Quantum Tunneling in Chemical Reactions

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MacMillan Group Meeting
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Lead References:

The Tunnel Effect in Chemistry; Bell, R. P.; Chapman and Hall: New York, 1980.
Electron Tunneling in Chemistry; Compton, R.G.; Elsevier: New York, 1989; in *Comprehensive Chemical Kinetics, Vol. 30.*

Overview

■ An Introduction to Tunneling

– Quantum Mechanical Basis of Tunneling

– Tunneling Correction to the Arrhenius Equation

– Experimental Clues that Point to Tunneling

■ Examples of Tunneling in Organic Chemistry

– Electron Tunneling

– Hydrogen Tunneling

– Carbon Atom Tunneling

– Whole Molecule Tunneling

The Origin of Tunneling: Quantum Mechanics

■ Tunneling arises from wave-particle duality, more specifically, the particle in a box problem

infinite barrier   **finite barrier**
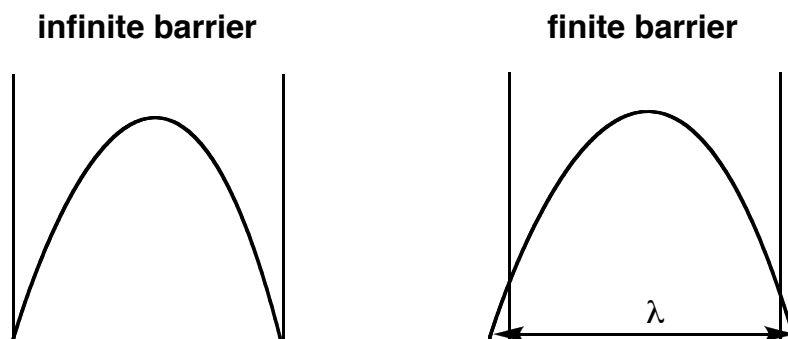
The probablility of finding the particle inside the box is 100% only when the energy barrier is infinite

$$\lambda = h / mv$$

λ: De Broglie wavelength
m: mass
v: velocity

■ Calculation of de Broglie wavelengths for a number of particles reveals that tunneling is more likely to happen with decreasing particle size
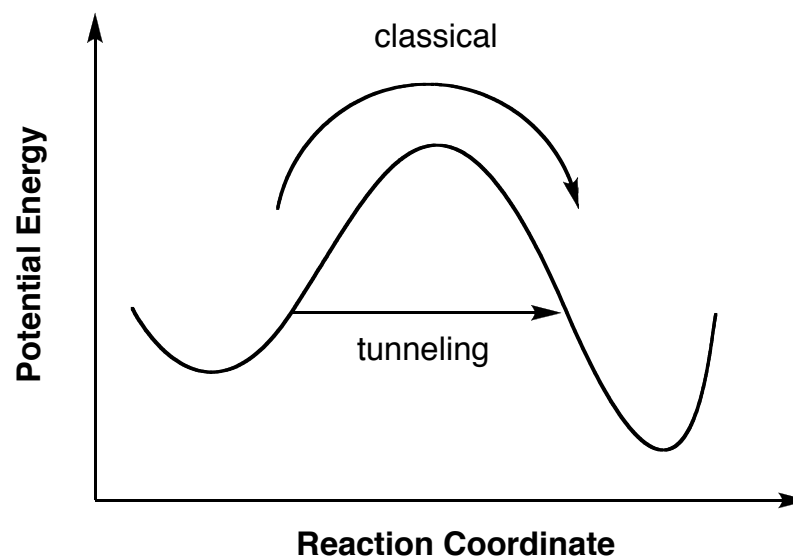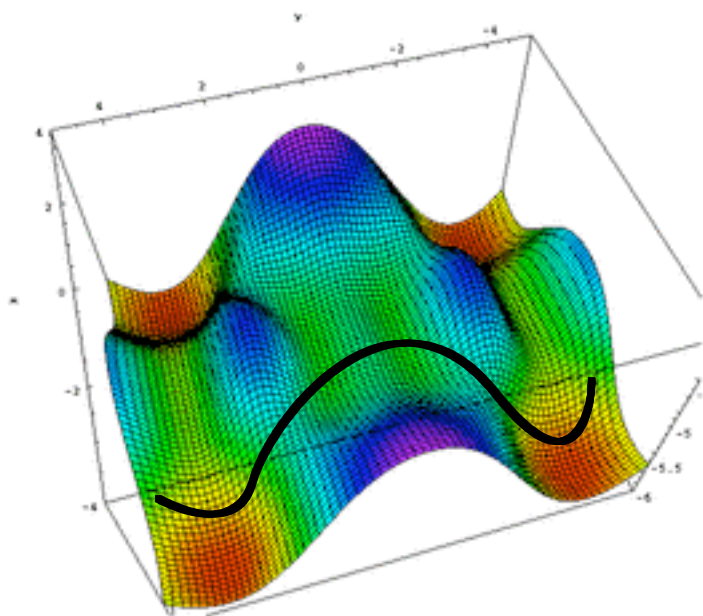
Particle	mass(a.m.u.)	λ(Å)
e^-	1/1750	26.9
H	1	.63
D	2	.45
C	12	.18
Br	80	.07

kinetic energy = 20kJ/mol

As λ approaches the scale of chemical reactions, tunneling becomes a factor in reaction mechanism

The Origin of Tunneling: A Graphical Explanation

■ The primary effect of quantum mechanical tunneling on organic chemistry is that we see deviations from classical kinetic behavior

Under the right conditions, a chemical system can react by going through the classical reaction barrier rather than over it

■ The first treatments of tunneling were done by particle physicists following the elucidation of quantum mechanics

