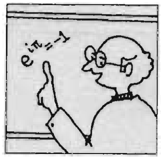
Classroom



In this section of* Resonance, *we invite readers to pose questions likely to be raised in a classroom situation. We may suggest strategies for dealing with them, or invite responses, or both. "Classroom" is equally a forum for raising broader issues and sharing personal experiences and viewpoints on matters related to teaching and learning science.

Reaction of RCOOH-NaHCO$_3$, a Convenient Illustration

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An improvised experiment involving the movement of water-band in a glass tube is used to illustrate the kinetics of RCOOH–NaHCO$_3$ reaction. A probable mechanism is derived from the kinetics of the reaction.

Introduction

Chemical kinetics is invariably an important component of senior secondary and first year college chemistry curricula. Although this topic is highly experimental in nature, in a majority of classrooms it is taught without the aid of experiments. It is because the experiments to illustrate the concepts of chemical kinetics involve complicated procedures and long time duration. Some improvised experiments involving the formation of a gas as a reaction product have been reported. The progress of reactions in such experiments is monitored by measuring the volume of gas formed at different time intervals with the help of gas syringes. A 100 ml gas syringe was first used by Max Schmidt in 1931. In an attempt to illustrate the concepts of chemical kinetics[1] by a single experiment we suggest the use of neutralization reaction of carboxylic acids with sodium hydrogen carbonate. Gas syringes cannot be conveniently used in this experiment because of high friction between the plunger and

[1] The goals of chemical kinetics are to determine the following: the rate of a reaction, order of reaction with respect to each reactant and the overall order of the reaction, half life period, specific reaction rate constant and a tentative mechanism of the reaction

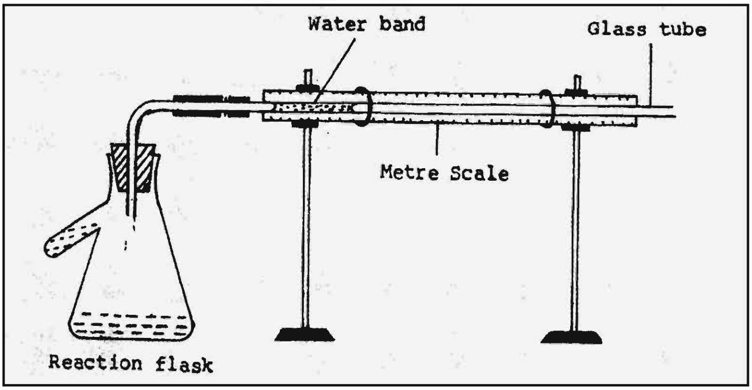


Figure 1. Set-up of apparatus.

the barrel of the syringe. Others have also reported the problem associated with the use of syringes. In the present experiment, an alternative and simple technique of movement of water-band in an ordinary glass tube is used to monitor the progress of reaction.

Experimental Setup

The apparatus is shown in *Figure 1*. A 6m mid ordinary glass tube is tied to a wooden metre-scale. One end of the glass tube is connected to an L-shaped delivery tube through a rubber tube. The other end of the delivery tube is connected to a specially designed 150 ml reaction flask. It is a conical flask fitted with a side tube of 5–6 ml capacity. The reaction flask is kept in a water bath at room temperature so as to ensure a uniform temperature throughout the reaction.

The rubber stopper is removed from the mouth of the reaction flask and about 1.5–2 ml of water is poured into the L-shaped delivery tube with a dropper. A water band of 5–7 cm length is formed in the glass tube. The position of the water-band in the glass tube is adjusted by moving the delivery tube upward or downward. Any air bubble in the water-band is also removed in this way.

One of the reacting solutions, 5 ml of sodium hydrogen carbonate of known concentration is taken into the side tube and the other, 5ml of carboxylic acid solution is taken into the reaction flask

Reaction Set	Concentration Acid / mol L^{-1}	Concentration $NaHCO_3$ / mol L^{-1}
I	1.0×10^{-1}	1.0×10^{-1}
II	5.0×10^{-2}	1.0×10^{-1}
III	5.0×10^{-2}	5.0×10^{-2}
IV	2.5×10^{-2}	2.5×10^{-2}

Table 1. Initial concentration of reactants CO_3.

containing a magnetic stir-bar. The rubber stopper is replaced over the mouth of the flask. The water-band gets pushed down a few centimetres into the glass tube. It is taken as the zero point on the scale. Tilting the flask mixes the two reacting solutions and a stopwatch is simultaneously started. The mixture is stirred gently with a magnetic stirrer. As carbon dioxide gas is formed, it pushes down the water-band in the glass tube. Even a negligibly small pressure exerted by the gas, perhaps much smaller than that required for displacing the liquid in an eudiometer tube, displaces the water-band. The positions of one end of the water-band on the metre-scale are recorded at 10-second intervals. Towards the end when the reaction becomes slow, the readings are recorded at appropriately longer time intervals. The experiment comprises the neutralization of four different carboxylic acids separately using sodium hydrogen carbonate. For each carboxylic acid, four different reaction sets using different concentrations of reactants are performed. The concentrations of reactants in any particular reaction set are the same while using different carboxylic acids. The strengths of acids and sodium hydrogen carbonate solutions used are shown in *Table 1*.

