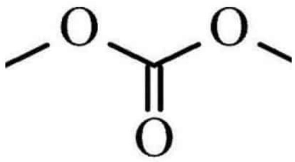
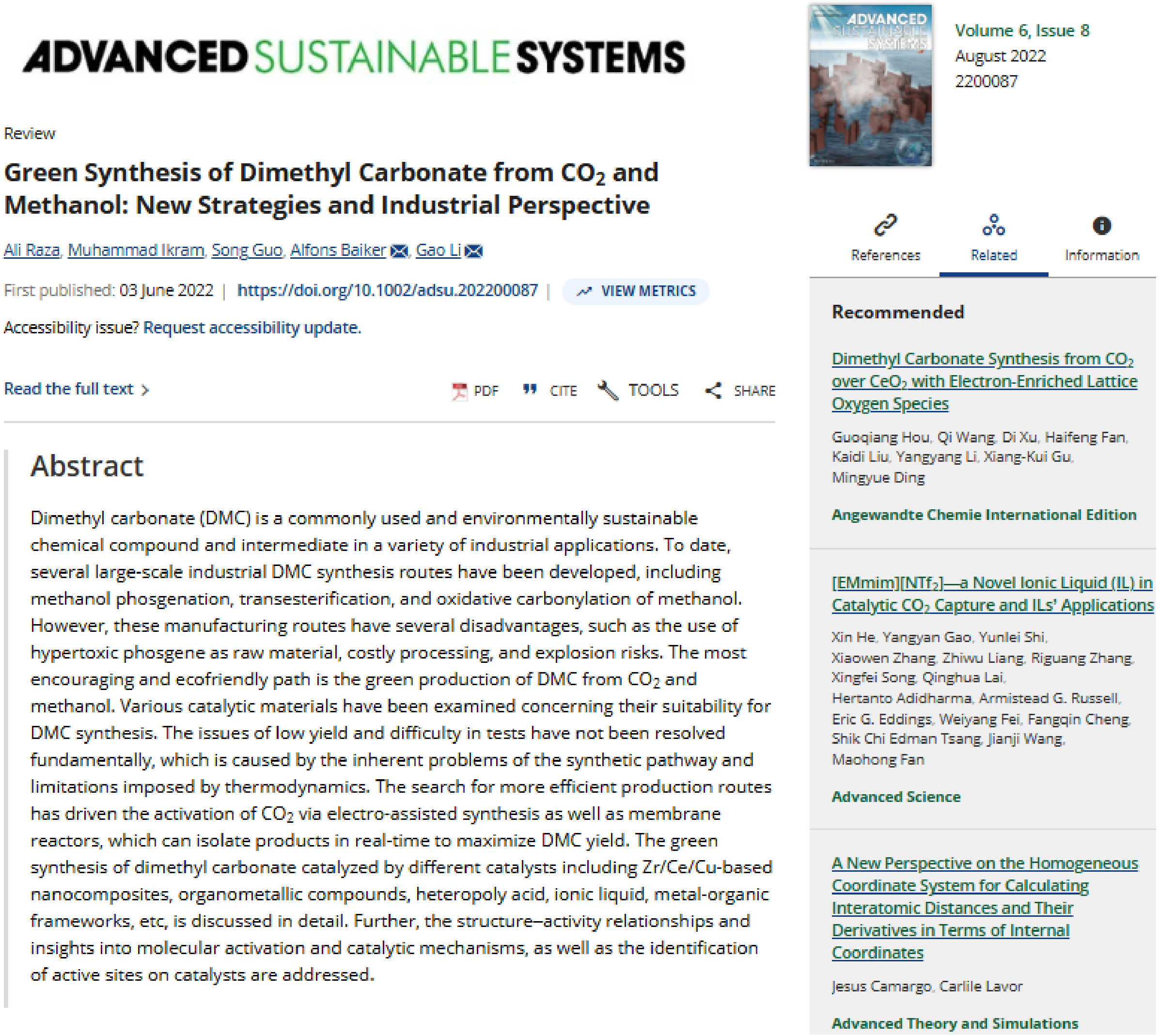
Solutions

Revision for Unit 4 AOS 1 outcome 1 – media article

Dimethyl carbonate (DMC) is an important, versatile and environmentally friendly chemical used in various chemical industries. Below are some products made using dimethyl carbonate.



