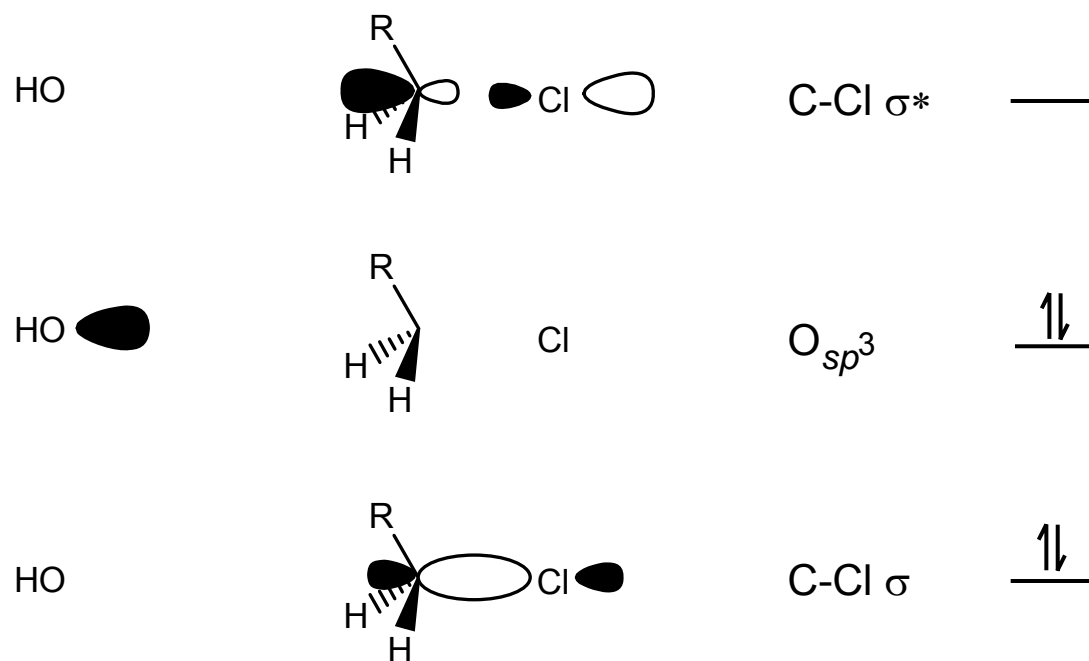
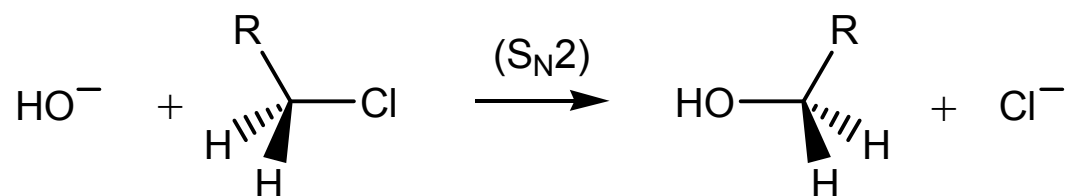


# Molecular Orbital (MO) Theory

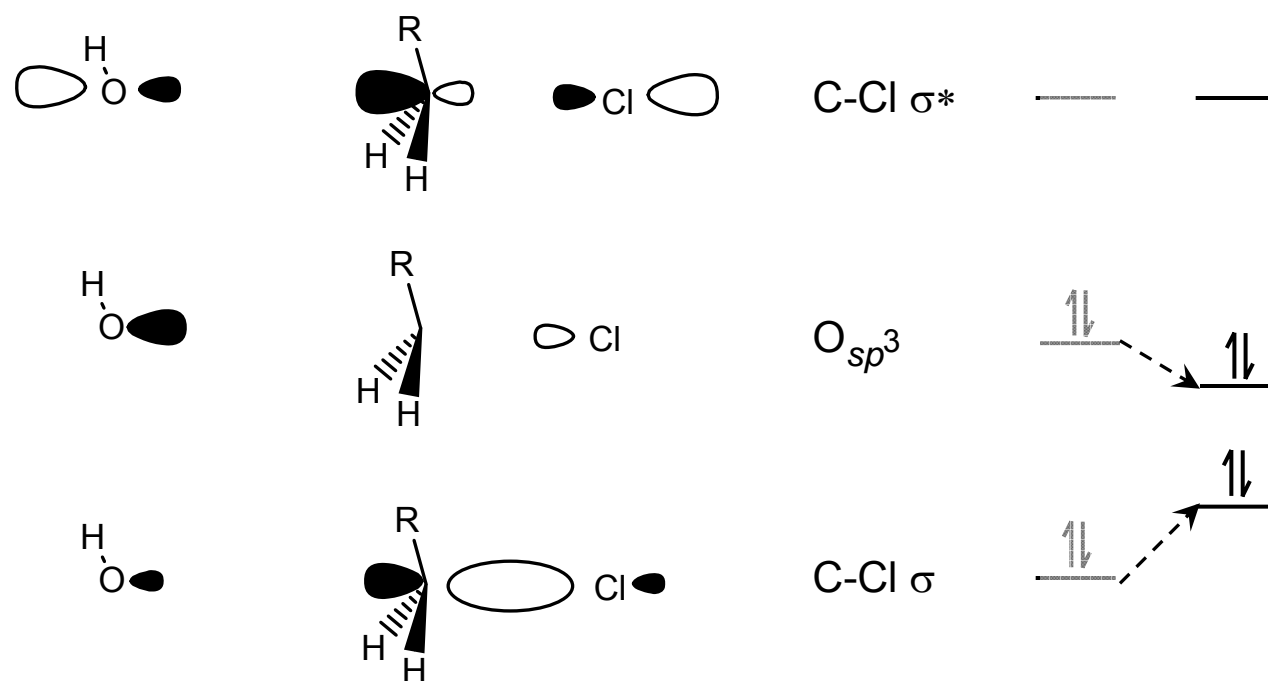
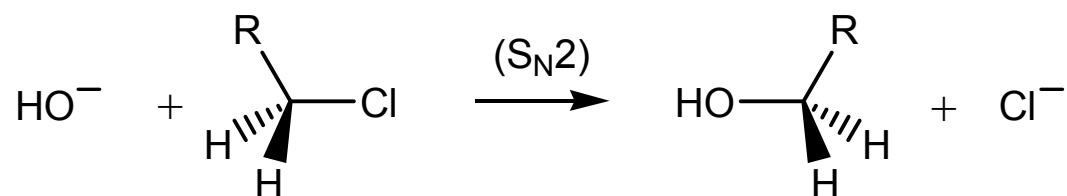
*Molecular orbital "mixing" takes place at all times along reaction coordinate.*



As  $\text{HO}^-$  approaches, and as  $\text{Cl}^-$  departs, orbitals mix.