α-decay of atomic nuclei: Gamow, Churney & Condon, 1928

cold emission of electrons from metals: Fowler & Nordheim, 1928
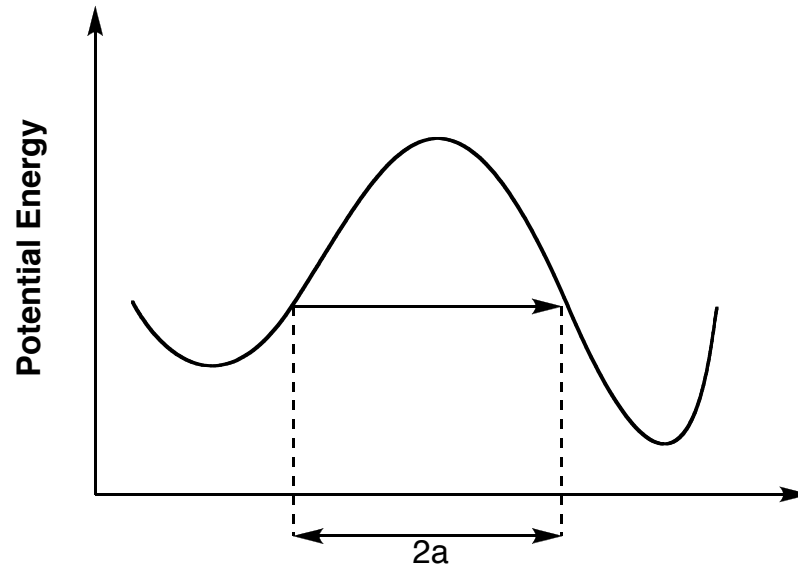
Consequences of Tunneling on Reaction Kinetics

■ R.P. Bell developed a quantum tunneling correction factor, Q, and explored its effect on an Arrhenius treatment of reaction kinetics

$$k = QAe^{-E/RT}$$

$$\text{where } Q = \frac{e^{\alpha}}{\beta - \alpha}(\beta e^{-\alpha} - \alpha e^{-\beta})$$

$$\alpha = E/RT \qquad \beta = 2a\pi^2 (2mE)^{1/2} / h$$

This equation relates measurable reaction parameters to the probablility of tunneling, allowing us to experimentally determine if tunneling is taking place

■ Four key experimental observations that imply tunneling is taking place
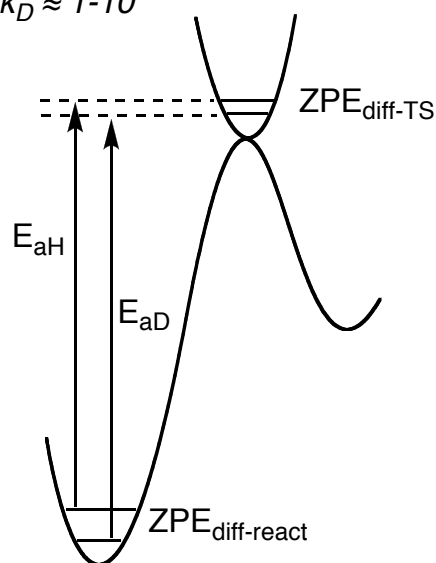
      1. Large Kinetic Isotope Effect

      2. Temperature Independence

      3. Anomalous A values

      4. Anomalous E_a values
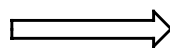
Consequences of Tunneling on Reaction Kinetics

■ **Large KIE**

classical kinetics: k_H / k_D arises from difference in ZPE's

$k_H / k_D \approx 1\text{-}10$

E_{aH}

E_{aD}

$ZPE_{\text{diff-TS}}$

$ZPE_{\text{diff-react}}$

$(E_{aD} - E_{aH})_{max} \leq 1.354 \text{ kcal / mol}$

tunneling: highly dependent on particle size moving from H to D doubles m

$k_H / k_D > 50$

$$k = QAe^{-E/RT}$$

$$\text{where } Q = \frac{e^{\alpha}}{\beta - \alpha}(\beta e^{-\alpha} - \alpha e^{-\beta})$$

$$\beta = 2a\pi^2 (2mE)^{1/2} / h$$

$$\alpha = E/RT$$

Temp (˚C)	k_H / k_{Dmax}
−30	17
−100	53
−150	260

■ **Anomalous E_a values**

$(E_{aD} - E_{aH})_{max} > 1.354 \text{ kcal / mol}$

E_a will decrease with temp, will be smaller than calulation would predict
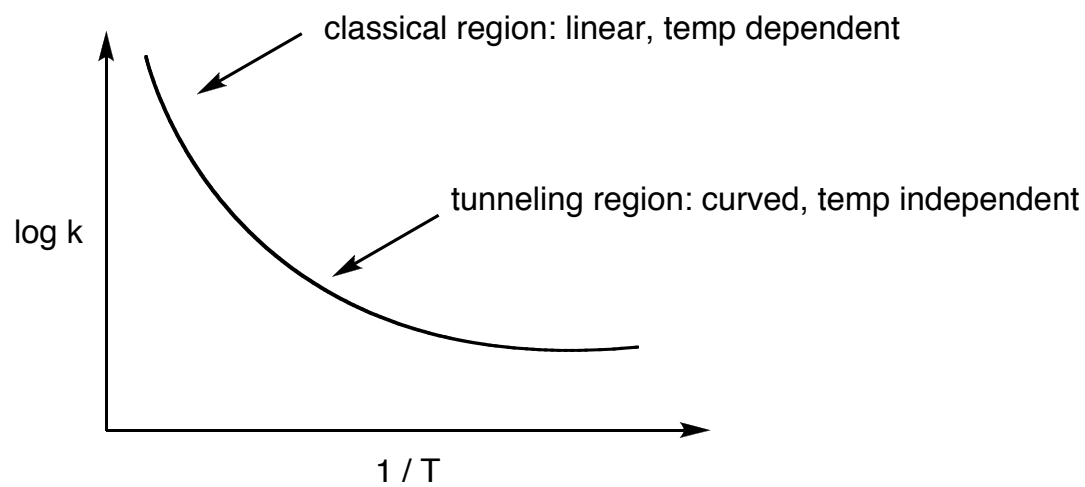
Consequences of Tunneling on Reaction Kinetics

■ Temperature Independence leading to nonlinear Arrhenius plots

Q is much less sensitive to temperature than A so as tunneling becomes relatively more important, positively curved Arrhenius plots are observed

Arrhenius plot: shows dependence
of rate on temperaure

slope $\implies E_a$

y-intercept $\implies$ A

classical region: linear, temp dependent

tunneling region: curved, temp independent

log k

1 / T

■ Anomalous A values

classical theory: A is related to entropy, so $A_H / A_D = 1$.

tunneling: Q is dependent of particle size, so $A_H / A_D \neq 1$

Ronald Percy Bell: A Giant in the Field of Quantum Tunneling

1907 – 1996

■ An Interesting Education

– Began at Balliol College in Oxford at age 16, graduating with First Class Honors in 1928
– Studied with Brønsted in Copenhagen from 1928-1933
  While in Denmark he learned thermodynamics and quantum mechanics from E. A. Guggenheim.
  Also met Niels Bohr, Heisenberg and Schroedinger
– Returned to Balliol in 1933

He never submitted his Ph.D.

