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## KINETICS AND MECHANISM OF OXIDATION OF BENZOPHENONE OXIME BY BISPYRIDINE SILVER (I) DICHROMATE

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### ABSTRACT

The oxidation of Benzophenoneoxime by Bispyridine silver (I) dichromate (BPSDC) has been studied in 50% (v/v) aqueous ethanol medium at 303K. The reactions show unit order dependence with respect to [Benzophenoneoxime]. The reaction is acid catalyzed, the effect of concentration of Manganous sulphate, sodium perchlorate and dielectric constant on the reaction rates was studied, Thermodynamic parameters were calculated from the Eyring's plot. Mechanism consistent with the observed kinetic results has been proposed and the related rate law derived.

**Keywords:** Kinetics, mechanism, Benzophenoneoxime, Bispyridine silver (I) dichromate.

### AIMS AND BACKGROUND

The Kinetics and mechanism of oxidation of Benzophenoneoxime was carried out in EtOH-H<sub>2</sub>O medium at 30°C and the rates were calculated. Further studies in this direction may be useful to understand the mechanistic aspects of the reaction. Regeneration of carbonyl compounds from their derivatives under mild conditions is an important process in synthetic organic chemistry. Several oxidative methods are available for deoxygenation<sup>1, 2, 3</sup>. Considerable research has been done in the last years on the mechanism of oxidation by the use of modified Cr (VI) reagents as oxidants<sup>4-16</sup>, pyridinium chlorochromate has been reported as a useful reagent for the formation of carbonyl compounds from the corresponding alcohols<sup>17</sup>. Bispyridine silver (I) dichromate is a recently

developed Cr(VI) oxidant and has been found quite useful as an oxidant in organic synthesis<sup>18</sup>. There seems to be no report on the kinetics and mechanism of oxidation of Benzophenoneoxime by BPSDC. Hence this paper reports on the kinetics and mechanism of oxidation of Benzophenoneoxime by Bispyridine silver (I) dichromate.

### EXPERIMENTAL

Benzophenoneoxime were prepared by the reported literature procedure<sup>19</sup>. Bispyridine silver (I) dichromate was prepared by the standard procedure<sup>18</sup>. Ethanol was purified as described in the literature<sup>19</sup>. Perchloric acid, manganous sulphate, acrylonitrile and sodium perchlorate were of AnalaR grade and used without further purification. All the kinetic measurements were carried out in a glass stoppered iodine flask protected from light and thermostated to within  $\pm 0.01^\circ\text{C}$ . Pseudo first order conditions were maintained throughout the

study. Reactions were carried out in aqueous ethanol (50-50 (v/v)) medium at 303K unless otherwise stated. The course of the reaction was followed by standard iodometric procedure. The reproducibility of rate constant was checked by duplicate measurement and were found to be within  $\pm 4\%$  error.

Product analysis; Benzophenone were found to be the products. The products have been confirmed by their melting point and IR spectra.

## RESULT AND DISCUSSIONS

### Oxidation of Benzophenoneoxime by BPSDC.

The kinetic results for the oxidation of Benzophenoneoxime by BPSDC along with the experimental conditions are given in tables 1 and 2.

The order of the reaction was found to be first with respect to the [BPSDC] as evidenced by the plot of  $\log[\text{BPSDC}]$  versus time ( $r = 0.999$ ). The rate constant increased with increase in the [Benzophenoneoxime]. A plot of  $\log k_{\text{obs}}$  versus  $\log [\text{benzophenoneoxime}]$  gave a straight line with a slope of 1.16 ( $r = 0.990$ )

indicating a first order dependence of the reaction with respect to [Benzophenoneoxime]. A fractional order dependence of the reaction with respect to  $[\text{HClO}_4]$  has been observed. The dependence of  $\log k_{\text{obs}}$  versus  $\log [\text{H}^+]$  is a straight line with a slope of 0.53 ( $r = 0.996$ ) indicating fractional order. The rate of the reaction has been found to increase with the decrease in the dielectric constant of the medium. This might probably be due to the reaction between two molecules forming a polar product<sup>20</sup>. The addition of sodium perchlorate increases the rate of the reaction suggesting that the reaction may be between an ion and a dipole type<sup>21</sup>. Added acrylonitrile has no effect on the reaction rate, i.e., the reaction did not induce polymerization of acrylonitrile indicating the absence of the radical pathway. The added  $\text{Mn}^{2+}$  ion enhances the rate confirming the formation of Cr (IV) in slow step. The reaction has been conducted at five different temperature and the activation parameters  $\Delta H^*$  and  $\Delta S^*$  were calculated;  $\Delta H^* = 50.224 \text{ KJ mol}^{-1}$ ,  $\Delta S^* = -113.3 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**Table1: Effect of varying [Benzophenoneoxime], [BPDC], solvent composition and temperature on reaction rate.**

[Benzophenoneoxime] $\times 10^2$ (mol dm <sup>-3</sup> )	[BPSDC] $\times 10^3$ (mol dm <sup>-3</sup> )	Ethanol-water % (v/v)	Temperature (K)	$k_{\text{obs}} \times 10^4 (\text{s}^{-1})$
1.00	1.00	50-50	303	3.35
1.50	1.00	50-50	303	5.33
2.25	1.00	50-50	303	7.67
2.75	1.00	50-50	303	9.12
3.25	1.00	50-50	303	13.14
1.50	0.63	50-50	303	5.47
1.50	1.25	50-50	303	5.23
1.50	2.50	50-50	303	5.31
1.50	3.13	50-50	303	5.11
1.50	3.75	50-50	303	5.03
1.50	1.00	30-70	303	2.38

