Tunnelling Effects in Chemistry

Molecules in the Strange Quantum World

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Most of the molecules react to form products by climbing a barrier. The energy involved in this climbing of the barrier is known as the activation energy of the reaction. Questions like how fast a reaction occurs can be answered by considering the height of the barrier. However, in some reactions, the reactants transform to products by directly tunnelling across the barrier instead of climbing over it. Such a purely quantum mechanical effect, which becomes more prominent for reactions at low temperatures can lead to interesting and even completely unexpected products. This effect and its consequences in representative examples are discussed.

Introduction

How molecules react to form products is a topic of fundamental interest in chemistry and biology. The ability of molecules to react and to form a product is governed mainly by the thermodynamics of the reaction. For example, whether two molecules A and B will spontaneously react to form a product C is determined by the Gibbs free energy of the reaction, ΔG_{react}:

$$A + B \rightarrow C, \text{ where } \Delta G_{\text{react}} = G_{\text{C}} - G_{\text{A}} - G_{\text{B}} \ .$$

If $\Delta G_{\text{react}} < 0$, the reaction is said to be spontaneous. Those reactions for which $\Delta G_{\text{react}} > 0$ are non-spontaneous and generally require additional favourable conditions like pressure, temperature, etc., to drive them forward.

However, the spontaneity of a reaction does not automatically ensure that the reaction shall indeed happen.

For example, in the process of respiration, carbohydrate is oxidized to be broken into CO_2 and H_2O to generate energy in the cell.

$$C_6H_{12}O_6 + 6O_2 = 6H_2O + 6CO_2; \ \Delta G_{react} < 0 \ .$$

The process is exothermic and certainly occurs (we feel hungry after 4–6 hours of lunch!). Nevertheless, this is not a simple process as it requires the help of a lot of complicated processes involving several enzymes. A similar reaction is the yellowish fading of the pages in our books where cellulose (the main component of paper) is slowly oxidized (it takes several years to see the effect of such slow oxidation – please visit the archive section of your institute library). Hence, the difference between the fast and slow oxidation of a similar material *does not* arise from the theromodynamics of the reaction but from the different kinetics of the processes. As shown in *Figure* 1, the pathways for these two oxidations are different. While oxidation of paper occurs via climbing a large barrier, for respiration, the process gets assisted by enzymes which provide an alternative smaller barrier pathway for the oxidation to occur. Therefore, we call respiration as a kinetically fast (facile or labile) reaction and oxidation of paper as slow (inert or sluggish) reaction.

Quantum Effects in a Chemical Reaction?

As seen from *Figure* 1, an enzyme (or catalyst) can provide an alternate and lower barrier pathway for a reac-
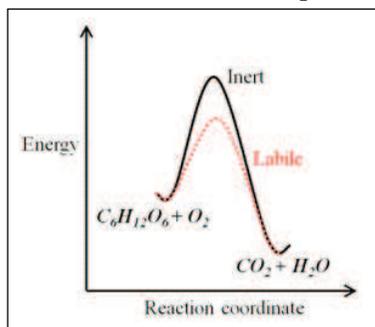
Figure 1. The height of the barrier for a reaction determines its reactivity. If barrier height is much larger than $k_B T$, then the reaction is slow, and if this is not so, the reaction is termed labile.

Table 1. de Broglie wavelengths of particles of various masses (calculated assuming a KE = 3.5 kJ/mol).