1. **Polycarbonates -** DMC is a building block in manufacturing polycarbonate plastics, which are used in electronic components, automotive parts, eyewear lenses, and construction materials.
2. **Pharmaceuticals -**It is involved in synthesizing intermediates and active pharmaceutical ingredients (APIs).
3. **Agrochemicals -** DMC helps produce herbicides, insecticides, and fungicides.
4. **Paints and Coatings -** As a solvent and chemical intermediate, it helps manufacture environmentally friendly paints and coatings.
5. **Lithium-Ion Batteries -** Electrolyte solutions using DMC improve battery efficiency in mobile devices and electric vehicles.
6. **Fuel additive**- It serves as an oxygenate additive to improve combustion efficiency and reduce emissions in gasoline.



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Review

Green Synthesis of Dimethyl Carbonate from CO_2 and Methanol: New Strategies and Industrial Perspective

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Abstract

Dimethyl carbonate (DMC) is a commonly used and environmentally sustainable chemical compound and intermediate in a variety of industrial applications. To date, several large-scale industrial DMC synthesis routes have been developed, including methanol phosgenation, transesterification, and oxidative carbonylation of methanol. However, these manufacturing routes have several disadvantages, such as the use of hypertoxic phosgene as raw material, costly processing, and explosion risks. The most encouraging and ecofriendly path is the green production of DMC from CO_2 and methanol. Various catalytic materials have been examined concerning their suitability for DMC synthesis. The issues of low yield and difficulty in tests have not been resolved fundamentally, which is caused by the inherent problems of the synthetic pathway and limitations imposed by thermodynamics. The search for more efficient production routes has driven the activation of CO_2 via electro-assisted synthesis as well as membrane reactors, which can isolate products in real-time to maximize DMC yield. The green synthesis of dimethyl carbonate catalyzed by different catalysts including Zr/Ce/Cu-based nanocomposites, organometallic compounds, heteropoly acid, ionic liquid, metal-organic frameworks, etc, is discussed in detail. Further, the structure–activity relationships and insights into molecular activation and catalytic mechanisms, as well as the identification of active sites on catalysts are addressed.

References Related Information

Recommended

Dimethyl Carbonate Synthesis from CO_2 over CeO_2 with Electron-Enriched Lattice Oxygen Species

Guoqiang Hou, Qi Wang, Di Xu, Haifeng Fan, Kaidi Liu, Yangyang Li, Xiang-Kui Gu, Mingyue Ding

Angewandte Chemie International Edition

[EMmim][NTf_2]—a Novel Ionic Liquid (IL) in Catalytic CO_2 Capture and ILs' Applications

Xin He, Yangyan Gao, Yunlei Shi, Xiaowen Zhang, Zhiwu Liang, Riguang Zhang, Xingfei Song, Qinghua Lai, Hertanto Adidharma, Armistead G. Russell, Eric G. Eddings, Weiyang Fei, Fangqin Cheng, Shik Chi Edman Tsang, Jianji Wang, Maohong Fan

Advanced Science

A New Perspective on the Homogeneous Coordinate System for Calculating Interatomic Distances and Their Derivatives in Terms of Internal Coordinates

Jesus Camargo, Carlile Lavor

Advanced Theory and Simulations

Figure 1 – An abstract from a research paper on the green synthesis of dimethyl carbonate (DMC)