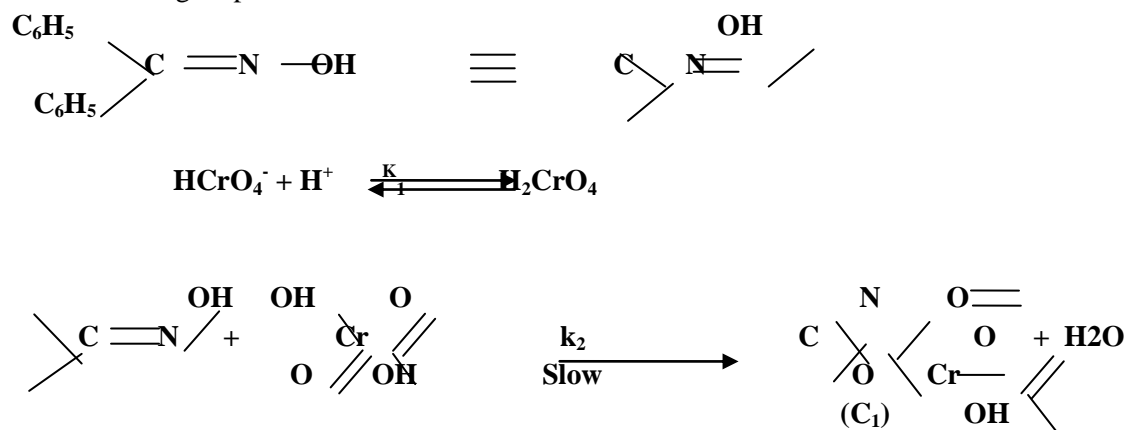
1.50	1.00	40-60	303	3.42
1.50	1.00	60-40	303	6.73
1.50	1.00	70-30	303	8.21
1.50	1.00	50-50	298	4.89
1.50	1.00	50-50	308	7.53
1.50	1.00	50-50	313	10.50
1.50	1.00	50-50	318	13.00

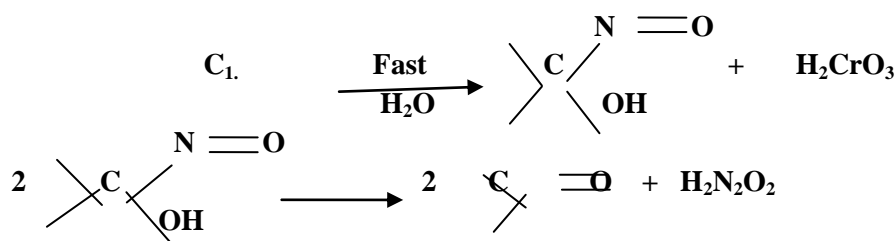
**Table 2: Effect of varying [perchloric acid] [sodium perchlorate] and [acrylonitrile] on reaction rate [BPSDC] =  $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ , [benzophenoneoxime] =  $1.50 \times 10^{-2} \text{ mol dm}^{-3}$ , 50-50 % (v/v) EtOH – H<sub>2</sub>O, Temperature 303K**

[HClO <sub>4</sub> ] x 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[NaClO <sub>4</sub> ] x 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[Acrylonitrile] x 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[MnSO <sub>4</sub> ] x 10 <sup>3</sup> (mol dm <sup>-3</sup> )	k <sub>obs</sub> x 10 <sup>4</sup> (S <sup>-1</sup> )
0.63	-	-	-	2.90
1.25	-	-	-	4.34
1.88	-	-	-	5.33
2.50	-	-	-	7.06
3.13	-	-	-	8.55
3.75	-	-	-	9.29
1.88	0.75	-	-	6.71
1.88	2.50	-	-	8.21
1.88	5.00	-	-	10.93
1.88	-	0.75	-	5.50
1.88	-	1.00	-	5.24
1.88	-	1.20	-	5.50
1.88	-	-	0.75	10.11
1.88	-	-	1.00	10.85
1.88	-	-	1.25	11.63

## MECHANISM

The HCrO<sub>4</sub><sup>-</sup> first protonates to give H<sub>2</sub>CrO<sub>4</sub> in equilibrium step. HCrO<sub>4</sub> reacts with benzophenoneoxime to give a complex (C<sub>1</sub>) in the slow step. Then this complex (C<sub>1</sub>) dissociates to give products as follows





The rate law is as follows

$$\text{rate} = \frac{K_1 k_2 [\text{oxime}] [\text{Cr (VI)}] [\text{H}^+]}{1 + K_1 [\text{H}^+]}$$

## CONCLUSION

Oxidative regeneration of carbonyl compounds from benzophenoneoxime by BPSDC follows different mechanistic pathway. The large negative entropies of activation support the formation of a rigid cyclic intermediate complex. The oxidation of benzophenoneoxime by BPSDC in the presence of perchloric acid in aqueous ethanol medium leads to the formation of benzophenone and a biologically active compound of hypo nitrous acid as end product.

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