# Molecular Orbital (MO) Theory

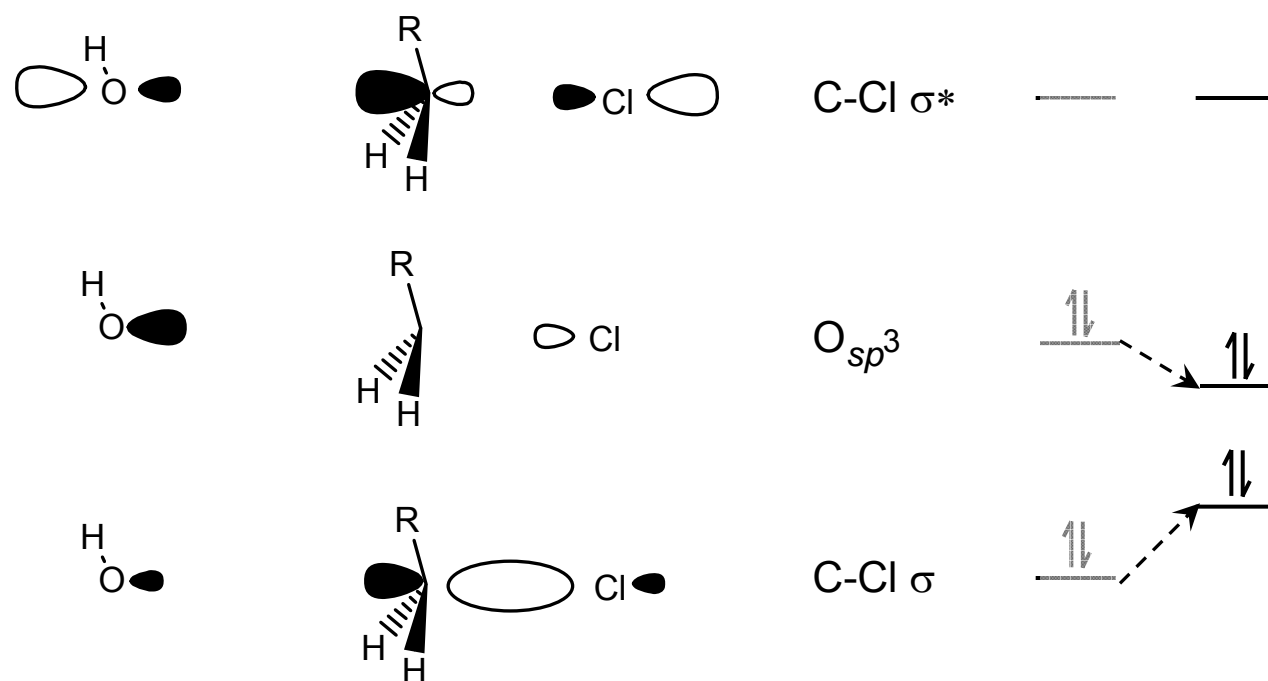
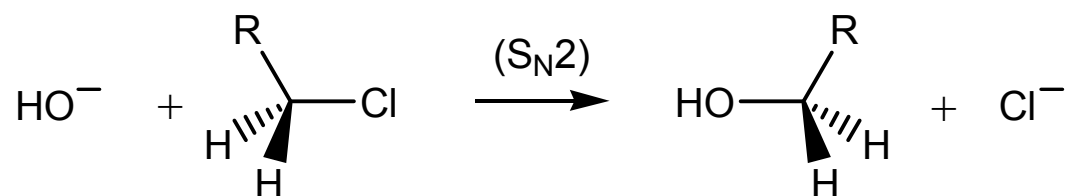
*Molecular orbital "mixing" takes place at all times along reaction coordinate.*



As reaction proceeds, C-Cl bonding mix is stretched apart; *destabilizing*

# Molecular Orbital (MO) Theory

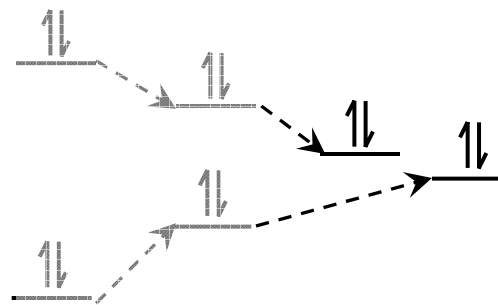
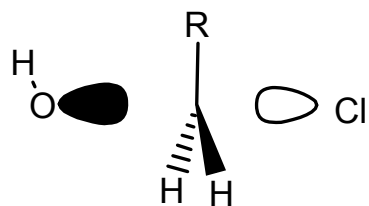
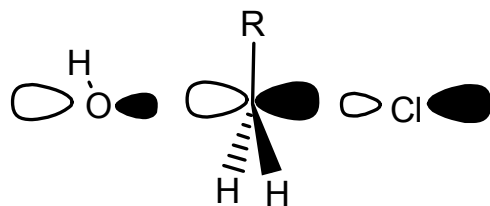
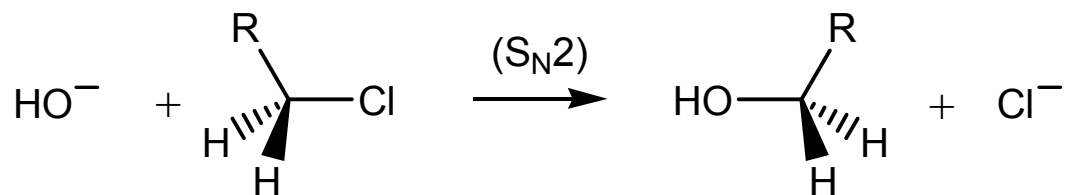
*Molecular orbital "mixing" takes place at all times along reaction coordinate.*