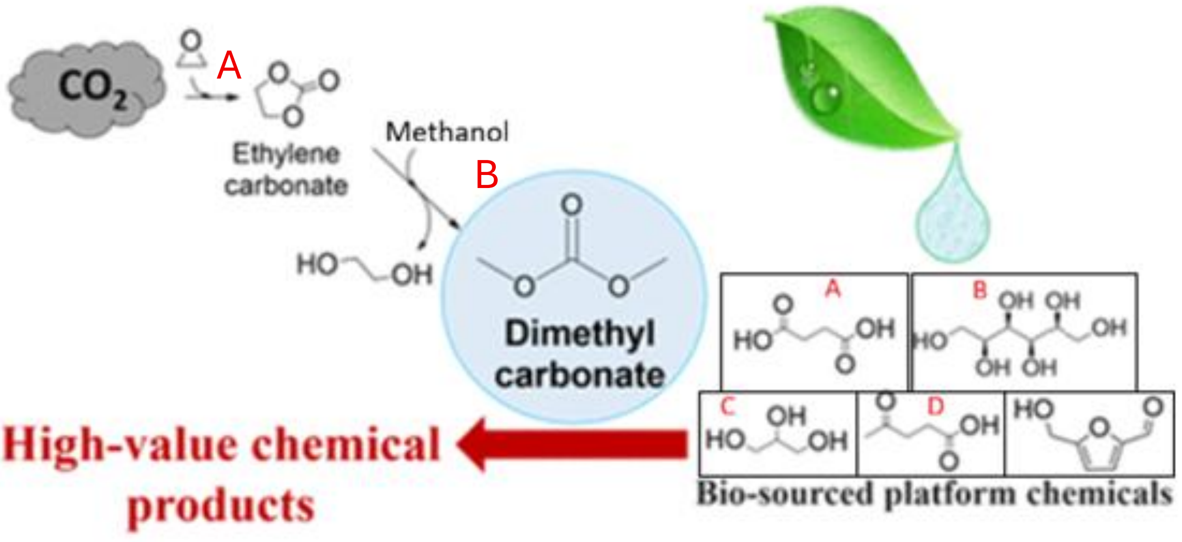


Figure 2 – A visual summary of the reaction to form DMC via CO_2 pathway and its use in the formation of other compounds

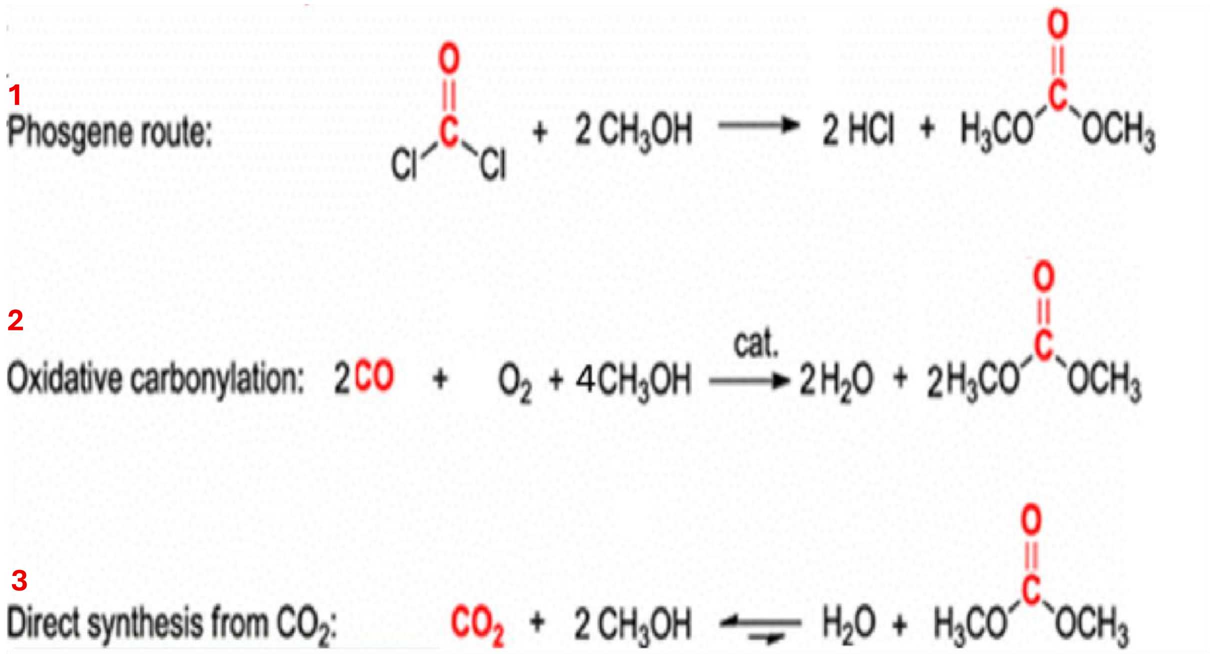


Figure 3 – Shows three chemical reactions forming DMC

Dimethyl carbonate (DMC) is a versatile, safe and environmentally friendly chemical widely used as a solvent, methylating agent, and intermediate in pharmaceutical and industrial synthesis. Its low toxicity and biodegradability make it an attractive alternative to more hazardous chemicals.

Currently, two main industrial processes produce DMC:

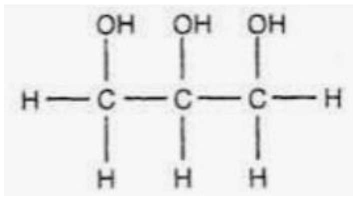
1. The phosgene reaction
2. The direct synthesis from carbon dioxide (CO_2)

The phosgene reaction involves the reaction of phosgene ($COCl_2$) with methanol (CH_3OH) to form DMC and hydrogen chloride (HCl) as a byproduct. Both phosgene and methanol are toxic, with phosgene infamously used as a chemical warfare agent during World War I. Handling phosgene requires stringent safety precautions, and the corrosive HCl byproduct necessitates careful neutralization and disposal. This method typically achieves high yields of around 90.0%.

