

# Kinetic studies on the oxidation of cyclohexanone by potassium dichromate in aqueous acetic medium

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## ABSTRACT

Kinetics of cyclohexanone oxidation by dichromate ion has been studied in acetic acid – water medium. The reaction showed first order kinetics with the concentration of substrate and oxidant. Adipic acid was obtained as the product which was proved by melting point determination and IR spectral analysis. The reaction failed to initiate the polymerisation of added acrylonitrile and involvement of any radical intermediate is ruled out from this result. The reaction rate is decreased with increase in dielectric constant of the medium. Thermodynamic variables like activation energy, enthalpy and entropy of activation and free energy change were determined and a suitable mechanism is proposed.

**Keywords:** Cyclohexanone, potassium dichromate, oxidation, kinetics, mechanism.

## 1. INTRODUCTION

Oxidation of organic compounds is very important and found useful in chemical industries for the production of various commercial products. Most of the industrially important organic compounds like aldehydes, ketones, carboxylic acids etc. can be produced by the oxidation of related substrates by various oxidizing agents (Lee, 1980; Wiberg, 1965). Permanganate, chromate, hypochlorite etc. are extensively used for the primary and secondary alcohol oxidation reactions in a selective manner to get corresponding aldehydes (Bijudas, 2015, 2014, 2004, Mahanti, 1990; Sharma, 2013). Kinetic studies of oxidation alcohols using permanganate and chromate were already reported. (Bijudas, 2004, 2015; Basheer, 2007, Joseph, 2007; Rao, 1986). But only few reports are available on the kinetics of oxidation of ketones by dichromate as oxidant and hence we carried out this work. Various forms of chromate can be employed for selective oxidation of alcohols and the oxidation of ketones to corresponding carboxylic acids.

The present paper reports the kinetics and mechanism of cyclohexanone oxidation in aqueous acetic acid medium using potassium dichromate. Stoichiometry of the reaction, isolation of product and its characterization, effect of oxidant and substrate concentration, effect of dielectric constant of the medium, effect of acid and added salt and effect of temperature on the reaction rate are carried out. Thermodynamic variables like energy of activation ( $E_a$ ), enthalpy of activation ( $\Delta H^\ddagger$ ), entropy of activation ( $\Delta S^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) were calculated and a suitable mechanism is suggested in accordance with the experimental observations.

## 2. EXPERIMENTAL

Analar grade potassium dichromate (Merck, India) was used as obtained and acetic acid was purified by reported methods (Perrin et al. 1966, Vogel 1967). Cyclohexanone (Merck, India) was purified by distillation and double distilled water was used for the entire experiment.

The stoichiometry of the reaction was studied under the condition  $[K_2Cr_2O_7] > [cyclohexanone]$ . Reaction mixture containing  $K_2Cr_2O_7$  and cyclohexanone in 20 % aqueous acetic acid medium was kept at 303 K in a thermostat for 6 hours to complete the reaction. Then 2 mL of the reaction mixture was pipetted out and the amount of unreacted dichromate was estimated iodometrically. This was repeated till a constant value obtains and from the concentration of unreacted  $K_2Cr_2O_7$ , stoichiometry of the reaction was determined. Product analysis was done by stirring excess of dichromate with cyclohexanone in 20% aqueous acetic acid medium for about five hours at room temperature. The obtained solution was treated with sodium metabisulphite and then extracted with ether. The organic layer obtained was again extracted with 10 % sodium carbonate and the aqueous layer is collected and acidified with concentrated HCl. The obtained product, on acidification and purification was identified by determining its melting point and by infra-red spectral analysis.

Kinetic investigations were done at various temperatures in a thermostat with an accuracy of  $\pm 0.1^\circ C$  by maintaining pseudo first order condition by keeping  $[cyclohexanone] \gg [dichromate]$ . A fixed volume of known concentration of dichromate in 20% aqueous acetic acid was equilibrated. The oxidation was initiated by mixing required volume of cyclohexanone in acetic acid which was previously thermostated to the already thermostated dichromate solution. The reaction mixture was shaken well and aliquots of it were withdrawn at regular intervals and the iodometric determination of concentration was done up to 90% completion of the reaction. The kinetic analyses were repeated and pseudo first order rate constants,  $k_{obs}$  were calculated from the linear least square plots of  $\log [dichromate]$  versus time.

