KINETICS EXPERIMENTS IN THE UNDERGRADUATE CHEMISTRY LABORATORY - MISTAKES AND MEASURES: ACID CATALYZED HYDROLYSIS OF METHYL ACETATE AS AN EXAMPLE

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Abstract. Kinetic study of acid catalyzed hydrolysis of methyl acetate is described in detail for undergraduate laboratory students. Identification and rectification of frequently encountered mistakes in this experiment are discussed.

Keywords: kinetics, hydrolysis of methyl acetate, first order reaction

Introduction

This article mainly aimed at the kinetics experiments, taking acid catalyzed hydrolysis of methyl acetate in water as an example in the BSc chemistry laboratory. The reasons for committing mistakes in the BSc laboratory are from many directions. I am just reminding some of the common mistakes that we are committing in the laboratory and I am trying to see how could avoid them.

About the apparatus

A reaction vessel with a quick-fit stopper would be appropriate. For that an iodination flask of 150 ml or 200 ml capacity would be ideal. Or even good airtight lid reagent bottle of 200 ml capacity would do its job. This will help to avoid the evapora-

tion of methyl acetate so that, there will not be any change in concentration of the reactant during the course of the reaction except its hydrolysis. About the care of other apparatus like burettes, pipettes and conical flasks need not be mentioned here. Any BSc laboratory should have these.

The first mistake and very often being committed in the kinetics laboratory is, not asking the students to keep the reaction vessel in a water-bath to keep the temperature of the reaction vessel constant at least during the course of the reaction. A plastic water tub will be nice for this purpose.

About quenching of the reaction

The kinetics experiment is meant for finding the rates, rate constants and order of the reactions. Coupled with these observations and with other kinetic parameters, like salt effect, solvent effect, and temperature effect on rates then one can write the probable mechanism of the reaction. So to get a better estimate of the rate, a better estimate of concentration of the reactant is needed at regular intervals of time. Therefore, for that purpose a proper quenching of the reaction at regular intervals of time is needed. Usually in the BSc laboratory, in the study of the hydrolysis of methyl acetate experiment, we do the quenching by putting the reaction aliquot in ice cold water. No doubt this will serve the purpose provided if the student (or the experimentalist) is quick enough for doing the titration at that time instant. We cannot expect that all the students are extraordinarily good. Well, we cannot escape if there is no other quenching possible except the ice cold water quenching. Here I suggest one reasonably good possibility for quenching the hydrolysis of methyl acetate at a desired time interval without using ice-cold water. (Probably some of you may already know it or might have already guessed it). Since it is acid catalyzed reaction, neutralize the acid with a known concentration of base, usually NaOH at regular intervals of time. So how do we this? We keep the burette ready with desired concentration of NaOH (usually 0.5 M if we do reaction with 1 M HCl) and a conical flask with ice cold water. Now we start the reaction by putting 10 ml of methyl acetate in to 100 ml of 1 M HCl. Then do the titration as quickly as possible. This we assume as V_0. From second titration onwards always keep ready the conical flask with V_0 ml of NaOH run from the burette (after that, fill the burette to the '0' if you wish) and quench the reaction aliquot in to NaOH. This will exactly neutralize the HCl present in the reaction mixture and acetic acid produced due to hydrolysis will be un-neutralized, which can be titrated with NaOH from the burette. Continue the rest of the titrations. Now V_0 will be assumed as 'zero'. The following readings are V_t. V_∞ evaluation is given in the further reading.

The second mistake and also very often being committed in the kinetics laboratory is about collection of number of observations/readings/points. Most often we tell the students that start the experiment and collect 5 or 6 measurements with 10

or 5 minutes interval. What does this mean? Does the teacher or the student have any idea behind this statement? Certainly students do not have.

Thumb rule in the kinetics experiment is to follow the experiment at least to the completion of 3 half-lives, i.e. 87.5% completion of the reaction provided if there is no effect of [products] on rates.

To find out the time required for known fraction of the reaction to be completed, it is essential first to know the total order of the reaction and the initial concentration/s of the reactant/s or the concentration/s of the end product/s i.e. what we call infinite reading. Then one can estimate the time required for completion of the known fraction of the reaction.

