

Second Order Rate Constant of Water Assisted Neutral Hydrolysis of Methyl Acetate: Project Based Activity for Post Graduate Students

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Abstract There were numerous reports on the kinetic study of acid catalyzed hydrolysis of methyl acetate. In all these studies emphasis was on the calculation of pseudo-first order rate constant. There were very few reports on the calculation of second order rate constant of uncatalyzed hydrolysis of methyl acetate; a small note regarding the second order rate constant is mentioned in the 12th class Central Board of Secondary Education (CBSE) Indian textbook. It is known that the hydrolysis of methyl acetate can proceed via two pathways: the un-catalyzed and the acid catalyzed. The un-catalyzed path of the reaction is too slow to be followed. It will take several days to follow the reaction. In the present article an attempt was made to calculate the second order rate constant of the un-catalyzed path. This rate constant was obtained by plotting k_{obs} (pseudo-first order acid catalyzed rate constants at different acid concentrations) versus $[\text{H}^+]$. The extrapolation to zero concentration that is the y-intercept divided by the water concentration yields the second order un-catalyzed rate constant. This second order rate constant was also determined theoretically. To the best of our knowledge, no one has determined the second order rate constant of this uncatalyzed reaction. This can be given as project-based activity to Graduate students.

Keywords: Methyl acetate, Second order, DFT

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1. Introduction

It would be interesting if the classroom teaching (both theory and laboratory sessions) commenced with the historical background of that topic. The first kinetics experiment was pioneered on the study of acid catalyzed inversion of sucrose by Ludwig Wilhelm in 1850 using polarimetry technique [1]. The first ever report on hydrolysis kinetics of methyl acetate was by Wilhelm Ostwald in 1883 [2]: $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$. Based on mole-to-mole ratio of methyl acetate to water, we anticipate this reaction to proceed via second order; but due to negligible change in concentration of H_2O during the course of the reaction it follows a (pseudo) first order path. Hence nobody ever thought of calculating its second order rate constant; though, the reaction is known for more than a century [2]. Ostwald did not even consider the course of the reverse reaction (since it was

negligible). This was followed by several studies on hydrolysis of kinetics of various esters in different mediums [3,4,5,6,7,8,9,10] including a study on the effect of structure of ester on hydrolysis kinetics by Hinshelwood [6] that is just a year after Hammett equation [11] was developed (and was getting popularized). One of the authors (VJ) has published a detailed study on the kinetics experiment, taking the acid catalyzed hydrolysis of methyl acetate in water, an undergraduate chemistry laboratory experiment [12]. In this study nothing was mentioned about the calculation of second order rate constant. However, commonly committed mistakes were highlighted, and measures were suggested. Besides this, many reports on the kinetic study of hydrolysis of methyl acetate appeared in literature [13,14,15,16,17,18,19]. In all these studies there was not a single instance where they had mentioned about the calculation of the second order rate constant of water assisted hydrolysis of methyl acetate; we could only find small note mentioned in an Indian textbook used by Central Board of Secondary Education,

New Delhi (CBSE, New Delhi) [20] where second order rate constant was determined. In the present article we have endeavored to calculate the second order rate constant of the un-catalyzed path with the help of Figure 1 (see Scheme 1) and the same was determined theoretically. In fact, determination of pseudo first order rate constant of acid catalyzed hydrolysis of methyl acetate is part of MSc first year chemistry syllabus of our college and many other colleges in our State. Hence this experiment can be given as Project-based activity for different groups of students. By carrying out this project-based activity, students learn basic aspects of chemical kinetic experiments, such as following the reaction titrimetrically at different time intervals, quenching of reaction at a particular time, maintaining ionic strength, using first order integrated equation for the determination of first order rate constant, plotting of appropriate graphs. While carrying out the theoretical aspect of this experiment, students would learn how to isolate a Transition state and calculate Gibbs energy computationally. It will also enable the students to use the Eyring equation for calculation of rate constant.

