Asian Journal of Chemistry Vol. 21, No. 1 (2009), 393-396

Kinetic Catalytic Method for the Estimation of Mn(II)

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Mn(II) has been estimated in simulated samples by kinetic catalytic method using D-glucose-Ce(IV) redox indicator reaction in sulphuric acid medium. The estimation have been made from the calibration plots obtained by using pseudo first order rate constant data of the indicator reaction and also by fixed time and fixed concentration procedures at different ppm concentration of Mn(II). The results of this study indicate that the estimated values of the simulated samples are consistent and responsible.

Key Words: Kinetic, Mn(II), Redox reaction.

INTRODUCTION

It is well known that the presence of certain substances (metals, non-metals and even ligands) accelerate some slow reactions through their catalytic effect. Metal ion oxidants have been widely been employed in synthetic organic chemistry[1-3] and also in elaborating reaction mechanistic pathway of their electron transfer reaction with carbohydrates. Catalytic determination constitute the most widely used analytical kinetic method[4-6]. The present work describes the catalytic determination of Mn(II) using oxidation of D-glucose by Ce(IV) as an indicator reaction.

EXPERIMENTAL

Commercially available chemicals of pure quality were used without further purification. Stock solutions of D-glucose (make: Merck) and Mn(II) (manganese chloride; purity: 99.0 %; make: SD Fine) were prepared in double distilled water. Ce(IV) stock solutions prepared by dissolving ceric sulphate (purity: 99.9 %; make: Loba Chemie) in aqueous sulphuric acid.

Kinetic method: Kinetic runs were performed in stoppered glass vessels in a controlled-temperature (± 0.1 ºC) water bath. The kinetics of redox reaction between D-glucose, Mn(II) and Ce(IV) in sulphuric acid medium

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was followed under pseudo first order condition by measuring absorbance at 316 nm (λ_{max} for Ce(IV)-Shimadzu Pharmaspec UV-1700) at constant temperature. The unknown is calculated in simulated sample by fix time method and fix absorbance method from the regression equations.

RESULTS AND DISCUSSION

Kinetic equation representing a catalyzed reaction can be formulated on the basis of mechanism involving formation of transient intermediate complex according to following scheme.

$$C + B \xrightarrow{k_1} CB + Y \tag{1}$$

$$C + A \xrightarrow{k_2} P + C \tag{2}$$

where C denotes catalyst, B an excess reactant forming the intermediate complex (CB) with the catalyst, A monitored reactant and P and Y are reaction products.

The indicator reaction between D-glucose, Mn(II) and Ce(IV) in sulphuric acid medium under kinetic run conditions can be represented in eqns. 3 and 4.

$$2Mn(II) + 2Ce(IV) \longrightarrow 2Mn(III) + 2Ce(III) \tag{3}$$

$$C_6H_{12}O_6 + Mn(III) + H_2O \longrightarrow C_5H_{10}O_5 + 2Mn(II) + HCOOH + 2H^+ \tag{4}$$

Kinetic estimation:

$$A + B \xrightarrow{C} P \text{ (Product)} \tag{5}$$

The rate equation when B is present in excess concentration, therefore according to whether reactant A or product P is monitored can be obtained as

$$\text{Rate (v)} = \frac{-d[A]}{dt} = k[A]\,[C]_0 + k_1[A] \tag{6}$$

or

$$\text{Rate (v)} = \frac{dP}{dt} = k([A]_0 - [P])[C]_0 + k_1([A]_0\ [P]_0) \tag{7}$$

where $[A]_0$ being the initial concentration of A and [P] the concentration of product formed and k and k_1 are the pseudo rate constant for the catalyzed and unanalyzed reactions. In either case the reaction must be pseudo-first-order with respect to monitored species, since the catalyst concentration, by definition, does not change during the reaction[7].

From the above equation assuming, $\Delta t = t_2 - t_1$ = constant

$$\ln\frac{[A]_1}{\Delta t} = \Delta(\ln[A]) = k'[C]_0 + k_1' \tag{8}$$

with $k' = k\Delta t$ and $k_1' = k_1\Delta t$. The plot of $\Delta(\ln[A])$ ν_S $[C]_0$ for a fixed concentration of A, $[A]_0$, constitute the calibration graph in this case.

