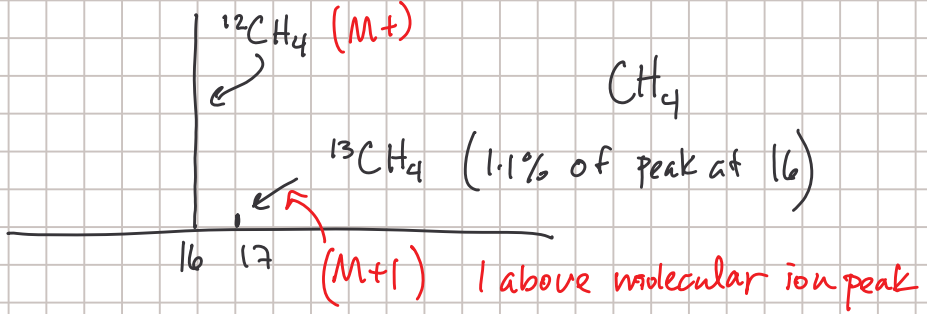
Ch 12

Note Title 10/18/2005

Heavier isotope peaks

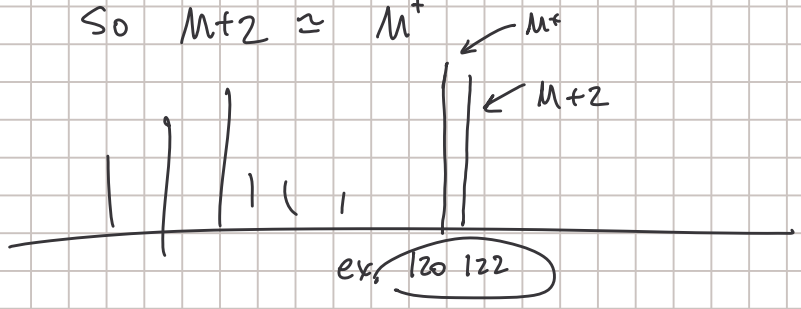
natural carbon mostly ^{12}C, 1.1% ^{13}C



recognizable isotope patterns:

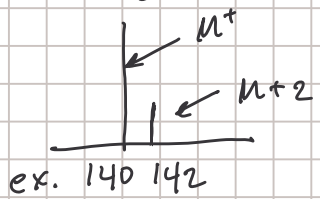
Br: ^{79}Br 50.5% / ^{81}Br 49.5%

So $M+2 \simeq M^+$



Cl: ^{35}Cl = 75.5% / ^{37}Cl = 24.5%

so $M+2 \simeq 1/3$ of M^+



S: M+2 4% of M^+

Other recognizable elements:

I = 127 amu = I^+ and 127 amu gap

CH_3I $M^+ = 142$

$I^+ = 127$

CH_3CH_2I — 156 amu

$M^+ = 156$ → molecular ion

$I^+ = 127$

127 amu gap

$CH_3CH_2^+ = 29$

N look for odd #'d M^+ (1 N or odd # nitrogens)

C, H, O compounds have even MW

$CH_4 = 16$ amu

$NH_3 = 17$ amu

CH_3NH_2 12 1S 29 **31**

Fragmentation

ionization process

$R:R' + e^- \longrightarrow [R \cdot R']^{+\cdot} + 2e^-$

original compound

the molecular ion, M^+

radical cation

missing 1 e^-

only charged particles are detected

radical cation $[R \overset{\curvearrowright}{\cdot} R']^{+\cdot}$ → $R^{\oplus}$ + $\cdot R'$

M^+

$R^{\oplus}$: cation — detected by MS

$\cdot R'$: radical — not detected

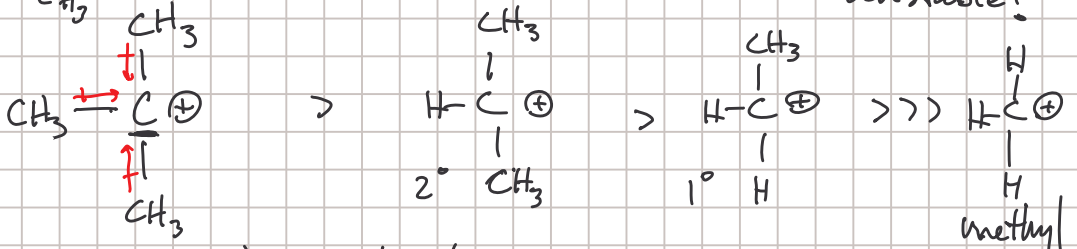
Fragmentation tends to occur to give the most stable cation

(stabilities of cations same as stabilities of radicals)

$3^\circ > 2^\circ > 1^\circ \ggg CH_3^+$

($CH_3-\dot{C}(CH_3)_2$ 3° radical)

methyl cations are horribly unstable!

