

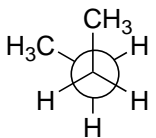


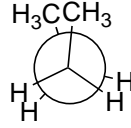


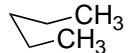

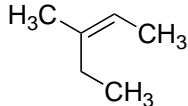

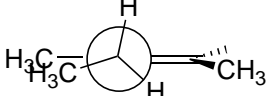

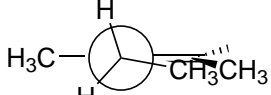
**pKa's.** Numbers are approximations for outside the range -2 - 16, but useful to know.  
For an extensive list, see <http://www.chem.wisc.edu/areas/reich/pkatable/>

Substrate	H <sub>2</sub> O	DMSO	Substrate	H <sub>2</sub> O	DMSO
<i>Inorganics</i>			<i>EWG-CH</i>		
CF <sub>3</sub> SO <sub>3</sub> H	-14			9	13
HCl	-8			11	14
CH <sub>3</sub> SO <sub>3</sub> H	-3	2		13	16
H <sub>3</sub> O <sup>+</sup>	-2		NO <sub>2</sub> -CH <sub>3</sub>	10	17
NH <sub>4</sub> Cl	9			20	27
H <sub>2</sub> O	16			25	30
<i>Organic X-H</i>					35
	-6			33	35
Ph-CH=O			<i>Hydrocarbons</i>		
Me <sub>2</sub> OH <sup>+</sup>	-4		H <sub>3</sub> C-CH <sub>3</sub>	50	
AcOH	5	12		44	
	5	3	R-C≡C-H	23	
PhOH	10	18	H-H	35	
	15	26			
MeOH	16	28			
tBuOH	17	29			
(iPr) <sub>2</sub> NH		36			
NH <sub>3</sub>	38	41			

**Bond Strength.** Take from Lowry and Richardson; by definition,  $\Delta H$  for:  $A-B \longrightarrow A + B^\bullet$

Bond	BDE (Kcal/mol)	Bond	BDE (Kcal/mol)
	98		84
	103		172 (2nd bond = 88)
	125		81
	85		148 (2nd bond = 67)
	82		194 (3rd bond = 46)
	69		
	54		
HO-H	119		
HO <sub>2</sub> -H	90		
HO-OH	50		
H-H	104		
Hydrogen bond X...H	2-10		

### Strain energy (energetic penalty for indicated strain)

Strain	Penalty (kcal/mol)	Strain	Penalty (kcal/mol)
 gauche	0.8	<i>ring strain</i>  or 	28
 eclipsed	2.2	 or 	26
 syn-pentane	3.7		6
<i>olefin conformations</i> for 			0
 A <sub>1,2</sub>	2.7		6
 A <sub>1,3</sub>	3.9		

### Kinetics and Thermodynamics

#### equilibrium processes

key equation:  $\Delta G = -RT \ln(K)$

for  $K = 10$ ,  $T = 298$ ,  $\Delta G = -1.4 \text{ kcal}$

$K = 100$ ,  $T = 298$   $\Delta G = -2.8 \text{ kcal}$

i.e. for every 1.4 kcal difference in energy there is an order of magnitude change in  $K_{\text{eq}}$

#### reaction rate

2nd key equation

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G^\ddagger}{RT}\right) \quad \text{or} \quad \Delta G^\ddagger = -RT \ln \frac{kh}{k_B T}$$

$k$  = rate constant

$h$  = Plank's constant

$k_B$  = Boltzmann's constant

$-\Delta G^\ddagger$  = free energy difference between ground state and transition state

for  $T = 298$ ,  $k = 1 \text{ s}^{-1}$

$\Delta G^\ddagger = 17.5 \text{ kcal/mol}$

i.e. activation energy for rxn occurring once a second is 17.5

As above, if  $k = 10 \text{ s}^{-1}$ ,  $\Delta G^\ddagger = 17.5 - 1.4 = 16.1$

For  $T = 308$  and  $\Delta G^\ddagger = 17.5$ ,  $k = 2.5 \text{ s}^{-1}$

i.e. increase in temp of 10K gives ~2.5 fold increase in rate

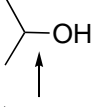
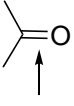
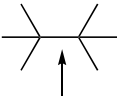
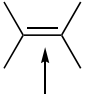
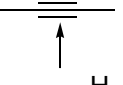
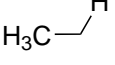
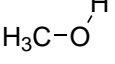
#### relative rates

for a system with 2 possible reaction pathways (e.g. kinetic enolization or asymmetric catalysis) for

$k_{\text{fast}}/k_{\text{slow}} = 10$  (would give 82% ee),  $\Delta\Delta G^\ddagger = 1.4 \text{ kcal/mol}$

$k_{\text{fast}}/k_{\text{slow}} = 100$  (would give 99% ee),  $\Delta\Delta G^\ddagger = 2.8 \text{ kcal/mol}$

## Bond distances

bond	length (angstroms [ $10^{-10}\text{m}$ ])
	1.43
	1.23
	1.53
	1.34
	1.20
	1.1
	0.97
X - - - H (hydrogen bond)	1.5 - 2.4