Now let us see the details of the experiment on the acid catalyzed hydrolysis of methyl acetate. (1) In the BSc kinetics experiments, we already have an idea of the total order of the reactions, which are in the syllabus. Hence we do not have to determine the order of the reactions; (2) we know the catalyst (acid) concentration and the amount of methyl acetate is being taken. Also we should know the sodium hydroxide concentration (approximately within ± 5%); (3) if we know the concentration of methyl acetate taken, we can calculate the infinite reading as follows. Generally in the laboratory we ask the students to heat the reaction mixture at about 40°C for half hour and cool, then titration for infinite reading. All this is thinking there is no evaporation of methyl acetate due to heating. The net reaction of hydrolysis is given by

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

So, 1 mole of methyl acetate gives 1 mole of acetic acid. In the reaction mixture we are taking 100 ml of 1M HCl and 10 ml of methyl acetate. Therefore the total volume of the reaction mixture is 110 ml. Therefore the [HCl] = 0.909 M. Density of methyl acetate = 0.932 g/ml. So, wt. of methyl acetate (10 ml) = 9.32 g/110 ml. So, wt. of methyl acetate in one liter = 84.73 gms. So molarity of methyl acetate = 84.73/74 (MW) = 1.145 M. Therefore, at the end of the reaction the acetic acid produced is 1.145 M. (mole to mole ratio). The total acid concentration in the reaction mixture is 0.909 M (HCl) + 1.145 M (acetic acid) = 2.054 M. We use normally 0.5 M NaOH for titration. Therefore for 10 ml of the reaction mixture the titre value (V_∞) at the end of the reaction would be 41.1 ml. ($M_{\text{total acid}} \times V_{\text{total acid}} = M_{\text{NaOH}} \times V_{\text{NaOH}}$) - V_o = 18.2 ml (100 ml of 1M HCl + 10 ml Methyl acetate = 0.909 M HCl, 10 ml of this with 0.5 M NaOH gives 18.2 ml), or V_o = 0 ml (if we follow NaOH quenching), V_∞ = 41.1 ml, or, V_∞ = 22.9 ml (if we follow the NaOH quenching). Hence, the initial concentration of methyl acetate would then correspond to (V_∞ - V_o) = 41.1 - 18.2 ≈ 22.9 ml. Therefore,

for completion of three half lives (87.5% completion) one should follow the reaction until the titre value becomes ≈ 38.25 ml [11.45 + 5.75 + 2.85 + V_o (= 18.2)] or 20.05 ml (if we follow the NaOH quenching). In order to decide the number of observations to be recorded, first the teacher must do a reaction, and then get the rate constant from which one can get the half-life.

From the half-life one should plan for the time of the reaction to be followed and then from that the number of observations. Care must be taken that at least 7 to 8 observations (excluding V_o and V_∞) must be made and those observations must spread over to 87.5% completion of the reaction. (4) The reasons for telling to take the observations that spread to 87.5% completion of the reaction are: if one follows the reaction up to only 50%, and then if you plot [C] vs time (zero order), or log [C] vs time (first order), or 1/[C] vs time (second order), or 1/[C^2] vs time (third order), all these plots yield always straight-line graphs. (Figs 1 - 4). All these plots are generated from a simulated data, by assuming some value for the initial concentration of the reactant and for a rate constant respectively.

Then it is not only difficult to determine the order of the reaction but also one cannot tell the order of the reaction is some thing.

