

Effect of Ring Size on Acid Dichromate Oxidation of Alicyclic Ketoximes: A Kinetic Study

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Kinetics of oxidation of three alicyclic ketoximes by acid dichromate have been studied in aqueous acetic acid medium. The oxidation of alicyclic ketoximes by acid dichromate is first order each in [oxidant] and [substrate]. The reactions are acid-catalyzed. The negligible effect of the added perchlorate and the decrease in rate constants with decreasing dielectric strength of the medium indicate that the reaction involves ion-dipole interaction. The rate data have been measured at different temperatures and the activation parameters computed. Based on the kinetic results obtained, a plausible mechanism is proposed. Among the alicyclic ketoximes the reactivity sequence observed is cyclohexanone oxime (CHexO) > cyclopentanone oxime (CPO) > cycloheptanone oxime (CHepO). This trend is rationalized in the light of I-strain.

Key Words: Kinetic, Ketoximes, Oxidation, Ring size.

INTRODUCTION

The chemistry of oximes is of great interest due to their wide synthetic and industrial applications and bioactivities. Since deoximation reaction is important from a synthetic point of view, a number of hydrolytic, reductive and oxidative methods have been developed¹⁻³ involving various reagents. Oximes have been converted to the corresponding aldehydes or ketones by treatment with reagents like thallium(III)⁴, manganese(III)⁵, pyridinium chlorochromate⁶, 1-chlorobenzotriazole⁷ and peroxomonosulphate⁸. However, extensive work in this field has not been carried out with chromium-containing oxidants. Hence, in the present investigation, the kinetics of oxidation of alicyclic ketoximes by acid dichromate has been chosen for study.

EXPERIMENTAL

AnalaR Glaxo sample of potassium dichromate was dissolved in conductivity water to give a stock solution of strength 5.0×10^{-3} mol dm⁻³. The alicyclic ketoximes were prepared by reported standard procedures⁹. Cyclopentanone oxime and cyclohexanone oxime were recrystallized from suitable solvents. Cycloheptanone oxime was purified by distillation under reduced pressure. The purity of the samples was confirmed by comparing the respective physical

constants with literature values which show good concordance. Acetic acid used for kinetic runs was thrice distilled adopting usual procedure¹⁰. All other chemicals used were of analytical grade.

Kinetic Procedure: Rate measurements were carried out in 80% (v/v) aqueous acetic acid medium in the temperature range of 288–308 K in the presence of sulphuric acid of strength 1.0 mol dm⁻³. The acidity of the medium and ionic strength were maintained constant using sulphuric acid. The reactions were carried out under pseudo-first order conditions keeping the substrate concentration in considerable excess over that of the oxidant. The progress of the reaction was followed spectrophotometrically at 355 nm up to 80% completion of the reaction. The pseudo-first order rate constants were evaluated and found to be reproducible within $\pm 2\%$.

Test for free radical intermediates: The possibility of free radical formation is ruled out since there was no polymer formation when freshly distilled acrylonitrile monomer was added to the reaction mixture. This is suggestive of a non-radical reaction pathway.

Stoichiometry and product analysis: A known excess of acid dichromate was allowed to react with a known concentration of oxime in 40% aqueous acetic acid medium. Estimation of the unreacted [Cr(VI)] from the reaction mixture after the completion of the reaction showed that the stoichiometry of the reaction is 1 : 1. The reaction mixture was also analyzed for the products by qualitative tests. The product was detected to be the corresponding ketone which was further confirmed by TLC experiments.

