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Kinetics of Oxidation of 2-Hydroxy-1-Naphthalidene-anil by Ce(IV) in Aqueous Sulphuric Acid

RAMESH S. YAMGAR, UMESH N. POL and S.S. DODWAD*
Physical Chemistry Division, The Institute of Science
15, Madam Cama Road, Bombay-400 032, India

The kinetics of oxidation of the Schiff base, 2-hydroxy-1-naphthalideneanil has been studied by $Ce^{4+} \rightarrow Ce^{3+}$ redox system in aquo-sulphuric acid medium. The reaction is found to obey the first order rate equation. The study is carried out at five different temperatures. The thermodynamic parameters ΔH, ΔG, ΔE and ΔS have been calculated. The frequency factor (A) is also determined and reported. The kinetic study is also carried out at various concentrations of oxidant and Schiff base which is also found to be the first order reaction. The effect of ionic strength on the reaction is also studied. A suitable possible mechanism has been suggested on the basis of kinetic results.

INTRODUCTION

Ce(IV) has been widely used as an oxidant in the oxidation of several organic substrates in sulphuric acid medium[1–9]. But the very few workers[10, 11] have studied the oxidation of some Schiff bases by ceric sulphate in sulphuric acid medium. The present communication deals with the kinetic study of oxidation of Schiff base, 2-hydroxy-1-napthalideneanil by ceric sulphate in aqueous sulphuric acid which has not been observed so far.

EXPERIMENTAL

All chemicals used were of AR grade. The Schiff base, 2-hydroxy-1-naphthalideneanil was prepared by refluxing 2-hydroxy-1-naphthaldehyde and aniline in ethanol for 2–3 h. It was then purified by recrystalisation and the purity was ascertained[12]. The stock solutions of ceric sulphate and ferrous ammonium sulphate were prepared in 2N sulphuric acid by the standard methods. The ferroin indicator was prepared and used in the titration. The solutions of ceric sulphate and ferrous ammonium sulphate were standardised by the known methods[13].

The kinetic study of oxidation of Schiff base was carried out by adding thermally equilibrated solution of ceric sulphate in sulphuric acid to the requisite amount of Schiff base solution. The course of the reaction was followed by removing 5 mL of aliquots at different time intervals and determining the amount of unreacted Ce(IV) by titration with ferrous ammonium sulphate using ferroin indicator.

RESULTS AND DISCUSSION

Effect of substrate

To determine the order of the reaction with respect to the substrate, the reaction was carried out at different concentrations of Schiff base and at fixed concentrations of oxidant, sulphuric acid and at constant temperature. The results are recorded in Table-1. A perusal of data of Table-1 indicates that the K_1 values are directly proportional to the concentration of Schiff base showing that the reaction follows first order kinetics with respect to Schiff bases. The values of K_2 (second order constant) calculated from K_1/[Schiff base] are practically constant which also proves the first order dependence of the reaction on Schiff base.

TABLE-1
EFFECT OF VARYING [OXIDANT] AND [SUBSTRATE] ON REACTION RATE

Temperature = 303 K, $[H_2SO_4]$ = 2.0 N, I = 0.3

[Substrate] $\times 10^{-3}$ M	[Oxidant] $\times 10^{-2}$ M	$K_1 \times 10^{-3}$ min^{-1} (Average)	$K_2 \times 10^{-2}$ mol^{-1} min^{-1}
0.60	2.40	08.52	14.20
0.70	2.40	10.13	14.47
0.80	2.40	11.13	13.91
0.90	2.40	12.64	14.04
1.00	2.40	14.21	14.21
1.00	2.16	14.87	—
1.00	1.92	15.25	—
1.00	1.68	16.84	—
1.00	1.44	19.51	—

Mean K_2 = 14.166 mol^{-1} min^{-1}

Effect of oxidant

In order to determine the order with respect to oxidant the reaction was studied at different initial concentrations of ceric sulphate and at fixed concentration of other reactants. The reaction follows first order kinetics with respect to Ce(IV). The K_1 values (average) are given in Table-1. The values decrease with the increasing concentrations of oxidant which is contrary to our expectation. Shorter[14] and others[4] also noted a similar effect in their studies. This fact shows the formation of an equilibrium complex between the reactants prior to the rate determining step. A plot of K_1 values against $[Ce(IV)]^{-1}$ is linear with an intercept on rate axes provides a positive evidence for the formation of complex (Fig. 1).