Alternatively, the direct synthesis from CO_2 uses carbon dioxide, a greenhouse gas and methanol, along with catalysts, to produce DMC and water as a byproduct. While far less toxic than phosgene, carbon dioxide's chemical stability demands high pressure and temperatures, and innovative catalysts to achieve high rates and moderate yields.

Developing sustainable and safe production methods for DMC remains a central challenge, as industries seek to balance yield, safety, environmental impact, and economic viability in line with green chemistry principles. This method typically achieves low yields of around 50.0%.

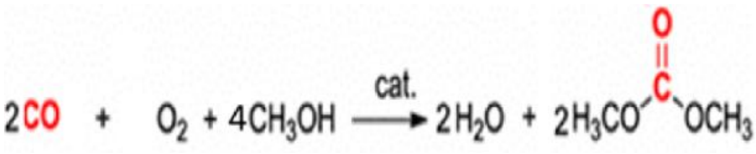
1. Consider fig. 2.
    a. Give the systematic name of the molecule labelled “C”
    propane-1,2,3-triol
    b. Draw the structural formula of compound C and give its molecular formula.



propane-1,2,3-triol

2. Consider fig. 3 reaction 2.

    a. Calculate the atom economy of reaction 2.



Working with a balanced chemical equation

%atom economy = (mass of desired product / mass of reactants) X 100
= (180 / 216) X 100 = 83.3%

    b. Under certain conditions reaction 2 has a %yield of 55%. Calculate the expected mass of DMC formed if 3.200 grams of methanol was placed in the rection vessel. Express your answer to the right number of significant figures.

Step 1 => convert
=> 3.200 /32.0 =0.100 mol
Step 2 => find mol of DMC
=> 0.0500
Step 3 Calculate the theoretical mass of DMC formed
=> 0.0500 X 90.0 X 0.55 = 2.5 grams (2 sig figs)

    c. Under totally different conditions 3.200 grams of methanol produced 3.587 grams of DMC. Calculate the %yield under these conditions.

Step 1 find he mol of methanol => 0.100
Step 2 find the mass of DMC produced => => 0.0500 X 90.0 = 4.50 grams
Step 3 find the %yield => (3.587 / 4.50) X 100 = 79.7%

d. What does the atom economy of reaction 2, as calculated in question 2 a, suggest about the reaction?

Any one of the following points

- *There is some waste generated, but it is relatively low compared to less efficient reactions.*
- *The reaction is relatively efficient in using the atoms of the reactants to form the desired product.*
- *From a green chemistry perspective, a higher atom economy (close to 100%) is preferable because it means less waste and better resource use.*
- *An atom economy of 83% is quite good, suggesting the process is reasonably sustainable but still has room for improvement.*

3. Figure 3 shows reaction 2 as a catalyst driven reaction.
   i. What green chemistry principle does using a catalyst in this reaction address?

      Any of the following
      - Catalysis

   ii. Discuss what the impact of a catalyst is on the reaction in regards to:

- *Temperature*
  The catalyst lowers the activation energy, allowing the reaction to proceed at a lower temperature or under milder conditions, which saves energy. This aligns with the green chemistry principles of energy efficiency and catalysis, reducing time and energy needed without changing the theoretical yield.
- *Yield*
  A catalyst does not affect the position of equilibrium in a reversible reaction, as in the production of DMC in reaction 2. This means it does not change the final yield of products when equilibrium is reached. Instead, a catalyst speeds up both the forward and reverse reactions equally, allowing the system to reach equilibrium more quickly.
- *Waste created*
  A catalyst can reduce waste by increasing reaction selectivity, minimizing unwanted by-products, and improving the overall efficiency.
- *Atom economy*
  The catalyst does <u>not affect atom economy</u>, because atom economy depends on the stoichiometry of the reaction, not on how fast or efficient it runs that depends on conditions.

4. A chemical reaction involves two reactant molecules combining to form a single product molecule, with no molecules lost or eliminated during the process.
    a. What class of reaction does this represent? Explain your answer, highlighting why the number of reactants and products matter in classifying this reaction.