■ His three main publications provide a theoretical foundation for fundamental chemical concepts

Acids & Bases - 1952

The Proton in Chemistry - 1959, 1973

The Tunnel Effect in Chemistry - 1980

His seminal work on tunneling provides the basis for all subsequent theoretical studies

■ Received many honors during his lifetime

Elected to the Royal Society 1944, President of the Faraday Society, Member National Academy
of Sciences 1972, Hon. Member American Association for the Advancement of Science 1974
Foundation Chair of Chemistry, Stirling University1967

■ Also a humanitarian, he was instrumental in bringing academic refugees to Oxford before
and during WWII, including his old colleague Niels Bohr

Direct Measurement of Tunneling: Ammonia Inversion

■ The splitting observed in the vibrational and rotational spectra of ammonia is explained by tunneling
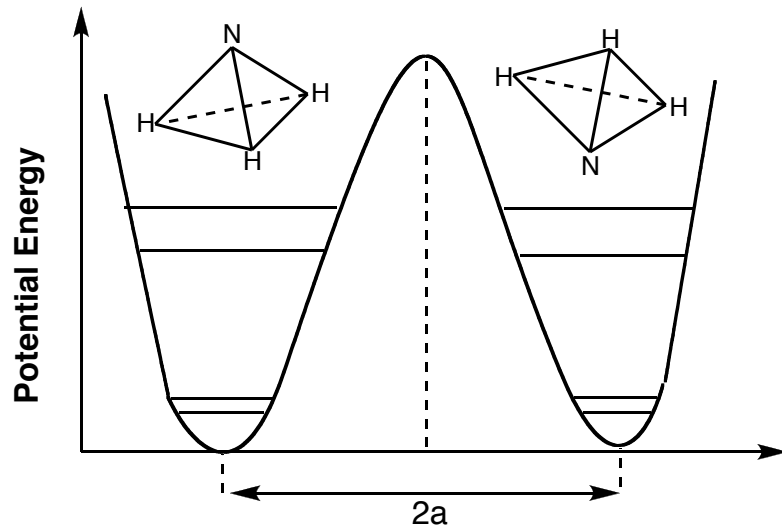

According to QM, the wave function describing nuclear vibrations in two symmetric potential wells is either symmetric or antisymmetric

In classical theory, these energy levels are identical, however when tunneling is taken into account they split

Dennison and Uhlenbeck derived this energy difference relative to a in 1932, later shown to match experimental data

The decrease in splitting magnitude for ND_3 is further experimental proof that tunneling is occuring

■ Cleeton and Williams use μwave spectroscopy to determine that the splitting of energies is greatest for fully symmetric deformational vibrations at 950cm^{-1}
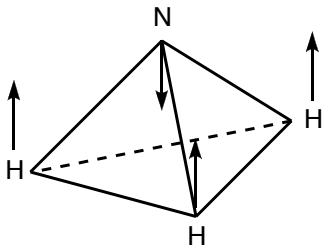
Manning (1935) showed that for ammonia inversion a = 0.39Å and E_a = 200cm^{-1}

Inversion splitting also occurs in PH_3 & AsH_3, however, inversion caused by tunneling is very rare due to increased reduced mass and occurs on a timescale such that it is unobservable by spectroscopy.

Electron Tunneling

■ Due to their small size, electrons can tunnel over relatively large distances (30Å) and this property has been harnessed for practical application in solids

superconductivity, scanning tunneling microscopy, dielectrics, semiconductors, metal junctions

Superconductive Tunneling and Applications; Solymar, L.; Chapman and Hall: London, 1972
Tunneling Phenomena in Solids; Duke, C.B.; Plenum Press: New York, 1969

■ Electron tunneling also plays an important role in biological processes

1960 Chance and Nishimura report the oxidation of cytochrome C at 77K

1966 Chance and DeVault propose tunneling as primary mechanism for charge transfer in biological systems

**1970s** Tunneling in metalloporphyrin chlorophyll analogs intensively studied

Tunneling has also been implicated in charge transfer across membranes (cellular respiration), protein-protein charge transfer, charge transfer across DNA

■ The use of Ru modified proteins as well as donor acceptor bridge molecules have shown that tunnelng of up to 20Å can occur on a biologically relevant timescale

For a good review of current research in distant charge transport se: *Proc. Nat. Acad. Sci.* **2005**, *102*, 3533

Hydrogen Tunneling: First Experimental Evidence

■ **Investigations by Williams provided some of the first evidence of tunneling in organic reactions**

$$CH_3\bullet + CH_3X \longrightarrow CH_4 + \bullet CH_2X \qquad X = CN, NC, OH$$
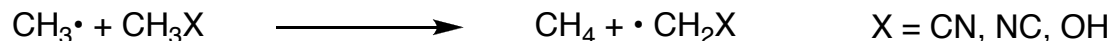
Methyl radical produced via "photo-bleaching" of acetonitrile crystals, irradiation by γ-rays followed by visible light produces solvated electrons

$$2CH_3CN \xrightarrow{\gamma\text{-rays}} e^-(CH_3CN)_2 \xrightarrow{h\nu} CH_3\bullet + CN^- + CH_3CN$$

measured by EPR
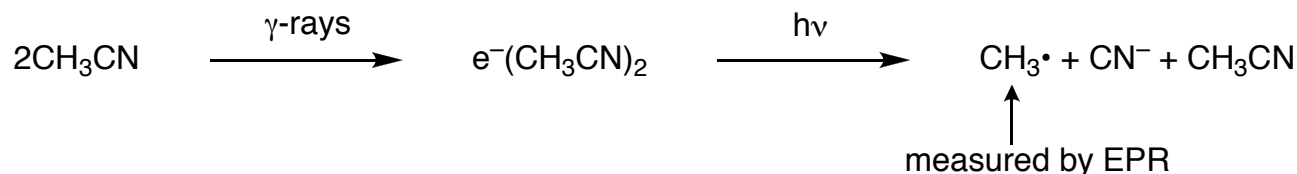
■ **Results**

X = CN:
- reaction rate measurable at 77K & 87K, classical theory predicts no reaction between 69-112K
- curved Arrhenius plot obtained with E_a = 3-10 kJ/mol
- Sprague later showed k_H / k_D = 28000 @ 77K

