

2,2'-Bipyridyl Catalyzed Oxidation of Cyclanols by Quinolinium Bromochromate-Kinetic Study

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Kinetic investigation in 2,2'-bipyridyl catalyzed oxidation of some cyclanols (cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol) by quinolinium bromochromate (QBC) in 60 % aqueous acetic acid medium in presence of mercuric (II) acetate as a scavenger have been studied. The reaction exhibits a first order rate dependence with respect to oxidant quinolinium bromochromate (QBC) and perchloric acid while it is fractional order in cyclanols and 2,2'-bipyridyl. The variation of ionic strength, $\text{Hg}(\text{OAc})_2$ and acrylonitrile have insignificant effect on reaction rate. Effect of varying dielectric constant of medium on the reaction rate has been studied. Activation parameters have been evaluated from Eyring plots by studying the reaction at different temperature. The rate law has been derived on the basis of obtained data.

Key Words: Quinolinium bromochromate, Cyclanols, 2,2'-Bipyridyl, Kinetic study, Oxidation.

INTRODUCTION

The literature study reveals that 2,2'-bipyridyl ($\text{C}_{10}\text{H}_8\text{N}_2$) is well known as a chelating agent for the metal ions¹ and used in the analysis of heavy metals. It has been reported that the ligand 2,2'-bipyridyl is oxidation resistant². 2,2'-Bipyridyl chromate (BPC) has been proposed as oxidant for oxidation of hydroxy group to the corresponding carbonyl group³. The kinetic investigations of the oxidation of various inorganic substrate ligands by $[\text{Ni}(\text{bipy})_3]^{3+}$ have been reported⁴⁻⁶.

Kinetics of oxidation of cyclanols with variety of oxidants such as $\text{Ce}(\text{IV})$ ⁷, potassium hexacyanoferrate⁸, thallium(III)acetate^{9,10}, barium manganate¹¹, KBrO_3 , NaIO_4 , quinolinium dichromate¹²⁻¹⁷, etc. are reported earlier. In the present investigation 2,2'-bipyridyl catalyzed oxidation of some cyclanols (cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol) by quinolinium bromochromate (QBC) in 60 % aqueous acetic acid medium has been reported.

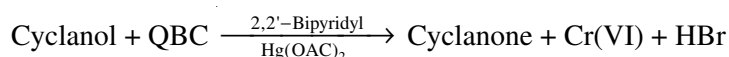
EXPERIMENTAL

All the cyclanols (cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol) used were of E-Merck samples. The oxidant quinolinium bromochromate (QBC) was prepared by the reported method¹⁸. Acetic acid was purified by the literature procedure. The standard solution of cyclanols was prepared in acetic acid. Double distilled water was employed in all kinetic runs. The concentration of quinolinium

bromochromate was checked iodometrically¹⁹ using 1 % solution of freshly prepared starch as an indicator.

Kinetics: Kinetic measurements were made under pseudo first order conditions, by keeping large excess of cyclanols over oxidant quinolinium bromochromate (QBC). Mixture containing requisite amount of solutions of cyclanols, Hg(OAc)₂ and 2,2'-bipyridyl in 60 % acetic acid were equilibrated at 308 K. To this mixture was added a measured amount of pre equilibrated standard solution of quinolinium bromochromate (QBC). To maintain the desired temperature (± 2 °C), the reaction mixture was kept in a thermostated waterbath and progress of the reaction was monitored iodometrically by withdrawing aliquots of the reaction mixture at regular time intervals. The pseudo first order rate constants K' were computed from linear least squares plot of $-\log [a-x]$ vs. time.

Stoichiometry and product analysis: Various sets of reaction mixtures containing an excess of the oxidant over cyclanols were kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unchanged oxidant showed that one mole Cr(VI) consumed one mole of the cyclanol.



The reaction mixture from the actual kinetic run after sufficient time, ensures completion of the reaction, it was then evaporated and extracted with ether. The layer was separated and dried. The product obtained was corresponding ketone which is characterized by TLC, spot test analysis²⁰, 2,4-dinitrophenylhydrazine (DNP) derivatives²¹ and its melting point.

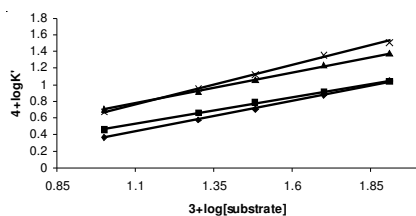
RESULTS AND DISCUSSION

Order of reaction: The kinetics of oxidation of cyclanols by quinolinium bromochromate in 60 % acetic acid in presence of 2,2'-bipyridyl as a catalyst was carried out at 308 K under pseudo first order conditions. The concentration of Hg(OAc)₂ was kept higher than QBC. The plot of $\log [\text{QBC}]$ vs. time found to be linear indicating first order dependence of the reaction rate and from the slope of the plots pseudo first order rate evaluated. The rate constant (K') have been found to increase with increase in the concentration of cyclanols and plot of $\log K'$ vs. $\log [\text{cyclanol}]$ was linear (Fig. 1) with the slope less than unity for all the cyclanols indicating a fractional order dependence on the rate (Table-1). The concentration of 2,2'-bipyridyl varied while the concentration of cyclanol, QBC and Hg(OAc)₂ kept at constant. The plot $\log K'$ vs. $\log [2,2'\text{-bipyridyl}]$ shows slope less than unity indicating fractional order dependence of rate on [2,2'-bipyridyl] (Table-1).