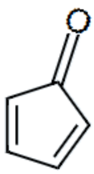
    Addition

    b. What is the atom economy of an addition reaction? Justify your answer.

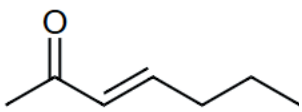
    100%. All the reactants are used up to form just one product.

5. Degree of unsaturation give an indication as to the structure of the molecule.

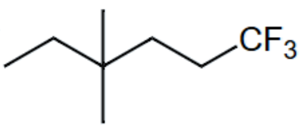
    a. Give the degree of unsaturation of molecules A, B, C and D shown below.



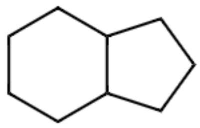
A



B



C

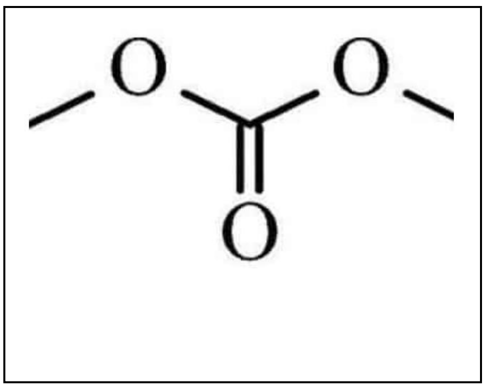


D

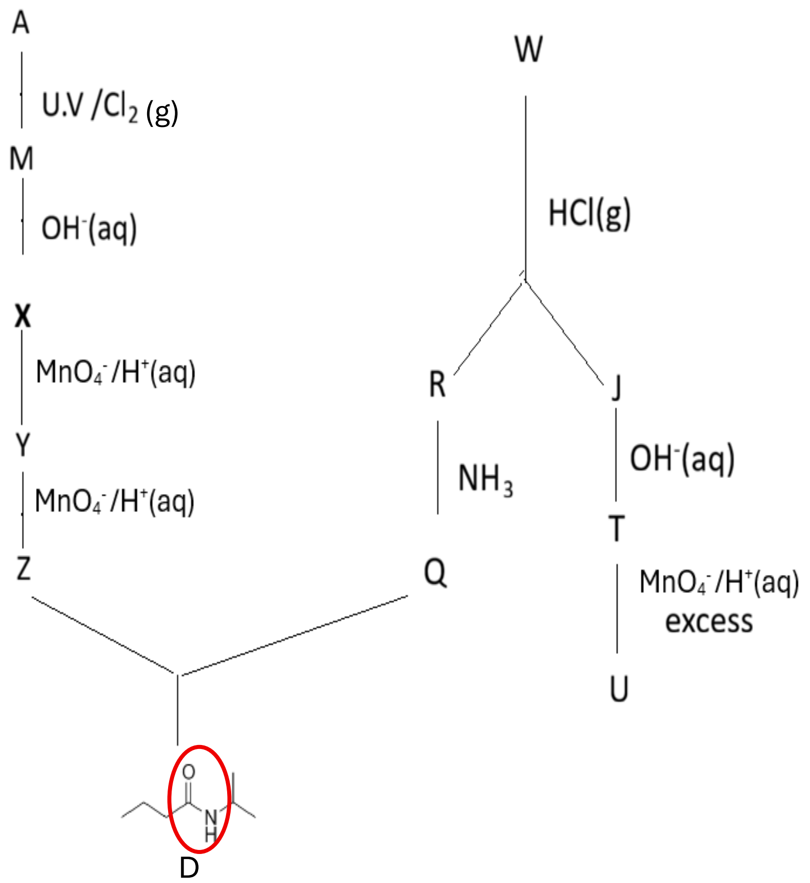
A = 4 - 2 C to C double bonds C=C, 1 C=O, and 1 ring structure
B = 2 – 1 C to C double bonds C=C, 1 C=O
C = 0
D = 2 – 2 ring structures

    b. What is the degree of unsaturation of DMC. Justify your answer.

1
it only contains a C=O group.



