CHEM 230 SEMESTER 01-2015 HOMEWORK 3

Print out this homework on letter sized paper. Answer the questions carefully (not on this sheet) and then submit your answers on Monday morning at the start of class. Note that if there is clear evidence of copying, the whole exercise may attract a zero mark, and the matter may be reported to the authorities.

1) The standard enthalpies of combustion of some *normal* (unbranched) alkanes at 25°C are given below:

Alkane	Molecular formula	ΔH_{c}^{Θ} /kJ mol ⁻¹
ethane	C_2H_6	-1560
propane	C_3H_8	-2219
butane	C_4H_{10}	-2877
pentane	C_5H_{12}	-3509
hexane	C_6H_{14}	-4163
heptane	C ₇ H ₁₆	-4817
octane	C_8H_{18}	-5470

- a) Using Excel, or otherwise, plot a graph of ΔH_c^{Θ} against number of CH_2 (not CH_3) groups. (For help, see footnote below.) From your graph determine the (average) value of ΔH_c^{Θ} per CH_2 group. (The equation gives you the values you need.)
- b) The difference between $\Delta H_c^{\Theta}(pentane)$ and $\Delta H_c^{\Theta}(butane)$ is 632 kJ mol⁻¹, somewhat different from your average value. Explain this difference by considering the states of the reactants.
- 2) The catalytic hydrogenation of alkenes is exothermic and its value depends to some extent on how the alkene is substituted, as shown below:

Situation of double bond	Description of alkene	$\Delta H_{\rm H}^{\Theta}$ /kcal mol ⁻¹ (average over many different molecules) ²
H H	unsubstituted	-32.5
R ¹ H	monosubstituted	-30.0
R ¹ P ²	cis-disubstituted	-28.2
R ¹ H	gem-disubstituted	-27.9
R ¹ H H R ²	trans-disubstituted	-27.4
$ \begin{array}{c} R^1 \\ R^2 \\ R^3 \end{array} $	trisubstituted	-26.8
$ \begin{array}{c} $	fully substituted	-26.3

¹ On older versions of Excel it is a little tricky to choose the values to put on the *x*-axis. Choose *scatter plot* as the type of chart. Select the ΔH_0^2 values to plot. Insert the chart in the spread sheet and then right-click on one of the data points. Select *source date*, select *series*, and, with the cursor in the box for *x*-values (which should be empty), select the required values. Click on OK. Right-click on one of the data points again, select *add trendline* and *linear*. Now click on *options* and check *display equation on chart*.

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² These are common, but obsolete, units. Multiply by 4.18 to convert to kJ mol⁻¹.

Name

- a) Which are the least and most stable types of alkene? Explain your choice and calculate the percentage difference, in terms of energy, between the least and most stable forms.
- b) Calculate the ΔH_H^{Θ} value for the hypothetical molecule, 1,3,5-cyclohexatriene. (Like benzene, but with alternate double and single bonds.) Explain the difference between your calculated value and the observed ΔH_H^{Θ} value for benzene of -49.8 kcal mol⁻¹.
- 3) Show, by means of stereochemical formulae and mechanisms, why the reaction of cyclohexene with bromine leads to the formation of *trans*-1,2-dibromocyclohexane, and not *cis*-1,2-dibromocyclohexane.
- 4) In each of the following cases, suggest a formula for the alkene which would give rise to the product (or products) of reductive ozonolysis. Give also the name of the alkene in each case.
 - a) |
 - b) $\stackrel{\text{\tiny H_3C}}{\longrightarrow}$ and $\stackrel{\text{\tiny H}}{\longrightarrow}$ in equimolar quantities
 - c) $\circ \downarrow_{\mathsf{H}} = \circ$ only.