The dependence of the reaction rate on hydrogen ion concentration has been investigated at different initial concentration of HClO₄ and keeping the concentration of the other reactants are constant. The rate increases proportionally with concentration of H⁺. Acidity dependence is first order throughout entire range of acidities studied as shown in Fig. 2. In absence of H⁺ no significant reaction takes place.

TABLE-1
EFFECT OF VARIATION OF REACTANT ON PSEUDO ORDER RATE CONSTANT K'
AT 308 K; $\text{Hg}(\text{OAc})_2 = 2.00 \times 10^3 \text{ mol dm}^{-3}$, 60 % ACETIC ACID MEDIUM

10^3 Cr(VI) mol dm^{-3}	10^2 [cyclanol] mol dm^{-3}	$10^2 [\text{H}^+]$ mol dm^{-3}	10^3 [bipyridyl] mol dm^{-3}	$10^4 K' (\text{s}^{-1})$			
				Cyclopentanol	Cyclohexanol	Cycloheptanol	Cyclooctanol
0.75	2.00	4.96	4.50	3.96	4.73	8.29	8.89
1.50	2.00	4.96	4.50	3.81	4.53	8.16	8.87
2.25	2.00	4.96	4.50	3.80	4.43	8.11	8.85
3.00	2.00	4.96	4.50	3.78	4.23	8.08	8.84
1.50	1.00	4.96	4.50	2.35	2.85	5.10	4.64
1.50	2.00	4.96	4.50	3.81	4.53	8.16	8.87
1.50	5.00	4.96	4.50	7.40	8.21	17.14	22.29
1.50	8.00	4.96	4.50	11.10	10.70	24.13	32.10
1.50	2.00	1.98	4.50	1.35	1.92	5.01	5.50
1.50	2.00	4.96	4.50	3.81	4.53	8.21	8.87
1.50	2.00	9.92	4.50	8.20	11.15	13.80	22.50
1.50	2.00	14.88	4.50	13.20	17.64	17.90	39.10
1.50	2.00	4.96	2.30	2.75	3.39	6.82	7.35
1.50	2.00	4.96	4.50	3.81	4.53	8.16	8.87
1.50	2.00	4.96	6.70	5.24	5.27	9.48	9.85
1.50	2.00	4.96	9.00	6.59	5.98	10.40	10.63



A = cyclopentanol, B = cyclohexanol, C = cycloheptanol, D = cyclooctanol

Fig. 1. Plot for order on substrate

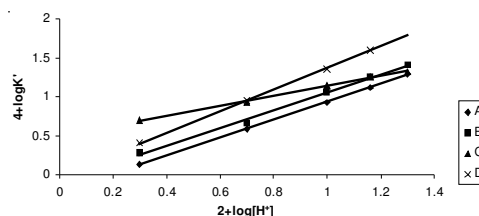


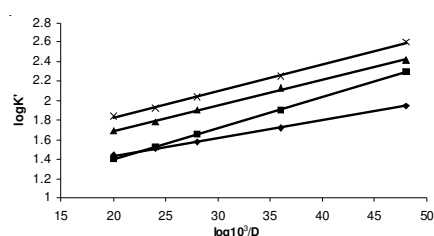
Fig. 2. Plot for order on perchloric acid

Effect of dielectric constant: The effect of varying dielectric constant of reaction rate was studied by varying concentration of acetic acid from 40-80 %. The rate constant (Table-2) suggests that the rate of the reaction increases with increasing acetic acid content of the solvent mixture. The plot of $\log K'$ vs. $1/D$ was found to be linear with positive slope (Fig. 3) indicating involvement of positive ion in the rate limiting step.