X = NC:
- curved Arrhenius plot obtained with E_a = 6-20 kJ/mol, value decreases with decreasing temperature
- could not detect KIE as $CD_3\bullet$ rapidly dimerized in isocyanide media

X = OH:
- curved Arrhenius plot obtained, below 40K the reaction is temperature independent
- k_H / k_D > 1000 @ 77K

Williams, F. *J. Am. Chem. Soc.* **1980**, *102*, 2325

Hydrogen Tunneling: Intramolecular H• Transfer

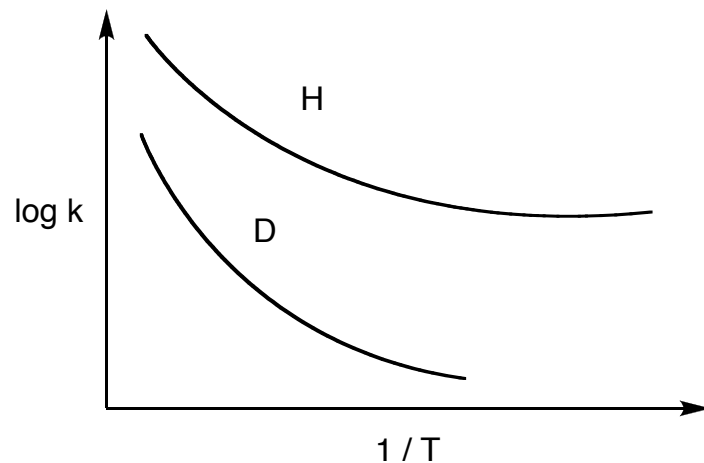■ Ingold also used EPR to monitor intramolecular hydrogen abstraction at low temp
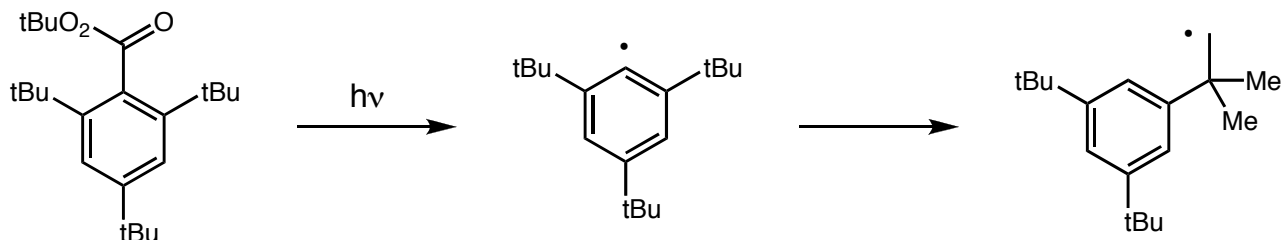
reaction rate measured from −26 to −160 ˚C (113 to 247 K)

■ Evidence for tunneling

k_H / k_D (theoretical max)	k_H / k_D (exp)	temp (˚C)
17	80	−30
53	1400	−100
260	13,000	−150

experimental KIE is much larger than max
value calculated according to classical theory


$E_D − E_H = 3.2$ kcal/mol (1.3 kcal/mol theoretical max)

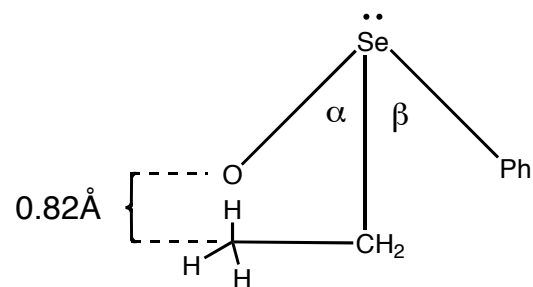reaction rate becomes temp independent below 40K

Ingold, K.U. *J. Am. Chem. Soc.* **1976**, *98*(22), 6803

Hydrogen Tunneling: Proton Tunneling in Selenoxide Elimination

■ Kwart found that tunneling can explain the difference in rate observed between sulfoxide and selenoxide elimination
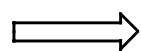
k_1

occurs through tunneling

$k_1 > k_2$

k_2

occurs through pericyclic mechanism
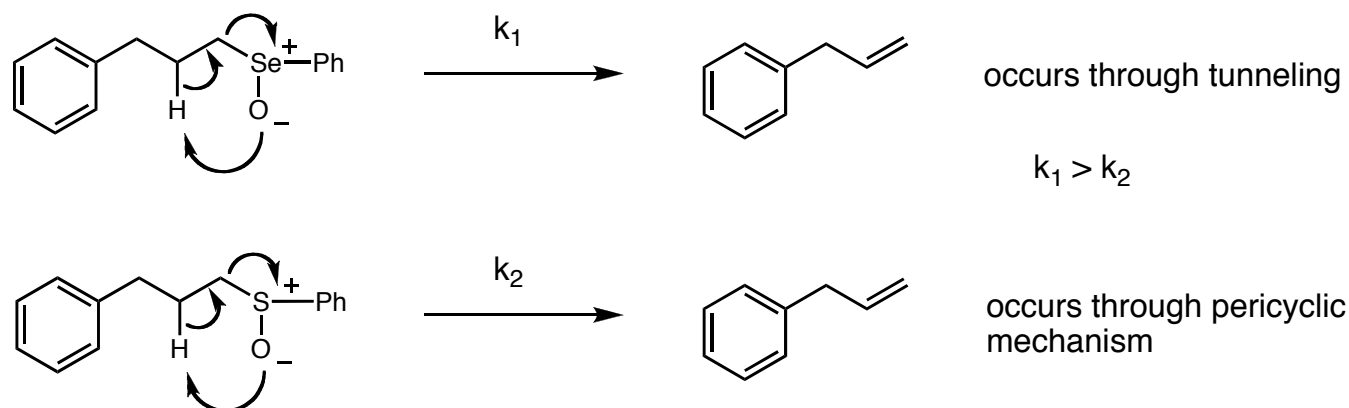
■ Evidence for tunneling

	A_H / A_D	ΔE (kcal/mol)	k_H / k_D
sulfoxide	0.76	1.15	2.7
selenoxide	0.092	2.52	72

0.82Å

α, β sulfoxide > α, β selenoxide

⟹ *The greater reactivity of the selenoxide system is due to shortening of the distance between the reacting centers*

Kwart, H. *J. Am. Chem. Soc.* **1981**, *103*, 1232
Kwart, H. *J. Am. Chem. Soc.* **1978**, *100*, 3927

