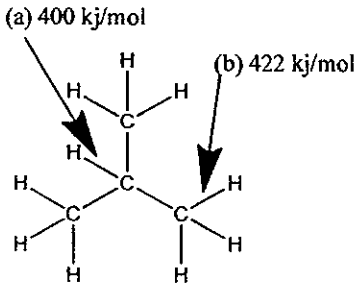
CHE 256 Phillips
Quiz 2, August 26, 2009 – **QUIZ IS DUE IN CLASS ON FRIDAY**

Name (print clearly) Key

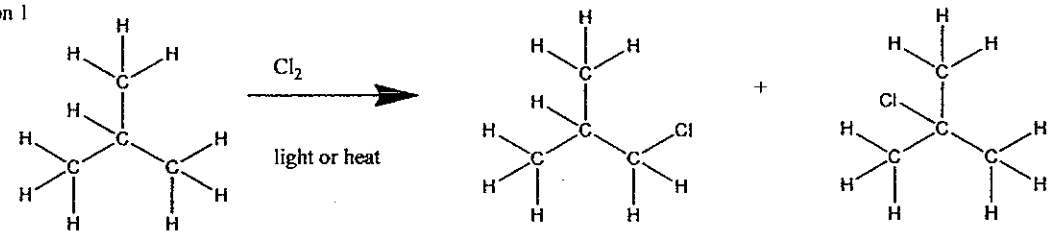
This quiz is designed to probe your understanding of the new topics presented in Chapter 10, as well as point out any areas where you need to review old material. Use your own paper, write your name on each sheet of paper, and attach to this sheet using staples.

1. (5 points) Two C-H bonds are labeled in the following structure of isobutane, (a) and (b), along with their corresponding homolytic bond dissociation energies (BDE).
   a. Using clearly drawn structures and the proper use of arrows to show electron flow, provide the radicals that are produced from the homolytic bond cleavage reactions of C-H bonds (a) and (b)
   b. Offer an explanation for the differences in BDE of the two C-H bonds (a) and (b)
   c. What is the hybridization of the carbon bearing the radical center?
   d. Does the radical have tetrahedral, pyramidal, or planar geometry?



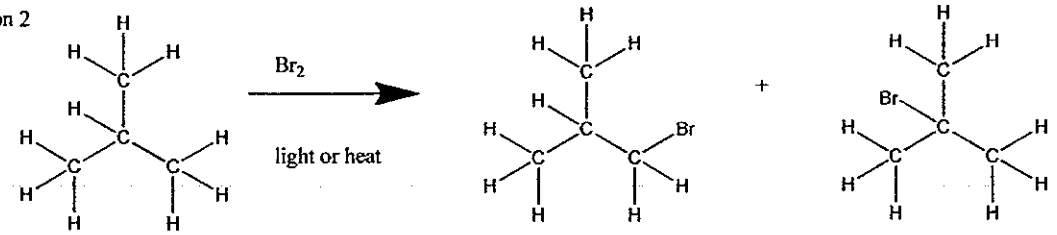
2. (5 points) Offer an explanation for the differences in product distributions resulting from the free radical halogenation reactions of isobutane with Cl_2 and Br_2. Full credit will require the use of an energy diagram and the Hammond-Leffler postulate. (For a quick review of the Hammond-Leffler postulate, see figure 6.10 on page 243)

Reaction 1



(48%) (29%)

Reaction 2

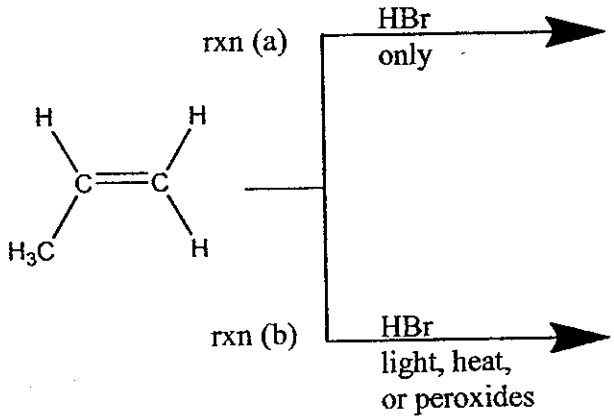


(<1%) (>99%)

3. (5 points) Radical halogenation reactions proceed through a chain reaction including initiation, propagation, and termination steps. Provide a VALID example of an initiation, propagation, and termination reaction specifically involved in the radical chlorination of isobutane.

