Investigation of the Overall Order of Reaction between Hydrogen Peroxide and Iodide in Acidic Medium (A Clock Reaction)

Student Handout

Purposes

To determine the order of the reaction between H_2O_2(aq) and I^-(aq) in acidic medium with respect to
1. H_2O_2(aq),
2. I^-(aq) and
3. H^+(aq).

Introduction

The kinetics of the reaction:

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

can be investigated by the introduction of a small and fixed amount of $S_2O_3^{2-}$(aq) and starch indicator.

$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$ ……….. *main reaction*
$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$ …….*monitor reaction*
Starch solution + I_2(aq) $\longrightarrow$ blue complex ………… ..*indicator reaction*

The added $S_2O_3^{2-}$(aq) ions consume the I_2(aq) ions produced from the *main reaction*. As long as there are $S_2O_3^{2-}$(aq) ions in the reaction mixture, I_2(aq) ions formed from the main reaction will be instantaneously consumed by the $S_2O_3^{2-}$(aq) ions and the starch indicator will not be affected. However, when all $S_2O_3^{2-}$(aq) ions are consumed, the I_2(aq) ions start to build up and will immediately turn the starch indicator to deep blue.

The overall result is that upon mixing different amounts of H_2O_2(aq), I^-(aq), H^+(aq), $S_2O_3^{2-}$(aq) and starch indicator, no change will be observed at the start of the experiment, but the reaction mixture suddenly changes to deep blue after a period of time. The time elapsed before the development of the blue colour depends on the amount of $S_2O_3^{2-}$(aq) used. The greater the amount of $S_2O_3^{2-}$(aq) is used, the longer will be the time taken for the development of colour. Thus the reaction responsible by the $S_2O_3^{2-}$(aq) is also known as the *monitor reaction*, as it controls the time taken for the development of colour.

Reactions using the above technique are collectively classified as '***clock reactions***'. If iodine is used to indicate the reaction time, it is called an iodine clock reaction. Likewise, if bromine is used, it is called a bromine clock reaction.

Time elapsed for colour development indicates the time (t) taken for the formation of a certain amount of iodine from the main reaction. $1/t$ would be proportional to the rate of formation of this amount of iodine. $1/t$ would also be proportional to the ***initial rate*** of decrease in concentration of I^-(aq) or H_2O_2(aq) if the amount of iodine formed is small or if the amount of $S_2O_3^{2-}$(aq) used is small. Hence there is a need to use small amount of $S_2O_3^{2-}$(aq).

Order of the reaction w.r.t. I^-(aq) will be investigated by keeping the concentrations of H_2O_2(aq) and H^+(aq) constant while varying the concentration of I^-(aq) in the ratio of 1 : 2 : 4 : 8. If the rate (1/*t*) doubles each time, the order of reaction w.r.t. to I^-(aq) will be determined as 1. If the rate (1/*t*) remains unchanged, the order can be regarded as zero. The experiment is then repeated for determining orders for H_2O_2(aq) and H^+(aq).

Safety

Avoid skin contact with the chemicals.

Materials and Apparatus

About 20 cm^3 of each of the following solutions in labelled plastic bottles:

1.50% H_2O_2(aq)

0.60 M H_2SO_4(aq), 0.60 M KI(aq), 0.08 M $Na_2S_2O_3$(aq), starch solution, deionised water.

Two rigid 8-well reaction strips (Fig. 1), micro-tip plastic pipette, stop watch, microspatula.