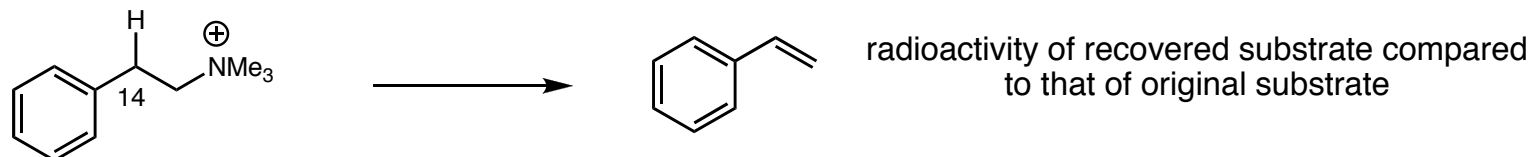## *Hydrogen Tunneling: Proton Tunneling in E2 Reactions*

■ Saunders used carbon isotope effects to examine the possibility of tunneling in hydroxide mediated elimination reactions
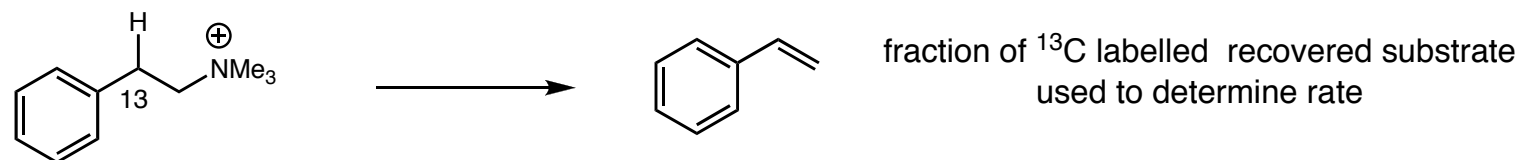

isotope effect observed on β carbon
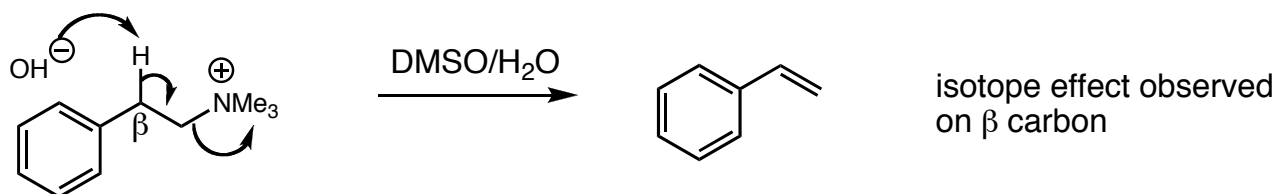
■ Both ^{13}C and ^{14}C isotope efects are measured to ensure accuracy of obtained KIE values

$$[\ln (k_{12} / k_{14})] / [\ln (k_{12} / k_{13})] = 1.9$$

k_{12} / k_{14} measured by radioactivity decay

radioactivity of recovered substrate compared to that of original substrate

k_{12} / k_{13} measured by $^{13}CNMR$

fraction of ^{13}C labelled recovered substrate used to determine rate

For T = 80, 60 ˚C, r was close to 1.9

Saunders, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 3519

Hydrogen Tunneling: Proton Tunneling in E2 Reactions

■ Calculations predict different isotope effects for the semiclassical and quantum mechanical situations

Semiclassical: inverse isotope effect $k_H / k_D < 1$
With tunneling: normal isotope effect $k_H / k_D > 1$

■ Experimental evidence points to tunneling

%DMSO	T (°C)	k_{12} / k_{14}	k_{12} / k_{13}
10	60	1.0348	1.0161
10	80	1.0281	1.0146
40	60	1.0318	1.0161
40	80	1.0301	1.0169
60	60	1.0338	1.0210

| %DMSO	$E_{a14} - E_{a12}$ (cal/mol)	A_{12} / A_{14}
10	84.4	0.911
40	84.3	0.912
60	110.5	0.873

k_{12} / k_{13} decrease with increasing temp implies tunneling

■ Why does tunneling show up in a heavy atom isotope effect?

"It should be kept in mind that the reacting system as a whole tunnels, not a particular atom. If heavy atom motion contributes significantly to the reaction coordinate, the effective mass m* will be less sensitive to changes in hydrogen mass and more sensitive to changes in carbon mass"

Saunders, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 3519

Carbon Tunneling: Cyclobutadiene Isomerization

■ In 1983, Carpenter postulates that tunneling could account for 97% of the total rate constant of bond shift in cycloutadiene below 0˚C
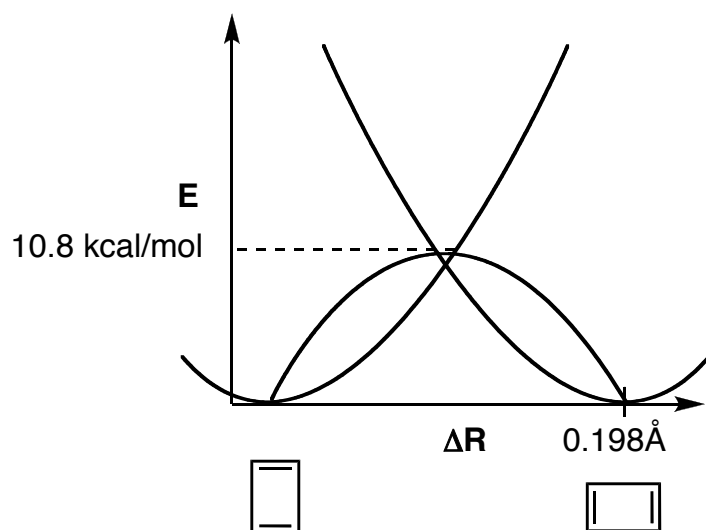
Bond shift can be approximated by a single bond stretching motion

1.34Å

1.52Å
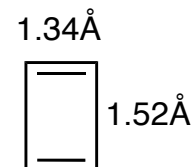
As ΔR is very small, tunneling from one isomer to another might be possible

E

10.8 kcal/mol

ΔR   0.198Å

Assuming 1000cm^{-1} for in plane recangular deformation, the potential energy barrier for automerization is 10.8 kcal/mol

■ Using the Bell formula, he is able to calculate tunneling rate constants and activation parameters