Since the $[A]_1/[A]_2$ ratio is constant for any catalyst concentration over a preselected time intervals if all reaction conditions are kept constant then it will be possible to calculate the overall pseudo first order rate constant, k_T, from

$$k_T = \frac{\Delta(\ln[A])}{\Delta t} = k[C]_0 + k \tag{9}$$

which, if plotted against the catalyst concentration, will give a straight line that can be used as the calibration plot.

Now, assuming $\Delta[A]$ to be constant

$$\frac{1}{\Delta t} = k''[C]_0 + k_1'' \tag{10}$$

where $k'' = k/\Delta(\ln[A]$ and $k_1'' = k_1/\Delta(\ln[A])$. This expression is equally valid whether the reaction is monitored through one of the reactant or product.

Kinetic estimation: The kinetic data of change in absorbance with initial concentrations of Mn(II) at fixed concentrations of cerium(IV), D-glucose and sulphuric acid has been given in Table-1. The variation of k_{obs}, absorbance at fixed time interval and time at fixed absorbance with initial concentration of D-glucose in different kinetic run is given by Table-2. The rate data of Table-2 has been used to obtain following linear regression equations (eqns. 11-15) to obtain unknown concentration of simulated samples of Mn(II). The results of these estimations with actual theoretical value are also given in Table-2.

TABLE-1
Mn(II) CATALYZED INDICATOR REACTION OF Ce(IV) WITH D-GLUCOSE IN H_2SO_4 MEDIUM
[Ce(IV)] = 350 ppm; $[H_2SO_4]$ = 1.45 mol dm^{-3}; λ = 316 nm
[D-glucose] = 2.7 %; Temperature = 296 ± 0.1 K

Time (s)	Mn(II) (ppm)						
	0.00	0.25	0.50	0.75	1.00	1.25	1.50
0	1.306	1.298	1.299	1.310	1.300	1.296	1.292
600	1.127	1.000	0.985	0.967	0.952	0.915	0.892
1200	0.973	0.789	0.764	0.733	0.700	0.650	0.600
1800	0.844	0.619	0.587	0.548	0.507	0.461	0.388
2400	0.725	0.487	0.456	0.413	0.349	0.293	0.247
3000	0.624	0.394	0.354	0.308	0.263	0.188	0.146
3600	0.528	0.313	0.269	0.219	0.178	0.118	0.082
4200	0.442	0.246	0.201	0.163	0.117	0.063	0.038
4800	0.376	0.194	0.152	0.113	0.074	0.028	0.012

TABLE-2
VARIATION OF k_{obs} (s^{-1}), ABSORBANCE AT FIXED TIME AND TIME AT FIXED ABSORBANCE WITH INITIAL CONCENTRATION OF Mn(II)

Mn(II) (ppm)	10^3 k_{obs}	Absorbance at fix time		Time at fix absorbance	
		2400	4200	0.9	0.7
0.25	24.396	0.487	0.246	880	1500
0.50	26.823	0.456	0.201	830	1400
0.75	29.563	0.413	0.163	790	1300
1.25	39.421	0.293	0.063	640	1030
1.50	44.408	0.247	0.038	580	980
Unknown	34.986	0.349	0.117	710	1150
[Unknown] ppm	**0.974**	**0.999**	**0.996**	**1.004**	**1.011**

Result: Unknown (ppm) = 0.997 ± 0.009 (calculated); 1.000 (Actual)

$$[Mn(II)] = 0.0598\,[k_{obs}] - 1.1177 \quad \text{Corre. Coeff.} = 0.9814 \qquad (11)$$

$$[Mn(II)] = -0.0040\,[A_{0.9}] + 3.8443 \quad \text{Corre. Coeff.} = 0.9903 \qquad (12)$$

$$[Mn(II)] = -0.0023\,[A_{0.7}] + 3.6559 \quad \text{Corre. Coeff.} = 0.9898 \qquad (13)$$

$$[Mn(II)] = -4.9428\,[t_{2400}] + 2.7243 \quad \text{Corre. Coeff.} = 0.9902 \qquad (14)$$

$$[Mn(II)] = -5.7980\,[t_{4200}] + 2.7243 \quad \text{Corre. Coeff.} = 0.9943 \qquad (15)$$

These equations have been used to determine the unknown concentration of simulated samples (Table-2).

ACKNOWLEDGEMENTS

Sincere thanks are due to Prof. and Head, Chemistry Department, Government Holkar Science College, Indore for permitting to undertake the present work and to Choksi Laboratories, Indore for providing facilities to carry out the experimental work.

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(*Received*: 20 December 2007; *Accepted*: 23 August 2008) AJC-6781