6. Consider the reaction pathway shown below.



Substance	Reaction with Br_2 water	Reaction with $Cr_2O_7^{2-}$	Reaction with blue litmus paper
W	Brown → clear	Remains orange	Remains blue
U	Remains brown	Remains purple	Turns red
Z	Remains brown	Remains purple	Turns red
A	Remains brown	Remains purple	Remains blue
T	Remains brown	Orange → green	Remains blue.

a. Name each compound in the table below

A	*Butane*
M	*1-chlorobutane*
X	*butan-1-ol*
Y	*Butanal*
Z	*Butanoic acid*
W	*Propene*
R	*2-chloropropane*
Q	*propan-2-amine*
J	*1-chloropropane*
T	*propan-1-ol*
U	*propanoic acid*

b. In the diagram above, circle and name the functional group of compound D.

amide

c. What general class of reaction forms compounds:

i. M ________________*substitution*____________________

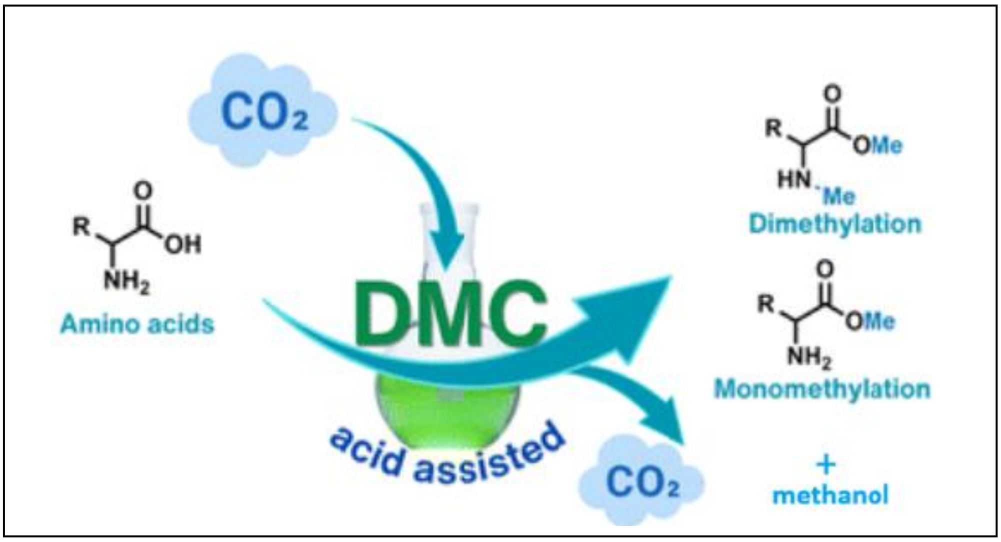
ii. R ________________ *addition* __________________________

iii. T __________________ *substitution* _____________________

iv. Z __________________ *oxidation* ________________________

v. D ________________ *condensation* _______________

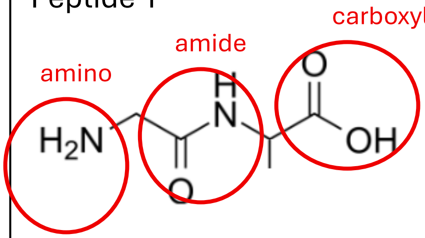
7. Dimethyl carbonate (DMC) is used for methylation in peptide synthesis because it is a mild, safe, and environmentally friendly methylating agent. Unlike traditional reagents such as diazomethane or methyl iodide, DMC has low toxicity and produces minimal hazardous waste, aligning with green chemistry principles. Its gentle reaction conditions help preserve the delicate structure and chirality of amino acids and peptides, minimizing the production of unwanted optical isomers and side reactions. Methylation itself is important in peptide synthesis because it protects reactive side chain groups, like carboxyl (–COOH) groups, from unwanted chemical reactions during the complex multistep synthesis process. By temporarily masking these functional groups, methylation improves the control, efficiency, and selectivity of peptide bond formation, ensuring the accurate assembly of biologically active peptides and enhancing stability and purity of the final product.



a. With reference to the 2026 data booklet:

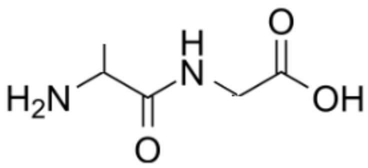
i. draw the <u>skeletal structure</u> of two possible dipeptides formed from the reaction between alanine and glycine, in the space provided below.