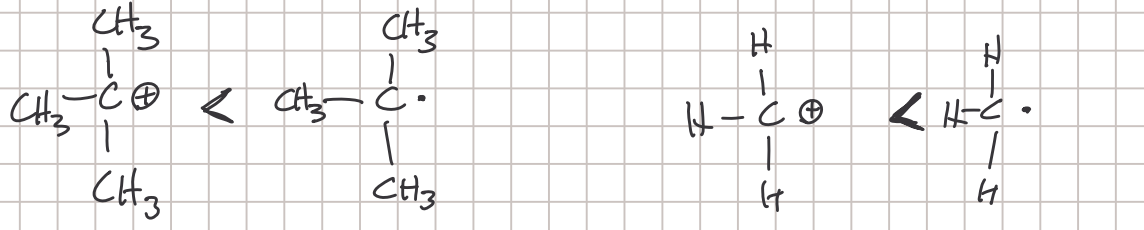


3° C's can donate e^- dens to C⊕

Carbocation = ⊕ on carbon

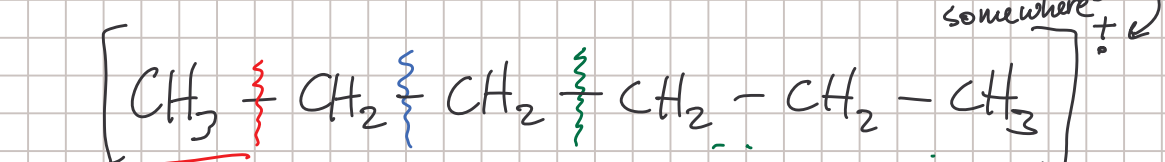
Overall carbocations are less stable than radicals

(more e^- missing)



less stable — more stable

less — more stable



hexane

$M^+ = 86$ amu

$CH_3\cdot$ + $^{\oplus}CH_2-(CH_2)_2-CH_3$ peak = 71

radical — not detected

cation — detected

$CH_3^{\oplus}$ cation + $\cdot CH_2-(CH_2)_3-CH_3$ radical

not detected

not detected

b/c CH_3^+ is not stable

not obs.

$CH_3CH_2\cdot$ + $^{\oplus}CH_2CH_2CH_2CH_3$ → obs. at 57 amu

$CH_3CH_2^{\oplus}$ + $\cdot CH_2CH_2CH_2CH_3$

not obs.

↓

obs at 29 amu

$CH_3CH_2CH_2\cdot$ + $^{\oplus}CH_2CH_2CH_3$

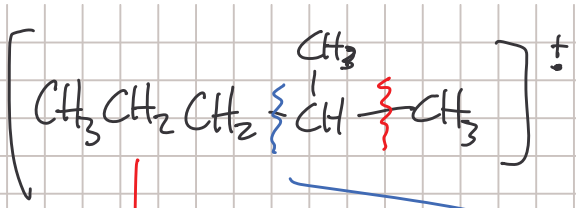
not obs obs at 43 amu

all peaks

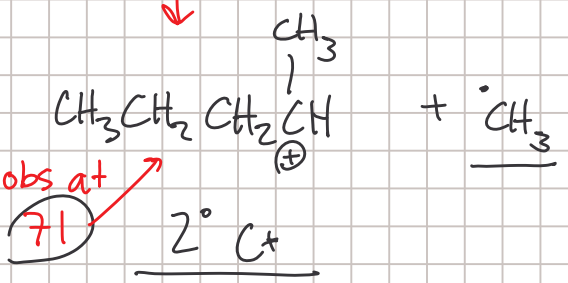
86	M^+
71	$M^+ - CH_3$
57	$M^+ - CH_2CH_3$
43	$M^+ - CH_2CH_2CH_3$ $(= {}^{\oplus}CH_2CH_2CH_3)$
29	$CH_3CH_2^+$