Particle	Mass (amu)	de Broglie wavelength (in Å)
Electron	1/1750	63.00
H	1	1.49
D	2	1.08
C	12	0.44
Br	80	0.18

tant to proceed to the product. This picture, though valid for all reactions does not consider the important fact that *atoms in molecules have a quantum mechanical behaviour as well*. This means that they are governed by laws of quantum mechanics and have a wave–particle dual nature. For example, the de Broglie wavelength of a particle of mass m and kinetic energy E is $\lambda = h/p = h/(2mE)^{1/2}$. In *Table* 1, the de Broglie wavelengths for some typical particles/atoms of interest in chemistry are listed (of course, electrons are of paramount interest in chemistry because atoms are *glued by pairs of electrons* in chemical bonds). Clearly, the wavelength of an electron (at kinetic energy of 3.5 kJ/mol which is typical of atoms at room temperature $T = 298$ K) has a very large wavelength which is spread across a linear length of dimensions of about 20 C–C bonds (each C–C bond $\sim$ 1.5 Å). However, as the mass of the particle increases, the de Broglie wavelength decreases. For all practical purposes, Br atom with a small de Broglie wavelength can be considered as a *classical* particle.

Nevertheless, for the lightest atom of the periodic table, namely H-atom, the de Broglie wavelength is about 1.5 Angstrom. This length is three times the radius of an H-atom in its ground state (measured by r_{mp}, the distance at which the probability of finding the electron is maximum, which is equal to 1 Bohr = 0.52 Å) [1]. Therefore, quantum effects should be most prominent in the case of reactions involving H-atoms. The list of such reactions is very long and includes important processes in chemistry and biology like proton transfer reactions, proton

Quantum mechanical tunnelling plays an important role in chemical reactions.

tautomerism, hydrogen atom transfer (HAT) reactions, C – H/N – H bond activation, Brønsted acid reactions[1], resonance assisted hydrogen bonds (RAHB) and proton transfer across the DNA base-pairs and H^+ hopping in the Grotthuss mechanism[2] for ionic conduction in water. In the next section, we discuss how the quantum mechanical process of tunnelling assists chemical reactions, in particular those involving H-atoms.

Simple Models for Quantum Mechanical Tunneling

Tunnelling Across Rectangular Barrier

Consider a particle moving from left to right from region A to region C via region B which has a finite one-dimensional rectangular barrier V_0 (see *Figure* 2). Finding a solution to this problem involves solving the Schrödinger equation for these three regions A, B and C piecewise. In quantum mechanics, for a wavefunction to be acceptable, both ψ and ψ' (first derivative of the wavefunction) have to be continuous and single-valued for all x including that for $x = 0$ and $x = a$ where the barrier V_0 begins and ends respectively. This problem is solved in most undergraduate textbooks on quantum mechanics [1]. The probability of tunnelling (i.e., going through the barrier) when the particle has an energy $E < V_0$ is given by

H-atom is the most quantum mechanical atom. So, QMT is most prominent in reactions involving H-atom.
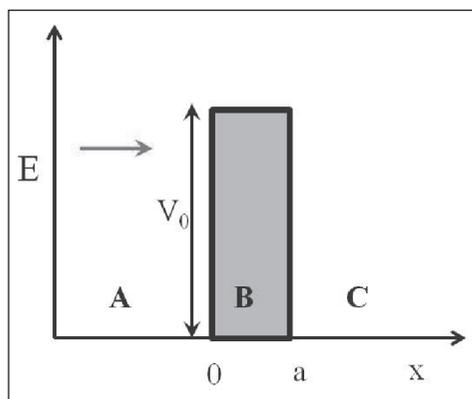
Figure 2. Tunnelling across one-dimensional rectangular potential barrier ($E < V_0$).
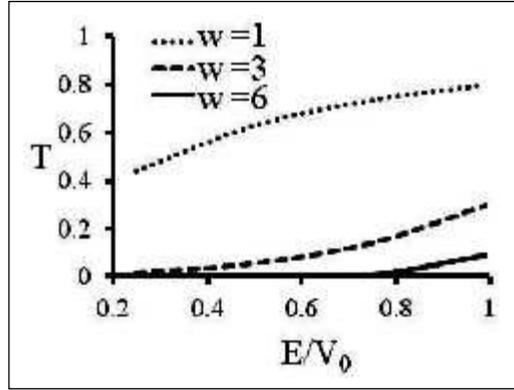
$$T = \frac{1}{1 + (e^{ka} - e^{-ka})^2 / \left(16(\frac{E}{V_0})(1 - (\frac{E}{V_0})) \right)} \ , \qquad (1)$$

