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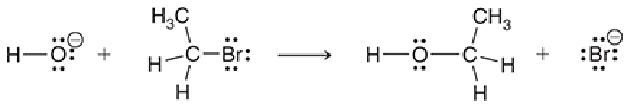
Chapter 6 Chemical Reactions, Curved Arrows & Carbocations

Some of these problems are from the Ch. 6 skeleton notes (page).

6.50 Consider the following reaction:

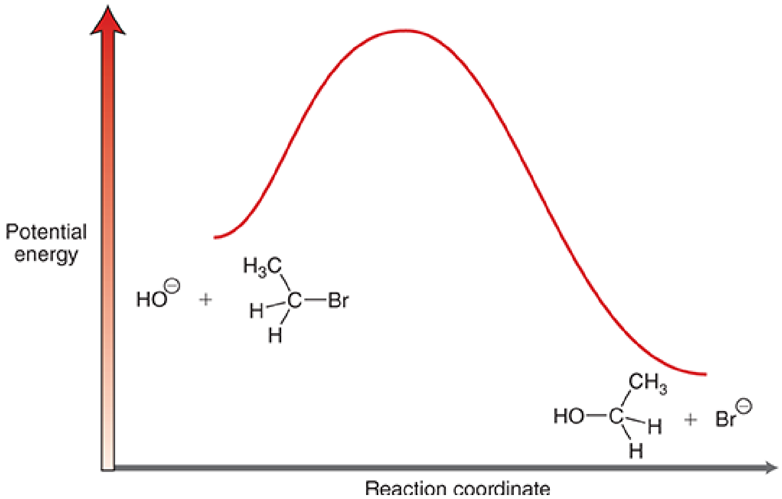
1



The following rate equation has been experimentally established for this process:

$$\text{Rate} = k[\text{HO}^-][\text{CH}_3\text{CH}_2\,\text{Br}]$$

An energy diagram for this process is shown below:



a. Identify the two characteristic arrow-pushing patterns that are required for this mechanism.

b. Would you expect this process to be exothermic or endothermic? Explain.

c. Would you expect ΔS_{sys} for this process to be positive, negative, or approximately zero?

d. Is ΔG for this process positive or negative?

e. Draw the transition state of this process and identify its location on the energy diagram.

f. Is the transition state closer in structure to the reactants or products? Explain.

g. Is the reaction first order or second order?

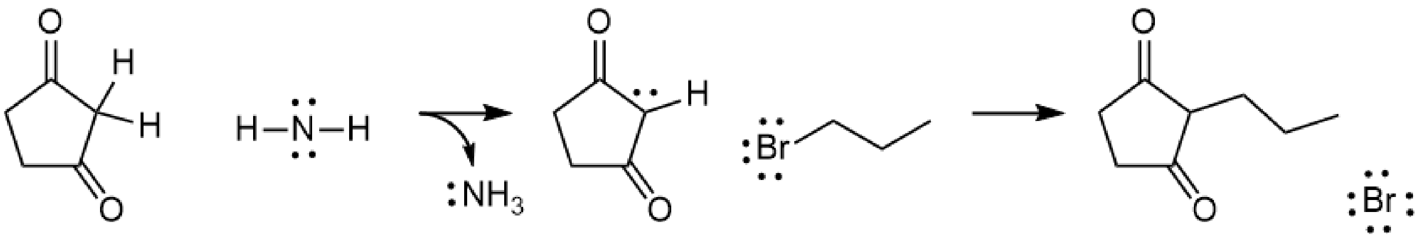
h. How will the rate be affected if the concentration of hydroxide is doubled?

i. Will the rate be affected by an increase in temperature?

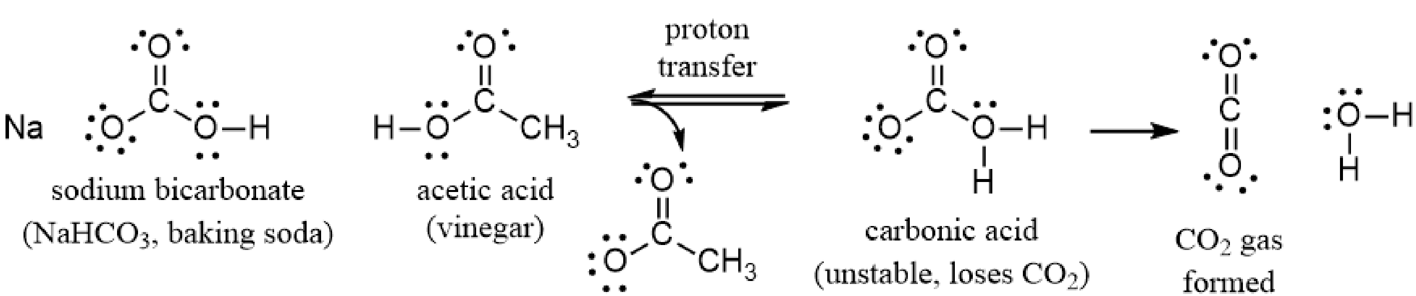
p.6-3 what happens to the rate of the above reaction of the amount of solvent is doubled?

a) it is 4x faster
b) it is twice as fast
c) no rate change
d) it is half the rate
e) it is 1/4 the rate

2 Add in any **missing formal charges**. **Draw curved arrows** for each step of the following mechanisms, and **describe each step** (e.g., proton transfer, loss of a leaving group, nucleophilic attack).