The plots of distance moved in centimetres by the water-band versus the time in seconds recorded for different sets of reactions using four different concentrations of all the four carboxylic acids, namely methanoic, ethanoic, propanoic and trichloroethanoic acids are used to determine the initial rates of reactions and half life periods (*Table 2*).

The shapes of the graphs formed by using different carboxylic

Reaction	Acid	Relative initial rate of reaction (R) per second	$t_{1/2}$ (s)	$k(10^2\ s^{-1})$
	HCOOH			
I		1.6	22	
II		0.78	21	
III		0.70	20	3.3 ± 0.2
IV		0.33	20	
	CH_3COOH			
I		1.2	24	
II		0.70	22	3.2 ± 0.1
III		0.60	22	
IV		0.25	26	
	CH_3CH_2COOH			
I		1.0	22	
II		0.60	22	3.0 ± 0.1
III		0.60	23	
IV		0.23	26	
	Cl_3CCOOH			
I		1.8	20	
II		0.78	20	3.5 ± 0.2
III		0.78	20	
IV		0.36	20	

* All measurements are expressed upto the appropriate numbers of significant figures.

Table 2. Kinetic Data.

acids are similar to the one shown in *Figure 2* for methanoic acid-sodium hydrogen carbonate reaction.

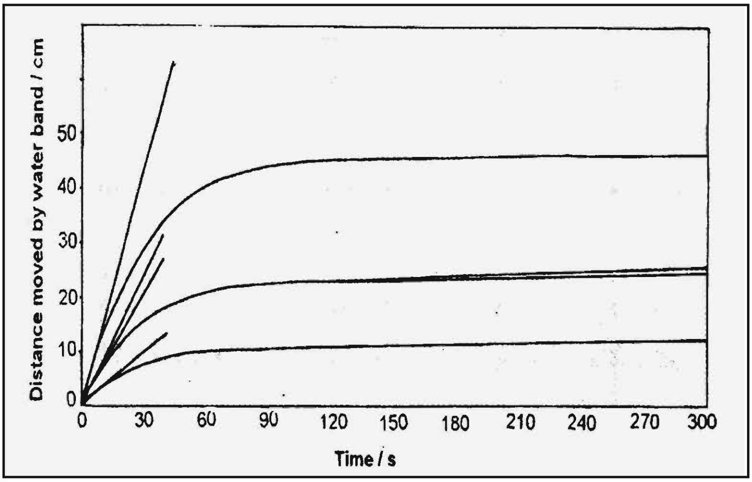


Figure 2. Kinetics of methanoic acid-sodium hydrogen carbonate reaction.

Discussion

As expected, the initial rate of reaction is maximum for reaction set I where the initial concentrations of reactants are maximum, and minimum for reaction set IV where the initial concentrations are minimum. In reaction sets I and II where the initial concentration of acid is halved and that of sodium hydrogen carbonate is unchanged, the initial rate of reaction is halved. The reaction sets II and III indicate that the rate of reaction remains almost unchanged on changing the concentration of sodium hydrogen carbonate. In reaction sets III and IV, the rate is halved as the acid concentration is halved. The same pattern is observed within the experimental error with all the four carboxylic acids.

Order of Reaction

The fact that the rate of reaction is independent of sodium hydrogen carbonate concentration leads to the conclusion that order of reaction with respect to sodium hydrogen carbonate is zero. The order of reaction with respect to both the reactants i.e. acid and $NaHCO_3$ may also be determined by the initial rate method. The initial rate of reaction, i.e. the rate when the reactant concentrations have not changed appreciably, is determined from the graphs of distance moved by water band vs time (*Figure 2*). The initial concentration of only one of the reactants is then changed and the initial rate is determined again. Assuming the orders of reaction with respect to acid and $NaHCO_3$ are p and q respectively, the rate law equation for the reaction is given as follows:

$$\text{Rate } (R) = k\ [\text{Acid}]^p\ [\text{NaHCO}_3]^q$$

The values of p and q for HCOOH-$NaHCO_3$ reaction are calculated as follows as an illustration.

