IB Chemistry: Electrophilic Addition to Alkenes

Topic 10: Organic Chemistry

Name: Answer Key **Date:**

Learning Objectives

By completing this worksheet, you should be able to:
- Draw detailed mechanisms for electrophilic addition reactions
- Apply Markovnikov's rule to predict major products
- Explain carbocation stability using the positive inductive effect
- Distinguish between major and minor products based on mechanism

Common Mistakes to Avoid:

1. Drawing arrows from the wrong place (they should start from bonds or lone pairs)
2. Forgetting to show the intermediate carbocation
3. Not showing formal charges on ions and carbocations
4. Confusing the electrophile (it's the H atom in HX, not the halogen)
5. Forgetting that Markovnikov's rule doesn't apply to symmetrical alkenes

Marking Criteria Reminder:

- Curly arrows must start from electron-rich regions (bonds or lone pairs)
- Partial charges (δ+ and δ−) should be shown where relevant
- Formal charges (+, −) must be shown on all ions and intermediates
- Two-step mechanism must be clearly shown
- Correct structural formulas with all atoms and bonds visible

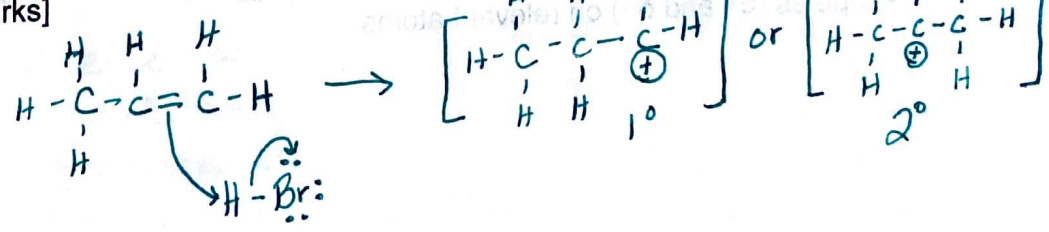
Section 1: Markovnikov's Rule and Carbocation Stability

Key Concepts: Markovnikov's rule states that in the addition of HX to an unsymmetrical alkene, the hydrogen atom bonds to the carbon with the greater number of hydrogen atoms already attached, while the halogen bonds to the carbon with fewer hydrogen atoms. This occurs because the reaction proceeds through the more stable carbocation intermediate.

Carbocation stability order: tertiary (3°) > secondary (2°) > primary (1°) > methyl

1. **Consider the reaction of propene ($CH_3CH=CH_2$) with hydrogen bromide (HBr).**

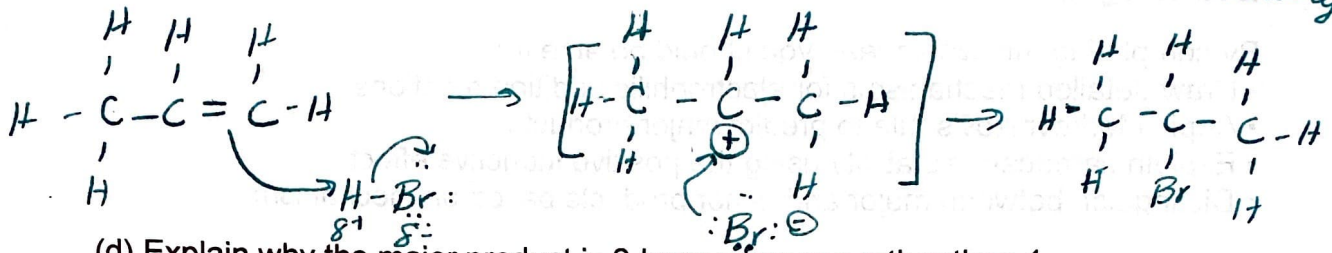
   (a) Draw the structure of the two possible carbocation intermediates that could form in the first step of this reaction. Label each as primary (1°) or secondary (2°). [2 marks]



(b) State which carbocation intermediate is more stable and explain your answer using the concept of the positive inductive effect. [3 marks]

The 2° carbocation is more stable. Alkyl groups have a positive inductive effect (more electron donating). The carbons attached to the carbocation can share electron density, partially neutralizing the positive charge.

(c) Draw the complete mechanism for the formation of the major product, showing all curly arrows, relevant dipoles, and formal charges. [4 marks]

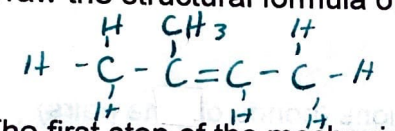


(d) Explain why the major product is 2-bromopropane rather than 1-bromopropane, with reference to Markovnikov's rule. [2 marks]

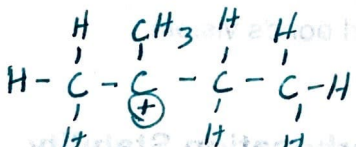
The 2° carbocation intermediate predominates due to its greater stability. Markovnikov's rule states the more substituted carbon will be more stable when forming an intermediate due to the positive inductive effect.

