

# Using Titration to Estimate Rate Law Parameters of the Reaction of Sodium Hydroxide and Ethyl Acetate

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**Abstract-** Determination of rate expression and rate law parameters i.e. rate constant and reaction orders of any reaction is an important step to design any type of reactors. In this research rate law parameters of the reaction of sodium hydroxide and ethyl acetate were determined using titration to measure final concentration of the limited reactant which is sodium hydroxide in this reaction, while the reaction was carrying out i.e. simultaneously. The standard solution used in the titration is hydrochloric acid. The usefulness of this technique is that the concentration at the time of measuring would be read and registered. Thus, accurate results could be obtained. After the final concentration being measured, rate of reaction was calculated as the difference between initial concentration and final concentration dividing by time of reaction. Then by extrapolating two rates at two different initial concentrations to zero time initial rate was calculated. Finally, several initial rates at different initial concentrations of sodium hydroxide and ethyl acetate were used to determine the rate law parameters using linearized least squares analysis method. According to this method the value of rate constant is about 0.11 L/mol.sec at 32°C and the reaction is first order with respect to each reactant.

**المستخلص -** تحديد صيغة لمعدل التفاعل و تحديد قيم معاملات صيغة المعدل أي قيمة ثابت المعدل و رتب التفاعل يعتبر خطوة مهمة لتصميم أي نوع من أنواع المفاعلات الكيميائية. وفي هذا البحث تم تقدير قيم معاملات قانون معدل التفاعل وذلك لتفاعل هيدروكسيد الصوديوم و خلات الإيثيل و ذلك باستخدام المعايرة لقياس التركيز النهائي للمتفاعل الحدي - هيدروكسيد الصوديوم في هذا البحث - بينما يحدث التفاعل بصورة متزامنة بين عمليتي المعايرة و التفاعل. المحلول العياري المستخدم للمعايرة هو محلول حمض الكلور. هذه الطريقة تضمن قراءة و تسجيل التركيز النهائي لهيدروكسيد الصوديوم عند لحظة القياس - نقطة نهاية التفاعل - و هكذا يمكن الحصول على نتائج دقيقة. بعد تحديد قيمة التركيز النهائي يمكن حساب معدل التفاعل كحاصل قسمة الفرق بين التركيزين الابتدائي و النهائي على زمن التفاعل - زمن المعايرة - ثم بإجراء الاستقراء على قيمتين لمعدل التفاعل - عند فترتين زمنيتين - يمكن إيجاد قيمة معدل التفاعل الابتدائي عند الزمن صفر، و أخيراً و بحساب عدة قيم لمعدل التفاعل الابتدائي بالطريقة المشار إليها عند تراكيز ابتدائية مختلفة من هيدروكسيد الصوديوم و خلات الإيثيل تم تقدير قيم معاملات معدل التفاعل باستخدام طريقة تحليل عدد المربعات الأصغر الخطية. و باستخدام هذه الطريقة اتضح أن التفاعل من الرتبة الأولى بالنسبة لكل من المتفاعلين و أن قيمة ثابت المعدل عند درجة حرارة 32 مئوية تبلغ حوالي 0.11 L/mol.sec.

**Keywords:** rate constant, reaction order, concentration, sodium hydroxide, ethyl acetate.

## INTRODUCTION

The reaction rate or rate of reaction for a reactant or product in a particular reaction is intuitively defined as how fast a reaction takes place. For example, the oxidation of iron under the atmosphere is a slow reaction which can take many years, but the combustion of butane in a fire is a reaction that takes place in fractions of a second<sup>[1,2]</sup>.

