Journal of **Engineering Research**

XXVI IBEROAMERICAN CHEMISTRY OLYMPICS MEXICO 2022: DISTANCE "EXPERIMENTAL" EXAM, PHYSICOCHEMISTRY-ORGANIC CHEMISTRY

David Corona-Martínez
Universidad de Sonora. Department of Biological Chemical Sciences

Héctor García-Ortega
Universidad Nacional Autónoma de México Department of Organic Chemistry, Faculty of Chemistry, UNAM

Fernando León-Cedeño
Universidad Nacional Autónoma de México Department of Organic Chemistry, Faculty of Chemistry, UNAM

José Manuel Méndez Stivalet
Universidad Nacional Autónoma de México Department of Organic Chemistry, Faculty of Chemistry, UNAM

1

Abstract: This work shows the experimental exam carried out by the students who participated in the XXVI Iberoamerican Chemistry Olympiad, which was held virtually in 2022. In this exam, the students were able to analyze an integrated experiment of two areas of chemistry: physical chemistry and organic chemistry. Based on that described in the literature, they examined the kinetic data of an S_N2 reaction and evaluated the description of the experimental steps for the synthesis, isolation, and purification of the product of this reaction.

Keywords: Iberoamerican Chemistry Olympiad, chemical kinetics, S_N2 reaction, virtual experimental exam.

INTRODUCTION

Every year the Ibero-American Chemistry Olympiad is held. On this occasion, the XXVI Olympiad was held from October 22 to 29, 2002, whose host country was Mexico. Given the problem that the pandemic had not been controlled on the dates already indicated, and given the lack of financial resources, it was decided to carry it out remotely. On this occasion the following countries participated: Argentina, Bolivia, Brazil, Chile, Costa Rica, Cuba, Ecuador, El Salvador, Spain, Guatemala, Honduras, Mexico, Peru, Portugal, Uruguay and Venezuela. In total 16 Latin American countries and it is established that each country participate with 4 high school students.

It is important to mention that since Chemistry is an empirical science, the importance of the laboratory in international Chemistry competitions that are carried out in person has a weight almost equivalent to that of theory (40% of the total).

For this reason we did not want that in this Olympiad there was no experimental test. The options to resort to the use of virtual laboratories (e.g. Labster, Cloud, LABS) were discussed and discarded as they were not viable for the proposed objective. Faced with this situation, we decided that the students would be evaluated through an experimental exam that would not only consider the manipulation ability of the students, but could also allow evaluating their ability to approach and solve an experimental problem.

The characteristics chosen for the proposed exam are:

a) Integrate a physicochemical part (analysis of kinetic data of a reaction) and another of organic chemistry.

b) That the student will interpret the enthalpy and entropy values of activation in the transition state, so that he can propose a reaction mechanism according to these parameters.

c) Choose the best procedure to carry out a halogenation reaction, in addition to isolating and purifying a brominated ketone.

d) That this exam be the guideline to distinguish, among the students who presented the virtual laboratory, which students were the most qualified to face this challenge in a limited period of time that also included digital skills for sending the required documents with their answers.

BACKGROUND

In the exam, students were given information on the following key points:

1) IMPORTANCE OF CHEMICAL KINETICS IN DETERMINING THE MECHANISM OF A SUBSTITUTION REACTION

He was given information about the reaction mechanisms and especially how they are determined based on chemical kinetics data. The reaction mechanisms are a hypothesis that is postulated based on the kinetic data of the effect of temperature on the rate constant

of a reaction, and which consist of a series of elementary reactions (elementary process), which can be unimolecular. or bimolecular.

2) THEORY OF COLLISION AND THE TRANSITION STATE

In the gaseous state, the molecules collide with each other. The frequency of collisions is of the order of 10^{30} collisions/second. However, if all collisions produced reactions, the speed of the reactions would be of the order of 10^6 mol L^{-1}·s^{-1}; but in reality they are much smaller. Only collisions between molecules that reach a certain kinetic energy produce a chemical reaction, and especially if they have a good orientation. The Arrhenius equation was analyzed ($k = Ae^{-Ea/RT}$) in its linearized form:

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

Next, they were shown an example of the expected trend and how to determine the activation energy with the slope on a graph with the data in Arrhenius coordinates.
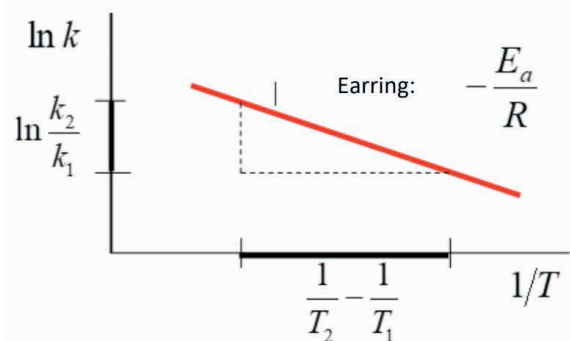
Graph 1. Arrhenius equation