2. **2-Methylbut-2-ene reacts with hydrogen chloride.**

(e) Draw the structural formula of 2-methylbut-2-ene. [1 mark]



(f) The first step of the mechanism involves the formation of a carbocation. Draw the structure of this carbocation and state whether it is primary, secondary, or tertiary. [2 marks]



(g) Explain why a tertiary carbocation is more stable than a secondary carbocation. Your answer should include reference to the positive inductive effect. [3 marks]

A 3° carbocation has 3 other alkyl groups attached, which means it is able to have positive inductive effects (electron-donating) from 3 sources, adding extra carbocation stability compared to a 2° carbocation (2 sources of inductive effect).

Section 2: Drawing Complete Mechanisms

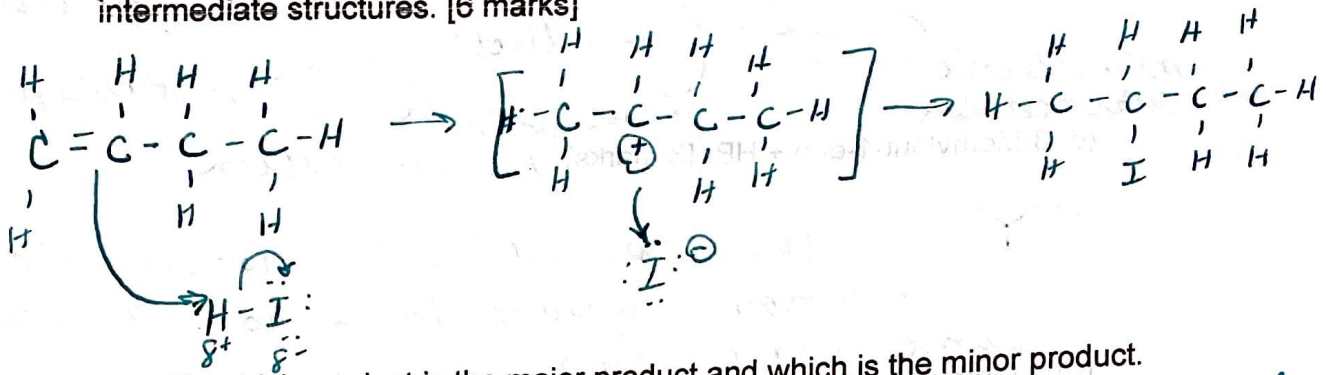
Remember: In a complete mechanism you must show:

- All curly arrows starting from electron-rich areas
- Dipoles (δ+ and δ−) on relevant atoms

- Formal charges on intermediates and ions
- Intermediate carbocation structure
- Both steps of the mechanism

3. **But-1-ene reacts with hydrogen iodide to form two products.**

(h) Draw a fully annotated mechanism for the reaction showing the formation of both possible products. Include all curly arrows, dipoles, formal charges, and intermediate structures. [6 marks]



(i) Identify which product is the major product and which is the minor product. Justify your answer. [2 marks]

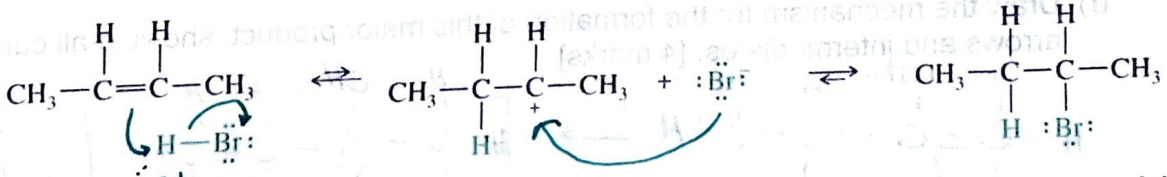
major : 2-iodobutane → formed from more stable 2° carbocation

minor : 1-iodobutane → formed from less stable 1° carbocation

(j) State the approximate percentage yield you would expect for the major product. [1 mark]

~ 90%.

4. **The mechanism for the electrophilic addition of HBr to but-2-ene is shown below:**



electrophile

(k) Add curly arrows to show the movement of electron pairs in both steps of the mechanism. [2 marks]

(l) Identify and label the electrophile in this reaction. [1 mark]

H atom in HBr

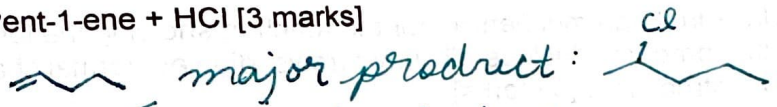
(m) Explain why but-2-ene produces only one product in this reaction, whereas but-1-ene produces two products. [2 marks]

but-2-ene is symmetrical, so the same 2° carbocation intermediate is formed no matter which side of the double bond loses e⁻ density. In but-1-ene, it is not symmetrical, so produces both 1° & 2° carbocation intermediate