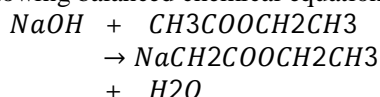
But first we must select one reaction component for consideration and define the rate in terms of this component  $i$ . If the rate of change in

number of moles of this component due to reaction is  $dN_i/dt$ , then the rate of reaction  $r_i$  based on unit volume of reacting fluid  $V$  is as follows<sup>[3]</sup>:

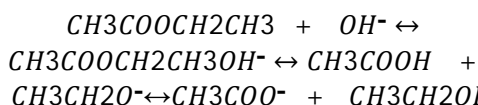
$$r_i = (1/V) (dN_i/dt) \quad (1)$$

The reaction of sodium hydroxide and ethyl acetate has been studied previously and literature values provided starting values for the reaction orders as 1 for both reactants<sup>[4,5,6]</sup>. But according to some literature there is no relationship between the values of the reaction orders and the stoichiometric coefficients which

both are 1 in the considered reaction as shown in the following balanced chemical equation:



This because the reaction may occur in more than one mechanistic step. The proposed mechanism for the reaction starts with the nucleophilic attack of the hydroxide ion on the carboxyl carbon to form a tetrahedral intermediate and the subsequent loss of the alkoxide as the leaving group. These steps are followed by a fast  $H^+$  ion transfer to give the acetate ion<sup>[7,8]</sup>:



There are several methods to determine values of rate constant (k), reaction order with respect to sodium hydroxide( $\alpha$ ) and reaction order with respect to ethyl acetate( $\beta$ ) using batch reactor data such as differential method, integral method, half-lives method and linearized least square analysis method.

If a rate law depends on the concentration of more than one species we may choose to use a linearized least squares method. In this method we can obtain a group of linear algebraic equations in more than one variable which could be solved simultaneously because the number of unknowns which are orders of reaction and rate constant equals the number of equation. This method of data analysis is also useful to determine the best values of the rate law parameters from a series of measurement where three or more parameters are involved (e.g., reaction orders  $\alpha$  and  $\beta$ , frequency factor and activation energy)<sup>[8,9]</sup>.

### MATERIALS AND METHODS

The following equipment was used for experimental work: Volumetric flasks, Titrimetric Flask (used as a batch reactor), Sensitive balance, Stirrer, Thermometer, Burette, Pipette, and Stop watch.

And the following materials were used:

1. Hydrochloric acid (concentrated solution 11M approximately).
2. Sodium Hydroxide (solid pellets)
3. Ethyl Acetate (concentrated solution 11M approximately).
4. Distilled water.
5. Phenolphthalein (indicator).

The procedure is as follows:

1. Oneliter of 1.08M HCl was prepared.

2. 4 samples each 800 ml of NaOH of 0.0805M, 0.10M, 0.119M and 0.141M were prepared.

3. 4 samples each 800 ml of  $CH_3COOC_2H_5$  of 0.62M, 0.72M, 0.90M and 1.02M were prepared.

4. The burette was filled with HCl solution.

5. 400 ml of NaOH and small amounts of the indicator was poured into the titri-metric flask. Then, 400 ml of  $CH_3COOC_2H_5$  was poured into the titri-metric flask and the reaction and titration were carried out simultaneously as shown in Table 1.

6. Each run was repeated using the remaining amount of each solution (400 ml) but at higher flow rate of HCl from the burette to the titri-metric flask. Thus, the reaction between NaOH and  $CH_3COOC_2H_5$  would be quenched early and as a result the time period of reaction would be reduced. Accordingly, two rates of reaction could be obtained.

7. During the reaction stirrer was used to agitate the reaction mixture, stop watch was used to read the time at the end point of the reaction (when the pink solution becomes colorless) and thermometer was used to read the temperature which could be considered constant (isothermal process) due to the short time of reaction.

8. For each run, temperature, time of reaction and titration, volume of HCl used to titrate remaining amount of NaOH which was not reacted with  $CH_3COOC_2H_5$  were registered as shown in Table 2.

### RESULTS AND ANALYSIS

Mole balance on a constant volume batch reactor gives:

$$-dCA/dt = -r_A = k CA^\alpha CB^\beta \quad (2)$$

where:  $-r_A$ : rate of reaction.  $C_A$ : concentration of sodium hydroxide.  $C_B$ : concentration of ethyl acetate. If we use the method of initial rates, then:

$$-r_{A0} = k C_{A0}^\alpha C_{B0}^\beta \quad (3)$$

Taking the natural logarithm of both sides, we have:

$$\ln(-r_{A0}) = \ln k + \alpha \ln C_{A0} + \beta \ln C_{B0} \quad (4)$$

Let  $Y = \ln(-r_{A0})$ ,  $X_1 = \ln C_{A0}$ ,  $X_2 = \ln C_{B0}$ ,  $a_0 = \ln k$ ,  $a_1 = \alpha$  and  $a_2 = \beta$