2. Experimental Section

Methyl acetate was purchased from Aldrich and other chemicals were of AR grade bought from the local market. All the other experimental methods adopted were similar to that reported in reference 12. KaleidaGraph software, (Reading, PA, USA) was used for the linear correlations. Effect of $[H^+]$ on rates of reactions was carried out at constant ionic strength of 2.0 M with the help of KCl. Experiments were initiated by keeping the HCl and KCl solutions of required concentration and methyl acetate in separate containers (which were thermostated at 25°C for about 15-20 minutes); the required volume of methyl acetate was extracted using a pipette and added to HCl solution. The reaction mixture was analyzed for acetic acid at regular intervals of time by titrating with standard sodium hydroxide solution taken in the burette using phenolphthalein indicator. The reactions were followed up to 2 half-life completions. Let V_0 be the volume of sodium hydroxide at time "0" and the volumes of sodium hydroxide are V_t at different time intervals. Further let V_∞ be the volume of sodium hydroxide after completion of the reaction. Slopes of the plots of $\log \frac{V_\infty - V_0}{V_\infty - V_t}$ versus time would yield the pseudo first order rate constants.

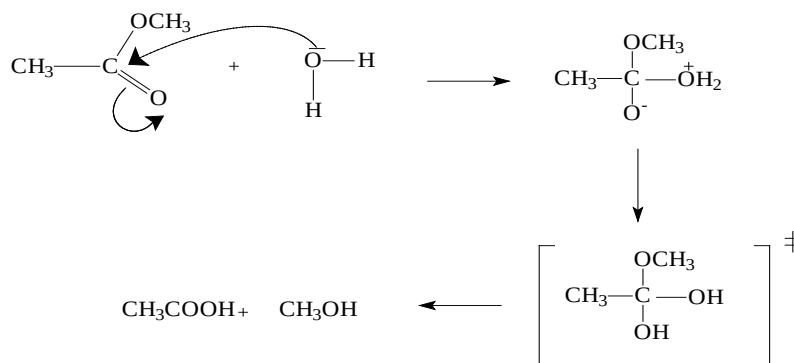
Gaussian 09 [21] program was utilized to for all the DFT calculations. B3LYP functional with 6-31G(d) was utilized. The transition State (TS) was isolated by performing Berny optimization. To convey in simple parlance Berny optimization is an algorithm which helps to find the minimum-energy geometry or a saddle point if one is hunting for a transition state (which we are). The

plausible Transition State is depicted in Scheme 1. Frequency calculations were performed to find the free energy of the TS and the reactants. The reactants did not have any imaginary frequency and only one imaginary frequency was observed in the Transition state. We had used opt plus frequency simultaneously during calculations. The implicit polarizable continuum model (PCM) with water as solvent was utilized in the calculations. This model factors in dielectric screening, polarization effects and bulk solvation energies, hence can be used for determination of rate constants of a reaction. Further, since the value of theoretical rate constant is almost same as that determined by experiment, the usage of implicit PCM model is apt. The free energy of activation was substituted in the well-known Eyring equation to determine the rate constant of the reaction [22]. Here transmission coefficient κ in the Eyring equation is assumed to be one. If you envisage the transition state on the the top of a mountain and the molecules ascending the mountain top, transmission coefficient κ is the index of how many actually slide down into products rather than roll back to reactants. We have made an approximation of ' κ ' to be one as it is very unlikely that Transition State would roll back to reactants. This approximation appears to be correct as the theoretical rate constant determined by use of this equation has almost the same value as that determined by experiment (as already conveyed).

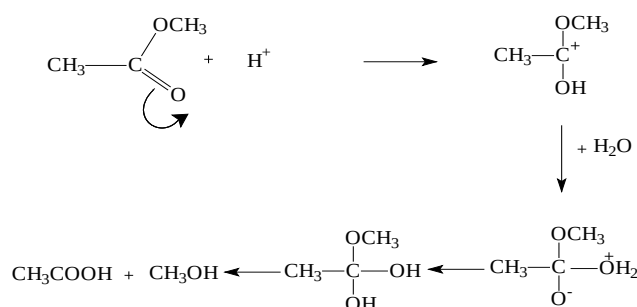
$k = (\kappa k_B T / h c^\ominus) e^{-\Delta^\ddagger G / RT}$
where k_B is Boltzmann constant; T = Temperature; h is Planck's constant; $\Delta^\ddagger G$ is the free energy of activation; R is gas constant; $c^\ominus = 1 \text{ mol dm}^{-3}$; κ = (kappa) transmission coefficient is assumed to be 1. Table 2 gives the theoretically determined free energies and the resulting rate constant of the reaction.