where $k = \sqrt{2mV_0 \left(1 - (\frac{E}{V_0}) \right)}/\hbar$. *Figure* 3 shows this
probability of tunnelling T as a function of the ratio
E/V_0. These three plots are for three different values of
$\sqrt{2mV_0 a^2/\hbar^2} = 1, 3$ and 6. For all the cases, $T \neq 0$
which means that the particle can *go* from the region
A to C even when $E < V_0$. In a way, the particle has
penetrated through the rectangular barrier even when it
clearly does not have the energy to do so. This is not
expected in our classical everyday life and is called the
non-classical, quantum mechanical tunnelling. As seen
from *Figure* 3, smaller the value of $w = \sqrt{2mV_0 a^2/\hbar^2}$,
higher is the probability of tunnelling. Therefore, one
must expect that smaller masses (m) and smaller barrier
heights (V_0) and narrower barriers (smaller a) should
have higher probabilities of tunnelling.

A similar consequence of quantum mechanical tunnelling
also occurs when the particle has enough energy to over-
come the barrier $(E > V_0)$. *Figure* 4 shows a simple
illustration for such a case. Classically, we expect that
the probability of the particle going from region A to
C should be 1 as there is no barrier. However, only a
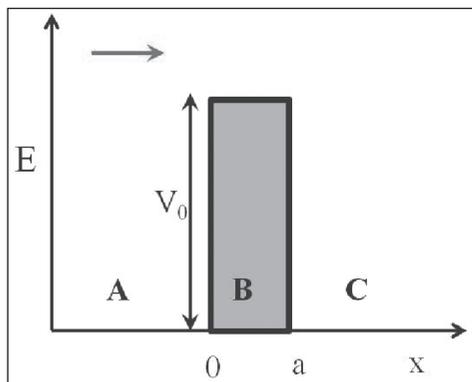fraction of this gets transmitted across the barrier and

Figure 4. Tunnelling across a one-dimensional rectangular potential barrier ($E > V_0$).

the rest of it is reflected back. This is again counterintuitive since $E > V_0$ and therefore, the particle is not expected to meet with any barrier to get reflected. This phenomenon is called *non-classical reflection* or *anti-tunnelling*.

Tunnelling Across Inverted Parabolic Barrier

Now consider a similar particle moving from left to right from region A to region C via an inverted one-dimensional parabolic potential in the region B (from $-a$ to $+a$). (See *Figure* 5). The form of the potential is $V(x) = V_0(1 - \frac{x^2}{a^2})$ for $-a \leq x \leq +a$ and $V(x) = 0$ in all other regions.
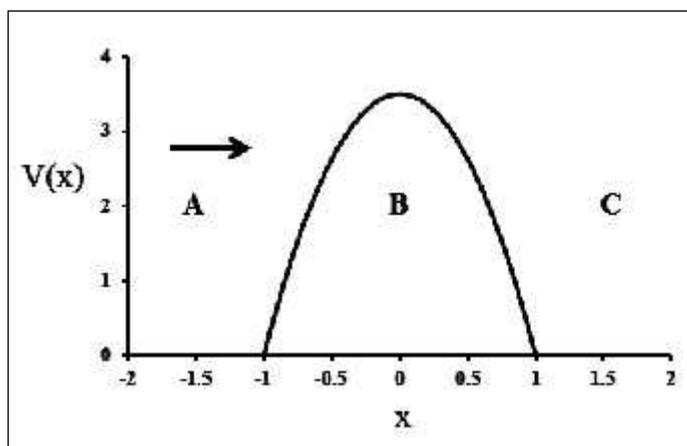

Figure 5. Tunnelling across an inverted parabolic potential with V_0= 3.5 kJ/mol and $2a$ = 2.0 Å; the units of $V(x)$ and x are kJ/mol and Å respectively.

