 H, d, methine protons at C-1), 2.78 (1 H, m, methine proton at C-2), 2.45 (1 H, s, hydroxyl proton).

2-Phenylethyl-*2-d*$_1$ *p*-Toluenesulfonate. Treatment of 2-phenylethanol-*1-d*$_1$ with *p*-toluenesulfonyl chloride in pyridine gave the *p*-toluenesulfonate in 80% yield, mp 87.0–37.5 °C.[20,21] From this reagent the remaining derivatives were prepared.

2-Phenylethyl-*2-d*$_1$ bromide was prepared in a reaction of 2-phenylethyl-*1-d*$_1$ *p*-toluenesulfonate with lithium bromide[11a] in dry acetone in 82% yield, bp 94 °C (15 mm).

(2-Phenylethyl-*2-d*$_1$)dimethylsulfonium Iodide. 2-Phenylethyl-*2-d*$_1$ *p*-toluenesulfonate was converted first to the methyl 2-phenylethyl-*2-d*$_1$ sulfide by treatment with sodium methylmercaptide[11a] (83% yield, bp 110 °C (70 mm). Then the iodide was synthesized in a reaction of methyl iodide with sulfide in nitromethane.[22] Recrystallization fromn ethyl ether gave a 75% yield of the product, mp 131.5–132 °C.

(2-Phenylethyl-*2-d*$_1$)trimethylammonium Iodide. As before, the 2-phenylethyl-*2-d*$_1$ *p*-toluenesulfonate was converted first to the dimethyl-(2-phenylethyl)amine-*2-d*$_1$ by treatment with anhydrous dimethylamine in anhydrous ether[11a] (79% yield, bp 100 °C (20 mm)). The bromide was prepared by treating dimethyl-(2-phenylethyl)amine-*2-d*$_1$ with methyl iodide in nitromethane. Recrystallization from ethyl ether gave the product in 75% yield, mp 236–237 °C.

Kinetic Procedure. A Pyrex pressure bottle was charged with a solution of sodium ethoxide in ethanol (0.1 M, 10-fold excess) and sealed with an inert elastomer stopper. The bottle was placed in a well-stirred oil bath regulated (±0.05 °C) by a Hallikainen Thermotrol. Each substrate was dissolved in a minimum of boiling solvent and slowly injected to the base solution (at such rate that no effect of local concentration on the apparent KIE need be feared), after it had equilibrated in the thermostat to ensure that the temperature of reaction was constant. 2,6-Di-*tert*-butyl-4-methylphenol was used as an inhibitor of styrene polymerization. Reactions proceeded to completion. The rates of elimination reactions of β-phenylethyl substrates ($C_6H_5CH_2CH_2X$, X = Br, p-$CH_3C_6H_4SO_3$, $S(CH_3)_2I$, $N(CH_3)_3I$) with sodium ethoxide in ethanol at several temperatures were determined previously.[11a,16] The product, consisting of a mixture of deuterated and undeuterated styrene, was quenched with ice water, extracted with pentane, dired ($MgSO_4$), stripped of solvent, and analyzed by chromatographic analysis. In addition, the product isolated from a given reaction run by a preparative GLC procedure was condensed in a chilled capillary in the line emerging from the thermal conductivity detector. The capillary was sealed to protect its contents from contact with air, and the product was later subjected to mass spectrometric analysis.

Instrumental Procedure. Preparative gas chromatography was performed on an F and M dual column gas chromatograph. Standard conditions were column (305 × 0.64 × 10^{-2} m) 10% SE-30 on chromosorb W, oven temperature 110 °C, injection and

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Table IV. Temperature Dependence of the Kinetic Isotope Effect (TDKIE) in the Weak Base Catalyzed Elimination Reaction in the Series

$$C_6H_5CHDCH_2X \xrightarrow[CH_3CN(-HX)]{Bu_4N^+F^-} [C_6H_5CH{=}CH_2 + C_6H_5CD{=}CH_2]^a$$

X	*T*, K ± 0.05 K	$(k_H/k_D)_{corr}{}^b$	$[\Delta E_a]_D{}^H$, kcal/mol	A_H/A_D
p-$CH_3C_6H_4SO_3$	293.00	2.99 ± 0.02	0.09 ± 0.08	2.6 ± 0.3
	313.00	2.96 ± 0.04		
	333.00	2.94 ± 0.04		
	353.00	2.91 ± 0.01		
Br	293.00	3.61 ± 0.02	0.06 ± 0.06	3.3 ± 0.3
	313.00	3.56 ± 0.04		
	333.00	3.55 ± 0.03		
	353.00	3.54 ± 0.03		
$S^+(CH_3)_2$	293.00	5.253 ± 0.009	0.07 ± 0.06	4.7 ± 0.4
	313.00	5.223 ± 0.008		
	333.00	5.18 ± 0.01		
	353.00	5.15 ± 0.01		
$N^+(CH_3)_3$	293.00	4.404 ± 0.008	1.97 ± 0.02	0.151 ± 0.007
	313.00	3.664 ± 0.007		
	333.00	2.929 ± 0.002		
	353.00	2.505 ± 0.005		

detector port temperatures 220 °C.