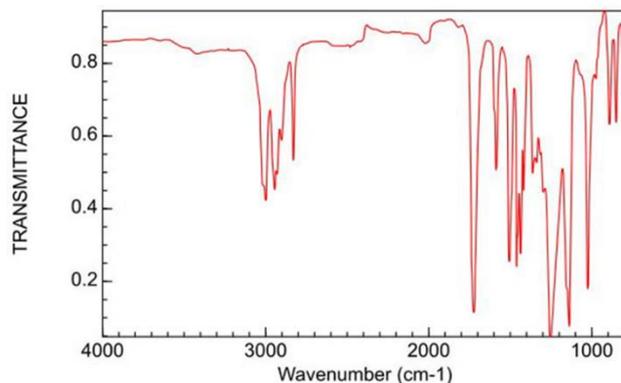
## 3. RESULTS AND DISCUSSION

Reaction stoichiometry was established by equilibrating known excess concentration of dichromate ion with

known amount of cyclohexanone. From the amount of unreacted  $K_2Cr_2O_7$  ratio of [cyclohexanone]: [ $K_2Cr_2O_7$ ] is 1:1 which confirmed the overall reaction sequence as given below.



The product was identified as adipic acid with above 90% yield. The recrystallised sample of product was characterized by its melting point ( $150 \pm 2^\circ C$ ). This result of melting point was in concordance with that of pure sample and proved that the obtained product may be adipic acid. IR spectral analysis of the product was done for further proof on characterization of the product. The IR spectrum was recorded from KBr pellets by using Jasco FT-IR 4100 spectrophotometer (Japan) and is shown in Figure 1.



**Fig.1. IR spectrum of the product**

The IR spectrum showed sharp peaks at  $2960\text{ cm}^{-1}$  (O-H stretching),  $2850\text{ cm}^{-1}$  (C-H stretching) and  $1720\text{ cm}^{-1}$  (C=O stretching). The occurrence of these peaks leads to the conclusion that the product formed may be adipic acid. Further the obtained spectrum on comparison with the IR spectrum of pure adipic acid also supported the formation of adipic acid.

The dichromate oxidation of cyclohexanone was carried out with different initial concentrations of the oxidant and substrate in 20% aqueous acetic acid medium at 303 K. The effect of oxidant and substrate concentration on oxidation is given in table 1. The plot of  $\log$  [dichromate] versus time was linear at various concentrations of oxidant. These results are showing that the reaction is first order with respect to the [oxidant]. This was again confirmed from the constant values of specific rates ( $k_{obs}$ ) for the different [oxidant] for a given concentration of the substrate. The effect of [substrate] on the rate of reaction was studied by taking different initial [substrate] and the observed rate constant increased linearly with the increase in [substrate]. Further, the second order rate constants ( $k_2$ ), were constant indicating the first order dependence of the reaction with respect to [cyclohexanone]. The first order dependence on the [substrate] was again confirmed by the plot of  $\log k_{obs}$  versus  $\log$  [substrate] which is linear with a slope of unity.

**Table.1. Effect of [oxidant] and [substrate] on the rate of oxidation of cyclohexanone**

Temperature - 303 K		Medium - 20% aq. HOAc (v/v)	
[Oxidant] x $10^3$ (mol dm <sup>-3</sup> )	[Substrate] x $10^1$ (mol dm <sup>-3</sup> )	$k_{obs}$ x $10^3$ (s <sup>-1</sup> )	$k_2$ x $10^3$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
5	2.0	3.45	17.25
10	2.0	3.43	17.15
15	2.0	3.45	17.25
20	2.0	3.43	17.15
10	1.0	1.76	17.60
10	2.0	3.43	17.15
10	3.0	5.43	18.10
10	4.0	7.20	18.00

The effect of dielectric constant of the medium on the oxidation reaction of cyclohexanone was carried under pseudo first order condition, by varying the acetic acid percentage and is given in table 2. The reaction rate is increased with decrease in dielectric constant of the medium. The plot of  $\log k_2$  versus  $1/D$  where D is the dielectric constant is found to be linear with a negative slope and is in accordance with Amis equation (E S Amis, 1966).