The probability for tunnelling T for such a case is given by [2]

$$T = \cfrac{1}{1 + \exp\left(2\pi^2 a \sqrt{\frac{2mV_0}{h^2}}\left(1 - \frac{E}{V_0}\right)\right)} \ .\qquad (2)$$

From (2) one can see that the tunnelling probability is inversely proportional to the exponential of the barrier width $(T \sim e^{-a})$, inversely proportional to the exponential of the square root of the mass of the particle $(T \sim e^{-\sqrt{m}})$ and inversely proportional to the exponential of the square root of the barrier height $(T \sim e^{-\sqrt{V_0}})$. Therefore, as a *rule of thumb*, lighter particles tunnelling across narrow and small barriers have a high probability to tunnel. Remember, the picture was similar in the case of the rectangular barrier discussed in the previous subsection.

Consequences of Quantum Mechanical Tunnelling in Chemical Reactivity

As seen from *Figure* 6, lighter particles are more efficient in tunnelling than heavier particles. From the above discussion, one expects that the hydrogen atom should tunnel faster than the deuterium atom. So, the rate of a chemical reaction that involves movement of H should
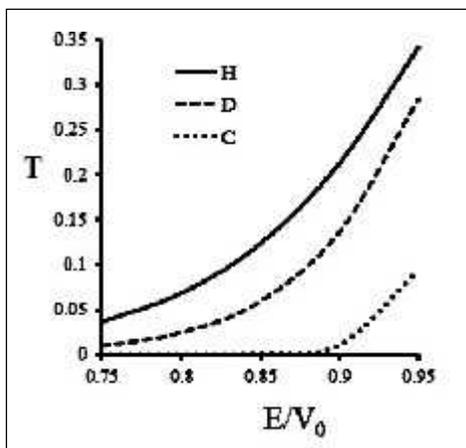
Figure 6. Tunnelling probability (T) across an inverted parabolic barrier (V_0= 3.5 kJ/mol) in the case of $E < V_0$ for hydrogen, deuterium and carbon.

be faster than that for D. This is the case for most reactions and is expected from even a classical picture. Let us consider a simple proton abstraction reaction from methane by fluoride anion:

$$H_3C - H + F^- = H_3C^- + H - F$$

(H-abstraction reaction)
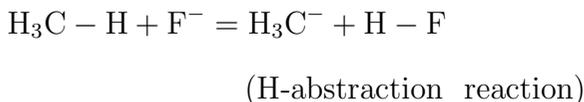
Now, we will also consider the same reaction where instead of hydrogen, deuterium is abstracted:
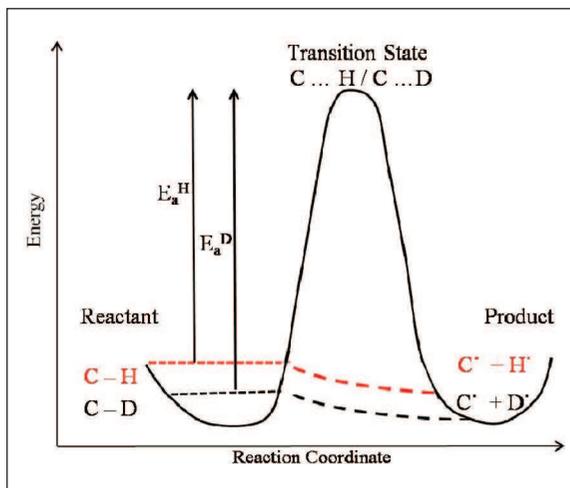
$$H_3C - D + F^- = H_3C^- + D - F$$