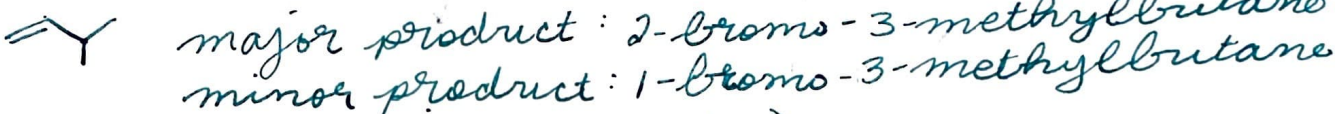
Section 3: Predicting Major and Minor Products

5. **Predict the major and minor products for each of the following reactions. Draw the structural formulas and explain your reasoning in each case.**

(n) Pent-1-ene + HCl [3 marks]



(o) 3-Methylbut-1-ene + HBr [3 marks]



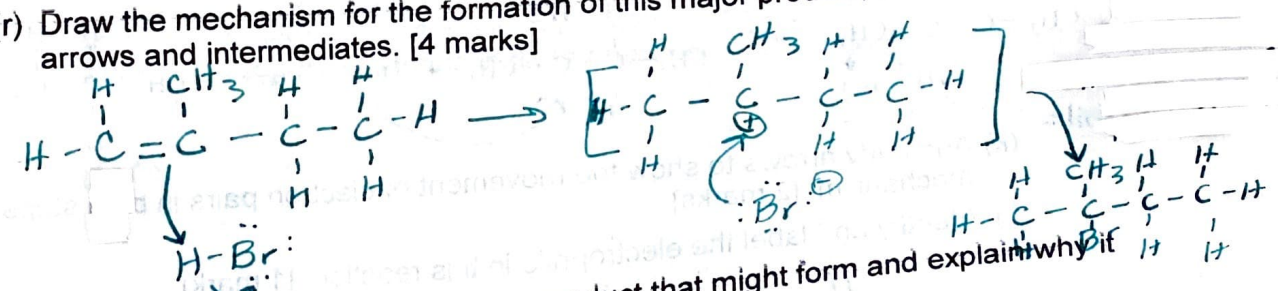
(p) 2-Methylpropene + HI [2 marks]

6. **An unknown alkene with the molecular formula C_5H_{10} reacts with HBr to form 2-bromo-2-methylbutane as the major product.**

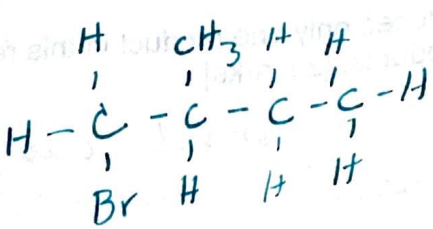
(q) Deduce the structure of the unknown alkene and draw its structural formula. [2 marks]

another possibility:

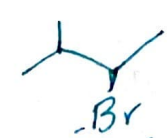
(r) Draw the mechanism for the formation of this major product, showing all curly arrows and intermediates. [4 marks]



(s) Suggest the structure of any minor product that might form and explain why it forms in smaller amounts. [3 marks]



1-bromo-2-methylbutane but realistically wouldn't form due to the much greater stability of the 3° carbocation intermediate



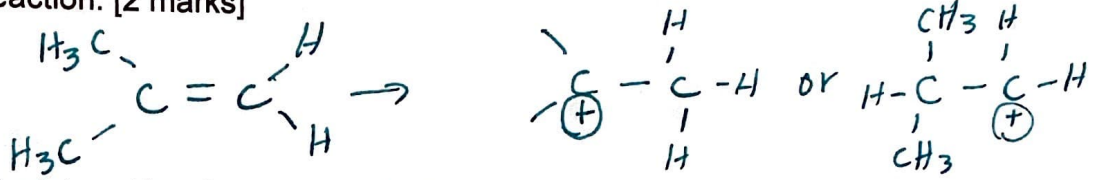
minor product that could form

Section 4: Application and Higher Level Analysis

7. **Consider the following reaction:**

$(CH_3)_2C=CH_2 + HBr \rightarrow$ *Product A (major) + Product B (minor)*

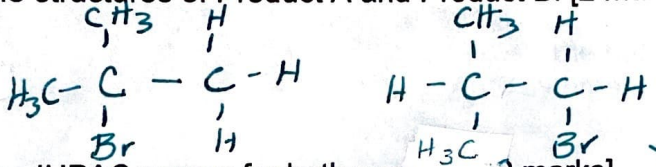
(t) Draw the structures of both carbocation intermediates that could form in this reaction. [2 marks]



(u) Explain, with reference to inductive effects, which carbocation is more stable. [3 marks]

3° carbocation → same reasoning as 2(g)

(v) Draw the structures of Product A and Product B. [2 marks]



(w) State the IUPAC names for both products. [2 marks]

2-Bromo-1-methylpropane

1-Bromo-2-methylpropane