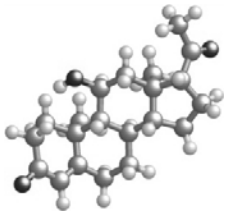

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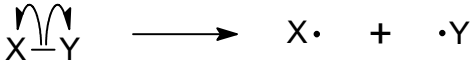
Date: …… **/** …… **/** ……

Homolytic Bond Fission and Free Radical Reactions

The cracking of a long chain alkane to form a short chain alkane and an alkene (and possibly hydrogen) requires the breaking or *fission* of a carbon-to-carbon single covalent bond. The fission of a covalent bond can be either *homolytic* or *heterolytic*.

• During *homolytic bond fission*, the shared pair of electrons that constitute the single covalent bond are shared evenly between the two atoms as the bond breaks. One electron is retained in the valence shell of one atom while the second electron is retained in the valence shell of the other atom. The products of this type of bond fission are *radicals*. A radical is an atom or a molecule which contains a *single unpaired electron* in its valence shell. The reaction sequence below shows homolytic bond fission. The half-headed arrow ( ) represents the movement of a single electron and the dot (·) represents a single unpaired electron:



Question 1.

What do the terms *homo* and *lysis* mean? Why is this type of bond breaking called *homolytic*?

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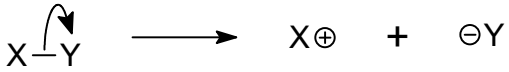
• During *heterolytic bond fission*, the shared pair of electrons that constitute the single covalent bond are *not* shared evenly between the two atoms as the bond breaks. Both electrons are retained in the valence shell of one atom, which becomes a negatively charged ion as a result. The other atom which has lost an electron becomes a positively charged ion.

The reaction sequence below shows heterolytic bond fission. The curved arrow ( ) represents the movement of a pair of electrons:



Question 2.

What do the terms *hetero* and *lysis* mean? Why is this type of bond breaking called *heterolytic*?

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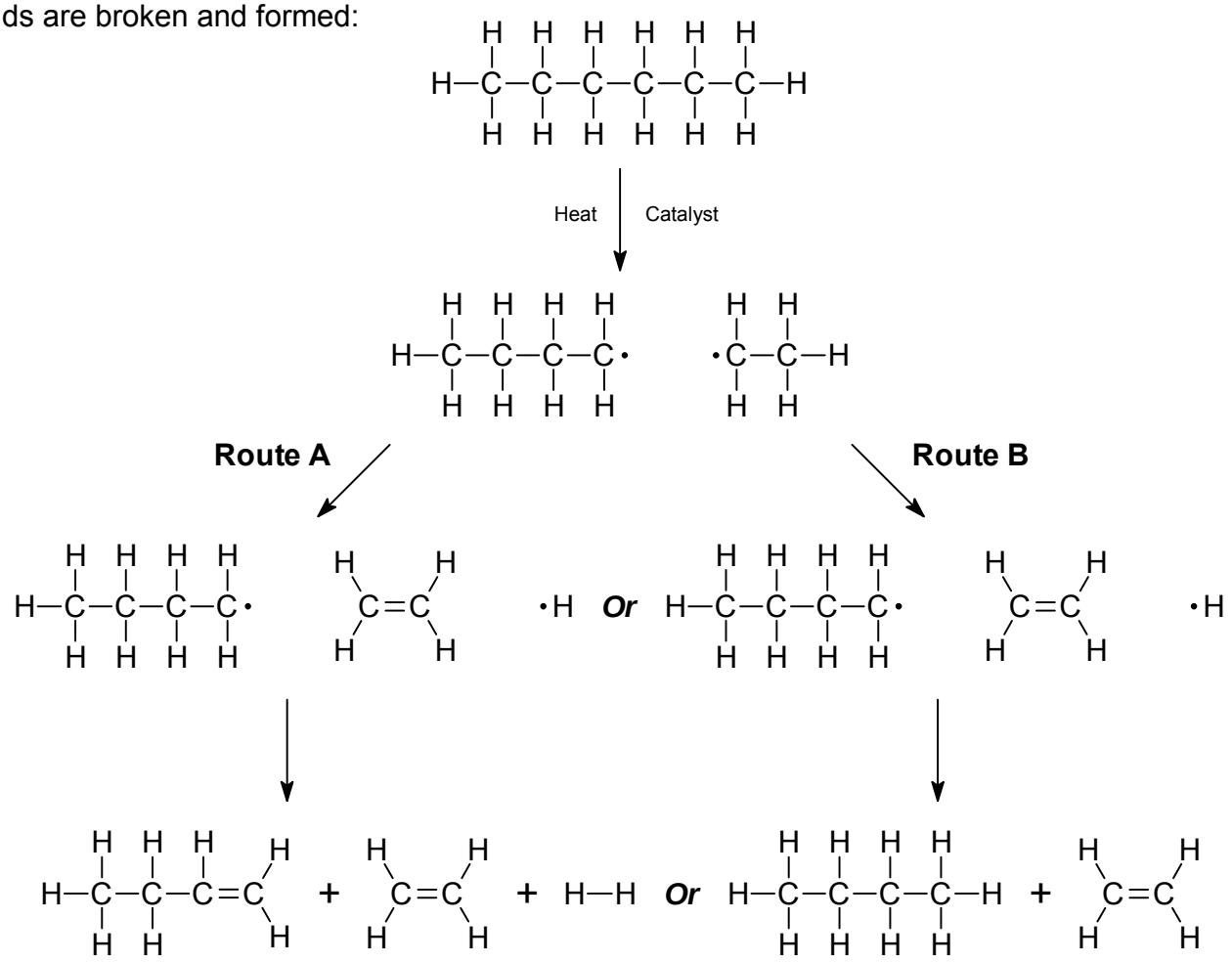
……...

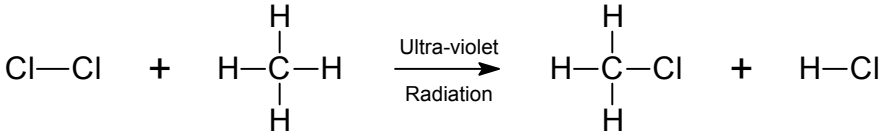
Question 3.

The diagram below shows the free radical reaction mechanism by which an alkane is cracked to form a smaller alkane and an alkene. Using half-headed arrows ( ) to represent the movement of single electrons, complete the reaction mechanism below to show how the various covalent bonds are broken and formed:



Question 4.

Chlorine (Cl_2) and methane (CH_4) react together in the presence of ultra-violet radiation to form chloromethane (CH_3Cl) and hydrogen chloride (HCl):



The reaction starts with *homolytic fission* of the chlorine-to-chlorine covalent bond. Write out the full mechanism for this reaction and explain why it can be described as a *chain-reaction*. Continue to write the reaction mechanism to show how dichloromethane (CH_2Cl_2), trichloromethane ($CHCl_3$) and tetrachloromethane (CCl_4) can also be formed as reaction products in the presence of excess chlorine.