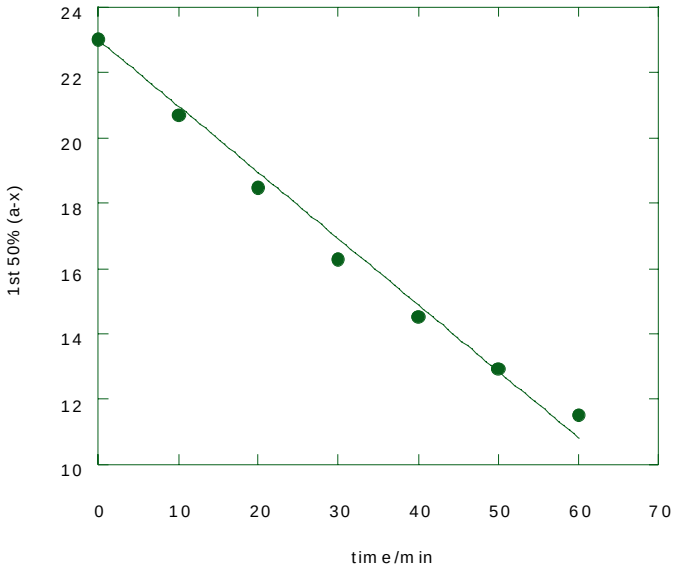

Fig. 1. Hydrolysis of MeCOOMe followed up to 1st half-life

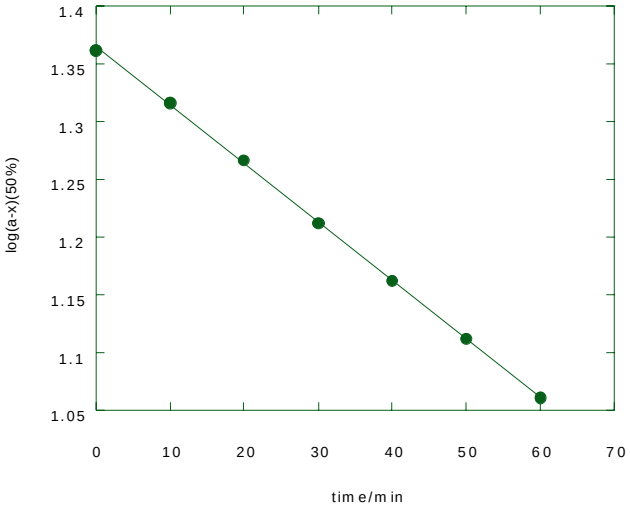

Fig. 2. Hydrolysis of MeCOOMe 1st 50%

Follow the reaction up to 3 half-lives, and then once again plot the graphs as above (Figs 5-8). Now look for which one will give the straight line. From the corresponding straight-line graph one can arrive at the total order of the reaction. (Here in this experiment we use water in excess over methyl acetate; hence we use 'psueodo' before the order term). Here Fig. 6 is linear therefore it is (psueodo) first order reaction.

