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Kinetics of the Oxidation of Hydroxylamine by Iodine in Aqueous Solution

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Kinetic of the rapid oxidation of hydroxylamine by iodine has been carried out voltametrically at various temperatures. From the results, kinetic parameters such as specific reaction rate, energy of activation, entropy of activation and frequency factor have been evaluated at 25°C in pH 3.0 and found to be 4.10^{-1} s^{-1}, 65.0 kJ mol^{-1}, –23.35 J K^{-1} mol^{-1} and 1.02×10^{12} mol^{-1} s^{-1} respectively. Further, the effect of H^+ ion concentration on specific reaction rate has also been determined.

Key Words: Kinetics, Oxidation, Hydroxylamine, Iodine.

INTRODUCTION

Oxidation of hydroxylamine is well known reaction. It was studied by Nazer *et al.*[1] with aqua vanadium (V) ion in aqueous perchloric acid. Gupta *et al.*[2] also studied the oxidation of hydroxylamine by platinum(IV) in sodium acetate-acetic acid buffer spectrophotometrically. Further, they studied its oxidation with chromic acid[3]. Kudesia[4] studied the kinetics of its oxidation by aqueous bromine at 25°C. Different workers used various oxidizing agents to study the oxidation of hydroxylamine[5–7].

In comparison with the oxidation of hydroxylamine by several reagents the oxidation of hydroxylamine by iodine in detailed acid medium has not yet been studied. Since the reaction is a fast one, the conventional methods of studying the kinetics of the reaction are not useful. Therefore, special methods have to be adopted. In the present work, this reaction has been studied by the use of rotating platinum electrode (RPE) technique. The technique had been successfully applied in the study of kinetics of rapid bromination of aromatic substrates[8, 9]. The RPE yield diffusion current is proportional to the concentration of the electro-reducible species[10]. Therefore, in reactions involving an electroreducible species, the course of reaction can be readily followed by measuring the diffusion current at intervals of time.

In the present work the kinetics of the reaction between hydroxylamine and iodine have been studied at different temperatures at particular pH. Also, the reaction has been studied at different pH but at particular temperature.

EXPERIMENTAL

All chemicals used were of analytical grade and water used for preparation of solution was double distilled. The stock solutions of hydroxylamine (5.0×10^{-2}M), iodine (5.0×10^{-2} M), potassium chloride (1.0 M), citric acid (2.0×10^{-1} M) and disodium hydrogen phosphate (4.0×10^{-1} M) were prepared by dissolving 2.052, 6.345, 74.5, 21.0 and 28.4 g respectively. Stock solution of iodine was standardized by adding sodium carbonate as buffer and titrating against sodium arsenite using starch as an indicator[10].

Kinetic Measurements : The saturated calomel electrode was dipped into an empty 500 mL beaker in which RPE was already rotated at 300 rpm. The whole assembly was kept in a thermostat at 25°C. 100 mL each of solution of iodine (1.0×10^{-3} M) and hydroxylamine (1.0×10^{-3} M) previously thermostated at 25°C were quickly poured into the beaker and a stopwatch was simultaneously started. The initial concentrations of iodine and hydroxylamine were each of 5.0×10^{-4} M in the resultant solutions. From the galvanometer deflection at various time intervals during the kinetics study the concentration of the iodine unreacted was estimated from the calibration curve (Table-1).

TABLE-1
KINETICS OF OXIDATION OF HYDROXYLAMINE BY IODINE IN AQUEOUS SOLUTION

Initial concentration of hydroxylamine	5.0×10^{-4} M
Initial concentration of iodine	5.0×10^{-4} M
pH of reaction medium	3.0
Concentration of potassium chloride	5.0×10^{-2} M
Temperature	25°C

Time (s)	Galvnometer deflection (cm)	Concentration of unreacted iodine ($\times 10^{-4}$ M)	$\frac{1}{\text{Iodine}} \times 10^{-3}$ M^{-1}
0	52.6	5.00	2.00
30	50.0	4.75	2.10
60	48.5	4.60	2.17
90	45.5	4.32	2.31
120	43.0	4.08	2.44
150	40.6	3.85	2.59
180	38.7	3.67	2.71
210	36.9	3.50	2.85
240	35.4	3.36	2.97
270	34.2	3.24	3.07
300	32.7	3.10	3.21
330	31.7	3.00	3.32