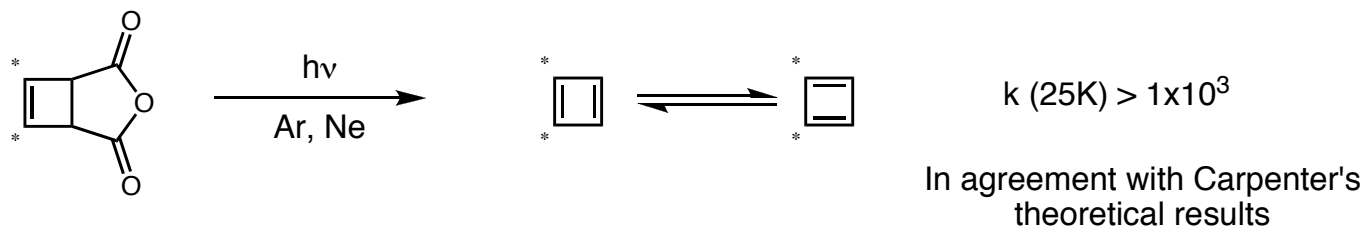| Temp (˚C)	$k_{classic}$	$k_{tunneling}$
−50	1.01×10^2	8.08×10^4
−10	4.82×10^3	4.65×10^5

$\Delta H^{\ddagger}$ = 4.6 kcal/mol

$\Delta S^{\ddagger}$ = −15 cal/mol K

Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700

Carbon Tunneling: Cyclobutadiene Isomerization

■ In 1988, Arnold is able to experimentally measure cyclobutadiene isomerization by ^{13}C NMR

$$k\ (25K) > 1 \times 10^3$$

In agreement with Carpenter's
theoretical results

Note: obtaining rate data is not easy, in order to get the NMR measurements the matrix
was irradiated during deposition with argon onto a sapphire plate cooled to 25K

Arnold, B. R. *J. Am. Chem. Soc.* **1988**, *110*, 2648

■ From Carpenter's calculations, an interesting result for substituted cyclobutadienes emerges
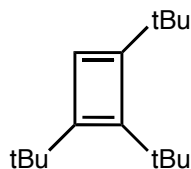
Why can automerization not be frozen out even at −185 °C?

*Sterically demanding substituents force the annulene to adopt a regular polygonal
structure, reducing barrier width and increasing the tunneling rate constant*

Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700

Carbon Tunneling: Ring Expansion

■ Zuev *et al* report that halogen substituted cyclobutylcarbene undergoes ring expansion to cyclopentene product at 8K via carbon tunneling
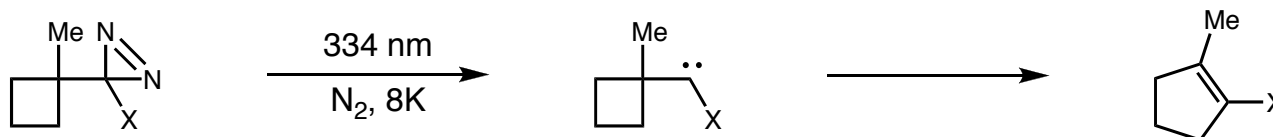
X = Cl, no carbene observed in IR spectrum
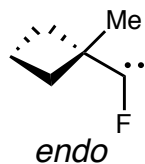X = F, new bands associated with carbene observed

In Ar matrix:

IR band	temp	k (s^{-1})
1108,1325	8K	4.0 x10^{-5}
	16K	9.0 x10^{-5}
956,1083	16K	6.0 x10^{-6}

In N$_2$ matrix:

IR band	temp	k (s^{-1})
1108,1325	8K	4.0 x10^{-6}
956,1083	8K	no rxn

■ Two possible conformers with different reaction rates
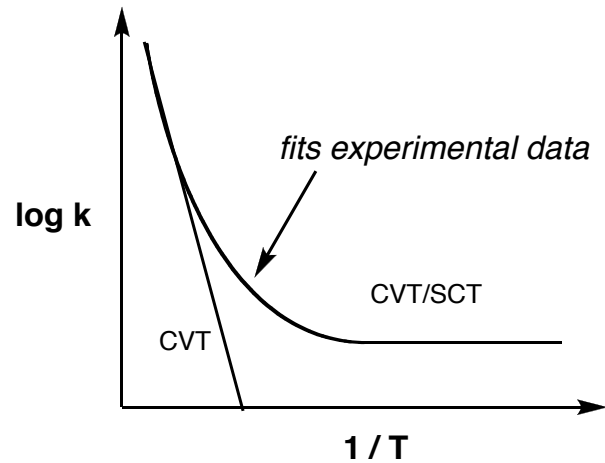

exo   *endo*

the more rapidly disappearing set of IR bands corresponds to the exo conformer as the F atom is appropriately aligned for expansion

Zuev, P. S. *Science* **2003**, *299*, 867

Carbon Tunneling: Ring Expansion

■ Experimental results validated by calculation

$\Delta E^{\ddagger} = 27$ kJ/mol, too large to be surmounted from 8 or 25K

log k on y-axis, **1 / T** on x-axis

fits experimental data

CVT/SCT

CVT

CVT: canonical variational transition state
SCT: small-curvature tunneling approximation

rate at 8K

CVT	CVT/SCT	experiment
2×10^{-158}	9.1×10^{-6}	4.0×10^{-6}

rearrangement of the chloro carbene calculated as 1.4×10^{4} at 8K, corresponding to a half life of 10^{-4}s

