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Pearson Edexcel International Advanced Level
In Chemistry (WCH04)
Paper 01 Rates, Equilibria and Further Organic
Chemistry

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Introduction

This paper was similar in style and standard to previous and parallel Unit 4 papers of this specification. A range of skills and knowledge were assessed, and the levels of difficulty allowed good discrimination between the different grades, while allowing well-prepared students at all levels to demonstrate their abilities. This is an A2 examination paper and therefore had a synoptic element but, for the most part, students seemed better prepared for the standard questions rather than those requiring application of knowledge and understanding. Many students lost marks because they did not answer the question that was actually set.

Multiple Choice Section (Questions 1–15)

This was the highest scoring section of the paper with a mean score across all students of 52.4%. 86% of students gave the correct answer to question 6c, while just 20% of students gave the correct answer to question 13a, the lowest scoring question.

Question 16

(a)(i) Most candidates realised that ΔS_{system} for this reaction would be positive and gave a sensible justification for their choice. Responses that did not refer to the change occurring in the reaction or just to an increase in disorder gained no credit. Some candidates confused ΔS_{system} and $\Delta S_{\text{surroundings}}$ and explained the sign in terms of the negative enthalpy change.

(a)(ii) The calculation of ΔS_{system} was usually completed successfully. Some candidates chose the wrong values for the standard molar entropies, the use of $69.9 \text{ J K}^{-1} \text{ mol}^{-1}$ (the value for liquid water) was a frequent error. Here and elsewhere in this sequence or calculations the omission of the sign or the use of incorrect units were common reasons for loss of a mark.

(a)(iii) The relationship between $\Delta S_{\text{surroundings}}$ and ΔH was well known, however, the conversion from celsius to kelvin seemed unfamiliar to many candidates. Some omitted this step altogether, some added 298 rather than 273 or attempted to scale a value from $25^\circ\text{C} = 298 \text{ K}$; a small number of candidates subtracted 273 from 160.

(a)(iv) Most candidates knew how to calculate ΔS_{total} but the instruction to express the final value to an appropriate number of significant figures was often ignored.

(b)(i) The equation relating ΔS_{total} to the equilibrium constant was known by most candidates, but the required algebraic manipulation caused many problems with the introduction of a negative sign being quite frequent.

(b)(ii) There were many excellent explanations of the effect of increasing temperature on $\Delta S_{\text{surroundings}}$ and hence the equilibrium constant but few of these mentioned ΔS_{system} ; those that did include ΔS_{system} assumed that it was unaffected by a change in temperature and use Route 1 in the mark scheme. A significant number of candidates gave an answer in terms of Le Chatelier which gained no credit.

Question 17

(a)(i) There was a wide range in the quality of responses to this item and many candidates devoted space and time to descriptions of the experiment before turning their attention to the measurement of the initial rate. The first mark was frequently scored but the use of a tangent was often omitted and the idea of the gradient at $t = 0$ was often poorly expressed or left out altogether.

(a)(ii) The reason for using a very much larger concentration of sodium hydroxide was well understood although the automatic ‘to ensure complete reaction’ was quite common, as were vague responses such as ‘to provide a nucleophile’.

(b)(i) The first mark was much more likely to be scored than the second when clear explanations of the effects of simultaneous changes in the concentrations of 2-bromobutane and sodium hydroxide were relatively rare. Some candidates essayed a general response ‘when the concentration doubles the rate doubles’, which gained no credit.

(b)(ii) Most candidates were able to calculate the value of the rate constant, although some chose results other than those from Experiment 1. The units of the rate constant were usually correct but sometimes omitted altogether.

(c)(i) Many candidates were uncertain of the relationship between reaction order and mechanism, leading to statements about the rate equation or linking the mechanism to the structure of the alcohol. Some responses referred to the rate determining step but then negated the mark by describing both reacting species as molecules.

(c)(ii) While there were some excellent mechanisms drawn, most candidates made at least one error. The most common mistakes were: inaccurate drawing of the curly arrows; placing the lone pair on the hydrogen of the hydroxide; drawing the transition state with the hydroxide hydrogen bonded to the carbon atom; drawing the transition state with an additional charge or no charge.

(d)(i) Candidates generally defined chirality in terms of a carbon atom bonded to four different atoms or groups and this idea was sufficient to score the mark even when the response was limited to the description of a chiral atom rather than the molecule. The preferred answer was relatively rare. Candidates were often imprecise in their use of the relevant terms, e.g. ‘a carbon atom bonded to four different molecules’ and just ‘chiral molecules are non-superimposable.’