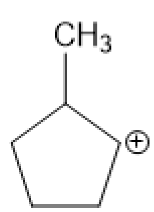
homemade "volcano" or chemistry experiment in a bag (www.youtube.com/ChemistryConnected)



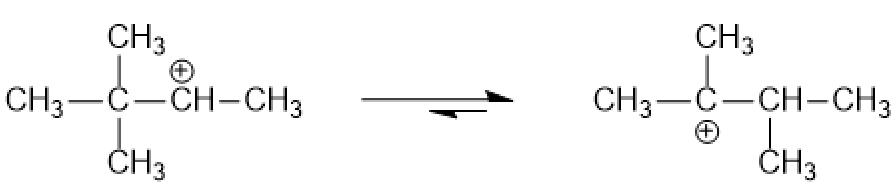
3 **B) Carbocation rearrangements (6.11)** p.6-6

It is possible for neighboring groups to "shift" over to the positively charged carbon, if the relocated positive charge ends up in a more favorable position.

Hydride shift:

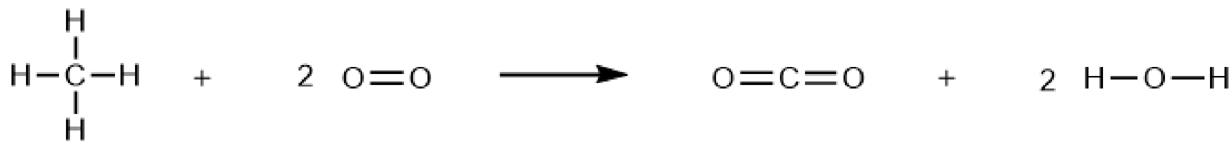


Methyl shift:



4 Group work: Estimate ΔH_{rxn} for the following reaction. Is it exothermic or endothermic?

p.6-3



Bonds broken:
(kcal/mol)

Bonds formed:
(kcal/mol)

Which best describes the process of BREAKING a sigma bond?

A) It always releases Energy (exothermic).

B) It always consumes Energy (endothermic).

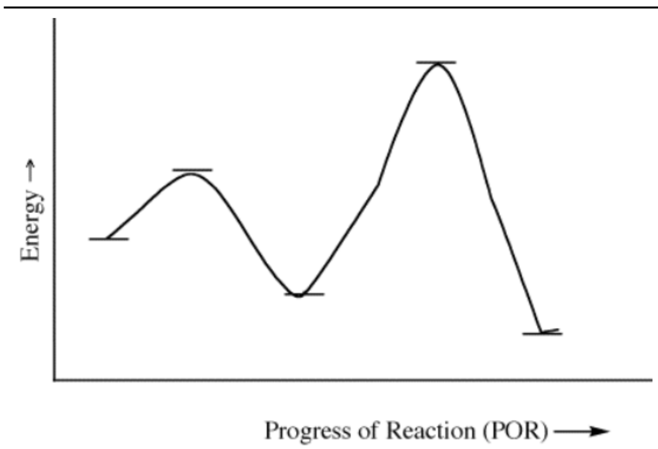
C) It can be exothermic or endothermic, depending on the bond involved.

ΔH° for Single Bonds (kcal/mol)

	H	C	N	O	F	Cl	Br	I	Si
H	104	99	93	111	135	103	87	71	76
C		83	73	86	116	81	68	52	72
N			39	53	65	46			
O				47	45	52	48	56	108
F					37				135
Cl						58			91
Br							46		74
I								36	56
Si									53

ΔH° for Multiple Bonds (kcal/mol)

C=C	C=N	O=O	C=O	C=O	C=O	C≡C	C≡N
146	147	119	176 aldehydes	179 ketones	192 CO_2	200	213



describe the reaction mechanism shown

A) Endothermic, with **two** transition states and **two** intermediates

B) Endothermic, with **two** transition states and **one** intermediate

C) Endothermic, with **one** transition state and **two** intermediates

D) Exothermic, with **two** transition states and **one** intermediate

E) Exothermic, with **one** transition state and **two** intermediates