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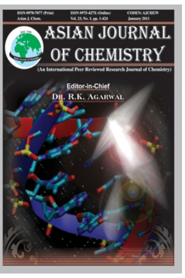

Kinetic Study of Decomposition of Aqueous Hydrogen Peroxide by Colloidal Manganese Dioxide

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The kinetics of the decomposition of aqueous hydrogen peroxide by water-soluble colloidal manganese dioxide (obtained by reduction of potassium permanganate with sodium thiosulphate) has been studied in the absence and presence of aqueous perchloric acid solution. The reaction followed pseudo first order kinetics with respect to [MnO_2], fractional order with respect to [$HClO_4$] and first order kinetics with respect to [H_2O_2].

Key Words: Hydrogen peroxide, Perchloric acid, Colloidal manganese dioxide.

INTRODUCTION

Manganese dioxide is a substance of certain importance owing to its catalytic[1] and oxidizing[2-5] properties, but its applications are notably limited because of its insolubility under ordinary conditions[6]. Recently, water-soluble colloidal manganese dioxide was prepared from reduction of aqueous potassium permanganate by sodium thiosulfate under neutral conditions[7-9]. This method yields a perfectly transparent solution of colloidal manganese dioxide, stable for several months. The kinetic study of colloidal MnO_2 towards oxidizing behaviour in redox reactions can be easily implemented by conventional spectrophotometric method[10]. It has been extensively used as an oxidant for oxidizing number of organic species like oxalic acid, formic acid, D-fructose, thiourea, lactic acid, L-methionine, l-tyrosine, gum arabic, citric acid, malic acid, ascorbic acid *etc*.[11-21]. Although it is used[22] to oxidize Mn^{2+}, its oxidizing behaviour towards inorganic species is limited. The present work deals with the study of the kinetics of the decomposition of hydrogen peroxide by colloidal MnO_2 in presence and absence of aqueous perchloric acid solution.

EXPERIMENTAL

Aqueous solutions of potassium permanganate (E. Merck, 98.5 %), sodium thiosulfate (E. Merck, 99 %) were prepared by dissolving the requisite amounts in doubly distilled and deionized water. All the other reagents (hydrogen peroxide and perchloric acid) were commercially available analytical reagents and used as received by proper dilution.

Preparation of colloidal MnO_2: A dark-brown colloidal MnO_2 (5.0×10^{-4} mol dm^{-3}) solution was prepared by reducing $KMnO_4$ with a stoichiometric amount of $Na_2S_2O_3$ according to the reaction,

$$8MnO_4^- + 3S_2O_3^{2-} + 2H^+ \longrightarrow 8MnO_2 + 6SO_4^{2-} + H_2O$$

A 2 L volumetric flask was filled with water to around 4/5 of its capacity. 20 mL of $Na_2S_2O_3$ (1.88×10^{-2} mol dm^{-3}) solution was added to it. Then 5 mL of $KMnO_4$ (0.2 mol dm^{-3}) solution was added and the mixture was diluted to 2 L with more water. Each addition was followed of homogenization by gentle shaking. A dark brown coloured colloidal solution was obtained, remaining perfectly transparent at least for several months.

Kinetic spectroscopic measurement: The reaction was initiated by adding the required quantity of hydrogen peroxide, maintained at constant temperature to the mixed solution of colloidal MnO_2 and perchloric acid maintained at the same temperature. The zero-time was taken when half of the hydrogen peroxide solution was added. The rate of disappearance of MnO_2 was monitored at 425 nm at different time intervals with a UV-visble spectrophotometer, using a cell of path length 1 cm. The pseudo-first order rate constants were calculated from the slopes of plots of log (absorbance) *versus* time. The first-order plots in almost all cases were linear to 80 % completion of the reaction with correlation coefficient *ca.* 0.998.