(d)(ii) The stereochemical outcomes of the different substitution mechanisms were often described with commendable accuracy and conciseness. Marks were most frequently lost by omitting mention of the S_N1 intermediate or the direction of attack on the nucleophile in S_N2 . Candidates do need to be aware of the need for precise language eg in S_N1 , the idea of the nucleophile attacking from above and below the plane of the intermediate is not the same as attacking from different directions. Some candidates confused S_N1 and S_N2 or even gave explanations without referring to the specific mechanisms at all.

Question 18

(a)(i) The reagents were well known, particularly for reactions 1 and 4. The common errors were the inclusion of an acid in reaction 2, the omission of acid in reaction 3 and failing to specify methanol in these reactions.

(a)(ii) The most likely answer was ‘heat under reflux’ and even where the mark was awarded the need to distil the butanal directly out of the reaction mixture was rarely made clear.

(a)(iii) The mark for an advantage was more likely to be scored, with the preferred answer and the various ‘allows’ in the mark scheme being equally popular. Candidates often opted for ‘automatic’ responses on cost, yield and impurities as a disadvantage.

(a)(iv) The key points of this question were that the oxidation of a primary alcohol proceeds through the corresponding aldehyde and that aldehydes are more easily oxidised than alcohols. These were appreciated by only a small minority of candidates with the most frequent response being ‘heat under reflux’.

(b) Most candidates correctly identified two relevant wavenumber ranges, but many failed to link these to bonds. Some referred to wavenumber ranges for functional groups (ester and carboxylic acid) or omitted mention of bonds altogether while others quoted the wavenumber range for the aldehyde carbonyl bond.

(c) Correct solutions to this problem were few and far between and the absence of any attempt at explanation made awarding one mark difficult. Candidates often presented the results of their calculations without regard to their feasibility and giving answers of the order of 10^6 mol dm^{-3} .

Question 19

The chemical tests were generally well-known although some candidates combined the first two tests to confirm that a ketone was present, and others linked reaction with sodium hydrogencarbonate with the presence of a hydroxyl group. However, the structures deduced did not necessarily match the inferences or the additional information given in the stem of the question resulting in aldehyde groups and branched carbon chains or the structures of three different molecules each with a single functional group. The mark for linking the molecular ion data to the deduced structure was the one most likely to be lost in high-scoring responses.

Question 20

(a)(i) This equation was given correctly by most candidates although the formula of the methanoate ion caused some difficulties.

(a)(ii) The expression for the dissociation constant was usually correct with the most common errors being the inclusion of the water concentration in the denominator and the use of $[\text{H}^+]^2$ as the numerator.

(a)(iii) The calculation of the concentration of the acid caused considerable difficulties in this question with some simply using a concentration of 30 mol dm^{-3} and others using $30/1000 \text{ mol dm}^{-3}$. Other common errors were the omission of the square root and incorrect rounding of the final answer.

(a)(iv) Most candidates knew the appropriate approximations although some responses duplicated the same marking point.

(b)(i) The standard buffer definition was known by most candidates although some responses still refer to constant pH or omit the proviso that any additions of acid and alkali must be small.

(b)(ii) There were some excellent descriptions of the methanoic acid / sodium methanoate buffer system. However, some candidates’ responses revealed issues in their understanding of buffer systems, eg giving

equations involving hydroxide ions reacting with methanoate ion, hydrogen ions reacting with methanoic acid and using 'base' or 'alkali' instead of 'salt'. Some candidates omitted the effect of either adding acid or alkali. Part of the challenge of this type of question is to adapt a general understanding of a buffer system to a specific pair of compounds, so general answers could not gain full marks.

(c)(i) The methods for calculating the pH of a buffer solution were not well understood, with many candidates attempting to repeat the calculation of a weak acid. Successful approaches were even split between those who used first principles, starting from the K_a equation and those who used the Henderson-Hasselbalch equation. The latter were more likely to invert the salt-acid ratio.

(c)(ii) Many candidates were unclear how to approach this calculation and those that did often failed to appreciate that the addition of alkali would affect the concentrations of both species. Here also, some candidates calculated the ratio of the concentrations of the acid and the alkali rather than acid and salt. Here, as elsewhere in the paper, candidates did not seem to react when the answer to their calculation was not chemically sensible. For example, the addition of an alkali to a buffer must result in an increase in pH.

Paper Summary

Based on their performance on this paper, students should:

- be aware that in this examination they will be tested, in part, on their ability to apply scientific knowledge and processes to unfamiliar situations
- remember to read questions carefully, be familiar with the meanings of command words and be alert for information that might be helpful in formulating their responses
- make sure that they understand the exact significance of curly arrows in organic mechanisms and practise their use with unfamiliar compounds
- try to ensure that they use the names of different particles and groups of particles correctly (e.g. atom, ion, molecule, group, functional group)
- learn to consider whether the values they obtain from their calculations are chemically realistic.

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