RESULTS AND DISCUSSION

Order with respect to oxidant

The dependence of rates of reaction on oxidant concentration was studied by varying [Cr(VI)] in the range 4.5–8.5 $\times 10^{-4}$ mol dm⁻³. From the linear plots of log [Cr(VI)] against time (min), the order with respect to [oxidant] is determined to be unity. However, the pseudo-first order rate constants were found to decrease with increase in the concentration of [Cr(VI)] (Table-1) Similar observations have been reported earlier in different oxidation studies involving various substrates^{11–14}. This decreasing trend in the rate constant may be due to the hydrolytic equilibrium between Cr₂O₇²⁻ and HCrO₄⁻ and it is to be expected that HCrO₄⁻ is the reactive oxidant species. The constancy of $k_{\text{cor}} = k_{\text{obs}} \times \frac{[\text{Cr(VI)}]}{[\text{HCrO}_4^-]}$ was checked at various Cr(VI) concentrations (Table-1a). As these ratios do not show constancy, it indicates that HCrO₄⁻ is not the only oxidizing species responsible for this oxidation. Similarly $k_{\text{cor}}^1 = k_{\text{obs}}[\text{Cr(VI)}]/[\text{Cr}_2\text{O}_7^{2-}]$ calculations were evaluated and these values also do not remain constant (Table-1a). This is indicative of the participation of both HCrO₄⁻ and Cr₂O₇²⁻ in the oxidation process. Similar views have been expressed in the oxidation of *p*-methoxy acetophenone¹⁵, malonic acid¹⁴ and α -hydroxy acids¹⁶ by Cr(VI).

TABLE-1
RATE DATA FOR THE OXIDATION OF CYCLOHEXANONE
OXIME BY ACID DICHROMATE

$[\text{Cr(VI)}] \times 10^4$ (mol dm ⁻³)	$[\text{CHexO}] \times 10^3$ (mol dm ⁻³)	$[\text{H}_2\text{SO}_4]$ (mol dm ⁻³)	μ (mol dm ⁻³)	AcOH : H ₂ O (%, v/v)	$k_1 \times 10^4$ (s ⁻¹) Temp. 293 K
4.5	6.5	1.0	3.00	80 : 20	10.41
5.5	6.5	1.0	3.00	80 : 20	9.02
6.5	6.5	1.0	3.00	80 : 20	7.79*
7.5	6.5	1.0	3.00	80 : 20	6.66
8.5	6.5	1.0	3.00	80 : 20	5.61
6.5	4.5	1.0	3.00	80 : 20	5.02
6.5	5.5	1.0	3.00	80 : 20	6.58
6.5	7.5	1.0	3.00	80 : 20	9.11
6.5	8.5	1.0	3.00	80 : 20	10.39
6.5	6.5	0.6	3.00	80 : 20	2.50
6.5	6.5	0.7	3.00	80 : 20	3.52
6.5	6.5	0.8	3.00	80 : 20	4.74
6.5	6.5	1.0	3.25	80 : 20	7.53
6.5	6.5	1.0	3.50	80 : 20	7.22
6.5	6.5	1.0	3.75	80 : 20	7.01
6.5	6.5	1.0	3.00	30 : 70	4.89
6.5	6.5	1.0	3.00	40 : 60	3.74
6.5	6.5	1.0	3.00	50 : 50	2.98
6.5	6.5	1.0	3.00	60 : 40	2.51

*at 288 K; 3.84; at 298 K; 10.92; at 303 K; 18.38.

TABLE-1a
EVALUATION OF CORRECTED RATE CONSTANTS k_{cor} AND k'_{cor}
FOR THE OXIDATION OF ALICYCLIC OXIMES BY Cr(VI) AT T = 293 K

$[\text{Cr(VI)}] \times 10^4$ (mol dm ⁻³)	$k_1 \times 10^4$ (s ⁻¹)	$[\text{HCrO}_4^-] \times 10^4$ (mol dm ⁻³)	$k_{\text{cor}} \times 10^4$ (s ⁻¹)	$[\text{Cr}_2\text{O}_7^{2-}] \times 10^4$ (mol dm ⁻³)	$k'_{\text{cor}} \cdot 10^3$ (s ⁻¹)
4.5	10.410	7.667	6.110	0.658	7.119
5.5	9.020	9.120	5.440	0.932	5.323
6.5	7.790	10.509	4.818	1.237	4.093
7.5	6.660	11.872	4.207	1.579	3.163
8.5	5.610	13.125	3.633	1.929	2.472

Order with respect to oxime

The dependence of the rates of reaction on substrate concentration was studied by varying [oxime] in the range $4.5\text{--}8.5 \times 10^{-3}$ mol dm⁻³ and fixed concentrations of the other reactants. The plots of log [Cr(VI)] vs. time (min) at different initial

concentrations of oxime were linear and the value of $k_{\text{obs}}(\text{s}^{-1})$ evaluated from the slopes were found to be dependent on the initial concentrations of the substrates. The plot of $\log k_{\text{obs}}$ vs. $\log [\text{oxime}]$ was linear with unit slope showing a first order dependence on [oxime]. The values of $k_{\text{obs}}(\text{s}^{-1})$ plotted against [substrate] gave straight lines passing through the origin, proving first order dependence on the oxime (Fig. 1). From the slopes of the above plots, the second order rate constants $k_2 (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ were evaluated.