RESULTS AND DISCUSSION

Characterization of colloidal MnO_2: The colloid's UV-vis spectrum was recorded with a Hitachi U 2000 UV-visible double-beam spectrophotometer and showed a large band covering the whole visible region of the spectrum, with absorbance maxima at 425 nm. So the wavelength of 425 nm was chosen to follow the kinetic runs.

Kinetic study: The kinetic results of the reduction of colloidal MnO_2 by H_2O_2 obtained in aqueous medium under different experimental conditions can be summarizes as follows.

Rate dependence on colloidal MnO_2: The order with respect to colloidal MnO_2 was determined by finding K_{obs} at different initial concentrations of MnO_2 (1.6×10^{-5}-2.8×10^{-5} mol dm^{-3}) with other parameters remaining fixed $[H_2O_2] = 2.8 \times 10^{-4}$ mol dm^{-3} $[HClO_4] = 0.4 \times 10^{-4}$ mol dm^{-3}. It has been found that the values of rate constants decreases up to $[MnO_2] < 2.0 \times 10^{-5}$ mol dm^{-3} and then remained constant for further increase of concentration of MnO_2 (Table-1). The initial decrease in the rate constant is due to the possible coagulation of the colloidal particles. The constant values of rate constants indicate that the rate is independent on concentration of colloidal MnO_2. According to the basic tenets of chemical kinetics the pseudo-first order rate constants should be independent of the initial concentration of MnO_2. So the reaction is pseudo 1st order with respect to colloidal MnO_2.

TABLE-1
EFFECT OF VARING THE [COLLOIDAL MnO_2], [H_2O_2] AND [$HClO_4$] ON THE PSEUDO-FIRST ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF H_2O_2 BY COLLOIDAL MnO_2

10^5 [MnO_2] (mol dm^{-3})	10^4 [H_2O_2] (mol dm^{-3})	10^4 [$HClO_4$] (mol dm^{-3})	10^3 k_{abs} (s^{-1})
1.6	2.8	0.4	114.9
1.8			111.2
2.0			39.7
2.2			39.8
2.4			40.4
2.6			39.6
2.8			39.6
2.8	1.8	0.2	22.8
	2.2		25.1
	2.6		30.9
	3.0		36.6
	3.4		41.9
	3.8		46.9
	4.2		56.4
2.8	2.8	0.2	33.1
		0.4	39.6
		O.6	45.6
		0.8	54.8

Rate dependence on [H_2O_2]: The order with respect to hydrogen peroxide was deduced from the values of k_{obs} obtained at several [H_2O_2] (1.8×10^{-4}-4.2×10^{-4} mol dm^{-3}) with fixed [MnO_2] (2.8×10^{-4} mol dm^{-3}) and [$HClO_4$] ($= 0.2 \times 10^{-4}$ mol dm^{-3}). The values of rate constant increased with increase in [H_2O_2]. A plot of log k *versus* log [H_2O_2] is linear with slope 1.079 which confirmed that the reaction is 1st order with respect to [H_2O_2] (Fig. 1).

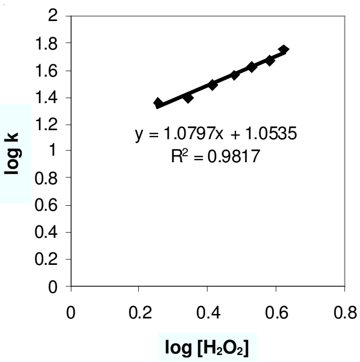

Fig. 1. Dependence of first order rate constants on the [H_2O_2] in presence of perchloric acid