3. Results and Discussion

The present work is the detailed study of calculation of the second order rate constant of the un-catalyzed (Scheme 1) path with the help of Figure 1. Pseudo-first order rate constant of the un-catalyzed hydrolysis of methyl acetate at 25°C and second order rate constant of acid catalyzed reaction was reported by Yih-Huang Hsieh et al [13]. Yih-Huang Hsieh et al determined the rate constant by carrying out the experiments at 90-100°C and then extrapolating to 25°C; whereas we carried out the acid (HCl) hydrolysis (Scheme 2) at different concentration of $[H^+]$ at 25°C and with the help of Figure 1 we got the second order rate constant of un catalyzed path (Scheme 1). The hydrolysis of methyl acetate can proceed via two pathways: un-catalyzed (scheme 1) and the catalyzed (scheme 2). The data of the acid catalyzed paths is summarized in Table 1. The un-catalyzed path of the reaction would be too slow to be followed (Scheme 1). It will take several days for the reaction to go for completion.

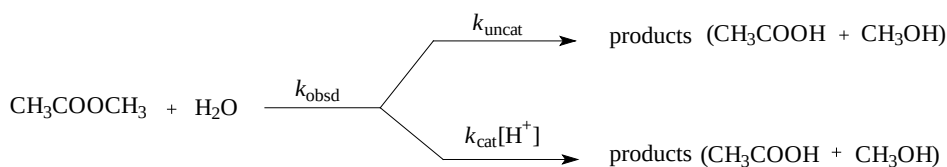


Scheme 1. un-catalyzed (water assisted) path



Scheme 2. Acid catalyzed path

The kinetic model of scheme 1 and 2 put together is shown as in scheme 3.



Scheme 3.

Therefore

$$\frac{-d[\text{CH}_3\text{COOCH}_3]}{dt} = k_{\text{uncat}} [\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}] + k_{\text{cat}}[\text{H}^+][\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}] \quad (1)$$

$$-\frac{d[\text{CH}_3\text{COOCH}_3]}{dt} \frac{1}{[\text{CH}_3\text{COOCH}_3]} = k_{\text{uncat}} [\text{H}_2\text{O}] + k_{\text{cat}}[\text{H}^+] [\text{H}_2\text{O}] \quad (2)$$

$$\begin{aligned} & -2.303 \frac{d(\log[\text{CH}_3\text{COOCH}_3])}{dt} \\ & = k_{\text{obsd}} = k_{\text{uncat}}[\text{H}_2\text{O}] + k_{\text{cat}}[\text{H}^+][\text{H}_2\text{O}] \end{aligned} \quad (3)$$

Table 1. Data of acid catalyzed rate constants of hydrolysis of methyl acetate at 25 °C and at constant ionic strength of 2.0M (KCl) in water. k_{obsd} in s^{-1} must be understood as k_{pseudo} in s^{-1}

Sl. No.	$[\text{H}^+]$ mol. L^{-1}	k_{obsd} in s^{-1}
1	0.00	0.00000199*
2	0.1190	0.000099190
3	0.2380	0.000154416
4	0.3428	0.000180069
5	0.7619	0.000253031
6	1.2380	0.000314221
7	1.4285	0.000339485
8	1.6190	0.000387388

*Obtained by interpolation of the locus of the plot of k_{pseudo} versus $[\text{H}^+]$ to zero concentration of the acid and dividing the intercept by 52.9 M (Figure 1)

At constant $[H_2O]$ a plot of k_{obsd} versus $[H^+]$ should yield a straight line (figure 1) with a slope of $k_{cat}[H_2O]$ and an intercept of $k_{uncat}[H_2O]$ (equation 3). The y-intercept (from equation 3) is equal to $k_{uncat}[H_2O]$. Thus, the y-intercept (in s^{-1}) divided by water concentration (52.9M) yields k_{uncat} (in $M^{-1}s^{-1}$) the second order rate constant of water assisted neutral hydrolysis of methyl acetate.

y-intercept = $0.000106 s^{-1}$ (Figure 1). This value is divided by water concentration that is = $0.00010577 / 52.9 = 1.99 \times 10^{-6} M^{-1}s^{-1}$ is the required second order rate constant of reaction between methyl acetate and water. The reported first order k_{uncat} value [13] is $0.17 \times 10^{-8} s^{-1}$. This rate constant was determined under entirely different conditions in the temperature range 90-110°C and the data at 25°C was drawn by extrapolation. At those high temperatures though the reaction is carried out in sealed tube, the reaction medium would be partly in vapor phase. So, we cannot compare our data with the reported data. The reported [13] k_{uncat} value is of first order; and what we have reported is the second order rate constant.

