

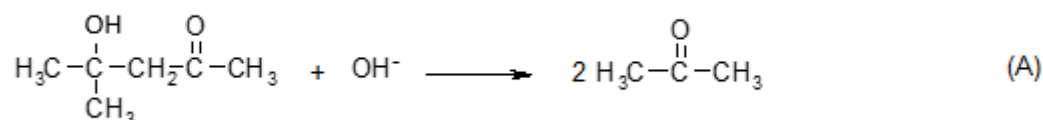
EXPERIMENT 4

DETERMINATION OF RATE CONSTANT OF A DISSOCIATIVE REACTION

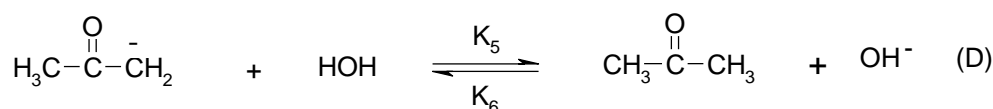
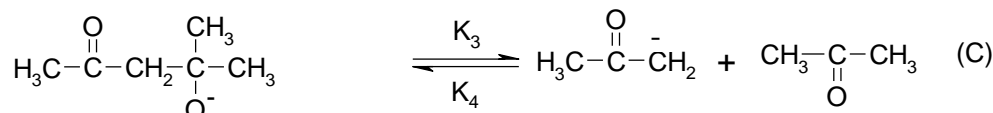
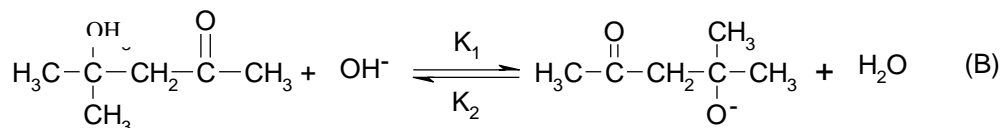
Objective: To determine the rate constant of a dissociative reaction of 4-Methyl-4-hydroxy-2-pentanone, MHP (diacetone alcohol)

1 Theory

4-Methyl-4-hydroxy-2-pentanone, MHP (diacetone alcohol), undergoes dissociation in the presence of hydroxyl ions to form acetone:



This reaction is reversible, though the equilibrium constant is quite large. It is assumed to occur via the steps shown below:



In step (B), the reactant, MHP, is in fast equilibrium with its ions. The ion then dissociates to form acetone and the carbanion as shown in step (C). Step (D) shows that the carbanion takes one proton from water to give acetone and a hydroxyl ion. Since step (B) is a fast equilibrium, the overall rate of reaction will depend on the step that is rate determining, i.e. step (C) or step (D).

CASE I

If (C) is the rate-determining step, the rate equation is:

$$d[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-] / dt = K_3 [\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-] \quad (1)$$

Since (B) is the fast step, thus,

$$K = K_1 / K_2 = \{[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-][\text{HOH}]\} / \{[\text{MHP}][\text{OH}^-]\}$$

$$\text{and } [\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-] = K [\text{MHP}][\text{OH}^-] / [\text{HOH}] \quad (2)$$

Substituting the above equation in equation (1), the rate equation becomes

$$d[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-] / dt = K_3 K [\text{MHP}][\text{OH}^-] / [\text{HOH}] \quad (3)$$

One molecule of $\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-$ is consumed in step (C) while one molecule of MHP reacts with OH^- to form one molecule of $\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-$ in step (B) so that equilibrium in step (B) is re-established. Thus, rate of change of MHP concentration is the same as rate of change of $[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-]$

$$d[\text{MHP}] / dt = d[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-] / dt$$

and equation (3) can be written as

$$- d[\text{MHP}] / dt = K_3 K [\text{MHP}][\text{OH}^-] / [\text{HOH}] \quad (4)$$

If OH^- and HOH are in excess, their concentrations will be the same as their initial concentrations and the reaction will be pseudo first order. Thus, equation (4) will be

$$- d[\text{MHP}] / dt = k [\text{MHP}] \quad (5)$$

where $k = K_3 K [\text{OH}^-] / [\text{HOH}]$

CASE II

If the forward reaction in step (D) is the rate-determining (slowest) step, the rate equation is:

$$-d[\text{CH}_3\text{COCH}_2^-] / dt = K_5 [\text{CH}_3\text{COCH}_2^-][\text{H}_2\text{O}] \quad (6)$$