However, as reaction proceeds, O lone pair is gradually redistributed over to Cl: *stabilizing*

# Molecular Orbital (MO) Theory

*Molecular orbital "mixing" takes place at all times along reaction coordinate.*



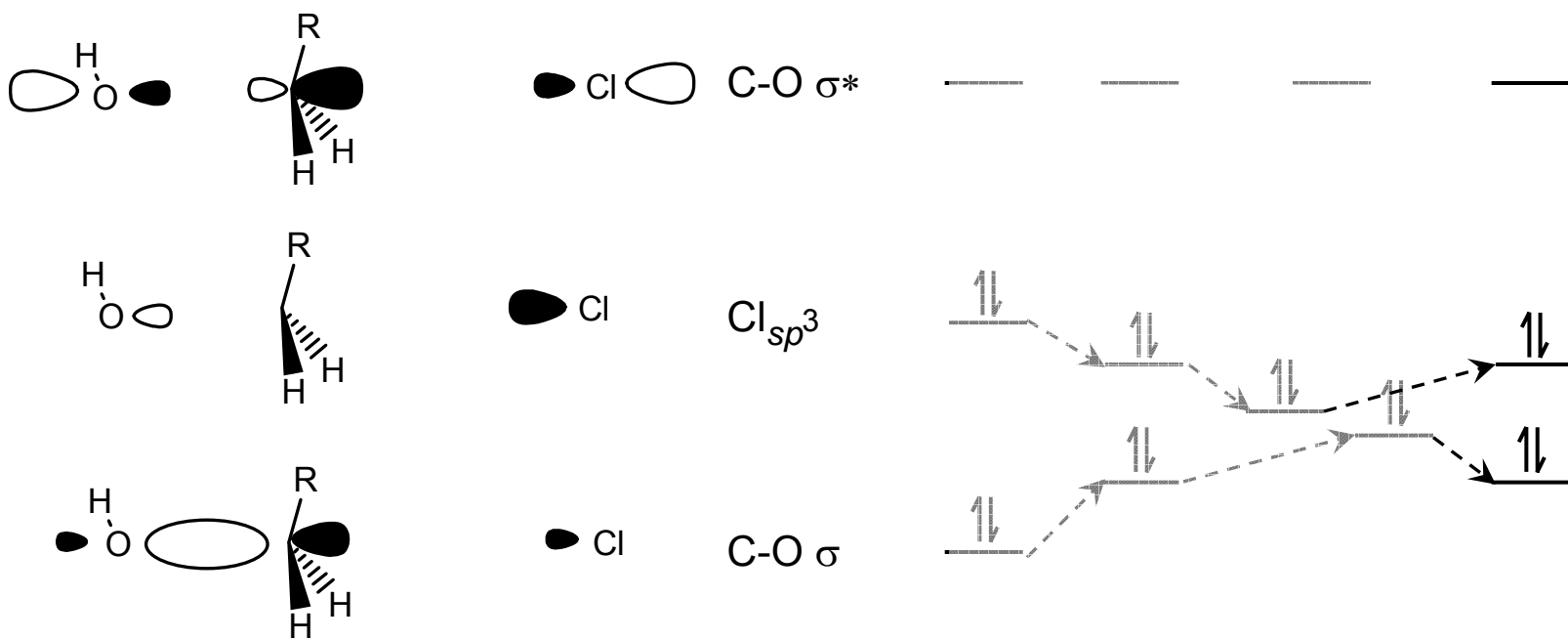
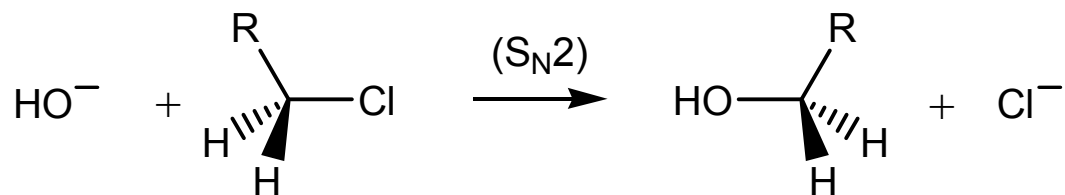
*(transition state)*