Peptide 1



Gly-ala

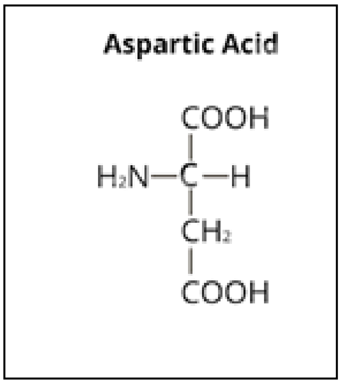
Peptide 2

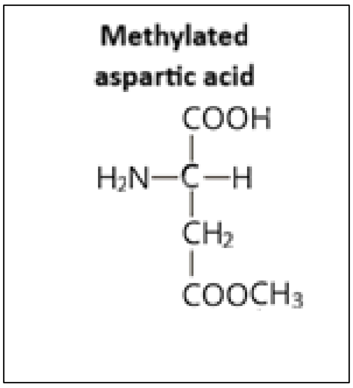


Ala-gly

ii. Circle and name three functional groups present in peptide 1.

b. During artificial peptide synthesis, aspartic acid tends to react with its acidic side chain to form crosslinks with neighbouring amino sidechains. Consider the methylated and unmethylated forms of aspartic acid, shown below.





i. How does methylation affect the solubility of the aspartic acid molecule in water?

Methylation makes aspartic acid less polar This decrease in polarity means the molecule interacts less easily with water, a polar solvent with relatively strong intermolecular forces of attraction, namely H-bonding.

ii. How does methylation influence the boiling point of aspartic acid?

Methylation can reduce hydrogen bonding because it modifies the carboxyl group, which normally forms two relatively strong hydrogen bonds. When the carboxyl group is methylated, it becomes an ester group. Ester groups do not have the acidic hydrogen available for hydrogen bonding and instead engage in weaker dipole-dipole interactions between the molecules. As a result, methylation decreases the molecule's ability to form strong hydrogen bonds, reducing the amount of energy required to break the intermolecular bonds.

***** Note when asked about BP or MP a reference to how changes impact on the amount of energy required to break intermolecular forces of attraction.*

iii. In what two ways does the methylation of the carboxyl functional group on the R group alter the ***chemical*** properties of aspartic acid?

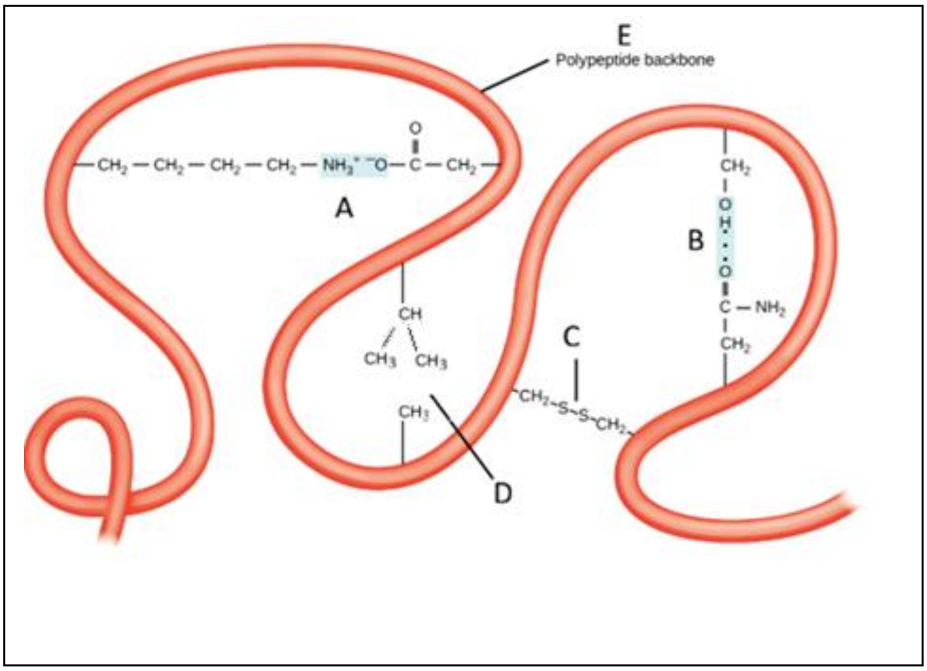
No longer acts as an acid.

No longer able to react with -OH or -NH_2 to form ester and amide links respectively.

iv. A student was quoted as saying " aspartic acid with a methylated R group would not be able to undergo condensation polymerisation to form a peptide" Is this statement chemical valid? Justify your answer.