**Table.2.Effect of dielectric constant of the medium on the rate of oxidation**[Oxidant] x 10<sup>3</sup> = 10.0 mol dm<sup>-3</sup> [Substrate] x 10<sup>1</sup> = 2.0 mol dm<sup>-3</sup>

Temperature - 303 K

Acetic acid: water	Dielectric constant	k <sub>obs</sub> x 10 <sup>3</sup> (s <sup>-1</sup> )	k <sub>2</sub> x 10 <sup>3</sup> (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
20 : 80	61	3.43	17.15
30: 70	53	4.01	20.05
40 : 60	47	4.42	22.10
50 : 50	40	5.80	29.00

The effect of salt added on the rate of oxidation of cyclohexanone by dichromate was carried out at 303 K and is given in table 3. The added salt had no influence on the rate of oxidation and this ruled out the possible interaction between two charged species during oxidation.

**Table.3.Effect of [salt] on the rate of oxidation of cyclohexanone [Oxidant] x 10<sup>3</sup> = 10.0 mol dm<sup>-3</sup>**[Substrate] x 10<sup>1</sup> = 2.0 mol dm<sup>-3</sup>

Temperature - 303 K		Medium - 20% aq. HOAc (v/v)
[NaCl] x 10 <sup>1</sup> (mol dm <sup>-3</sup> )	k <sub>obs</sub> x 10 <sup>3</sup> (s <sup>-1</sup> )	k <sub>2</sub> x 10 <sup>3</sup> (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
2	2.18	10.90
3	2.18	10.90
4	2.19	10.95
5	2.17	10.85

Dependence of rate of reaction on acid concentration was done at 303 K and is shown in table 4. The rate of reaction was increased with increase in the [acid]. Reaction rate showed unit dependence on [acid].

**Table 4: Effect of [acid] on the rate of oxidation of cyclohexanone**[Oxidant] x 10<sup>3</sup> = 10.0 mol dm<sup>-3</sup> [Substrate] x 10<sup>1</sup> = 2.0 mol dm<sup>-3</sup>

Temperature - 303 K		Medium - 20% aq. HOAc (v/v)
[Acid] x 10 <sup>1</sup> (mol dm <sup>-3</sup> )	k <sub>obs</sub> x 10 <sup>3</sup> (s <sup>-1</sup> )	k <sub>2</sub> x 10 <sup>3</sup> (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
2	3.43	17.15
3	6.15	30.75
4	11.08	55.40

The effect of temperature on the reaction rate of cyclohexanone using dichromate ion in 20% aqueous acetic acid (v/v) were studied in the temperature range 303 K to 318 K. The magnitude of various thermodynamic variables were calculated and presented in Table 5.

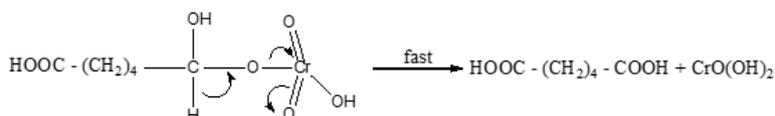
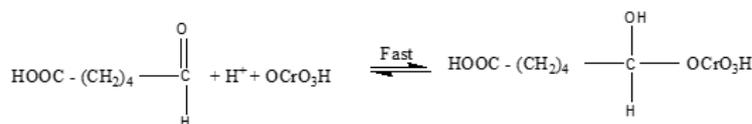
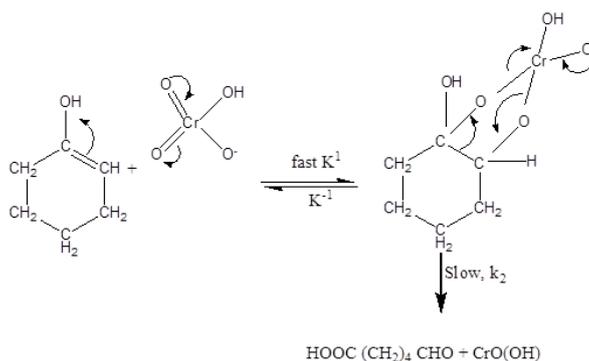
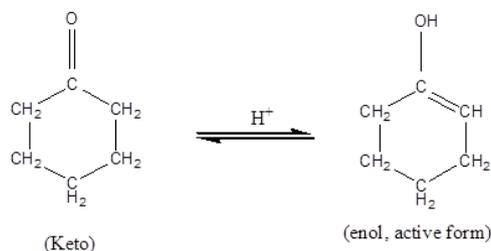
**Table 5: Activation parameters for the oxidation of cyclohexanone**