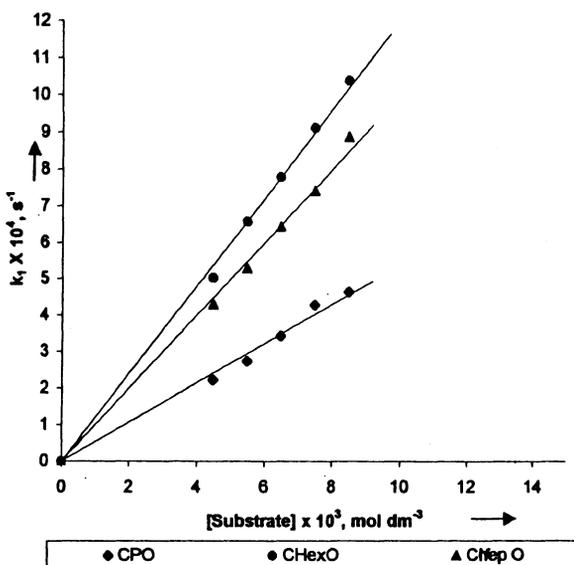


Fig. 1. Evaluation of k_2 at 293 K

Effect of $[\text{H}^+]$: The acidity of the medium was varied from 0.6–1.0 mol dm^{-3} to learn the effect of acid on the reaction rate at constant $[\text{Cr(VI)}]$, [oxime] and ionic strength (3.00 mol dm^{-3}). The oxidation reactions were found to be acid catalyzed. The plot of $\log k_{\text{obs}}$ vs. $\log [\text{H}^+]$ were linear and the slope indicates fractional order with respect to $[\text{H}^+]$.

Influence of ionic strength: The rate studies were made at different ionic strengths of the medium, varied by the addition of sodium perchlorate maintaining constant $[\text{H}^+]$. The influence of ionic strength on the rates of oxidation was negligible indicating the interaction of an ion and a dipole in the rate-determining step¹⁷.

Dependence on solvent polarity: The effect of dielectric constant on the reaction rate was examined by varying the percentage of acetic acid in the range 30–80% (v/v). The rate constants were found to decrease on lowering the dielectric constant of the medium. This trend reveals that there is formation of a charge separated complex in the rate-limiting step.

Rate and activation parameters: From the observed kinetic data, the second order rate constants for the three alicyclic ketoximes were found to increase with increase in temperature. The plots of $\log k_2$ vs. $1/T$ were linear indicating that the Arrhenius law is being obeyed. The thermodynamic parameters E_a (kJ mol^{-1}), ΔG^\ddagger (kJ mol^{-1}), ΔH^\ddagger (kJ mol^{-1}) and ΔS^\ddagger (J $\text{K}^{-1} \text{mol}^{-1}$) have been computed and tabulated (Table-2).

Influence of Structure of Reactivity

The differences in reactivity between five and seven-membered ring compounds on the one hand and six-membered ring compound on the other are quite large due to I-strain. Changes in I-strain were attributed by Brown²² primarily to changes in the state of hybridization of C atom from sp^2 to sp^3 or *vice-versa* during the course of the reaction. The rate-determining step of the oxidation reaction studied involves a change from sp^2 to sp^3 . Based on the concept of I-strain, the observed trend in reactivity can be readily accounted for, in the present study. Thus, the oxidation of cyclohexanone oxime by Cr(VI) is faster than the oxidation of cyclopentanone oxime or cycloheptanone oxime by Cr(VI). The same trend in reactivity is observed in the oxidation of cyclic ketones by PFC²³ and oximes by PMS⁸.

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