Point of  
most e<sup>-</sup>  
redistribution

Point of  
least  
bonding  
overlap

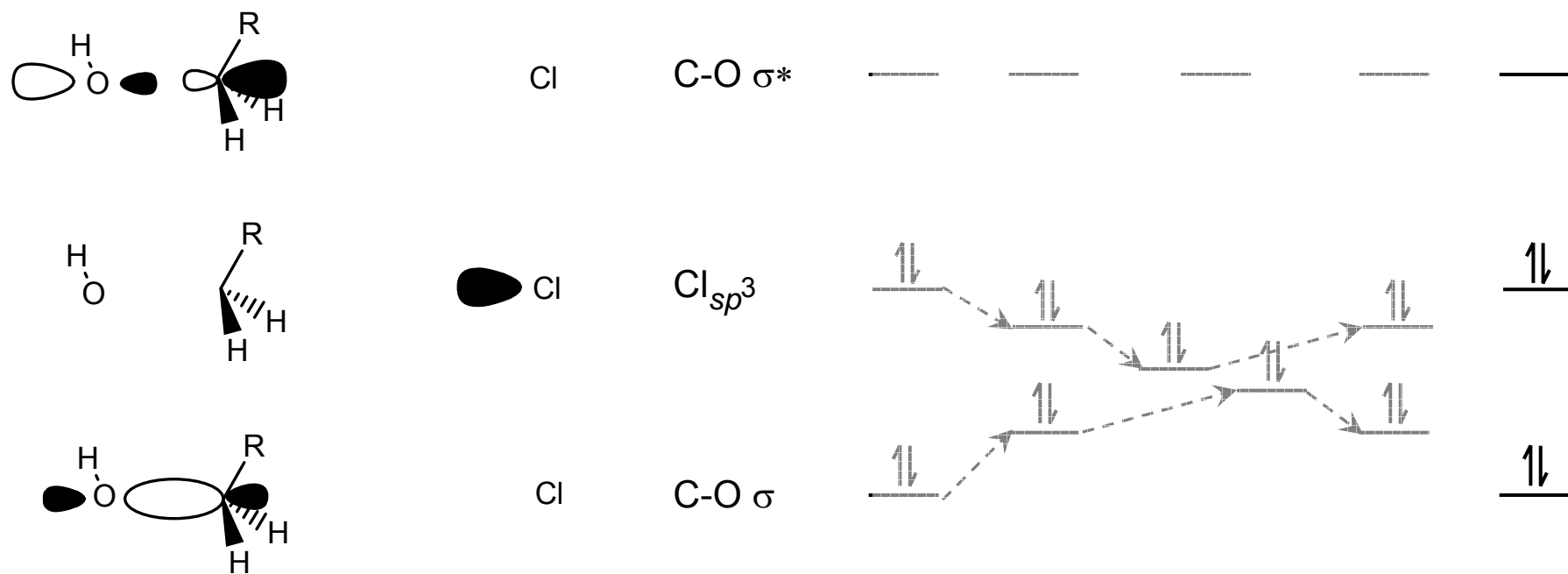
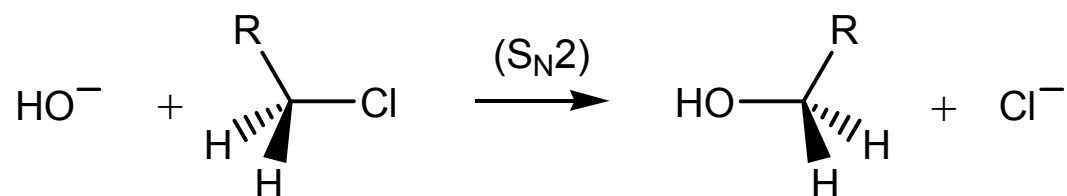
# Molecular Orbital (MO) Theory

*Molecular orbital “mixing” takes place at all times along reaction coordinate.*



# Molecular Orbital (MO) Theory

*Molecular orbital "mixing" takes place at all times along reaction coordinate.*



# Thermodynamics “On the Fly”

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= RT(\ln K)\end{aligned}$$

*Reminder of some good rules of thumb:*

- At room temperature,  $\Delta G = 1.4$  kcal/mol is equivalent to an order of magnitude in equilibrium constant  $K$ .
- Creating a new molecule in the gas phase yields  $\Delta S \approx 50$  cal/mol K (“entropy units”, eu); 15 kcal/mol at room temperature
- New molecules in solution are worth less (< 35 eu)



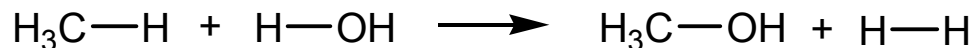
*(Standard energy means units refer to 1 M of all reactants and products.)*

# Thermodynamics “On the Fly”: Reaction Energetics from Standard Bond Dissociation Energies (BDEs)

*Concept:*  $\Delta H$  for reaction can be estimated from types of bonds that are created and broken in reaction.

Don't need to know mechanism to do this; just look at bonds.

*Example:* Oxidation of methane to methanol (to convert gas to liquid fuel).



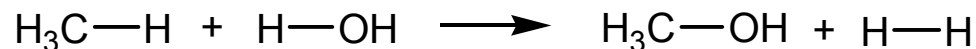
We don't know the mechanism of this reaction.

What if we just pulled bonds apart and put them back together again?

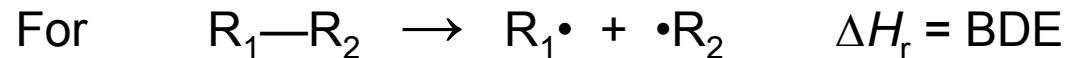
Enthalpy of reaction (state function) would be the same.



# Thermodynamics “On the Fly”: Reaction Energetics from Standard Bond Dissociation Energies (BDEs)



*Strategy:* Use Bond Dissociation Energies (BDEs), enthalpy of individual homolytic bond cleavage, to calculate sum of bond breaking and bond making processes.



# Standard Bond Dissociation Energies (BDEs)

Bond Type	BDE (kcal/mol)
H-H	104.2
C-C	83
N-N	38.4
O-O	35
F-F	36.6
Si-Si	52
P-P	50
S-S	54
Cl-Cl	58
Br-Br	46
I-I	36
H-C	99
H-N	93
H-O	111
H-F	135
H-Cl	103

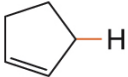

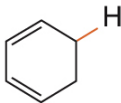
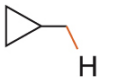

Bond Type	BDE (kcal/mol)
H-Br	87.5
H-I	71
H-B	90
H-S	81
H-Si	75
H-P	77
B-F	150
B-O	125
C-N	73
N-CO	86
C-O	85.5
O-CO	110
C-S	65
C-F	116
C-Cl	81
C-Br	68

Bond Type	BDE (kcal/mol)
C-I	51
C-B	90
C-Si	83
C-P	70
N-O	55
S-O	87
Si-F	135
Si-Cl	90
Si-O	110
P-Cl	79
P-Br	65
P-O	90
C=C	146
N=N	109
O=O	119
C=N	147

Bond Type	BDE (kcal/mol)
C=O (CO <sub>2</sub> )	192
C=O (aldehyde)	177
C=O (ketone)	178
C=O (ester)	179
C=O (amide)	179
C=O (halide)	177
C=S (CS <sub>2</sub> )	138
N=O (HONO <sub>2</sub> )	143
P=O (POCl <sub>3</sub> )	110
P=S (PSCl <sub>3</sub> )	70
S=O (SO <sub>2</sub> )	128
S=O (DMSO)	93
P=P	84
P≡P	117
C≡O	258
C≡C	200
N≡N	226
C≡N	213