Since steps (B) and (C) are in fast equilibrium,

$$K_1 / K_2 = [\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-][\text{HOH}] / [\text{MHP}][\text{OH}^-] \quad (7)$$

$$\text{and } K_3 / K_4 = [\text{CH}_3\text{COCH}_2^-] [\text{CH}_3\text{COCH}_3] / [\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-] \quad (8)$$

Since the rate equation must be expressed using measurable quantities,

$$\begin{aligned} [\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-] &= (K_1 / K_2) [\text{MHP}][\text{OH}^-] / [\text{HOH}] \\ [\text{CH}_3\text{COCH}_2^-] &= K_3 / K_4 [\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}^-] / [\text{CH}_3\text{COCH}_3] \\ &= (K_3 K_1 / K_4 K_2) [\text{MHP}][\text{OH}^-] / [\text{HOH}][\text{CH}_3\text{COCH}_3] \end{aligned} \quad (9)$$

$$\text{and } d[\text{CH}_3\text{COCH}_2^-] / dt = d[\text{MHP}] / dt \quad (= - \text{rate}) \quad (10)$$

Thus, the rate equation becomes

$$d[\text{MHP}] / dt = \{K_5 K_3 K_1 / K_4 K_2\} \{[\text{MHP}][\text{OH}^-] / [\text{CH}_3\text{COCH}_3]\} \quad (11)$$

This shows that the decomposition rate of MHP is inversely dependent on the concentration of acetone.

As such, Case I and II can be differentiated because the added acetone will reduce the rate in Case II but will not disturb the rate in Case I.

This reaction is accompanied by a change in volume. Thus, the extent of reaction can be followed from the volume measurement.

For the condition involving excess MHP, the rate is not influenced by the addition of acetone. The kinetics of this reaction will obey the rate law (4) and not (11). By arranging the conditions so that the concentrations of OH^- and H_2O remain constant, the reaction will achieve the pseudo-first order and the rate will only depend on the concentration of MHP.

$$-d[\text{MHP}] / dt = k [\text{MHP}] \quad (12)$$

where $k = K_3 K_1 [\text{OH}^-] / K_2 [\text{H}_2\text{O}]$

$$\text{From here} \quad \ln \{[\text{MHP}]_0 / [\text{MHP}]\} = kt \quad (13)$$

$$\text{or} \quad \ln \{a / (a - x)\} = kt \quad (14)$$

It can be shown that equation (14) can be re-presented as,

$$(V - V_\infty) / (V_0 - V_\infty) = e^{-kt} \quad (15)$$

[Show how equation (15) can be derived from equation (14) in your report].

2 Materials

Apparatus: Dilatometer, conical flask, burette, pipette, thermometer, stopwatch.

Chemicals: NaOH, MHP(diacetone alcohol), acetone.

3 Experimental Procedure

The change in volume during a reaction can be measured with a dilatometer as shown in Figure 1. It involves a bulb connected to a capillary with graduated small diameter; a small change in volume can be measured from the height of the meniscus of the liquid in the capillary.

The dilatometer is very brittle and must be handled with care. Before each test is carried out, it has to be properly washed and dried.

TEST 1

- (1) Place the dilatometer in a water bath at 30 °C with only its bulb immersed in the water.
- (2) Add 34 cm³ of 0.1 mol dm⁻³ NaOH into a conical flask through a burette. The flask is then stoppered and placed in the same water bath.

- (3) After 15 minutes, 1 cm³ of acetone is added to the above conical flask step (2) through a pipette, followed by addition of 2 cm³ of MHP from another pipette. The contents are then poured into the funnel of a dilatometer. The stopcock is opened and the solution is allowed to fill up the bulb until it is exactly below the capillary.
- (4) With the stopcock closed, the position of the meniscus is determined every 30 seconds for 600 seconds.
- (5) After allowing it to remain for another 600 seconds, a similar set of readings is taken (i.e. $\Delta = 600$ seconds).
- (6) The height of the meniscus can be measured "relative" to any suitable scale attached to the capillary column.



Dilatometer

TEST 2

Repeat the above procedure using 35 cm³ of NaOH solution and 2 cm³ of MHP only (without acetone).

4 Calculations

Guggenheim¹ has suggested a method to determine the rate constant of a first order reaction in which the amount of x_i that had reacted can be determined directly but the initial concentration is not known. This method can be used in this experiment as it involves a first order reaction, using a physical measurement in which the final reading cannot be made, or equilibrium cannot be achieved.