29 43 57 71 86

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

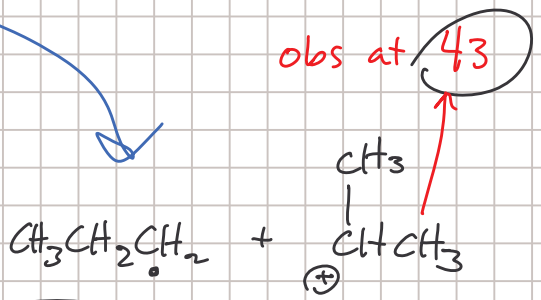


$M^+ = 86$



obs at 71

2° C+



obs at 43

2° C+

all other fragmentations give 1° C+

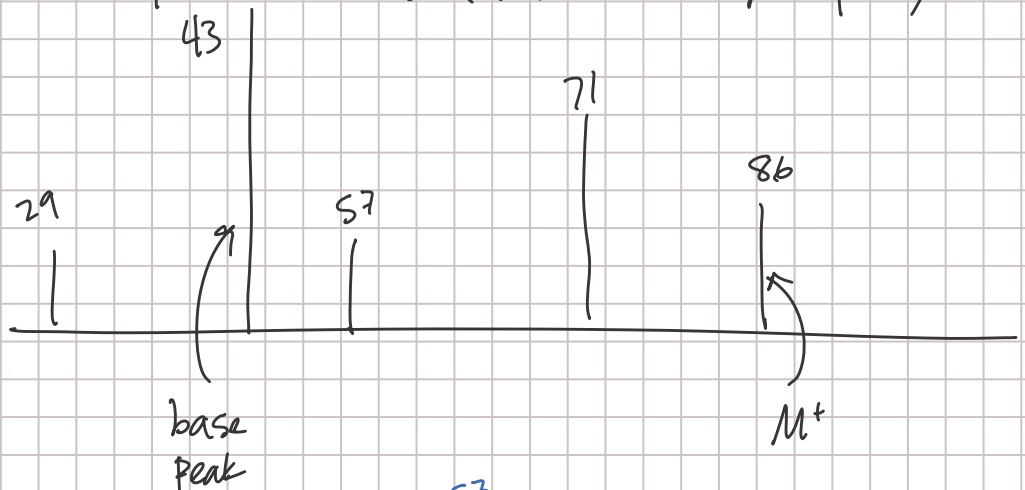
stable carbocations form strong peaks

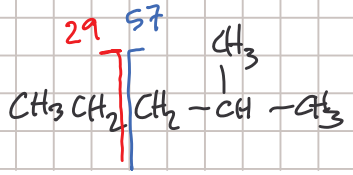
(propyl radical is more stable than $\cdot CH_3$

this fragmentation is preferred over other b/c both C+ similar stability, C• is more stable

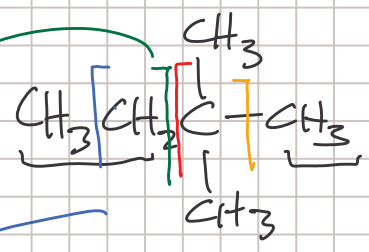
the base peak

peak w/ highest abundance (tallest/strongest peak)





- M^+ peak usu not strongest
- Base peak comes from most stable fragmentation (look at C+ stability first, then C• stability)
- All other C+'s will be observed on spec. except CH_3^+ (too unstable)



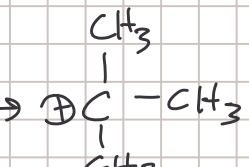
- predict all peaks
- ident. base peak

C_6H_{14}

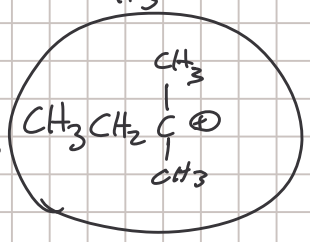
$72 + 14 = 86 = M^+$

$86 - 15 = 71$

$CH_3CH_2^+ = 29$

red = $86 - 29 = 57 \rightarrow$ 

orange = $86 - 15 = 71$



red = base peak