In order to have evidence of a possible mechanism, it is very useful to analyze the enthalpy change ($\Delta H^\ddagger$) and the activation entropy. With the activation energy in reactions in solution, it is found that there is a relationship with $\Delta H^\ddagger$, which is:

$$E_a \approx \Delta H^\ddagger + RT$$

However, to know not only the enthalpy of activation but also the entropy of activation, it is better to use the same values of the dependence of the rate constant on temperature in an analysis using Eyring's equation (Henry Eyring (1901– 1981) theoretical chemist who was born in Chihuahua, Mexico and became a US citizen):

$$k = \frac{k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}}$$

where k_B=1.38x10^{-23} j/K, h=6.626x10^{-34} j . s, y R=8.314 j/(mol.K) *are the Boltzmann, Planck and ideal gas constants respectively. The linearized form of Eyring's equation is:*

$$\ln\frac{k}{T} = \ln\frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{R}\left(\frac{1}{T}\right)$$

The magnitudes of the activation parameters $\Delta H^\ddagger$ y $\Delta S^\ddagger$ They provide information about the difference between the enthalpies and entropies between the activated complex in the transition state with the reactants. In the activated complex, some bonds could be weakened or even broken, which can lower their formation energy in relation to the reactants. This means that the values of $\Delta H^{\wedge\ddagger}$ are regularly positive, since a value of zero or negative would mean that stronger bonds are formed (or simply more bonds are formed) in the activated complex, compared to the reactants. An example of the above are reactions via radicals.

In the case of $\Delta S^{\wedge\ddagger}$, it can give us an idea of the disorder produced or lost when reaching the transition state (because this property measures the possible arrangements). A negative value of the activation entropy implies a decrease in the translational and rotational degrees of freedom, indicating the combination of two molecules (ie, a concerted mechanism). While a positive value implies an increase in the degrees of translational and rotational freedom, which indicates the creation of more molecules (dissociative

mechanism). This information is very useful when you want to propose reaction mechanisms from the kinetic parameters.

In order to obtain the parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, $\ln k/T$ is graphed as a function of $1/T$ where a line must be obtained whose slope gives the activation enthalpy and whose intersection allows estimating the activation entropy.

### 3) TECHNIQUE FOR OBTAINING 2-(BROMOACETYL)NAPHTHALENE (Raghunath, et al.; 2015).

To obtain the substrate to determine the kinetics of the substitution reaction, the following transformation is carried out:
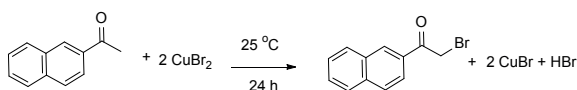
The steps to follow were described in the experimental part (Raghunath, et al.; 2015), (León and Corona, 2022).

SUBSTITUTION REACTION (SHAB, T. B. *ET AL*.; 1982).

For the following reaction, the following rate constants have been observed at different temperatures:
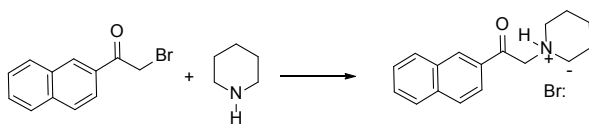
T (K)	$k \times 10^2$ (L·mol^{-1}·s^{-1})
293	4.55
298	6.05
303	7.50
308	9.46
313	12.27

With these values, the following graph was obtained, in which the adjustment equation is indicated.

$$y = 5.423 - 4156.339\, x$$
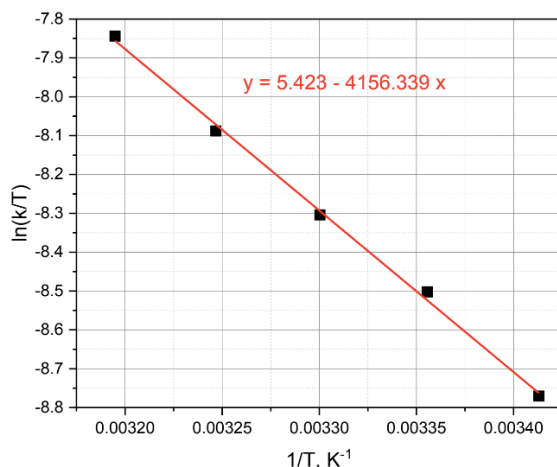
Graph 1. Variation of the equilibrium constant as a function of temperature.

Taking into account Eyring's equation and the data from graph 1, the student determined the enthalpy and entropy values of the transition state for the reaction of 2-(bromoacetyl)naphthalene with piperidine.