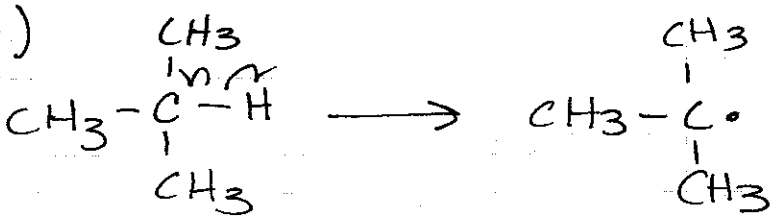
4. (5 points) Draw all the potential mono-chlorinated products, including stereoisomers, produced in the free radical chlorination of pentane. Clearly label all stereogenic centers and denote as R or S configuration (draw stereoisomers in wedge-and-dash form to show stereochemistry – for a quick review on how to determine absolute stereochemistry, see Section 5.7 beginning on page 190).

5. (5 points) Provide the products from the following reactions (a) and (b) and indicate in each case whether the addition has occurred in a Markovnikov or anti-Markovnikov fashion (for a review of polar addition reactions of alkenes and Markovnikov's rule, see section 8.2 beginning on page 314).

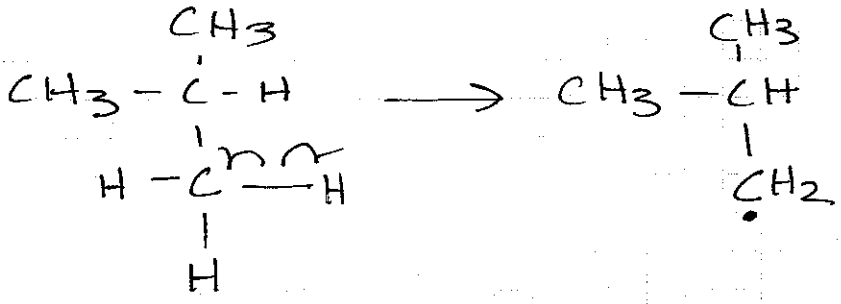


Quiz 2

1(a)

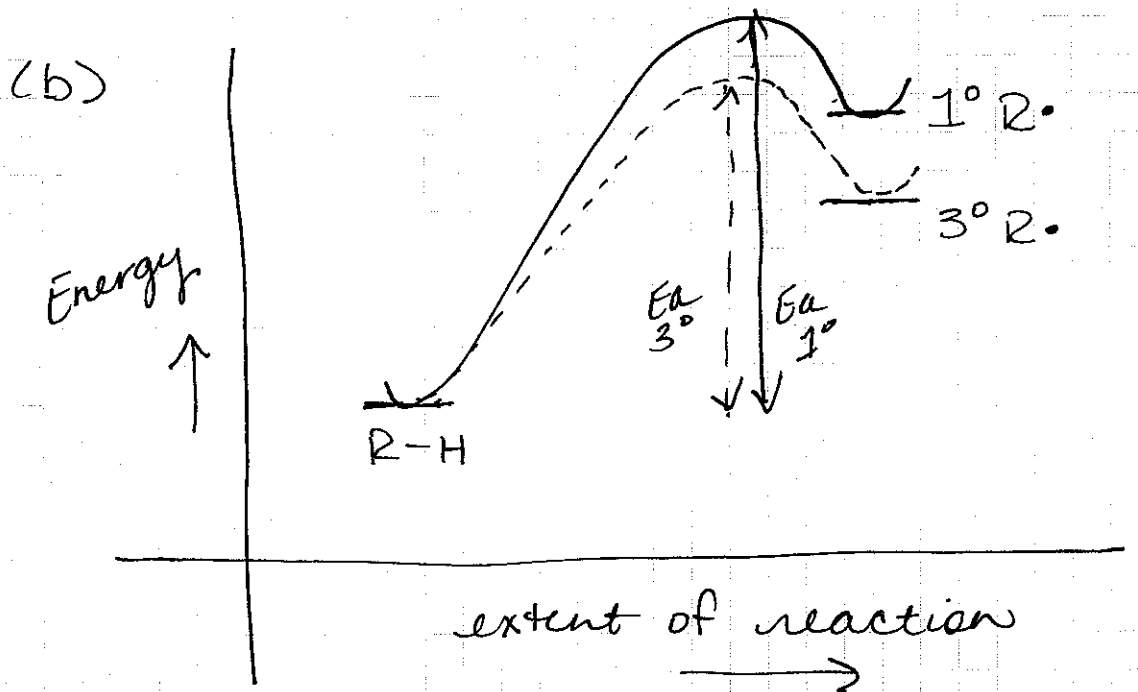


Structure (a) bond gives 3° radical



Structure (b) bond gives 1° radical

(b)



3° Radicals are more stable because of the R groups ability to donate electron density via induction and hyperconjugation more R groups = more stable for both cations and radicals (electron-deficient centers)

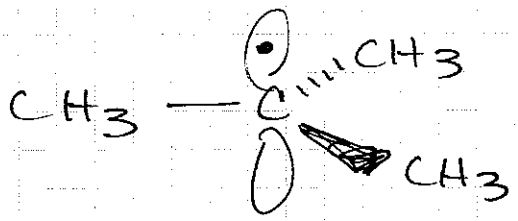
Because 3°R· are more stable than 1°R· less energy is required for their formation. Revisit Hammond postulate.