(D-abstraction reaction)
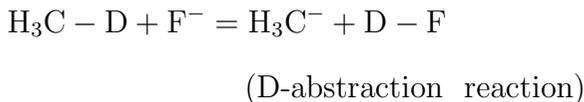
We will denote the rate of hydrogen and deuterium abstraction as k_H and k_D respectively. The ratio of these rates (k_H/k_D) is called the kinetic isotope effect (KIE) [3]. Since we are considering the ratio of the rates of H and D abstraction from the primary bond which is being broken in the reaction, it is called primary kinetic isotope effect (PKIE). However, if instead of substituting the H atom of the primary bond which we are breaking, we had substituted H by D at a different position, like in the CH_3 end, it would be called secondary kinetic isotope effect (SKIE). The reason why this case is called secondary is that the H/D of the methyl group act as mere spectators in the chemical reaction while the primary C–H bond is being cleaved. Therefore, SKIE is generally less prominent and we will avoid discussing tunnelling effects on SKIE in this article.

What do we expect for PKIE *without quantum mechanical tunnelling*? For understanding that we consider a simple schematic diagram as shown in *Figure* 7. As you might have studied in your physical chemistry course, molecular vibrations are also quantized and hence, even at $T = 0$ K where no thermal effects exist, any bond vibrates with a minimum energy known as the zero-point energy (ZPE). The ZPE of a bond is equal to

The ratio of the rate of a reaction with and without deuterium substitution (Kinetic Isotope Effect) is an important tool to detect tunnelling.

$(1/2)\,h\nu_0$, where ν_0 is the frequency of vibration of the bond. One can assume that the bond vibrates with a harmonic frequency in which case the frequency will be given by $\nu_0 = (1/2\pi)\sqrt{k/\mu}$, where k is the force constant of the bond and μ is the reduced mass of the system which is defined as $\mu = m_1 m_2/(m_1 + m_2)$. Therefore, the reduced masses for C–H and C–D bonds will be 12/13 amu and 24/14 amu respectively. The experimental force constant (k) for the C–H bond stretching is 456.7 N/m which we shall assume to be the same for a C–D bond stretch as well. Using these values, we get $\text{ZPE}_{\text{C–H}} = 17.34$ kJ/mol and $\text{ZPE}_{\text{C–D}} = 12.72$ kJ/mol. Clearly, the ZPE of a C–H bond is more than that for a C–D bond. This is represented in *Figure* 7 with the C–D bond stretching energy being placed lower in energy than that for a C–H bond. As the reaction progresses (moving from left to right along the reaction coordinate), the C–H/C–D bond is slowly cleaved and when it crosses the hump, the bond is completely broken. Therefore, just at the topmost point of the hump or hilltop, a transition (or crossover) occurs, namely from a C–H/C–D to $C^\bullet + H^\bullet/C^\bullet + D^\bullet$. This is referred to as the *transition state* (TS) and we shall denote it as C...H/C...D. The activation energy (E_a) is therefore the energy difference

between the energy of the TS and that of the ground state.

According to the Arrhenius equation, the rate constant of a chemical reaction $k = Ae^{-E_a/k_B T}$, where k_B, T and A are respectively the Boltzmann constant, the temperature at which the reaction occurs (in Kelvin) and pre-exponential factor (which is a constant for a particular reaction). Therefore, assuming that the pre-exponential factors are not very sensitive to H/D substitutions, we get $k_{C-H}/k_{C-D} = \exp-((E_a^{C-H} - E_a^{C-D})/k_B T)$. For $T = 298$ K (room temperature) and ZPE of C–H and C–D bonds calculated above, we get PKIE = 6.45. Hence, we expect that even in the absence of tunnelling, the rate of H reaction should be greater than that for D. Taking the logarithm of the Arrhenius equation, we get $\ln k = \ln A - E_a/(k_B T)$. Therefore, if we plot $\ln k$ with respect to $1/T$, we should get a straight line with a slope of $-E_a/k_B$. Such a plot is called the Arrhenius plot. So, for a reaction that occurs completely by *classical* above the barrier crossover (*no tunnelling*), the *Arrhenius plot should be a straight line*. This is shown in *Figure* 8, plot (a).