Quantitative GLC analyses were conducted on an F and M 5750 chromatograph connected to a Hewlett-Packard 3370 A electronic integrator. Standard conditions were column (3.05 m × 0.32 cm) 10% SE-30 on Chromosorb W, oven temperature 90 °C, injection and detector port temperatures 220 °C.

Mass spectral determinations were recorded at 70 eV by using a Hewlett-Packard 5930 A mass spectrometer equipped with a 5932 data system.

Nuclear magnetic resonance spectra confirming the structures of the substrates used in these studies were obtained on a Perkin Elmer R-12B spectrometer using Me_4Si as the reference.

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Appendix

Calculation of k_H/k_D from Mass Spectrometer Data. In elimination reactions of $C_6H_5CHDCH_2X$, the rates k_H and k_D are directly proportional to the mass spectrometric intensities of the $C_6H_5CD{=}CH_2$ (M_D) and $C_6H_5CH{=}CH_2$ (M_H) ions, respectively. To obtain values of M_D and M_H, the observed intensities of the M_{105} and M_{104} ions must be corrected for contributions to M_{105} from the ^{13}C isotope peak of M_H, and to M_{104} by the M − 1 peak of M_D. Thus $M_{104} = M_H + M_{D-1}$ and $M_{105} = M_D + M_{H+1}$. To obtain M_H and M_D from the measured ratios M_{104}/M_{105} for any sample, we can express the ratio M_D/M_H in these terms and rearrange algebraically to give

$$\left(\frac{k_H}{k_D}\right)_{corr} = \left(\frac{M_D}{M_H}\right)_{corr} = \frac{M_{105} - M_{H+1}}{M_{104} - M_{D-1}} = \frac{M_{H+1}}{M_H}\left[\frac{\dfrac{M_H}{M_{H+1}} - \dfrac{M_{104}}{M_{105}}}{\dfrac{M_{104}}{M_{105}} - \dfrac{M_{D-1}}{M_D}}\right]$$

The terms M_H/M_{H+1} and M_{D-1}/M_D are obtained from the observed ratios of the M_{104} and M_{105} peaks for reference samples of styrene and styrene-α-d with the same mass spectrometer operating conditions. In the present study the values for the reference samples were

$$C_6H_5CH{=}CH_2\text{:}\quad \frac{M_H}{M_{H+1}} = 9.794$$

$$C_6H_5CD{=}CH_2\text{:}\quad \frac{M_{D-1}}{M_D} = 0.541$$

The correction equation is then

$$\left(\frac{k_H}{k_D}\right)_{corr} = \frac{1}{9.794}\left[\frac{9.794 - R}{R - 0.541}\right] = 0.102\left[\frac{9.794 - R}{R - 0.541}\right]$$

where $R = (M_{104}/M_{105})_{obsd}$ for any sample.

The values of $(k_H/k_D)_{corr}$ in Table I were obtained by use of this equation. In the previous paper[11c] on the fluoride ion catalyzed elimination of these same phenylethyl substrates, an incorrect form of this correction equation was used, with the result that values for $(k_H/k_D)_{corr}$ are too high by a factor of 0.143/0.102. We present below Table IV giving recalculated values for $(k_H/k_D)_{corr}$, $[\Delta E_A]_D{}^H$, and A_H/A_D. The estimated angles of H transfer would be corresponding smaller. (This is a correction to Table I, *J. Org. Chem.* **1983**, *48*, 756.)

Registry No. $C_6H_5CH_2CH_2Br$, 103-63-9; $C_6H_5CH_2CH_2SO_3C_6H_4CH_3$-$p$, 4455-09-8; $C_6H_5CH_2CH_2S^+(CH_3)_2{\cdot}I$, 28289-44-3; $C_6H_5CH_2CH_2N^+(CH_3)_3{\cdot}I$, 1077-11-8; $C_6H_5CHDCH_2Br$, 84649-06-9; $C_6H_5CHDCH_2SO_3C_6H_4CH_3$-$p$, 84649-05-8; $C_6H_5CHDCH_2S^+(CH_3)_2{\cdot}I$, 92471-90-4; $C_6H_5CHDCH_2N^+(CH_3)_3{\cdot}I$, 92471-91-5; D_2, 7782-39-0.