$$\frac{R\text{set}-\text{I}}{R\text{set}-\text{II}} = \frac{1.6}{0.78} = \frac{k[0.1]^p[0.1]^q}{k[0.05]^p[0.1]^q}, \qquad p=1$$

$$\frac{R\text{set}-\text{II}}{R\text{set}-\text{III}}=\frac{0.78}{0.70}=\frac{k[0.5]^{p}[0.1]^{q}}{k[0.05]^{p}[0.5]^{q}}, \qquad q=0$$

The overall order of reaction (1+0) is one. The orders of reaction for the remaining three acids are similarly determined. These are recorded in *Table 2*. Thus the RCOOH-$NaHCO_3$ reaction is a first order reaction.

The half-life period, the time taken for half of the reaction to complete (*Table 2*) is independent of the initial concentrations of reactants. It is valid for first order reactions only.

The order of reaction can also be determined using van't Hoff's method:

$$R=\text{K}\,C^{n} \qquad (1)$$

where R is the initial rate of reaction, k the specific reaction rate constant, C the initial concentration and n the order of reaction.

$$\log R = n\log C + \log k \qquad (2)$$

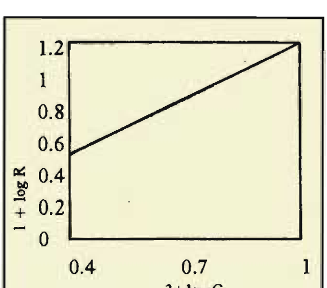
[2] Constants 1 and 2 have been added in order to convert negative numbers to positive ones for ease in plotting.

The plot of equation (2), (1+log R) versus (2 + log C) gives a straight line (*Figure 3*)[2]. The slope of the line gives the order of reaction n. The slope of four graphs is 1.1. The order of reaction turns out to be one within the experimental limits by this method as well.

The value of k, the specific reaction rate constant can be determined from half-life period values by the following equation:

$$t_{1/2} = 0.693/k$$

Figure 3. 1+ log R vs. 2+ log C.



The average values of k are recorded in *Table 2*.

A comparison of initial rates of reactions (R) and half life periods ($t_{1/2}$) with the acid dissociation constants (K_a) of carboxylic acids indicates that R decreases and $t_{1/2}$ increases with decrease in K_a values, the measure of acid strength of acids. R is maximum and $t_{1/2}$ is minimum for the reaction involving trichloroethanoic acid, the strongest acid. Also, R is minimum

and $t_{1/2}$ maximum for propanoic acid reaction. In fact there is only a little difference in the values of R and $t_{1/2}$ in the reactions involving ethanoic and propanoic acids. This is because their acid strengths are almost the same. The K_a values of the four acids are as follows:
$HCOOH = 1.8\times10^{-4}$, $CH_3COOH = 1.8\times10^{-5}$, $CH_3CH_2COOH = 1.3\times10^{-5}$ and $Cl_3C\,COOH = 1.3\times10^{-1}$ mol L^{-1}.

Mechanism of Reaction

Chemical kinetics plays an important role in deciding the mechanism of reaction. The following steps may be proposed for the neutralization of carboxylic acids using sodium hydrogen carbonate:

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+ \quad \text{(i)}$$
$$NaHCO_3 \rightleftharpoons Na^+ + HCO_3^- \quad \text{(ii)}$$
$$H_3O^+ + OH^- \rightleftharpoons 2H_2O \quad \text{(iii)}$$
$$H_2CO_3 \rightleftharpoons CO_2 + H_2O \quad \text{(iv)}$$

Carboxylic acids are weak acids and are only partially ionized. Sodium hydrogen carbonate solution is mildly alkaline due to hydrolysis. The hydronium ion from step – (i) and hydroxyl ion from step (ii) neutralize each other according to step (iii). Carbonic acid so formed is unstable and largely decomposes to carbon dioxide and water. As step (i) is the slowest, it is the rate-determining step. It is in agreement with the rate law equation, $R = k$ [RCOOH].

Thus kinetics of the neutralization of four acids provides sufficient supporting data to propose a mechanism for the reaction. The present technique of movement of water-band in a glass-tube is an alternative and convenient method to monitor the progress of reactions. It can be successfully used to illustrate a number of concepts of chemical kinetics. The use of complicated and time consuming methods of estimating the concentrations of reactants or products are avoided. The experiment also illustrates the application of chemical kinetics in the investigation of reaction mechanisms.

Suggested Reading

[1] Rogers M. *Gas Syringe Experiments*. Heinemann Educational Books Ltd. London, 1970
[2] Laidler K J. *Reaction kinetics*. Pergamon. Vol.1. 16, 1963.