If we now carry out N experimental runs, for the jth run, the equation above takes the form:

$$Y_j = a_0 + a_1 X_{1j} + a_2 X_{2j} \quad (5)$$

The best values of the parameters  $a_0$ ,  $a_1$  and  $a_2$  are found by solving the following simultaneous equations system:

$$\Sigma Y_j = N a_0 + a_1 \Sigma X_{1j} + a_2 \Sigma X_{2j} \quad (6)$$

$$\Sigma X_{1j} Y_j = a_0 \Sigma X_{1j} + a_1 \Sigma X_{1j}^2 + a_2 \Sigma X_{1j} X_{2j} \quad (7)$$

$$\Sigma X_{2j} Y_j = a_0 \Sigma X_{2j} + a_1 \Sigma X_{1j} X_{2j} + a_2 \Sigma X_{2j}^2 \quad (8)$$

We have three linear equations and three unknowns which we can solve for  $a_0$ ,  $a_1$  and  $a_2$  [9,10].

But to calculate the initial rate we need firstly to calculate two rates at two different time periods and extrapolate them to zero time. And to calculate any of these two rates we need firstly to measure final concentration of a reactant which is used as a base of calculation or limited reactant, this could be achieved by titration.

The titration of an acid with a base or vice versa and the precipitation of an ion in an insoluble compound are example of chemical method of analysis used to determine the concentration of a species in a liquid - sample removed from a reactor, such methods are often suitable for relatively slow reactions. This is because of the length of time that may be required for the analysis, the mere collection of sample does not stop further reaction from taking place, and the method of quenching the reaction may be required. For batch reactor, there is the associated difficulty of establishing the time at which the concentration is actually measured [10]. To solve this problem, carrying out the main reaction, reaction between sodium hydroxide and ethyl acetate, and the titration reaction, reaction between sodium hydroxide and hydrochloric acid, simultaneously could be used. This means that titration of the reaction mixture against solution of hydrochloric acid could be used to quench the reaction and cease it at a specific point of time on one hand and to determine the final concentration of sodium hydroxide - its concentration after some amount has reacted with ethyl acetate during the period between the start of the reaction and the specific time point at which the reaction had been ceased or the end point of the titration - on the other hand. Thus, rate of reaction would be obtained as a result of division of the difference between initial concentration and final concentration by the period of time.

Taking two rates of reaction at two different periods of time and extrapolating them to zero time results in obtaining the initial rate of reaction - the rate of reaction at the beginning of the reaction ( $t = 0$ ), this is shown in Table 3. Using different initial rates at different initial

concentration of sodium hydroxide (A) and ethyl acetate (B) and substituting into equations (5), (6) and (7) results in evaluating the values of  $k$ ,  $\alpha$  and  $\beta$  i.e. rate law parameters. Final concentration of sodium hydroxide  $C_{Af}$  was calculated as follows:

$$C_{Af} = V_{HCl} * C_{HCl} / V_A \quad (9)$$

where:  $V_{HCl}$  : volume of HCl as read from the burette.  $C_{HCl}$  : concentration of HCl used in the titration which equals 1.08M.  $V_A$ : volume of NaOH i.e. volume of the reaction mixture which equals 800ml.

Rate of reaction for each run was calculated as follows:

$$-r_A = (C_{Ai} - C_{Af}) / t \quad (10)$$

where:  $C_{Ai}$ : initial concentration of NaOH which equals half of the concentration before mixing NaOH with  $CH_3COOC_2H_5$  in the reaction vessel (equimolar reaction mixture).

$t$ : Time period of reaction.

Using two reaction rates for each couple of runs (same initial concentrations of NaOH and  $CH_3COOC_2H_5$  but different reaction time) the initial reaction rate (reaction rate at  $t = 0$ ) was calculate by extrapolation.

