

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/>

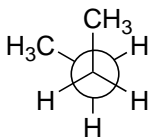


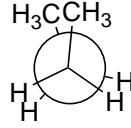


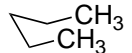

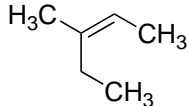

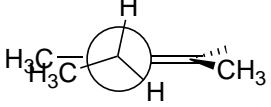

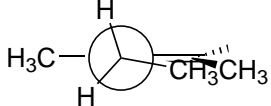
Substrate	H ₂ O	DMSO	Substrate	H ₂ O	DMSO
<i>Inorganics</i>			<i>EWG-CH</i>		
CF ₃ SO ₃ H	-14			9	13
HCl	-8			11	14
CH ₃ SO ₃ H	-3	2		13	16
H ₃ O ⁺	-2		NO ₂ -CH ₃	10	17
NH ₄ Cl	9			20	27
H ₂ O	16			25	30
<i>Organic X-H</i>					35
	-6			33	35
Me ₂ OH ⁺	-4		<i>Hydrocarbons</i>		
AcOH	5	12	H ₃ C-CH ₂ -H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

Bond Strength. Take from Lowry and Richardson; by definition, ΔH for: $A-B \longrightarrow A^{\bullet} + B^{\bullet}$

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 ₂ -H	90		
HO-OH	50		
H-H	104		
Hydrogen bond X---H	2-10		

for a large list of BDE's see Prof. Thomas Lectka's web page:
<http://www.jhu.edu/chem/lectka/Bond%20Strengths.html>

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 _{1,2}	2.7		6
 A _{1,3}	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_{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



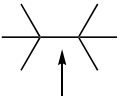

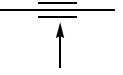
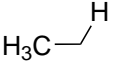
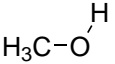
relative rates

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}m])
	1.43
	1.23
	1.53
	1.34
	1.20
	1.1
	0.97
X - - - H (hydrogen bond)	1.5 - 2.4