However, if instead of always going over the barrier, the particles (H and D) also tunnel across it (as shown in the lower portion of *Scheme* 2), the picture changes. This is because now the particles can travel across the barrier
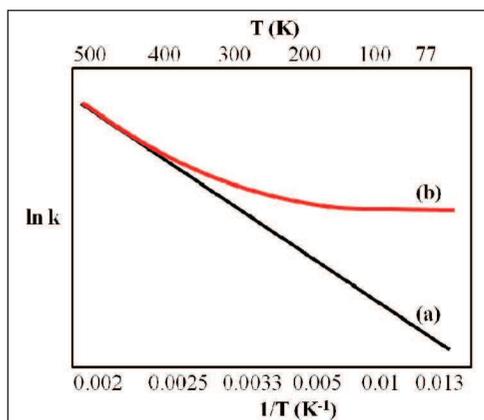

Figure 8. A typical Arrhenius plot for a reaction showing (a) linear plot for a classical over the top of the barrier process and (b) with effects of quantum tunneling. Note the curvature in the plot at low temperatures.

A curved and finally a flat Arrhenius plot (at low T) is a strong indication for quantum mechanical tunnelling.

without actually climbing it. Therefore, effectively there is no barrier and therefore the activation energy (E_a) reduces. This becomes very prominent at low temperatures since most of the reactants are in the lowest possible state and have no energy to go over the barrier. The only thing that they can do is to tunnel. The result is shown by a red plot in *Figure* 8. As discussed in the previous paragraph, the negative slope of the Arrhenius plot is the activation energy; so when the particles are tunnelling, the activation energy reduces which results in a *curvature of the Arrhenius plot*. Finally, when one goes to low temperatures (typically to liquid nitrogen temperature, 77 K), the plot is almost parallel to the horizontal axis, giving $E_a \sim 0$.

A curved and finally a flat Arrhenius plot (at low T) is a strong indication for quantum mechanical tunnelling. It means that the rate of the reaction is almost independent of temperature. This is in strong deviation from the original (over the barrier) classical process (plot (a) in *Figure* 8) which should have meant that the rate of the reaction (k) should have decreased (exponentially) with decreasing temperature. So, *at low temperatures, quantum mechanical tunnelling (QMT) should lead to higher rate of reaction than what is expected from a classical jumping over a barrier process.* Therefore, QMT ensures a fast reaction at low temperature. This is an important application of QMT in chemical reactivity because QMT is assisting a reaction just as catalysts do.

As you might have guessed by now, H being lighter than D and assisted by the fact that the barrier width for H tunnelling is smaller than that for D (as seen from *Figure* 7), the rate of a C–H bond cleavage should be larger than that for a C–D due to QMT. This leads to a value of PKIE > 6.45 at room temperature. Therefore, *QMT leads to primary kinetic isotope effect (PKIE) which is larger than that expected from a classical jumping over a barrier process.*

Some Examples Where QMT Plays an Important Role

Let us consider the first reaction (**1**) as shown in *Scheme 1*. As shown by the arrow, the H-atom moves from one end of the cyclopentadiene ring to the other end (such reactions are called [1,5] H–shift reactions since the hydrogen atom is moving from 1-position to the 5-position of the five membered ring)[4]. At 300 K, the rate of the H-atom transfer $k_H = 2.48 \times 10^7$ sec^{-1}. When the H-atom is replaced by D, the rate of the D-atom transfer $k_D = 4.34 \times 10^6$ sec^{-1}. For the H-atom case, 87.9% of the reaction occurs via tunnelling while for the D-atom, the percentage of tunnelling decreases to 73.1. The PKIE is[3] 5.7 at 300 K. In the absence of QMT, this value should have been 2.6 only [4]. Therefore, QMT leads to a faster rate of reaction than that expected classically.