Ea 3° < Ea 1°

(a) 3° more stable < energy

sp^2 planar

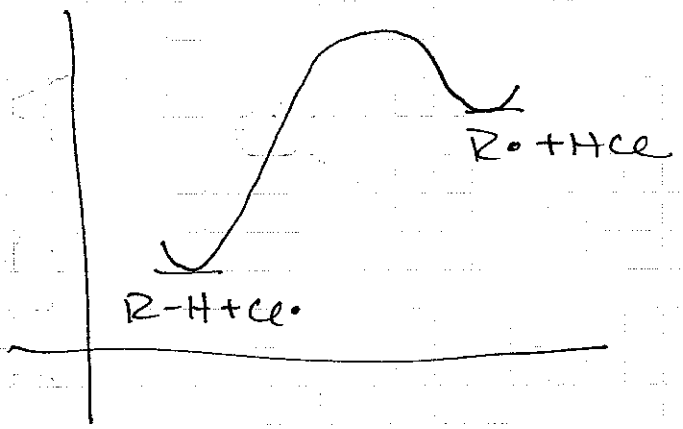
1(c) hybridization of radical center is sp^2



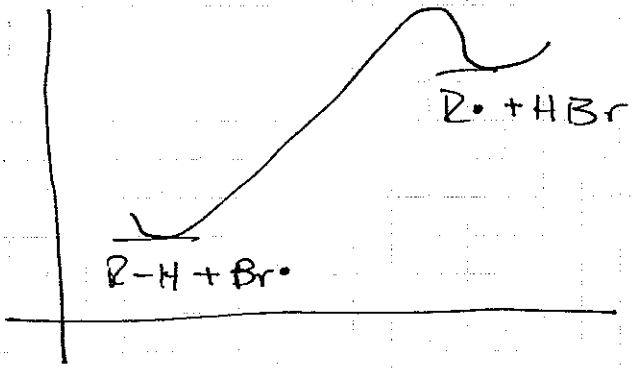
(d) geometry is planar
(specifically trigonal planar)

Quiz 2

2.



chlorination has earlier transition state more reactive and less selective than bromin.



bromination has later transition state so structure of forming radical is more important. Stability of radical produced is reflected in T.S. less reactive and more selective than chlorin radical.

3. $Cl-Cl \xrightarrow{h\nu} 2\,Cl\bullet$ initiation

$Cl\bullet + R-H \longrightarrow R\bullet + HCl$

$R\bullet + Cl-Cl \longrightarrow R-Cl + Cl\bullet$

} propogation

$Cl\bullet + R\bullet \longrightarrow R-Cl$

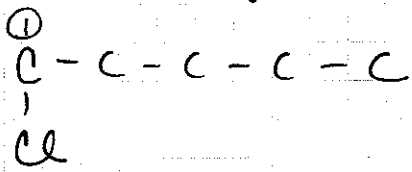
$Cl\bullet + Cl\bullet \longrightarrow Cl-Cl$