Slope of the graph of 1/[Iodine] *vs.* time = specific reaction rate = $K_2 = 4.10$ M^{-1} s^{-1}

The reciprocal of unreacted iodine was plotted *vs.* time. The curve was a straight line showing that the reaction was of second order. The experiment was repeated three times and the specific reaction rates determined by the RPE technique were satisfactorily reproducible to within ±3%; from similar kinetic measurements the specific reaction rates were determined at various temperatures and from Arrhenious plot, the energy of activation for the reaction was obtained (Table-2). Further, the entropy of activation and frequency factor were also evaluated.

TABLE-2
ENERGY OF ACTIVATION FOR THE OXIDATION OF HYDROXYLAMINE BY IODINE IN AQUEOUS SOLUTION

Temperature		Specific reaction rate, k_2 (M^{-1} s^{-1})	$\log k_2$
T (K)	$1/T \times 10^{-3}$ K^{-1}		
293	3.412	2.60	0.4150
298	3.355	4.10	0.6128
303	3.300	6.60	0.8195
308	3.246	11.00	1.0414
313	3.195	13.50	1.1303

Slope of the graph of $\log k_2$ *vs.* $1/T = -3.39 \times 10^{-3}$

$$\text{Energy of activation} = \frac{-2.303 \times 8.314 \times (-3.39 \times 10^{3})}{1000} = 65.0 \text{ kJ mol}^{-1}$$

RESULTS AND DISCUSSION

The oxidation of hydroxylamine by iodine is a rapid reaction and its kinetic parameters at 25°C at pH 3.0 are:

Specific reaction rate = 4.10 M^{-1} s^{-1}; Energy of activation: = 65.0 kJ mol^{-1}; Entropy of activation = −23.35 J K^{-1} mol^{-1}; Frequency factor 1.02×10^{12} mol^{-1} s^{-1}.

In order to study the possible dependence of specific reaction rate on the acidity of the reaction medium, the specific reaction rate was also determined at various pH values, *i.e.*, 3.0, 3.2, 3.4, 3.6, 3.8 and 4.0 at 25°C. At pH 3.0 the specific reaction rate was found to be 4.10 M^{-1} s^{-1}at 25°C, while at pH 4.0 it was found to be 790.8 M^{-1} s^{-1}. It was observed that at low pH, the reaction was comparatively slow but at higher pH, the reaction was very fast.

Hydroxylinium salt undergo hydrolysis as

$$NH_3OH^+ + H_2O \rightleftharpoons NH_2OH + H_3O^+$$

Hence, hydrolysis constant K_h for this reaction is

$$K_h = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{6.6 \times 10^{-9}} = 1.5 \times 10^{-6}$$

which is in fact the dissociation constant of the hydroxylinium ion acting as weak acid. Therefore, the ionization constant (K_a) can be represented as

$$K_a = \frac{[NH_2OH][H_3O^+]}{[NH_3OH^+]}$$

It indicates that there would be less equilibrium concentration of the unprotonated form of hydroxylamine at lower pH and larger concentration at higher pH. Since the reaction rate is low at low pH and larger at higher pH, the unprotonated form of hydroxylamine must be the active species in the reaction between iodine and hydroxylamine. Moreover, since the specific reaction rate is significantly increased with increasing pH, it is also possible that the reaction may be base catalyzed with the concentration of disodium hydrogen phosphate at higher pH. Therefore, the simultaneous effect of both reactivity of the basic form of hydroxylamine and catalysis by disodium hydrogen phosphate may cause a significant increase in the specific reaction rate of the reaction between iodine and hydroxylamine at higher pH.

Since, specific reaction rate of the reaction increases with increasing pH (Table-3) it seems that the basic form of hydroxylamine may be more reactive than its acidic form. It is likely to be an unprotonated form of hydroxylamine that is reacting with iodine species rather than the protonated form of hydroxylamine.

TABLE-3
VARIATION OF SPECIFIC REACTION RATE WITH pH

pH of reaction medium	Specific reaction rate at 25 °C (M^{-1} s^{-1})
3.0	4.10
3.2	22.10
3.4	52.00
3.6	80.00
3.8	455.50
4.0	790.00

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