Theoretical rate constant was determined by finding the free energy of the TS and the reactants. The difference in free energy of the TS and the sum of the free energies of the reactants yielded $\Delta^\ddagger G$ i.e., the free energy of activation. This value was substituted in the Eyring equation (this is already explained in the methods section). The theoretical rate constant turned out to be $6.44 \times 10^{-6} M^{-1} s^{-1}$.

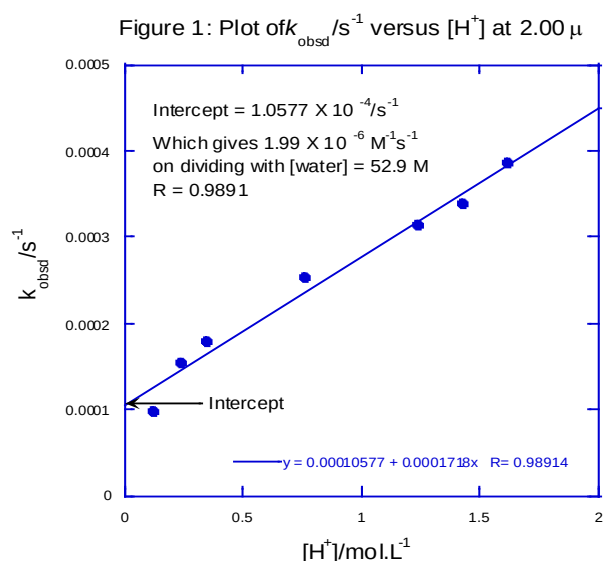


Figure 1.

Table 2. Theoretically determined Free Energies and Rate constant

Sl. No.	Name	Free energy in Hartree units	Rate constant of the reaction
1	Transition State	-344.707345	$6.44 \times 10^{-6} M^{-1}s^{-1}$
2	Water	-76.412841	
3	Methyl acetate	-268.333604	

$$\begin{aligned}\Delta^\ddagger G &= (\text{Transition state}) - \{(\text{Methyl acetate}) + (\text{Water})\} \\ \Delta^\ddagger G &= -344.707345 - \{(-268.333604 + (-76.412841))\} \\ \Delta^\ddagger G &= -344.707345 - (-344.746445) \\ \Delta^\ddagger G &= 0.0391 \text{ Hartree units}\end{aligned}$$

$$\Delta^\ddagger G = 0.0391 \times 627.5095 \text{ kcal/mol}$$

$$\Delta^\ddagger G = 24.535621 \text{ kcal/mol}$$

$$\text{or } \Delta^\ddagger G = 102633.52 \text{ J/mol}$$

Substituting the above $\Delta^\ddagger G$ in Eyring equation [22]

$$\begin{aligned}k &= (\kappa k_B T / hc^\ominus) e^{-\Delta^\ddagger G / RT} \quad [\text{here } \kappa \text{ is } 1 \text{ and } c^\ominus = 1 \text{ mol dm}^{-3} \text{ as already mentioned in methods section}] \\ &= [1.380662 \times 10^{-23} (298.15) / 6.626176 \times 10^{-34}] \\ &\quad \exp(-102633.52 / 8.314 \times 298.15) \\ &= 6.2125 \times 10^{12} \exp(-41.41) \\ &= 6.2125 \times 10^{12} \times 1.0372 \times 10^{-18} \\ &= 6.44 \times 10^{-6} M^{-1} s^{-1}\end{aligned}$$

4. Conclusion

In the present article an attempt was made to calculate the second order rate constant of the un-catalyzed path that is water assisted hydrolysis of methyl acetate, by finding the acid catalyzed pseudo-first order rate constants at various $[H^+]$ and then by extrapolation to zero concentration of the acid to the locus of the plot of k_{obsd} versus $[H^+]$; this value was finally divided by the concentration of water. The second order rate constant turned out to be $1.99 \times 10^{-6} M^{-1}s^{-1}$. The theoretical determined rate constant turned out to be $6.44 \times 10^{-6} M^{-1}s^{-1}$. The fact that we are getting similar rate constant by theoretical and experimental methods, it does reflect that the obtained second order rate constant of water assisted hydrolysis of methyl acetate is reasonably correct. This project-based activity will help the students learn both experimental and theoretical determination of rate constants.

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Conflict of Interest Statement

The authors declare no conflicts of interest

Availability of Data and Material

The supplementary files contain all the input and output files of the Gaussian calculations.

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