Not Valid.
Polymerisation to form a peptide takes place via a condensation reaction between the carboxyl and amino groups coming off the carbon, numbered 2, of the amino acids not the R group.

c. Below is a section of a protein chain. Name the labelled intermolecular forces acting between different parts of the protein chain and give two amino acids that can produce the interaction labelled.



i. A _____*ionic bond*_________

Amino acid 1 _____*lysine*__________ + amino acid 2 __*aspartic acid*___

ii. B __________*H-bonding*_________________

iii. Amino acid 1 ____*asparagine*__________ + amino acid 2 __*serine*___

iv. C ___________*covalent (disulfide links)* __________________

v. Amino acid 1 _____*cystine*__________ + amino acid 2 __*cystine*___

vi. D ____________*Dispersion forces*_______________

vii. Amino acid 1 _____*alanine*__________ + amino acid 2 __*valine*___

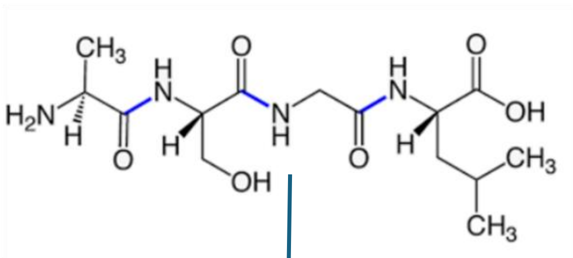
d. What type of covalent bond of produces structure E ? Describe the type of reaction taking place to form these bonds and name the functional groups involved.

Covalent bonds via amide links (or peptide links).
Condensation polymerization between the carboxyl groups and amino groups linked to carbon number 2 of adjacent amino acids.

e. Consider the peptide chain shown below.

i. How many amino acids formed this peptide? *4*

ii. Name three amino acids produced from the breakdown of the peptide shown below and name the general class of reaction that reaction A belongs to.



Reaction A ___*Hydrolysis*____

Alanine

Serine

Leucine or glycine

f. Consider the four sketches below of protein structures. Complete the table.

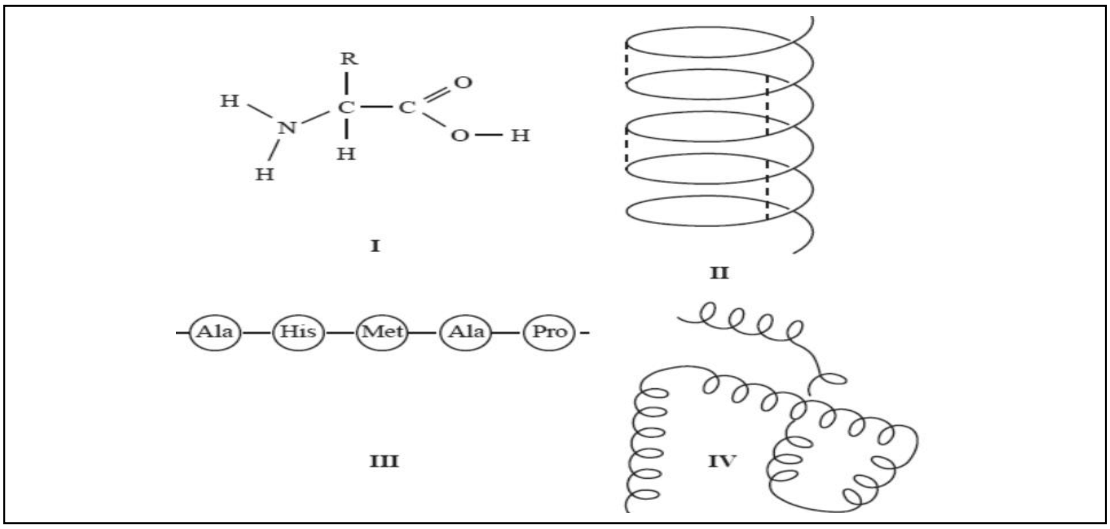


Diagram	Structure	Intermolecular forces	Property
i.	Monomer	Covalent ionic dispersion only H-bonding Dipole-dipole	Contains carboxyl and amino functional groups
iii	*primary*	Covalent ionic dispersion only H-bonding Dipole-dipole	Breaks at very high temperatures
ii	*Secondary structure*	Covalent ionic dispersion only H-bonding Dipole-dipole	Interaction between amide bonds (peptide links)
iv.	*Tertiary structure*	*Covalent* *ionic* *dispersion only* *H-bonding* *Dipole-dipole*	Breaks at low temperatures around 40-50 °C
iv	*Tertiary structure*	*Covalent* *ionic* *dispersion only* *H-bonding* *Dipole-dipole*	Forms from R group interactions