Barrier Width: A Powerful Parameter for Hydrogen Transfer Reactions

By MIKLÓS SIMONYI* and ISTVÁN MAYER

(*Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, Pf.17*)

Summary Observable consequences of tunnelling are reproduced by calculating kinetic parameters as a function of barrier width and limiting values are predicted.

SINCE theoretical prediction on tunnelling[1] are now well supported by experimental evidence[2,3] making semi-classical treatments[4] of primary kinetic isotope effects (PKIE) insufficient, we have lost the convenience of having predicted maximum values for k_H/k_D, $E_D - E_H$ and A_D/A_H. In the light of experiments which have yielded anomalously large PKIE and anomalous isotopic Arrhenius parameters[3,5] we now need new upper limits for these quantities.

Considering the one-dimensional penetration of potential barriers by a Boltzmann incident flux of particles, rate constants have been calculated according to equation (1)

$$k = \frac{1}{kT}\int_0^\infty f(\epsilon)e^{-\frac{\epsilon}{kT}}\,d\epsilon \qquad (1)$$

by numerical integration. The energy dependent probability of transmission, f(ε) was chosen using the following assumptions. (i) The reduced mass was taken as equal to one, two or three times the mass of the proton. (ii) The barrier height, V_H = 10·00 kcal mol^{-1} for the hydrogen isotope. (iii) The barrier height for both heavier isotopes, V_D and V_T = 10·00 kcal mol^{-1} (neglecting zero-point-energy differences, ΔZPE), and V_D = 11·26 kcal mol^{-1}, V_T = 11·81 kcal mol^{-1} (allowing for ΔZPE). (iv) The barrier width at base (2*a*) was varied within the limits of 0·3—2·0 Å. (v) Calculations have been performed for both parabolic[6] and symmetrical Eckart[7] barriers. Some of the results are shown in the Table and the Figure.

Using the results obtained we can make the following conclusions. (i) Experimental indications on the importance of tunnelling can be reproduced by the calculations without

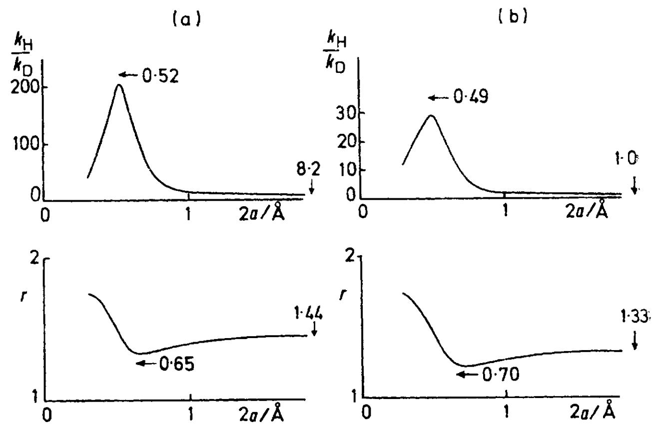

FIGURE. PKIE (k_H/k_D) and the Swain–Schaad exponent[8] (*r*) as functions of barrier width calculated for parabolic barri *T* 300 K. (a) V_H = 10·0 kcal mol^{-1}, V_D = 11.26 kcal mol^{-1}, V_T = 11·81 kcal mol^{-1}; (b) $V_H = V_D = V_T$ = 10·0 kcal mol^{-1}. The horizontal arrows indicate the positions of the extrema, the vertical ones the limiting values for 2a→∞.

making assumptions on the properties of the transition state (except the dimensions of the barrier). (ii) The type of dependence of observable indicators on barrier width is due to tunnelling and ΔZPE give only quantitative contributions.[11] (iii) Predicted limiting values of PKIE for both barriers are larger than experimental data published so far. Predicted Arrhenius parameters are consistent with experi-

TABLE. Observable indicators of tunnelling calculated[a] as functions of barrier width (2*a*)

Observable indicator	Type of dependence	Limiting values[b] Parabolic barrier	Eckart barrier[c]	Classical limit (2*a* → ∞)
k_H/k_D	maximum	200 at 0·52 Å (28·5 at 0·49 Å)	85·1 at 0·35 Å (14·1 at 0·32 Å)	8·2 (1·0)
k_H/k_T	maximum	3095 at 0·45 Å (>163; 0·40 < 2a < 0·45)	>907; 2a < 0·3 Å (>61·3; 2a < 0·3 Å)	21·0 (1·0)
$(E_D - E_H)$[d]	maximum	⩾5·8; 0·65 < 2a < 0·70 (⩾4·7; 0·65 < 2a < 0·70)	3·5 at 0·5 Å (2·5 at 0·48 Å)	1·26 (0·0)
A_D/A_H	maximum[e]	⩾270; 0·65 < 2a < 0·70 (⩾280; 0·65 < 2a < 0·70)	7·5 at 0·55 Å (9·0 at 0·55 Å)	1·0 (1·0)
$(E_T - E_D)$[d]	maximum	4·2 at 0·51 Å (3·0 at 0·51 Å)	2·2 at 0·4 Å (1·5 at 0·4 Å)	0·55 (0·0)
A_T/A_D	maximum[e]	102 at 0·52 Å (41 at 0·52 Å)	4·5 at 0·4 Å (3·8 at 0·4 Å)	1·0 (1·0)
r[f]	minimum	1·33[g] at 0·65 Å (1·22 at 0·70 Å)	1·40 at 0·7 Å (1·3165 at 0·8 Å)	1·443 (1·330[g])
ln A = f(ε)	isokinetic plot[10]	T_I = 410 K; 2a > 0· 7Å	T_I = 540 K; 2a > 0·5 Å	ln A = 0

[a] PKIE at 300 K; Arrhenius parameters from rate constants relating to 290 and 310 K. [b] For values in parentheses, $V_H = V_D = V_T$ = 10·00 kcal mol^{-1}. Other values imply ΔZPE. [c] The width of an Eckart barrier is defined as the width at the base of the parabola having the same curvature at the top. [d] In kcal mol^{-1}. [e] For extra narrow barriers (2*a* < 0·3 Å) $A_T < A_D < A_H$ in agreement with Stern and Weston[7] indicating that tunnelling correction factors, Γ_H and Γ_D^* may have crossover at certain low tempeature. [f] The Swain-Schaad exponent.[8] [g] Cf. Ref. 9.

ment only in the case of the parabolic barrier. (iv) Compensation phenomena (isokinetic relationships[10]) can be reasonably explained by tunnelling[12] in contrast with ideas that isokinetic plots are artefacts.[13]

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