E_a (J / mol)	Temp (K)	% $\nu = 1$
0.3	8	0.04
	16	6
0.45	30	
1.2	40	50
23.6	150	

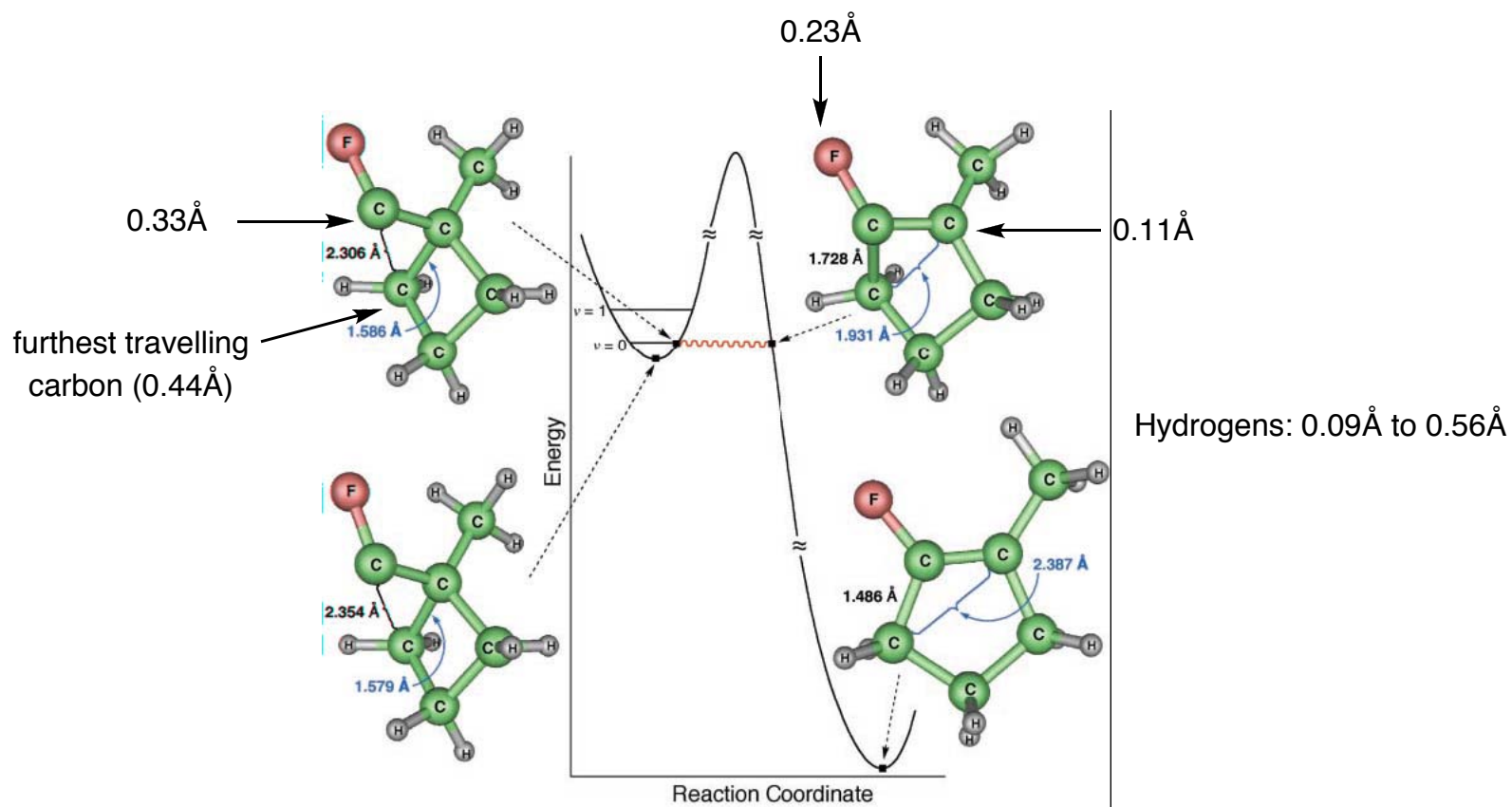transition from $\nu = 0$ to $\nu = 1$ tunneling corresponds to curve in Arrhenius plot

■ One point of disagreement

Theory predicts a negligible change in rate as one moves from 8K to 16K but experiment shows that the rate doubles, why?

⟹ "matrix softening" explains rate inrease, greater reactivity in Ar and *endo* reacivity

Carbon Tunneling: Ring Expansion

■ The change in 3-dimensional positions of individual atoms at termini of tunneling pathway reveals tunneling distances
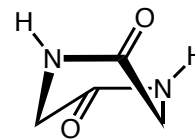

0.23Å

0.33Å

0.11Å

furthest travelling carbon (0.44Å)

2.306 Å

1.586 Å

2.354 Å

1.579 Å

1.728 Å

1.931 Å

1.486 Å

2.387 Å

Hydrogens: 0.09Å to 0.56Å

Energy

Reaction Coordinate

Conformer Tunneling: Diketopiperazine

■ Controversy in the literature over the solution structure of diketopiperazine
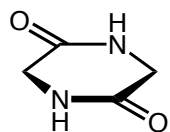
planar ring structure
X-ray crystal structure

puckered boat structure
favored by calculation

Though all theoretical studies argued for the boat structure as most stable, they vary widely in the value of energy difference between the planar and boat form, $2 cm^{-1}$ to $2000 cm^{-1}$

■ Godfrey *et al* found that the microwave spectrum of diketopiperazine is split into a series of doublets, indicative of a tunneling pathway between conformers

Spectroscopic data was successfully fit a two vibrational state model incorporating tunneling