Rate dependence on [$HClO_4$]: The rate constant, obtained as a function of [$HClO_4$], at constant [MnO_2] ($= 2.8 \times 10^{-5}$ mol dm^{-3}) and [H_2O_2] ($= 2.8 \times 10^{-4}$ mol dm^{-3}) was found to increase with increasing [$HClO_4$] (0.2×10^{-4}-0.8×10^{-4} mol dm^{-3}). The plot of log k_{obs} *versus* log [H^+] is linear with slope 0.34, indicating the order to be fractional with respect to [$HClO_4$] (Fig. 2). In order to confirm the role of $HClO_4$, a series of experiments were performed in the absence of $HClO_4$ as a function of [MnO_2] and [H_2O_2]. The results of these experiments are summarized in Table-2. It has been found that in the absence of $HClO_4$ the rate constants also decreases first with increase in concentration of MnO_2 to $< 2.0 \times 10^{-5}$ mol dm^{-3} and then remain constant for further increase of concentration of MnO_2 at constant [H_2O_2] (2.8×10^{-4} mol dm^{-3}). Similarly the rate constant increases for increase in concentration of H_2O_2 at constant [MnO_2] ($= 2.8 \times 10^{-5}$ mol dm^{-3}). Here also the plot of rate constant *versus* [H_2O_2] is linear (Fig. 3). However all the rate constant values obtained in presence of $HClO_4$ are more than the corresponding values obtained in the absence of $HClO_4$ (Table-3). Thus both pH-dependent and independent pathways are involved for this decomposition reaction of H_2O_2 using colloidal MnO_2.

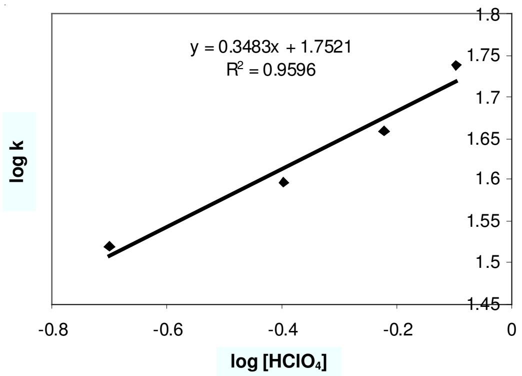

Fig. 2. log-log plot of concentration of perchloric acid with rate constant

TABLE-2
VALUES OF FIRST ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF H_2O_2 BY COLLOIDAL MnO_2 IN THE ABSENCE OF $HClO_4$

10^5 [MnO_2] (mol dm^{-3})	10^4 [H_2O_2] (mol dm^{-3})	10^3 K_{abs} (s^{-1})
1.6	2.8	36.90
1.8		30.40
2.0		26.80
2.2		26.90
2.4		26.90
2.6		26.70
2.8		26.80
2.8	2.8	26.80
	3.2	36.15
	3.6	39.90
	4.0	46.90
	4.4	49.30

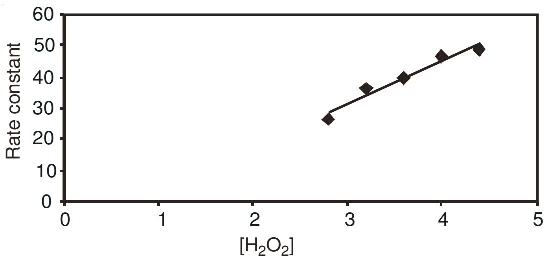

Fig. 3. Dependence of first order rate constants on the $[H_2O_2]$ in absence of perchloric acid

TABLE-3
COMPARISON OF 1ST ORDER RATE CONSTANTS IN THE PRESENCE AND ABSENCE OF $HClO_4$

10^5 $[MnO_2]$ (mol dm^{-3})	10^4 $[H_2O_2]$ (mol dm^{-3})	10^3 k_{abs} (s^{-1}) in presence and absence of $HClO_4$	
		Presence	Absence
1.6	2.8	114.9	36.9
1.8		11.2	30.4
2.0		39.7	26.8
2.2		39.8	26.9
2.4		40.4	26.9
2.6		39.6	26.7
2.8		39.6	26.8

Conclusion

The colloidal MnO_2 first prepared by Perez-Benito *et al.*, can be used for the decomposition of H_2O_2. This decomposition process obeys Pseudo-first order kinetics, which is both pH dependent and pH independent.

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