If times t_1 , t_2 , t_3 and so on, and $(t_1 + \Delta)$, $(t_2 + \Delta)$ and $(t_3 + \Delta)$ and so on, are chosen as a time interval constant, the following equations are true:

$$(V - V_{\infty}) = (V_0 - V_{\infty}) e^{-kt} \quad (16)$$

$$(V' - V_{\infty}) = (V_0 - V_{\infty}) e^{-k(t + \Delta)} \quad (17)$$

where V and V' are volumes at times t_1 and $(t_1 + \Delta)$.

Equation (17) minus equation (16) gives:

$$(V - V') = (V_0 - V_\infty) e^{-kt} (1 - e^{-k\Delta}) \quad (18)$$

or

$$kt + \ln(V - V') = \ln[(V_0 - V_\infty)(1 - e^{-k\Delta})] \quad (19)$$

The right hand side of equation (19) is a constant. Thus,

$$\ln(V - V') = -kt + \text{constant} \quad (20)$$

or

$$\log(V - V') = -(k/2.303) t + \text{constant} \quad (21)$$

From here, a graph of $\ln(V - V')$ against time, t gives a straight line of slope $-k$ (or alternatively, a graph of $\log(V - V')$ against time gives a straight line of slope $-k/2.303$).

5 Discussion

Compare the two tests carried out at the same temperature. What is the effect of acetone on the rate of reaction? Are the rate constants similar to each other within experimental error? Is this conclusion consistent with the mechanism expressed in equation (4) or in equation (11)? Give your reasons.

6 References

1. E. A. Guggenheim, *Phil. Mat.*, 1926, 2, 538.
2. V. K. La Mer and M. L. Miller, *J. Am. Chem. Soc.*, 1935, 57, 2674.
3. Atkins, P. W. (1998), *Physical Chemistry*, 7th ed. Oxford.
4. Levine, I. N. (2002), *Physical Chemistry*, 5th edn. McGraw Hill.

nb: Please quote experimental error estimates for all your data presented.

Plagiarism Warning!

Some of these experiments are carried out in groups of usually a pair of students. Therefore expectedly, each member of a group should follow an identical procedure in the laboratory and has the same set of raw data. Members of a group are allowed to discuss the analysis of data with one another. However, preparation of the report including data analysis, interpretation and discussion must be prepared by the individual student submitting the report.

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APPENDIX

To measure the rate of reaction from changes in a physical property

Consider a general reaction,



where Z includes all the products. Let the value of a physical property at any time t,

$$\lambda = \lambda_M + \lambda_A + \lambda_B + \lambda_C + \lambda_Z, \quad (B)$$

where λ_M is the contribution from the first reactant and the all the other λ s change with concentration, for example,

$$\lambda_A = \zeta_A [A] \quad (C)$$

where ζ_A is a proportionality constant. Let the initial concentrations of reactants be a, b, c respectively and the change in the extent of reaction x is the no. of moles that have reacted during time t, then,

$$\lambda = \lambda_M + \zeta_A(a - nx) + \zeta_B(b - mx) + \zeta_C(c - px) + \zeta_Z rZ \quad (D)$$

and

$$\lambda_0 = \zeta_M + \zeta_A a + \zeta_B b + \zeta_C c \quad (D1)$$

$$\lambda_\infty = \lambda_M + \zeta_B(b - ma/n) + \zeta_C(c - pa/n) + \zeta_Z ra/n \quad (D2)$$

where λ_0 and λ are initial and final values of λ , and in equation (D2) it is assumed that A is the is the reactant in infinite excess.

Subtraction of (D1) from (D2) gives:

$$\lambda_\infty - \lambda_0 = \zeta_Z(ra/n) - \zeta_A a - \zeta_B(ma/n) + \zeta_C(pa/n) \quad (D3)$$

and subtraction of (D1) from (D) gives:

$$\lambda_\infty - \lambda_0 = \zeta_Z rx - \zeta_A nx - \zeta_B mx + \zeta_C px \quad (D4)$$

which may be summarized as

$$\lambda - \lambda_0 = x\Delta\zeta; \quad \zeta_\infty - \lambda_0 = (a/n)\Delta\zeta \quad (D5)$$

$$\text{and} \quad \lambda_\infty - \lambda = (a/n - x)\Delta\zeta \quad (D6)$$

$$\text{where} \quad \Delta\zeta = \zeta_Z r - \zeta_A n - \zeta_B m + \zeta_C p \quad (E)$$

From here, we can derive a useful kinetic expression.

$$nx/a = (\lambda - \lambda_0) / (\lambda_\infty - \lambda) \quad (F)$$

$$a / (a - nx) = (\lambda - \lambda_0) / (\lambda_\infty - \lambda) \quad (F1)$$