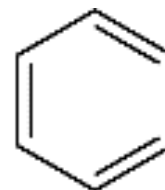


UNDERSTANDING BENZENE STRUCTURE

LESSON 3 SOME FURTHER EVIDENCE

From the last two LESSONS on Benzene, you have discovered that;

- the **molecular formula of benzene is C₆H₆**
- There are many possible structures that could have the formula **C₆H₆**
- **Kekulé** suggested a structure that we refer to as **Kekulé benzene**.
- There are reasons to doubt this proposed theoretical structure. These include,
 - Failure to react with **bromine water**
 - **Bond lengths between carbons are all equal AND between the length of a C-C and C=C**



Stretch and Challenge conclusions also show that $\Delta_a H$ data can be used in conjunction with **mean bond enthalpies** to show that **Kekulé benzene** is **thermodynamically less stable than real benzene**. **This evidence is not required by OCR!**

This week we will look at another key piece of evidence that you will need to know and understand. This will cast further doubt on the **Kekulé benzene** structure.

3. Enthalpy of Hydrogenation

Hydrogenation is a very important reaction in organic chemistry. The simplest example is:

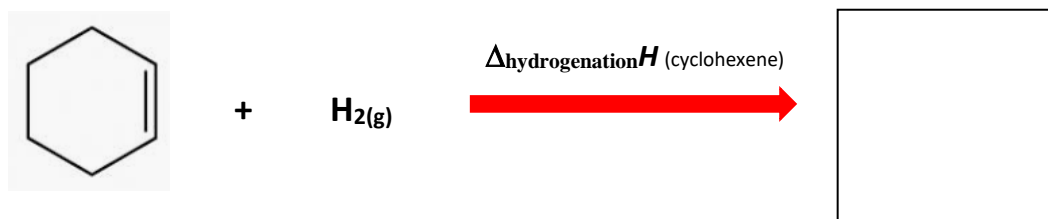


1. What type of organic reaction is this?
2. What catalyst is typically used in this reaction?
3. What is the atom economy of this reaction?
4. 7.00g of ethene was placed in a reactor vessel with a catalyst.

Hydrogen was then added from a container in which it was stored at **5000 kPa** and at **18°C**. What **volume** of hydrogen in cm^3 would need to be added if it was at this temperature and pressure?

Volume of hydrogen cm^3

Consider the following hydrogenation reaction:



5. Draw the skeletal formula of the product of the reaction in the space, above.

We now need to calculate the value for this **enthalpy change**, $\Delta_{\text{hydrogenation}}H$ (cyclohexene).

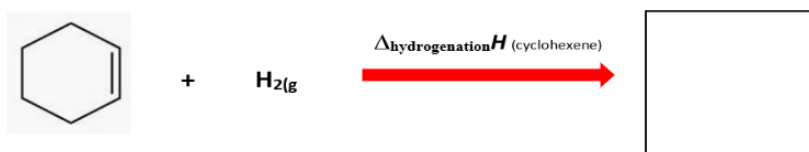
We can do it in **two possible ways** thanks to Hess's Law.

Here is some relevant data.

Chemical	Enthalpy of formation, $\Delta_f H$ /kJ mol ⁻¹	Enthalpy of combustion, $\Delta_c H$ /kJ mol ⁻¹
hydrogen	-286
cyclohexane	-156.4	-3920
cyclohexene	-38.2	-3752
cyclohex-1,3-diene	+71.41	-3576
benzene	+48.7	-3273

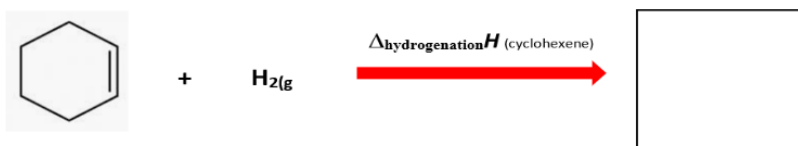
6. Fill in the blank cell in the table!

7. Draw a Hess Cycle that uses the **enthalpies of formation** to calculate the enthalpy change for the hydrogenation of cyclohexene. It has been started for you. Then calculate the value.



$\Delta_{\text{hydrogenation}}H(\text{cyclohexene})$ kJ mol⁻¹

8. Draw a Hess Cycle that uses the **enthalpies of combustion** to calculate the enthalpy change for the hydrogenation of cyclohexene. Then calculate the value.



$\Delta_{\text{hydrogenation}}H(\text{cyclohexene})$ kJ mol⁻¹

The answers for $\Delta_{\text{hydrogenation}}H(\text{cyclohexene})$ should be **identical (or pretty close)**!

9. Now, **repeat** this exercise to calculate the $\Delta_{\text{hydrogenation}}H(\text{cyclohexa-1,3-diene})$

You can use either Δ_cH or Δ_fH data. Maybe do both methods as it's good revision of Hess Cycles!

enthalpy of hydrogenation using formation data $\Delta_{\text{hydrogenation}}H(\text{cyclohexa-1,3-diene})\dots\dots\dots \text{kJ mol}^{-1}$


enthalpy of hydrogenation using combustion data $\Delta_{\text{hydrogenation}}H(\text{cyclohexa-1,3-diene})\dots\dots\dots \text{kJ mol}^{-1}$

10. Finally, **repeat** the exercise in 9. and 10. to calculate the $\Delta_{\text{hydrogenation}}H(\text{benzene})$

$\Delta_{\text{hydrogenation}}H(\text{benzene})\dots\dots\dots \text{kJ mol}^{-1}$

So, you now have calculated three **enthalpies of hydrogenation for cyclohexene, cyclohexa-1,3-diene and benzene** using **experimental** data. Write the values below.