Experimental Procedures

Part A: Order of reaction w.r.t. iodide ion

1. Using a fresh and clean micro-tip plastic pipette, transfer 1 drop each of 1.5% H_2O_2(aq), 0.6 M H_2SO_4(aq) and starch indicator solution to 4 separate wells of a 8-well reaction strip (call it strip A) so that each well has a total volume of 3 drops.
2. Take another 8-well reaction strip (call it strip B), again using a fresh and clean micro-tip plastic pipette, transfer 1 drop of 0.08 M $Na_2S_2O_3$(aq) to each of the first 4 wells.
3. In strip B, add 1 drop of 0.6 M KI(aq) to the first well, 2 drops to the second, 4 drops to the third and 8 drops to the fourth. Add 7 drops of deionised water to the first well, 6 drops to the second and 4 drops to the third so that the total volume of reactant mixture in each of the 4 wells of strip B is 9 drops. (see Table A)
4. Stir the solution mixture in each of the wells of strip B with a microspatula.
5. Invert strip B and stack it atop strip A so that the first 4 wells of strip B is directly above the first 4 wells of strip A.
6. Hold the two strips firmly together by means of two small pieces of rubber tubing, one at each end. Lower the strip combination suddenly (“shake-down” technique) so that the two solution mixtures mix thoroughly (see Fig. 2). Start the stop watch at the same time.
7. Turn the strip combination upside down ***repeatedly*** and look for the sudden appearance of a deep blue colour. Record the time taken. Record the time until all the 4 wells have developed colour in the correct sequence.
8. Clean the reaction strips thoroughly with deionised water and empty the water in the wells.

Fig. 1

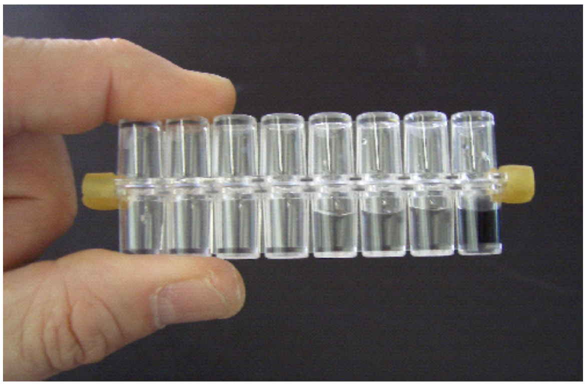

Fig. 2

Table A

	Number of drops					
	Strip A			Strip B		
Well	H_2O_2(aq)	H_2SO_4(aq)	Starch solution	I^-(aq)	H_2O(l)	0.08M $S_2O_3^{2-}$(aq)
1	1	1	1	1	7	1
2				2	6	
3				4	4	
4				8	0	

Part B: Order of reaction w.r.t. H_2O_2(aq)

9. Repeat steps (1) to (8) according to Table B.

Table B

	Number of drops					
	Strip A			Strip B		
Well	I^-(aq)	0.08 M $S_2O_3^{2-}$(aq)	Starch solution	H_2O_2(aq)	H_2O(l)	H_2SO_4(aq)
1	1	1	1	1	7	1
2				2	6	
3				4	4	
4				8	0	

Part C: Order of reaction w.r.t. H^+(aq)

10. Repeat steps (1) to (8) according to Table C.

Table C

	Number of drops					
	Strip A			Strip B		
Well	$I^-(aq)$	0.08M $S_2O_3^{2-}(aq)$	Starch solution	$H_2SO_4(aq)$	$H_2O(l)$	$H_2O_2(aq)$
1	1	1	1	1	7	1
2				2	6	
3				4	4	
4				8	0	

Results

Variable	Relative concentration	t (s)	Rel. initial rate, 1/t (s^{-1})	Deduced order
$[I^-(aq)]$	1			
	2			
	4			
	8			
$[H_2O_2(aq)]$	1			
	2			
	4			
	8			
$[H^+(aq)]$	1			
	2			
	4			
	8			

Note: If initial rate doubles when the concentration of a species is doubled, the reaction is first order with respect to that species.

Discussion Questions

1. With the help of an appropriate sketch, illustrate the meaning of "initial rate".
2. Why is it assumed that in order to obtain initial rate, time (t) has to be small?
3. Why are initial rate preferred to rates at other times of a reaction, i.e. instantaneous rates?
4. Explain why the amount of $S_2O_3^{2-}(aq)$ added to the reaction mixture has to be small.
5. From the deduced order w.r.t. each reactant, give a rate equation for the reaction.
6. A proposed mechanism for the reaction consists of the following three elementary steps:

$$H_2O_2(aq) + I^-(aq) \longrightarrow X + H_2O(l) \text{ .... (slow)}$$
$$H^+(aq) + X \longrightarrow Y \text{ .... (fast)}$$
$$Y + H^+(aq) + I^-(aq) \longrightarrow I_2(aq) + H_2O(l) \text{ ...... (fast)}$$

Suggest species for X and Y in the above elementary reactions so that the rate expression for the rate determining step fits with the experimental rate equation.