Then solving the system of simultaneous equations (5), (6) and (7) as shown in Table 4, the following results were obtained:

$$a_0 = -2.2087, a_1 = 1.23, a_2 = 1.09$$

That means rate constant ( $k$ ) equals 0.1098, order of reaction with respect to NaOH ( $\alpha$ ) equals 1.23 and order of reaction with respect to  $CH_3COOC_2H_5$  ( $\beta$ ) equals 1.09. These values deviate slightly from the values in some literature [4,5,6]. These deviations could be justified by the following reasons:

1. Some literature suggest a mechanism for the reaction considered consists of more than one step i.e. the reaction is non elementary. Accordingly, values of the reaction orders deviate from stoichiometric coefficients values - 1 for both reactants-.
2. Measurement error and calculations approximation error.

## CONCLUSION

It could be concluded that the reaction is second order approximately - first order with respect to each reactant- and the rate constant at 32.5°C is about 0.11 L/mol.sec - rate constant is a function of temperature-, and the method used to calculate these parameters in this research through calculating final concentration of the limited reactant may be considered a suitable method.

## RECOMMENDATIONS

The following recommendations could be considered:

1. Carrying out this experiment at other temperature, this is because If  $k$  is determined at more than one temperature the activation energy of the reaction,  $E$  and the pre-exponential factor,  $A$  can be determined

Using the following form of the Arrhenius equation and a plot of  $\ln k$  vs.  $1/T$ <sup>[11,12,13,14,15]</sup>:

$$\ln k = -E/RT + \ln A \quad (11)$$

In addition, this will assure the results obtained.

2. Carrying out the experiment to other reactions of similar type - one of reactant is an acid or a base. This is to give more reliability for this method which is suggested to estimate rate law parameters of this kind of reactions.

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TABLE 1: EXPERIMENTAL DATA FOR REACTION AND TITRATION.

Run	NaOH initial concentration (M)	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> initial concentration (M)
1	0.0805	0.90
2	0.100	1.02
3	0.119	0.72
4	0.141	0.62

TABLE 2: TEMPERATURE, TIME OF REACTION AND TITRATION, VOLUME OF HCL USED TO TITRATE REMAINING AMOUNT OF NAOH.

Run	Temperature (°C)	Volume of HCl (ml)	Time period (sec)
1.a	33	16.5	70
1.b	32.5	17.5	48
2.a	32.5	9.6	45
2.b	32.6	10.5	36
3.a	33	14	60
3.b	32	16.2	37
4.a	32.6	18.5	82
4.b	31.5	22.5	54

Notes:

1. runs named as n.a (n = 1, 2, 3 or 4) were carried out at low flow rates of HCl whereas those named as n.b were carried out at high flow rates of HCl.
2. Average temperature of the experiment was 32.5 °C.

TABLE 3: RESULTS OF EXTRAPOLATING REACTION RATE TO ZERO TIME.

Run	$C_{Af}$	$-r_A * 10^4$	$-r_{A0}$ (initial rate) $* 10^4$
1.a	0.02228	2.57	5.4
1.b	0.02363	3.46	
2.a	0.01296	8.23	16.83
2.b	0.01418	9.95	
3.a	0.01989	6.60	15.1
3.b	0.02302	9.86	
4.a	0.02498	5.55	11.06
4.b	0.03038	7.43	

TABLE 4: RESULTS OF SUBSTITUTING INITIAL RATES AND RELATED INITIAL CONCENTRATIONS OF NAOH AND  $CH_3COOC_2H_5$  FOR VARIABLES OF EQUATIONS (5), (6) AND (7).

$X_1$	$X_2$	Y	$X_1 * X_2$	$X_1^2$	$X_2^2$	$X_1 * Y$	$X_2 * Y$
-2.996	-0.673	-6.39	2.02	8.98	0.45	19.14	4.30
-3.213	-0.798	-7.52	2.60	10.32	0.64	24.14	6.02
-2.822	-1.022	-6.50	2.90	7.96	1.04	18.33	6.64
-2.652	-1.171	-6.81	3.11	7.03	1.37	18.05	7.97
$\Sigma X_1$	$\Sigma X_2$	$\Sigma Y$	$\Sigma X_1 * X_2$	$\Sigma X_1^2$	$\Sigma X_2^2$	$\Sigma X_1 * Y$	$\Sigma X_2 * Y$
-11.68	-3.66	-27.22	10.63	34.30	3.50	79.66	25.00