Enthalpy of hydrogenation of **cyclohexene**,  $\Delta_{\text{hydrogenation}}H(\text{cyclohexene}) \dots\dots\dots \text{kJ mol}^{-1}$

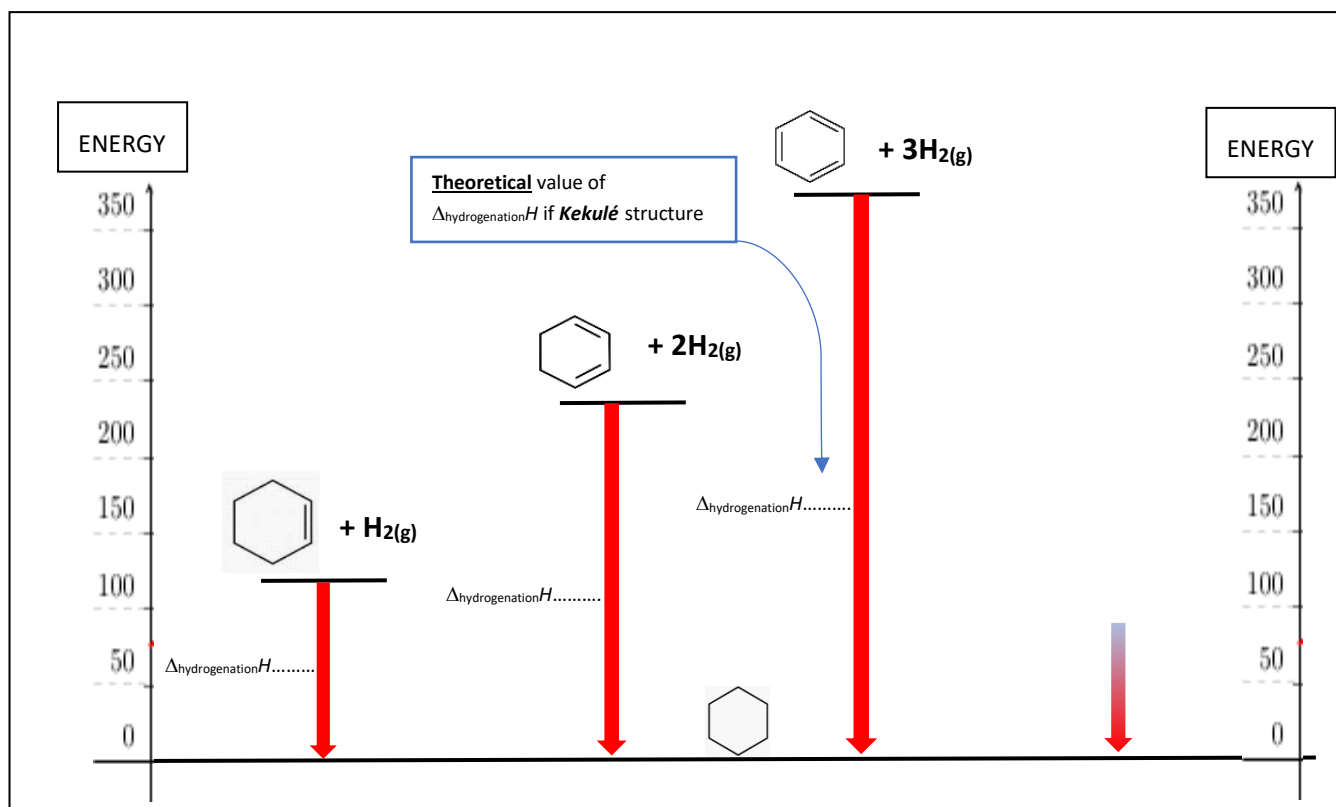
Enthalpy of hydrogenation of **cyclohexa-1,3-diene**,  $\Delta_{\text{hydrogenation}}H(\text{cyclohexa-1,3-diene}) \dots\dots\dots \text{kJ mol}^{-1}$

Enthalpy of hydrogenation of **benzene**,  $\Delta_{\text{hydrogenation}}H(\text{benzene}) \dots\dots\dots \text{kJ mol}^{-1}$

11. Now look at your calculated values for **enthalpies of hydrogenation for cyclohexene and cyclohexa-1,3-diene**. What would you **predict** the value of **enthalpy of hydrogenation for benzene** to be if the **Kekulé benzene structure** was correct, i.e. cyclohexa-1,3,5-diene?

..... kJ mol⁻¹

Now we are going to complete a diagram that clearly illustrates that 'real benzene' must be significantly more chemically stable than the structure that **Kekulé** proposed.



12. On the diagram above, draw a fourth **arrow** that would represent the **true enthalpy of hydrogenation for benzene** that you calculated in question 10. It is 'true' because it was obtained experimentally. Think about where the level would be on the diagram. The arrow has been started for you. Represent 'real benzene' using the following structure.

13. Calculate the difference between the predicted value for $\Delta_{\text{hydrogenation}}H(\text{Kekulé benzene})$ and the actual value for $\Delta_{\text{hydrogenation}}H(\text{'real' benzene})$ obtained from **experimental data**.

..... kJ mol⁻¹

The **conclusion** is that 'real' benzene is around 150 kJ mol⁻¹ **more stable** than the Kekulé benzene.

Next week, we will consider a structure of benzene that is consistent with these 3 pieces of evidence that have been discussed. To do this we will introduce a modification to the standard covalent bond.