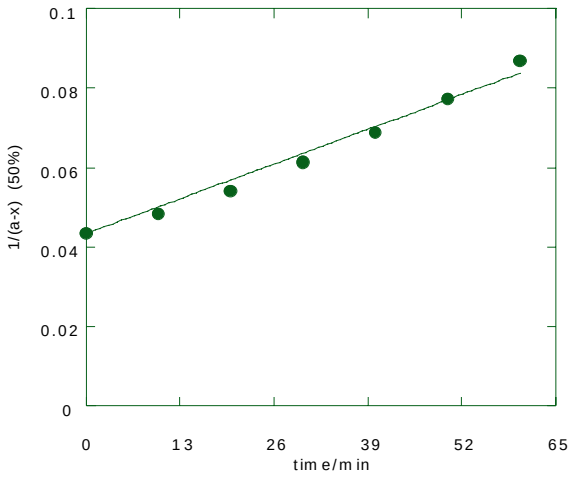

Fig. 3. Hydrolysis of MeCOOMe 1st 50%

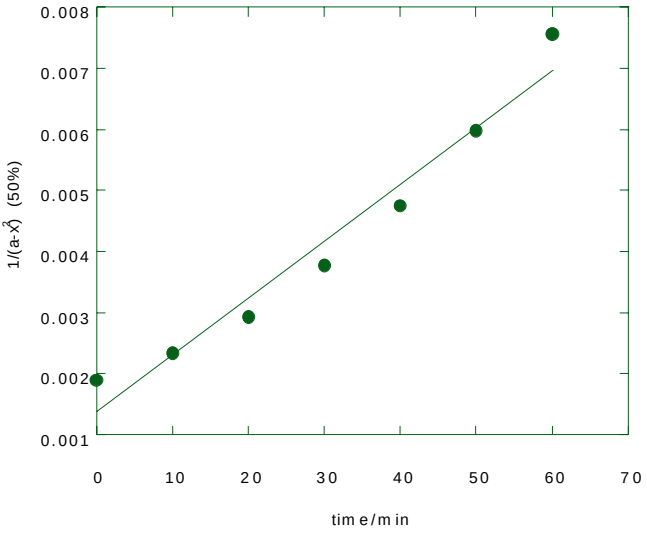

Fig. 4. Hydrolysis of MeCOOMe 1st 50%

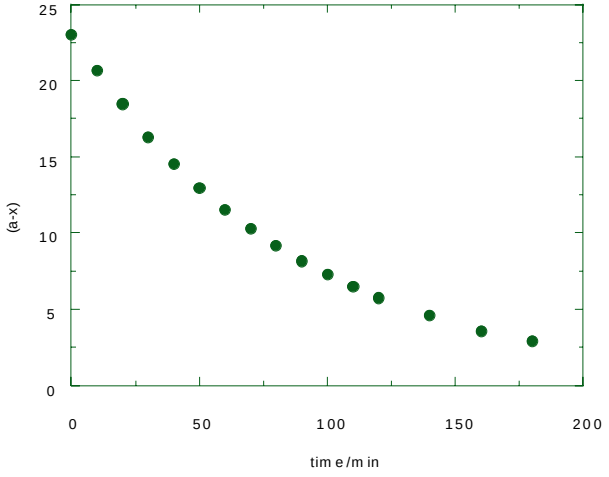

Fig. 5. Hydrolysis of MeCOOMe until three half-lives

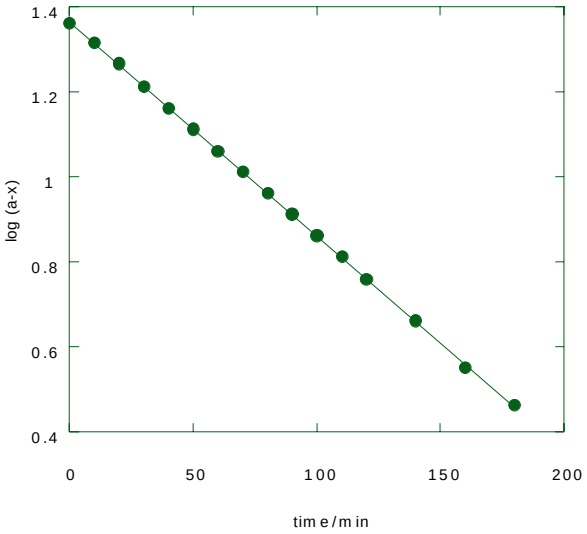

Fig. 6. Hydrolysis of MeCOOMe up to three half-lives

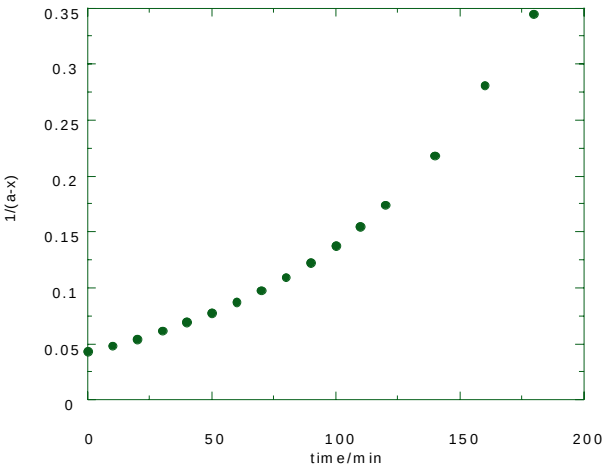

Fig. 7. Hydrolysis of MeCOOMe up to three half-lives

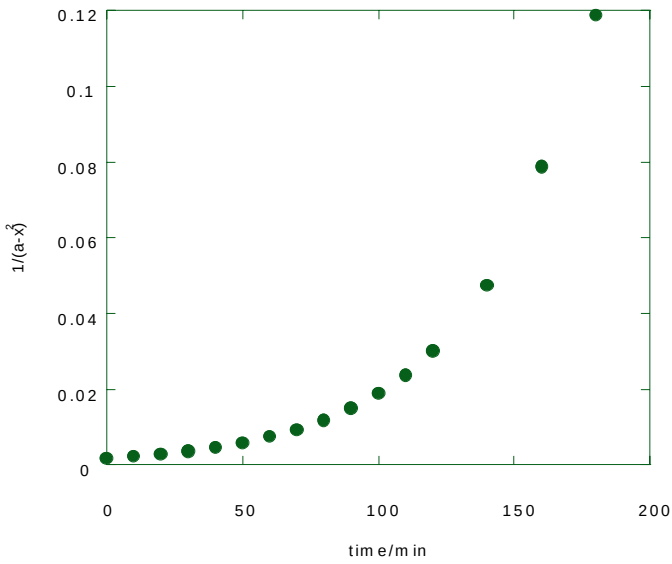

Fig. 8. Hydrolysis of MeCOOMe up to three half-lives

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