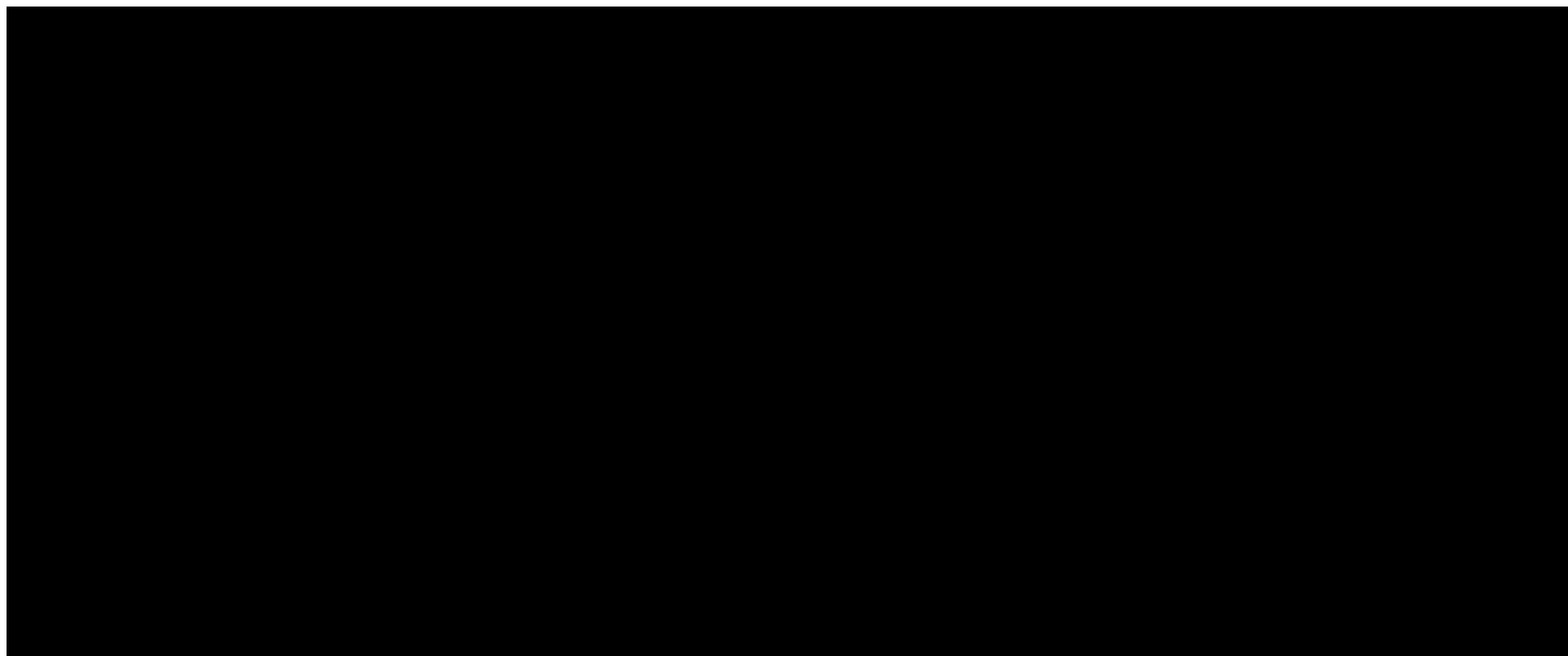
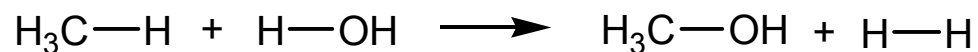
From <http://www.cem.msu.edu/~reusch/OrgPage/bndenrgy.htm>.

# Standard Bond Dissociation Energies (BDEs)

Bond	BDE	Bond	BDE	Bond	BDE
H-H	104.2 (104.2)	CH <sub>2</sub> =CH-H	110 (110.7)	CH <sub>3</sub> -CH <sub>3</sub>	90.4 (90.1)
CH <sub>3</sub> -H	105.1 (105.0)	C <sub>6</sub> H <sub>5</sub> -H	110.9 (112.9)	CH <sub>3</sub> -F	109.9 (115)
CH <sub>3</sub> CH <sub>2</sub> -H	98.2 (101.1)	HC≡C-H	132 (131.9)	CH <sub>3</sub> -Cl	84.6 (83.7)
(CH <sub>3</sub> ) <sub>2</sub> CH-H	95.1 (98.6)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -H	88 (89.7)	CH <sub>3</sub> -Br	70.9 (72.1)
(CH <sub>3</sub> ) <sub>3</sub> C-H	93.2 (96.5)	CH <sub>2</sub> =CHCH <sub>2</sub> -H	86.3 (88.8)	CH <sub>3</sub> -I	57.2 (57.6)
c(CH <sub>2</sub> ) <sub>3</sub> -H	106.3	CH <sub>3</sub> C(O)-H	86 (88.1)	CH <sub>3</sub> -OH	92.3 (92.1)
c(CH <sub>2</sub> ) <sub>4</sub> -H	96.5	HO-H	119 (118.8)	CH <sub>3</sub> -NH <sub>2</sub>	84.9 (85.2)
c(CH <sub>2</sub> ) <sub>5</sub> -H	94.5	CH <sub>3</sub> O-H	104.4 (104.6)	CH <sub>3</sub> -SH	74
c(CH <sub>2</sub> ) <sub>6</sub> -H	95.5	NH <sub>2</sub> -H	107.4 (107.6)	CH <sub>3</sub> -SiH <sub>3</sub>	88.2
	82.3	CH <sub>3</sub> S-H	90.7 (87.4)	CH <sub>3</sub> -SiMe <sub>3</sub>	89.4
		HO-OH	51	CH <sub>3</sub> -GeMe <sub>3</sub>	83
	71.1	CH <sub>3</sub> O-OCH <sub>3</sub>	37.6 (38)	CH <sub>3</sub> -SnMe <sub>3</sub>	71
		HOCH <sub>2</sub> -H	94 (96.1)	CH <sub>3</sub> -PbMe <sub>3</sub>	57
	73	H <sub>2</sub> C=CH <sub>2</sub>	(174.1)	CH <sub>3</sub> -OCH <sub>3</sub>	(83.2)
	97.4	HC≡CH	(230.7)	CH <sub>3</sub> -C <sub>2</sub> H <sub>5</sub>	(89.0)
	90.6	H <sub>2</sub> C=O	(178.8)	CH <sub>3</sub> -CH(CH <sub>3</sub> ) <sub>2</sub>	(88.6)
CH <sub>3</sub> -CH=CH <sub>2</sub>	(101.4)	CH <sub>3</sub> -C <sub>6</sub> H <sub>5</sub>	(103.5)	CH <sub>3</sub> -C(CH <sub>3</sub> ) <sub>3</sub>	(87.5)
C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>5</sub>	(118)	CH <sub>3</sub> -CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	(77.6)	CH <sub>3</sub> -CH <sub>2</sub> CH=CH <sub>2</sub>	(76.5)