$R\bullet + R\bullet \longrightarrow R-R$

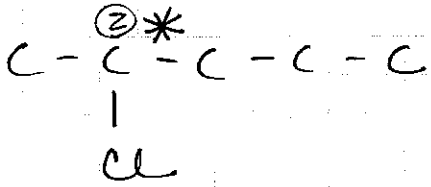
} termination

4. ①C–②C–③C–④C–⑤C pentane

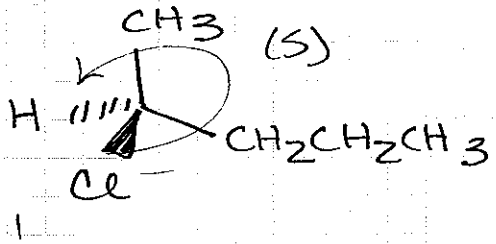
$h\nu \downarrow Cl_2$

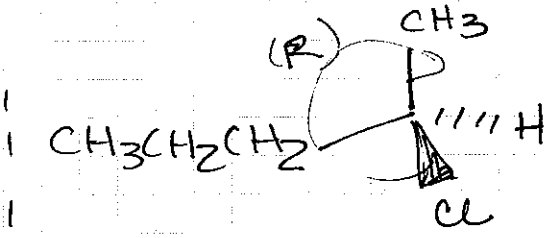


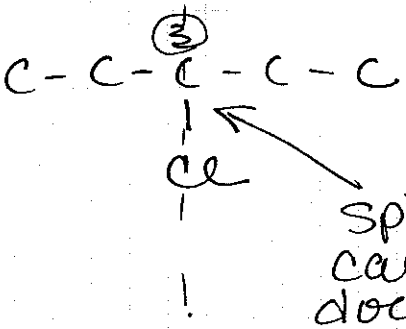
① same as chlorination at ⑤
1 product



② same as chlorination at ④ produces a stereogenic center
2 products (R) & (S)





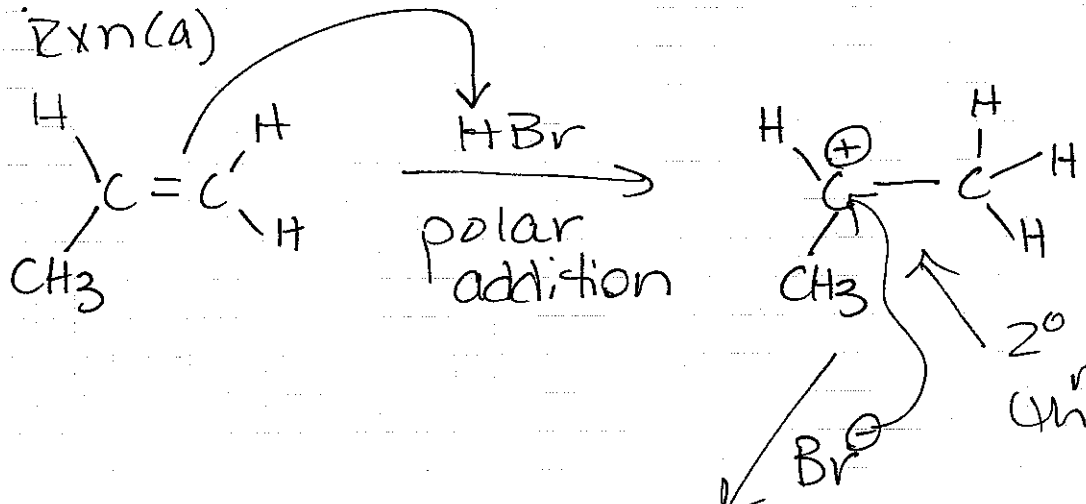


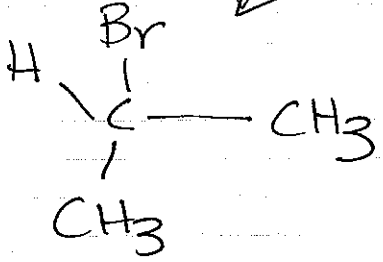
③ molecule has mirror plane and no stereogenic center
1 product, no stereoisomers

4 total products.

5.

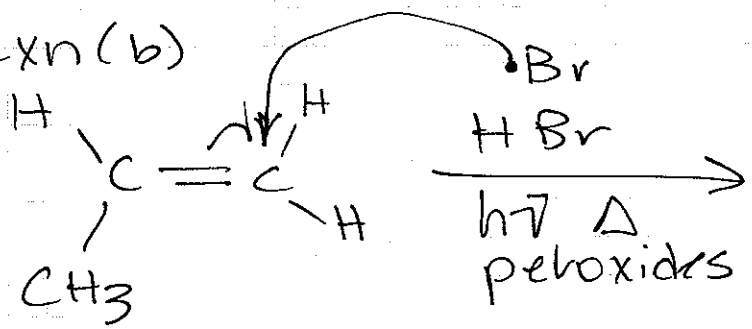
Rxn(a)

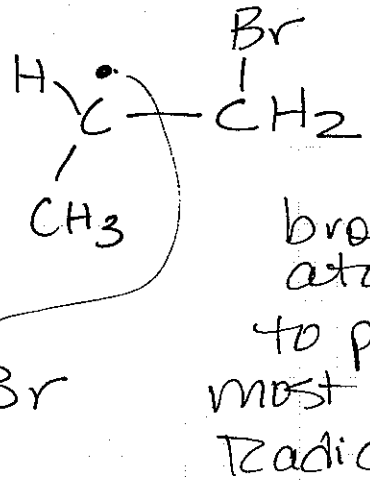




Bromine goes to most substituted carbon 3D markovnikov addition

Rxn(b)





bromine atom adds to produce most stable radical followed by •H abstraction

$CH_3CH_2-CH_2Br$

anti-markovnikov