Difference in vibrational levels is similar to that observed with trideuteroammonia
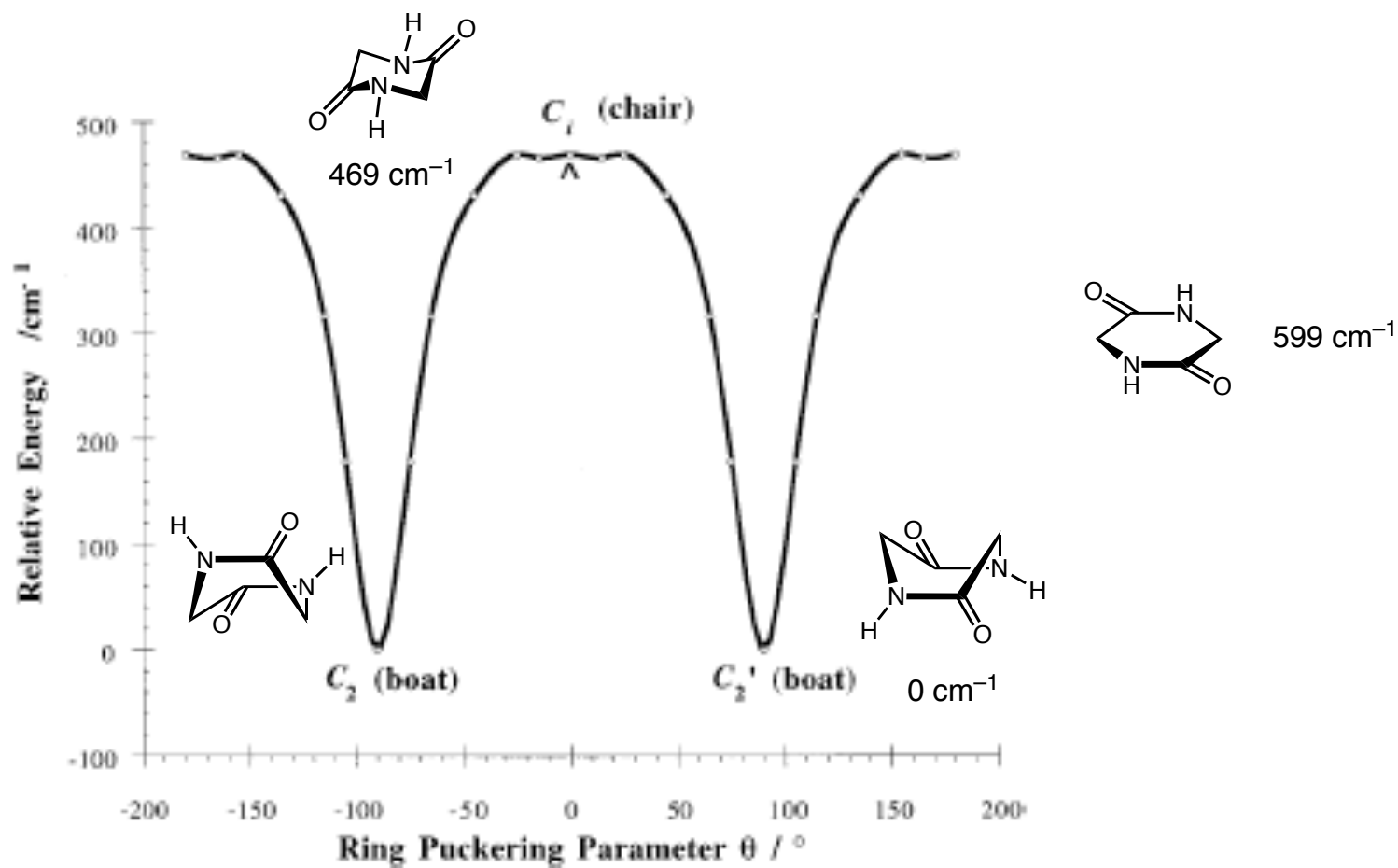
tunneling splitting parameter

from fit data: Δ GHz = 1.075

compare to ND_3: Δ GHz = 1.6

Godfrey, P.D. *J. Am. Chem. Soc.* **2000**, *122*, 5856

Conformer Tunneling: Diketopiperazine

■ Using calculations, they determine energy differences between the three conformers

"The energy barrier of 470cm^{-1} separating the two equivalent boat confromers is of appropriate size to result in the tunnel splitting found in the measured spectrum"
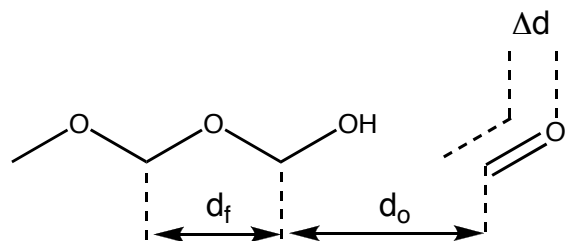
Tunneling in Condensed Media: Formaldehyde Polymerization

■ Goldanskii showed in 1976 that formaldehyde poymerization is a tunneling process

solid state rxn occurs as low as 4K
k independent of temp from 4.2-10K

$$k_H / k_D = 1$$
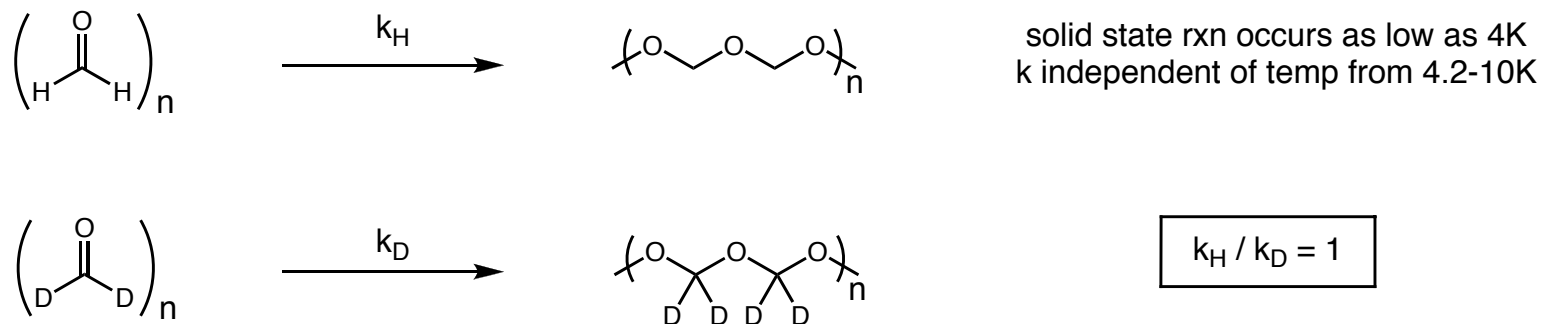
⟹ **the entire formaldehyde molecule tunnels**

■ Polymerization is associated with monomer movement onto the end of the polmer chain

*formaldehyde monomer must tunnel
Δd in order to join polymer chain*

$\tau_0 = 10^{-2}$ sec ⟹ $\Delta d = 0.4\text{-}0.5\text{Å}$

τ_0: time of polymer chain growth

Goldanskii, V.I. *Ann. Rev. Phys. Chem.* **1976**, *27*, 85

Conclusions

■ Tunneling is a direct consequnce of quantum mechanics and its effects can be found thoughout the physical sciences

Particle physics: explains phenomena such as α-particle emission and can be exploited for practical use (STM)

Material Science: superconductors, smeiconductors and dielectric materials all make use of charge transfer via tunneling

Biology: the main mechanism of charge transfer in cellular respiration and other biological procceses

Chemistry: electron, hydrogen and heavy atom tunneling is found throughout a number of chemical transformations

■ Though less common than electron tunneling, heavy particle tunneling does play an important role in chemistry

explains spectroscopic splitting patterns as well as reactivity at extremely low temperatures

■ Chemists habitually speak of individual particles tunneling but it's important to keep in mind that according to QM the entire system is tunneling

ammonia inversion, diketopiperazine puckering, formaldehyde polymerization