*From Anslyn & Dougherty, p. 72. Plenty more available on the Web.*

# Thermodynamics “On the Fly”: Reaction Energetics from Standard Bond Dissociation Energies (BDEs)

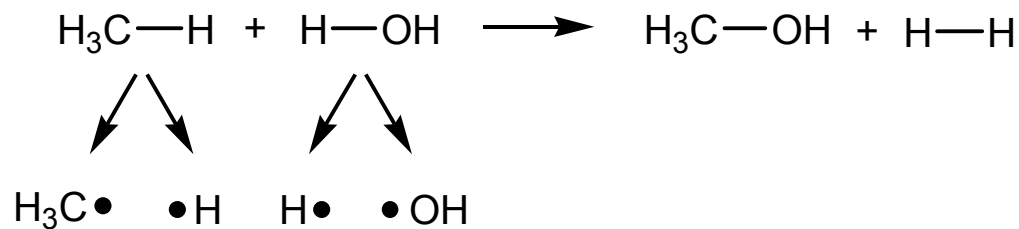


# Thermodynamics “On the Fly”: Reaction Energetics from Standard Bond Dissociation Energies (BDEs)

*Concept:* So, to determine  $\Delta H$  for entire reaction, sum up  $\Delta H$  values (BDEs) for all bonds broken and made.

Don't need to know mechanism to do this; just look at bonds.

*Example:* Oxidation of methane to methanol (to convert gas to liquid fuel).



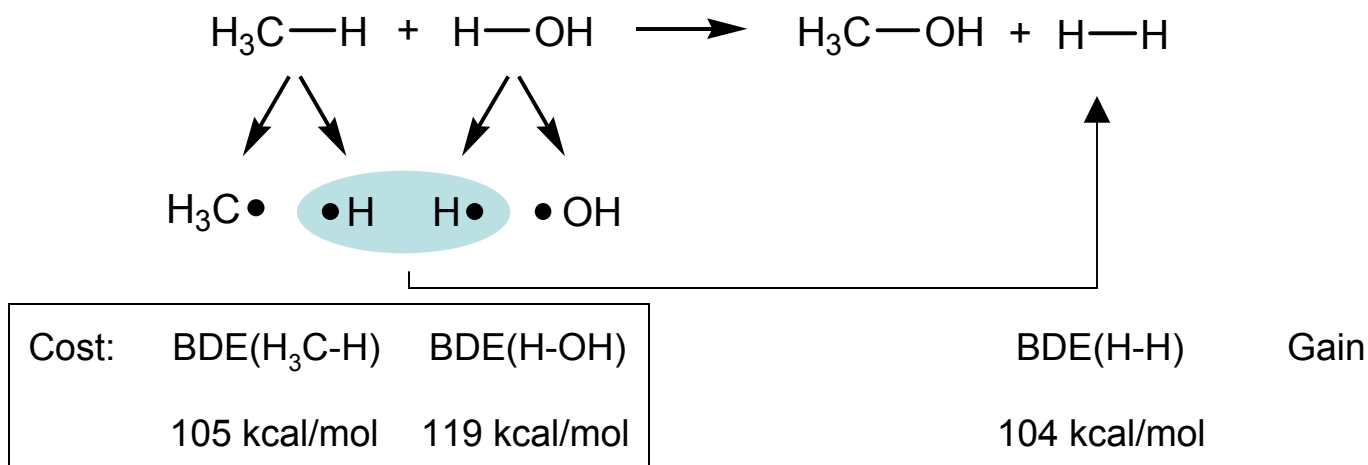
Cost:    BDE(H<sub>3</sub>C-H)    BDE(H-OH)  
          105 kcal/mol    119 kcal/mol

# Thermodynamics “On the Fly”: Reaction Energetics from Standard Bond Dissociation Energies (BDEs)

*Concept:*  $\Delta H$  for reaction can be estimated from types of bonds that are created and broken in reaction.

Don't need to know mechanism to do this; just look at bonds.

*Example:* Oxidation of methane to methanol (to convert gas to liquid fuel).