For the second reaction (**2**), the hydroxyl radical abstracts one H-atom from H_2S to form H_2O and HS radical [5]. At 300 K, the rate of H-atom abstraction, k_H is 4.23×10^{-12} cm^{3}molecule^{-1}sec^{-1} in the presence of tunnelling and 4.17×10^{-12} cm^{3}molecule^{-1}sec^{-1} in the absence of QMT. The value for PKIE (at 300 K) is 1.73

> Examples of heavy atom tunnelling like that by carbon are rare.

[3] The values for the PKIEs discussed in the examples are actually less than 6.45 at 300 K, the classical expected value for a C–H mode. However, if you look carefully, the value of 6.45 that we derived was for a C–H stretching mode of vibration. In the examples, most of the time it is C–H/O–H bending mode which is being lost in the transition state. Since the energy associated with a C–H bend is less than that for a C–H stretch, the KIEs are also less.
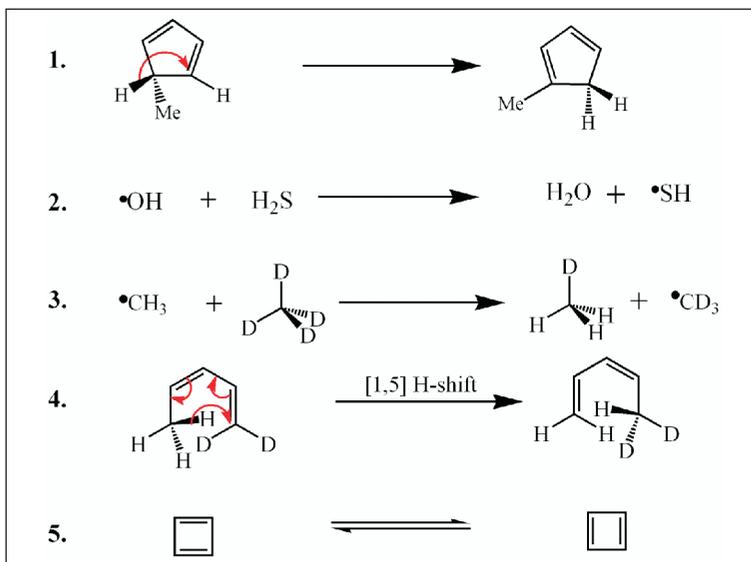
Scheme 1.
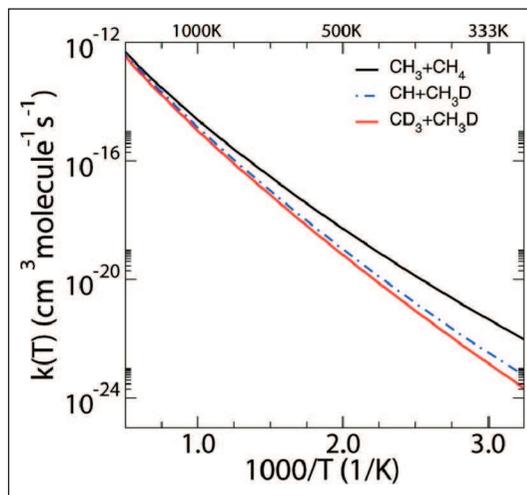
and 1.71 in the presence and absence of QMT respectively.

For the third reaction (**3**), a D-atom is exchanged from perdeuterated methane (CD_4) to a methyl radical to form CH_3D and CD_3 radical. These reactions are called self–exchange reactions because in the absence of any isotopic substitution, the reactant and the product are the same though a H-radical moves from one molecule to the other in the course of the reaction. The Arrhenius plots for this reaction for various isotopic substitutions are shown in *Figure* 9 [6]. The curvature for Arrhenius plot is maximum in case of H-exchange reaction (CH_3 radical + CH_4) and is visible below $T = 400$ K. The least curvature occurs for the maximally deuterated system (CD_3 radical + CH_3D) and curvature starts to appear only below 333 K. This is again expected from QMT because H-atom being light can tunnel across the barrier with much more ease than D.