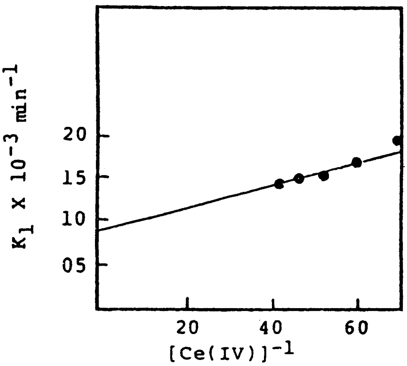


Fig. 1. Plot of K_1 vs. $[Ce(IV)]^{-1}$

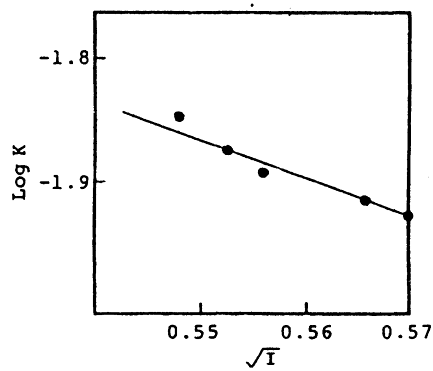


Fig. 2. Plot of log K vs. $\sqrt{I}$

Effect of ionic strength

In order to study the effect of ionic strength on the reaction rate, the reaction was carried out at five different values of ionic strength. The ionic strength of the reaction mixture was maintained by the addition of requisite amounts of potassium chloride. The other parameters were kept constant. The results are tabulated in Table-2 which indicates that K_1 values decrease with the increase in ionic strength. Thus, the retarding effect is observed on addition of potassium chloride. A plot of log K_1 against $\sqrt{I}$ is a straight line with negative slope shown in Fig. 2, which indicates that the rate determining step of reaction probably involves the ions with opposite charges.

TABLE-2
EFFECT OF IONIC STRENGTH

Temperature = 303 K, $[H_2SO_4]$ = 2.0 N, [Oxidant] = $2{\cdot}40 \times 10^{-2}$ M, [Substrate] = $1{\cdot}0 \times 10^{-3}$ M.

$I \times 10^{-1}$	3.00	3.05	3.10	3.20	3.25
$K \times 10^{-3}$ min^{-1}	14.21	13.38	12.87	12.19	11.85

Effect of temperature

The reaction was carried out at five different tempreatures over a range of 303–323 K. The frequency factor (A) and other thermodynamic parameters ΔH, ΔG, ΔS and ΔE have been calculated and reported in Table-3. The low values of frequency factor and the negative value of entropy change indicate the formation of more rigid activated complex. The end product analysis shows that a quinone is formed at the end of the reaction. This is confirmed by recording IR spectra of oxidised product and the qualitative tests.

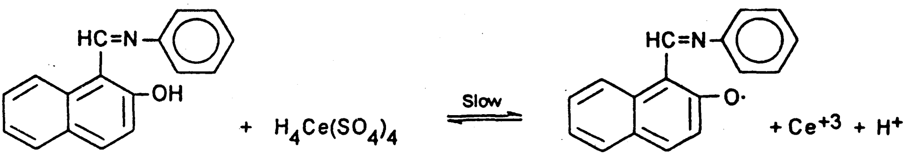
TABLE-3
EFFECT OF TEMPERATURE

[Oxidant] = $2{\cdot}40 \times 10^{-2}$ M, [Substrate] = $1{\cdot}0 \times 10^{-3}$ M, [H_2SO_4] = 2.0 N, Ionic strength, I = 0.3.

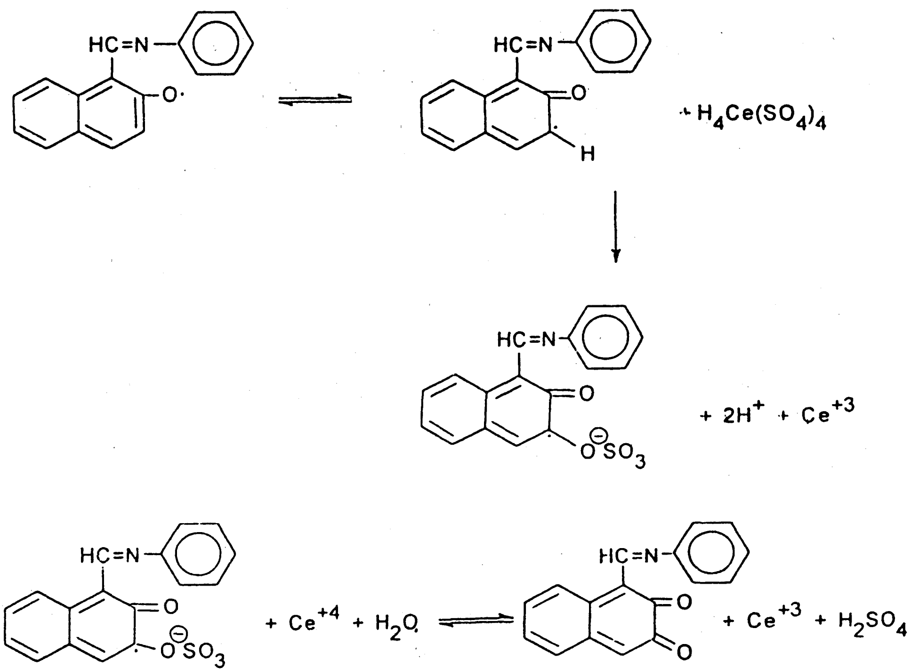
Temp. K	$K \times 10^{-3}$ min^{-1}	ΔH KJ deg^{-1} mol^{-1}	ΔG KJ deg^{-1} mol^{-1}	ΔS J deg^{-1} mol^{-1}	$A \times 10^3$ min^{-1}	ΔE KJ mol^{-1}
303	14.21	25.920	87.482	–194.86	1.1363	
308	16.90	25.878	88.523	–195.08	1.1251	
313	20.18	25.837	89.543	–195.22	1.1250	28.439
318	22.18	25.795	90.764	–195.99	1.0413	
323	24.58	25.754	91.957	–196.65	0.9770	

Mechanism

The existence of ceric sulphate in acidic medium in the various states[15–20] have been reported. Based on the observation recorded above and the mechanism proposed by Singh and others[21], the possible mechanism for the oxidation of Schiff base is shown as:



Followed by fast reactions



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