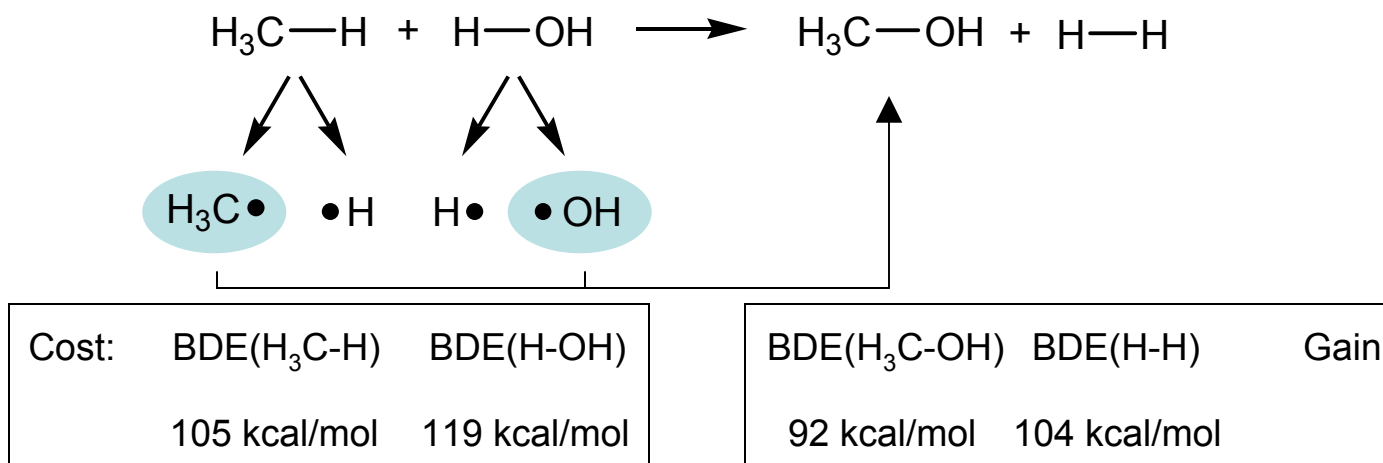


# Thermodynamics “On the Fly”: Reaction Energetics from Standard Bond Dissociation Energies (BDEs)

*Concept:*  $\Delta H$  for reaction can be estimated from types of bonds that are created and broken in reaction.

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*Example:* Oxidation of methane to methanol (to convert gas to liquid fuel).

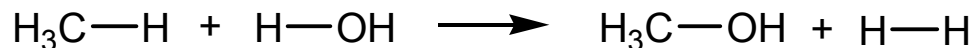


# Thermodynamics “On the Fly”: Reaction Energetics from Standard Bond Dissociation Energies (BDEs)

*Concept:*  $\Delta H$  for reaction can be estimated from types of bonds that are created and broken in reaction.

Don't need to know mechanism to do this; just look at bonds.

*Example:* Oxidation of methane to methanol (to convert gas to liquid fuel).



Overall  $\Delta H = 105 + 119 - 92 - 104 = +28$  kcal/mol. (*Endothermic.*)

Cost:	BDE(H <sub>3</sub> C-H)	BDE(H-OH)
	105 kcal/mol	119 kcal/mol

BDE(H <sub>3</sub> C-OH)	BDE(H-H)	Gain
92 kcal/mol	104 kcal/mol	



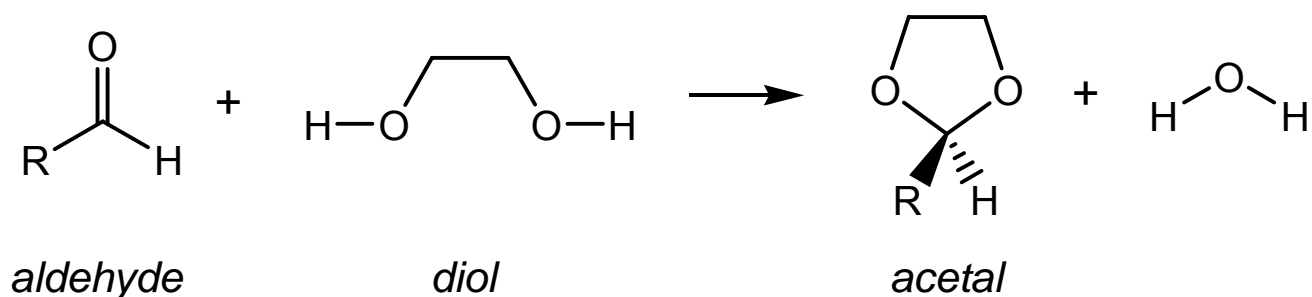
# Thermodynamics “On the Fly”: Reaction Energetics from Standard Bond Dissociation Energies (BDEs)

*Concept:*  $\Delta H$  for reaction can be estimated from types of bonds that are created and broken in reaction.

Don't need to know mechanism to do this; just look at bonds.

*Warning:* Using BDEs to calculate  $\Delta H_r$  works okay, but is not very accurate. Good enough for thermo “on the fly” though.

