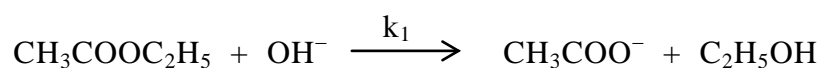


TO BE ADAPTED TO THE HANNA CONDUCTIVITY METER

KINETICS OF HYDROLYSIS OF ETHYL ACETATE

1. Purpose

This experiment illustrates the use of conductivity measurements to follow the progress of a reaction in solution. The reaction studied is the hydrolysis of ethyl acetate which can be represented by the chemical equation:



The kinetics data will be obtained

- at 25 C under three different initial mixing conditions (Ethyl acetate in excess, hydroxide in excess, second order conditions – ie. 1:1 mixing),
- at ~35 C under second order conditions.

From these data, the order of the reaction, the rate constant and the enthalpy of activation can be deduced.

2. Safety

Mercury is used in the conductivity cell to make electrical contact to the platinum electrode; do not turn this cell upside down. If some mercury spills, notify the instructor immediately.

Please, wear eye protection at all times in the laboratory.

3. Experiment

Perform the experiment as described in Daniels *et al.*, "Experimental Physical Chemistry", Exp 23. A copy of the write-up can be downloaded from the course web site; a copy of this book is in the reserve section of the library. See also the experiment, "Dissociation of Acids" in the Chem 366 lab manual and in S&G, for hints on conductance measurements.

The proper interpretation of the data obtained in this kinetic experiment depends crucially on an accurate knowledge of the reagent concentrations. This is so because the reaction conditions are chosen *not* to be the usual

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pseudo-first order conditions¹, and actually, two of the runs are performed under second-order conditions which assume an exact 1:1 stoichiometric mixture. Make sure that your solutions are prepared accurately and do calculate the exact concentrations before proceeding with the experiment.

Before starting a kinetic run, place the cell together with all flasks and solutions in the constant temperature bath for at least 10 min to bring them to thermal equilibrium. If the experiment is performed over several days, fresh solutions have to be prepared each day. The cell constant should be measured at each new temperature using a KCl solution (≈ 0.02 M) of precisely known concentration.

For each run it is sufficient to monitor the reaction for $\approx 20 - 25$ min. At the end of the run, empty out the cell into a capped labelled vial in which the reaction can be allowed to proceed to completion while you are doing other things. The resistance of these solutions may be measured at the end of the session to obtain a value for R_c (see below).

Note: be gentle with the cell; the platinum electrode arrangement is delicate. Also, do not turn the electrode assembly upside down; the contact between the platinum electrodes and the outside world is effectuated by some mercury which might spill.

4. Data analysis

Data may be analysed as suggested in Daniels. Be aware that in Eqn. 5 the equivalent ionic conductance must be expressed in $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, the concentration in mol l^{-1} and the cell constant in cm^{-1} . With these units, the factor 1000 in the denominator of Eqn. 5 has the dimension of $\text{cm}^3 \text{ l}^{-1}$. In the method of analysis described in Daniels, the values of the resistance of the reacting mixtures at $t = 0$ (R_0) and at $t = \infty$ (R_c) appear explicitly in the expression used to calculate x (Eqn. 8). R_0 may be estimated by extrapolating at time zero the values of R_t while R_c may be measured on a sample which has been allowed to react to completion. Process at least one set of data in this way. Below, an alternate method to process the data is suggested. Do process at least this same set of data using this procedure, and compare the results.

By rearranging Eqn. 5 in Daniels, x the number of mole l^{-1} which has reacted can be obtained:

$$x = \frac{1}{\left(\ell_{\text{OH}^-} - \ell_{\text{CH}_3\text{COO}^-}\right)} \left[b \left(\ell_{\text{OH}^-} + \ell_{\text{Na}^+} \right) - \frac{1000K}{R_t} \right] \quad (1)$$

¹ Pseudo-first order conditions mean that the concentration of one of the reagent (the excess reagent) is much larger such that effectively its concentration stays constant during the reaction while the other reagent is totally consumed.

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in which Daniels notations have been kept.

$$\text{Let } x = A - \frac{B}{R_t} \quad (2)$$

$$\text{where } A = \frac{b(\ell_{\text{OH}^-} + \ell_{\text{Na}^+})}{\ell_{\text{OH}^-} - \ell_{\text{CH}_3\text{COO}^-}} \quad \text{and} \quad B = \frac{1000K}{\ell_{\text{OH}^-} - \ell_{\text{CH}_3\text{COO}^-}} \quad (3)$$

The constants A and B may be calculated for each run knowing K the cell constant and the various ℓ_i (found in references).

4.1 Case 1: $a = b$

$$\text{One has } \frac{x}{a-x} = k_1 at \quad (\text{Eqn. 4 in Daniels}) \quad (4)$$

$$\text{Define the new variable } Y = \frac{1}{a} \frac{x}{(a-x)} \quad (5)$$

Eqns. 4 and 5 show that a plot of Y versus time should be linear with slope k_1 (and an intercept of zero). This analysis will work properly only if the conditions are truly second-order, *i.e.* the concentrations a and b are equal (within $\approx 1\%$); if a and b are significantly different, one has to process the data as in **Case 2** below.

4.2 Case 2: $a \neq b$

$$\text{One has } \ln \frac{b(a-x)}{a(b-x)} = k_1(a-b)t \quad (\text{Eqn. 3 in Daniels}) \quad (6)$$

$$\text{Now define the new variable } Y = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} \quad (7)$$

Eqns. 6 and 7 show that a plot of variable Y versus time should be linear with a slope of k_1 (and an intercept of zero). Deviation from linearity may come from an inaccurate knowledge of the concentrations, or from other reasons. In this case, try using the initial slope to determine k_1 . An EXCEL spreadsheet (HYDROLYS.XLS) is provided to facilitate some of these calculations; it is available on some of the computers in the lab or can be

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downloaded from the course web site. When you are handing in your report, submit the raw data by filling in the MS-Excel spreadsheet hydrolysis_results.XLS (available also from the course web site).

5. References

F. Daniels, J.W. Williams, P. Bender, R.A. Alberty and C.D. Cornwell, *Experimental Physical Chemistry*, 6th ed., Expt 23, MacGraw Hill, Toronto (1962).