The following values were also given for another example of the same SN2 reaction, but now using aniline as the nucleophile. The calculated values were $\Delta H^{\ddagger}$ = -111.4 kJmol 1 and $\Delta S^{\ddagger}$ = -234.4 Jmol 1K 1.

With all these data, the student had to answer a series of questions about the formation of 2-(bromoacetyl)naphthalene regarding the experimental procedure, and later about the two substitution reactions with piperidine and aniline (León and Corona, 2022).

QUESTIONNAIRE (León and Corona, 2022).

1) Bromination reaction of acetylnaphthalene.

Questions were asked about the type of reaction using copper(II) bromide, a process via radicals. Questions included balancing the reaction equation and determining the limiting reactant. In addition, he had to choose what kind of labware (or equipment) could be used to isolate the product and purify it.

1) Bimolecular nucleophilic substitution

4

reaction on 2-(bromoacetyl)naphthalene.

With piperidine as a nucleophile, the student had to determine the transition state, its activation enthalpy and activation entropy using Eyring's linearized equation. And based on this, determine what the nature of the transition state would be and compare it with the transition state when aniline is used as a nucleophile.

He was also asked how the separation of the products from the reactants would be carried out in a flowchart, for the following reaction:
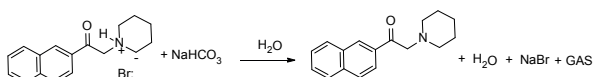

In the end, he had to decide how the compounds would look like on a silica-gel chromatoplate.:
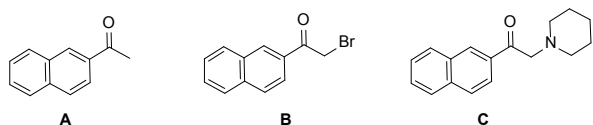
For which the dipole moments of compounds A, B and C were provided.

RESULTS OBTAINED BY STUDENTS

According to the graphs of figures 1 and 2, we can conclude that the "virtual" physicochemical-organic chemistry exam did fulfill its objective, since it allowed distinguishing between the student skills. The analysis showed that 15 students obtained between 9 and 10, 23 between 70 and 90, 16 between 40 and 70, and 5 less than 40, Graph 1.
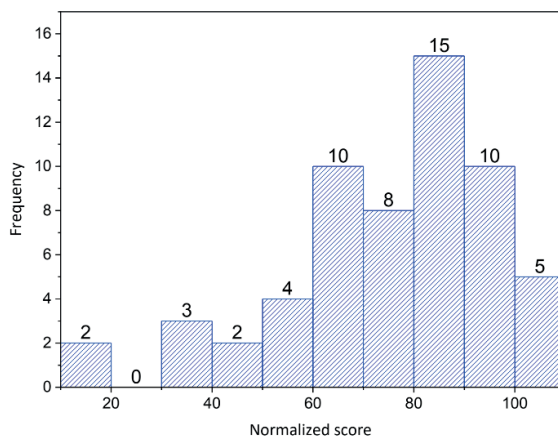
Graph 1. Experimental problem 1. The importance of chemical kinetics to determine the mechanism of a substitution reaction.

Mean: 74.94 Standard deviation: 20.36

CONCLUSIONS

1) According to the results obtained, this virtual experimental exam made it possible to distinguish between students with good performance and was of great importance as another criterion to select the best students among the participants.

2) Although there is always the undeniable risk that the student can consult material through electronic media, the results do not indicate that this has occurred.

3) We believe that our approach gave the expected results. Our proposal did allow us to approach the students who participated in this contest, in determining the type of mechanism, and the transition state based on chemical kinetics data with the use of the Eyring equation.

THANKS

REFERENCES

1. Raghunath, A., Manjula, A., Sowjanya, P., Nishant, J.; *European Journal of Medicinal Chemistry*, **2015**, *100*, 18-23. CAS Method Number 3-119-CAS-14836341.

2. Shab, T. B., Soni, A. N., Patel, S. R.; *J. Prakt. Chem.*, **1982**, *324*, 158-162.

3. Vogel, A. I.; Vogel's Textbook of Practical Organic Chemistry. Fifth Edition Revised edition by Furniss, B. S.; Hannaford, A. J., Smith, P. W. G., Tatchell, A. R., Ed. Longman Scientific & Technical, 1989.

4. Brewster, R. Q.; VanderWerf, C. A.; McEwen W. E.; (1977). Unitized Experiments in Organic Chemistry. Ed. Van Nostrand.

5. León-Cedeño, F.; Corona-Martínez, D. (**2022**). Examen profesores XXVI Olimpiada Iberoamericana de Química, México. Se puede bajar el archivo pdf en el siguiente vínculo:

https://nube.quimica.unam.mx/index.php/s/cDu2sDJ3g6SZ81t