The fourth reaction (**4**), is again an example of [1,5] H–shift reaction where the H atom moves from the one end of *cis*-1, 3-pentadiene to the other end. At 470 K, the rate of H-atom abstraction k_H is 7.8×10^{-4} cm³molecule^{-1}sec^{-1} in the presence of tunnelling and 1.5×10^{-4}cm³ molecule^{-1}sec^{-1} in the absence of QMT [7]. The value

for PKIE (at 470 K) is ~ 5.0. In the absence of QMT, this value should have been ~ 2.5 only [8].

The last reaction that we discuss here (**5**) is an example where a *heavy atom like carbon tunnels*. As discussed in *Table* 1, the de Broglie wavelength of a carbon atom is only ~ 0.2 Å. Nevertheless, in the reaction in which a bond-shift occurs in 1, 3-cyclobutadiene (CBD), it is indeed possible. For this reaction, CBD with alternate single and double bonds gets converted to alternate double and single bonds. The average C=C bond length is about 1.4 Å while that for a C–C bond is 1.54 Å. So, going from the reactant to the product, the C-atoms move on an average by only ~ 0.15 Å. Hence, the barrier width for this reaction is small. The activation energy E_a for this reaction is also very small (~ 6.3 kcal/mol) [8]. Therefore, in agreement with what we learnt for an inverted parabolic barrier, a small and narrow barrier in CBD favours QMT of carbon atoms in its bond-shift reaction [9].

> Tunnelling can increase the rate of many reactions substantially at low temperatures.

Conclusion

In this article, we have learnt about some examples of tunnelling probability for particles across simple models like a reactangular barrier and an inverted barrier. QMT leads to interesting effects in the rates of reactions particularly for those involving hydrogen atoms (in rare cases, of course even carbon may tunnel, as discussed above). The signatures for QMT become prominent at low temperatures. Therefore, while the students may forget the formulae in this article, whenever they see chemical reactions involving H-atoms or protons at low temperature, the possibility of quantum mechanics assisting it via tunnelling should also be thought of.

Suggested Reading

[1]   P Atkins and R Friedman, *Molecular Quantum Mechanics*, 5th Edition, Oxford University Press, 2011.

[2]   M D Harmony, Quantum Mechanical Tunneling in Chemistry, *Chem. Soc. Rev.*, Vol.1, pp.211–228, 1972.

[3]   T H Lowry and K S Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd Edition, Addison Wesley Longman Inc. 1998. This book has a nice discussion on various types of KIE and their origin with examples and also mentions the role of QMT in KIE.

[4]   G Robert Shelton, David A Hrovat and Weston Thatcher Borden, *J. Am. Chem. Soc.*, Vol.129, pp.164–168, 2007.

[5]   Benjamin A Ellingson and Donald G Truhlar, *J. Am. Chem. Soc.*, Vol.129, pp.12765–12771, 2007.

[6]   Sarah M Remmert, Simon T Banks and David C Clary, *J. Phys. Chem. A*, Vol.113, pp.4255–4264, 2009.

[7]   Yi–Ping Liu, Gillian C Lynch, Thanh N Truong, Da-hong Lu, Donald G Truhlar and Bruce C Garrett, *J. Am. Chem. Soc.*, Vol.115, pp.2408–2415, 1993.

[8]   Mijana Eckart-Maksic, Mario Vazdar, Mario Barbatti, Hans Lischka and Zvonimir B Maksic, *J. Chem. Phys.*, Vol.125, p.064310-1-9, 2006.

[9]   Barry K Carpenter, *J. Am. Chem. Soc.*, Vol.105, pp.1700–1701, 1983. This short communication discusses the probability of carbon tunnelling in CBD using a very similar model that we learnt for the inverted parabolic barrier.

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