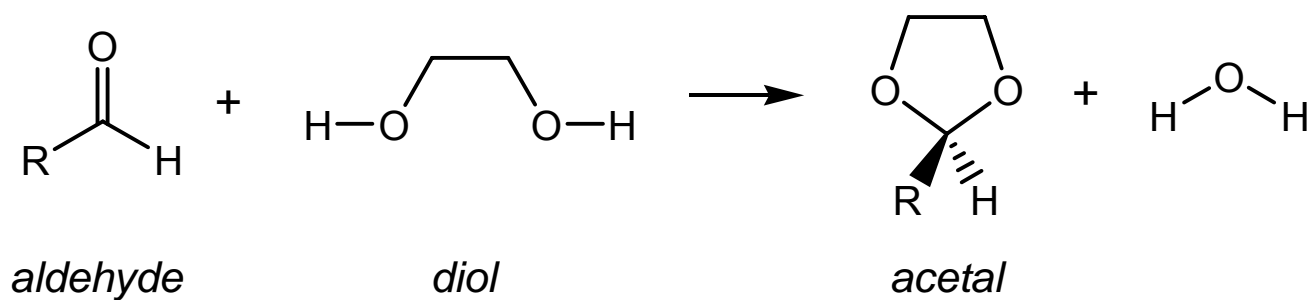
# Discussion Question



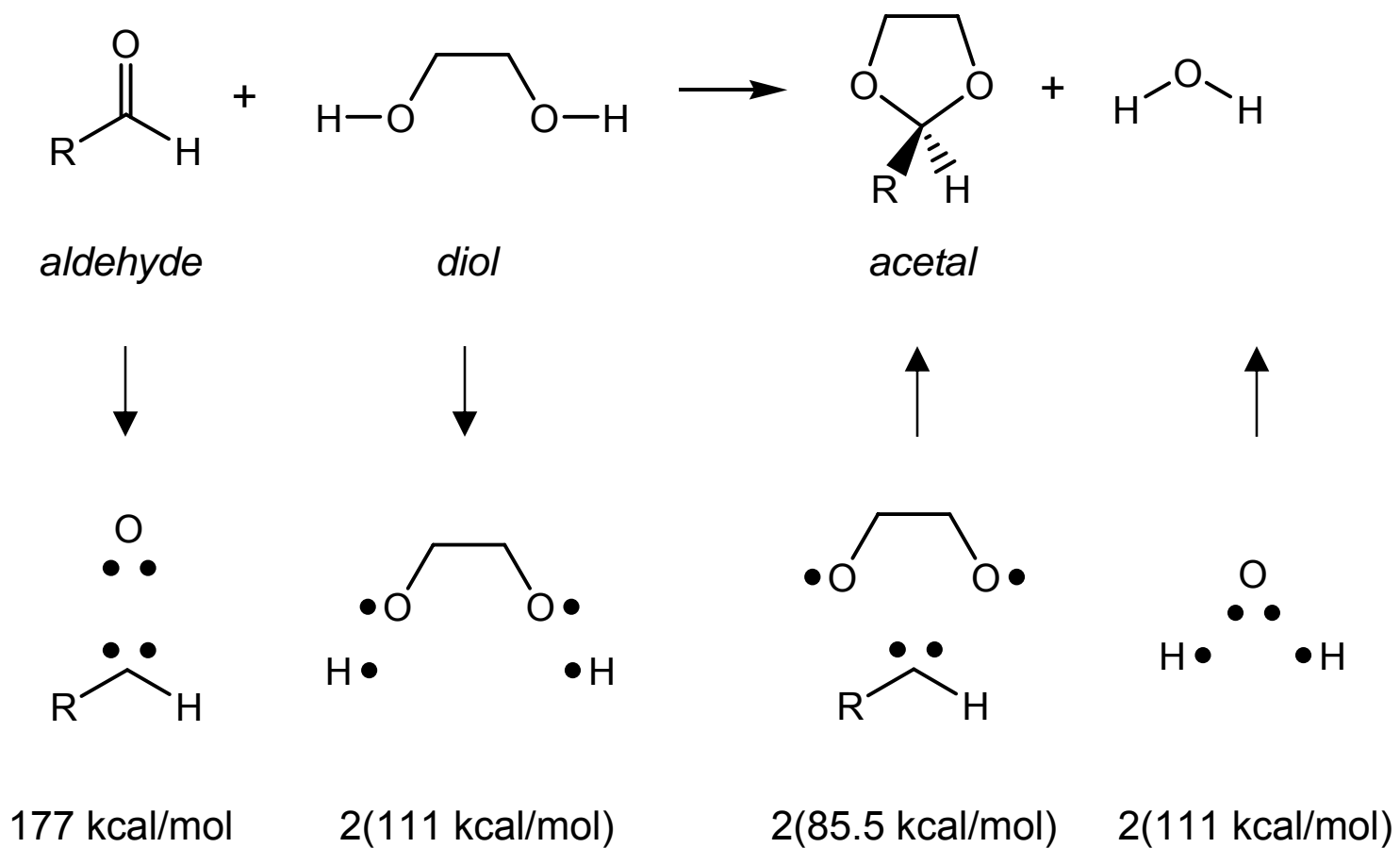
For the reaction above,

1. What bonds are made and broken?
2. What do the BDEs of these bonds mean for the overall  $\Delta H$  for this reaction?
3. If you wanted the reaction to proceed to 99% completion ( $[\text{acetal}]/[\text{aldehyde}] = 100$ ), what would the ratio  $[\text{H}_2\text{O}]/[\text{diol}]$  have to be? How might you pull/push this reaction to this degree of completion (if necessary)?

# Discussion Question

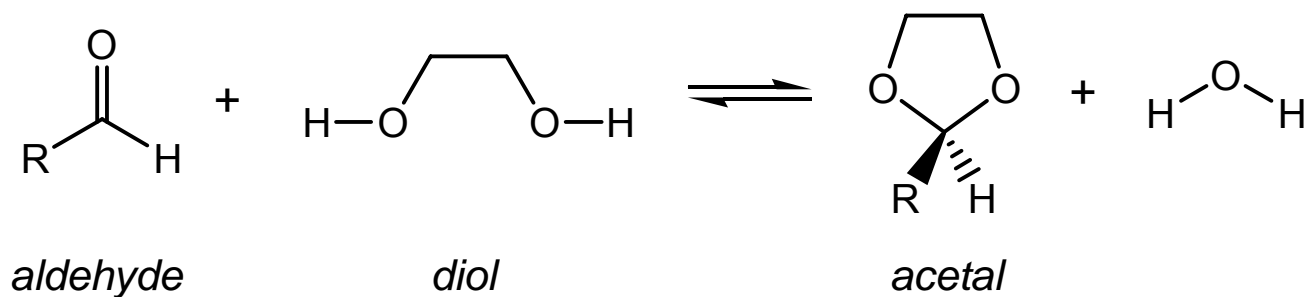


# Discussion Question



$$\Delta H_r = +6 \text{ kcal/mol}$$

# Discussion Question



$$\Delta H_r = +6 \text{ kcal/mol.}$$

Assuming  $\Delta S \approx 0$  (number of molecules is the same on both sides),

$$\Delta G_r = +6 \text{ kcal/mol.}$$

Our rule of thumb says that this means  $K_{\text{eq}} = \frac{[\text{acetal}][\text{H}_2\text{O}]}{[\text{aldehyde}][\text{diol}]} \approx 0.0001.$

So, to reach  $\frac{[\text{acetal}]}{[\text{aldehyde}]} = 100,$   $\frac{[\text{H}_2\text{O}]}{[\text{diol}]}$  must  $\approx 1 \times 10^{-6}.$