The ionic strength of the reaction varied by the addition of NaClO_4 and the influence of ionic strength on the reaction was studied. It was found that the ionic strength of the reaction medium has negligible effect. The concentration effect of $\text{Hg}(\text{OAc})_2$ in present study showed negligible effect on the reaction rate but

TABLE-2
EFFECT OF VARIATION OF DIELECTRIC CONSTANT ON REACTION RATE

AcOH:H ₂ O	D	1/D	10 ⁴ K' (s ⁻¹)			
			Cyclopentanol	Cyclohexanol	Cycloheptanol	Cyclooctanol
40:60	49.60	0.020	2.70	2.50	4.86	5.25
50:50	42.37	0.024	3.20	3.24	6.01	6.93
60:40	35.14	0.028	3.81	4.53	8.16	8.87
70:30	27.90	0.038	5.25	8.10	13.34	16.40
80:20	20.67	0.048	8.85	19.72	25.90	29.80



A = cyclopentanol, B = cyclohexanol, C = cycloheptanol, D = cyclooctanol

Fig. 3. Amis plot

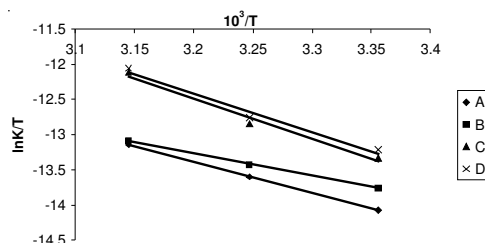


Fig. 4. Eyring plots of cyclanols at 308 K

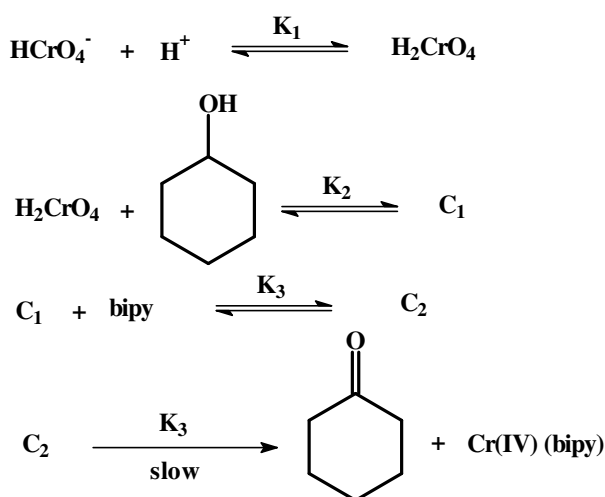
found its utility to fix bromide ion during the course of the reaction and avoiding the oxidation of the latter to molecule bromide²². The addition of acrylonitrile to reaction mixture also does not affect the rate of the reaction and this observation rules out the formation of any free radical in the reaction.

Effect of temperature: The rate of oxidation was determined at three different temperatures *viz.*, 298, 308 and 318 K. The Eyring plots of $\ln k/T$ vs. $1/T$ were all linear (Fig. 4) from these plots, the activation parameters were evaluated (Table-3). The thermodynamic parameter for equilibrium step and rate determining step of the scheme was evaluated.

TABLE-3
ACTIVATION PARAMETERS OF CYCLANOLS

Cyclanol	10 ⁴ K' (s ⁻¹)			ΔH^\ddagger (KJ mol ⁻¹)	ΔG^\ddagger (KJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)
	298 K	308 K	318 K			
Cyclopentanol	2.30	3.18	6.22	44.60	95.82	-166.30
Cyclohexanol	3.18	4.52	6.65	26.38	95.18	-223.40
Cycloheptanol	4.84	8.16	17.40	47.56	93.49	-149.12
Cyclooctanol	5.39	8.89	18.40	38.18	93.44	-179.42

Mechanism and rate law: As all the cyclanol show similar mechanics, the tentative mechanism of the oxidation of cyclohexanol by QBC is given below:



$$\text{Rate} = k_4 [\text{C}_2]$$

$$v = \frac{K_1 K_2 K_3 k_4 [\text{Cr(IV)}][\text{S}][\text{bipy}][\text{H}^+]}{\{(1 + K_3[\text{bipy}])(1 + K_2[\text{S}])\}}$$

$$k_{\text{obs}} = \frac{K_1 K_2 K_3 k_4 [\text{S}][\text{bipy}][\text{H}^+]}{\{(1 + K_3[\text{bipy}])(1 + K_2[\text{S}])\}}$$

The protonated form of the oxidant in acidic medium has already been postulated. Decomposition of the complex C_2 to give the product is assumed to be slow and rate limiting step. Large negative entropy of activation values suggest a cyclic complex in the transition state which is in the agreement with the proposed mechanism. The linear relationship in the Exner's plot further supports a similar mechanism operating in the cyclohexanol. The above rate law satisfies all the above experimental observations.

Conclusion

Kinetic studies demonstrate that the [2,2'-bipyridyl-QBC-cyclanol] complex decomposes in a slow rate determining step to give corresponding ketone as the main product, low dielectric constant of the medium favourable for the reactivity. First order to oxidant, H^+ and fractional order to cyclanol, catalyst is supported by derived rate law. The rate of oxidation of cyclic alcohols was found to be in the order of cyclopentanol < cyclohexanol < cycloheptanol < cyclooctanol.

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