Medium - 20% aq. HOAc

Temperature - 303 K

Substrate	k <sub>2</sub> x10 <sup>3</sup> (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	E <sub>a</sub> (kJ mol <sup>-1</sup> )	ΔH <sup>#</sup> (kJ mol <sup>-1</sup> )	-ΔS <sup>#</sup> (JK <sup>-1</sup> mol <sup>-1</sup> )	ΔG <sup>#</sup> (kJ mol <sup>-1</sup> )
Cyclohexanone	17.15	63.76	58.40	215.56	71.15

Based on the evidences obtained experimentally, the proposed mechanism is as explained below. A hydrogen abstraction mechanism which leads to the formation of free radicals is negated in view of the failure to initiate the polymerisation of added acrylonitrile. The reaction is first order with respect to the concentration of both oxidant and substrate. The reaction rate is increased with decrease in dielectric constant of the medium. This indicates the possible interaction between either two dipoles or between a dipole and an ion. The added salt had no influence on the reaction rate and this discards any possibility of interaction between two charged species. Study of influence of mineral acid showed that the reaction rate is increased with increase in [acid], keeping first order with [H<sup>+</sup>]. This increase in rate may be due to increase in the active enol form concentration of the substrate. The enol form of cyclohexanone is the active form in this reaction. But the formation of enol cannot be the rate determining step since the oxidation rate had a first order dependence on chromium (VI) concentration and measurement of rate of enolisation showed may be more rapid than oxidation. In aqueous medium dichromate exists as HCrO<sub>4</sub><sup>-</sup> as the active species which again protonates to H<sub>2</sub>CrO<sub>4</sub> in presence of mineral acid. The chromate ion or chromic acid is attached to the double bond of cyclohexanone which is in enol form by a fast equilibrium step to form a cyclic chromate ester as intermediate. This chromate ester then undergoes a rate determining slow decomposition giving an aldehydic carboxylic acid. This aldehydic carboxylic acid further reacts with chromate ion in acid medium in a fast step to form adipic acid.



The suitable rate expression in consistent with above observation can be formulated as follows:

$$-\frac{d}{dt} [\text{Cr}_2\text{O}_7^{2-}] = -\frac{d}{dt} [\text{HCrO}_4^-] = k_2 [\text{Chromate ester}]$$

Applying steady state Approximation,  $\frac{d}{dt} [\text{Chromate ester}] = 0$

$$\text{ie. } K_1[\text{enol}] [\text{Chromate}] - K_{-1}[\text{Chromate ester}] - k_2[\text{Chromate ester}] = 0$$

$$K_1[\text{enol}] [\text{HCrO}_4^-] = K_{-1}[\text{Chromate ester}] + k_2 [\text{Chromate ester}]$$

$$= [\text{Chromate ester}] (K_{-1} + k_2)$$

$$\therefore [\text{Chromate ester}] = K_1 \frac{[\text{enol}][\text{HCrO}_4^-]}{K_{-1} + k_2}$$

$$\text{Rate} = -\frac{d}{dt} [\text{Cr}_2\text{O}_7^{2-}] = -\frac{d}{dt} [\text{HCrO}_4^-] = k_2 K_1 \frac{[\text{enol}][\text{HCrO}_4^-]}{K_{-1} + k_2}$$

Since  $k_{-1} \gg k_2$ ,  $k_2$  is negligible in the denominator.

$$\begin{aligned} \therefore \text{Rate} &= -\frac{d}{dt} [\text{HCrO}_4^-] = k_2 \frac{k_1}{k_{-1}} [\text{enol}] [\text{HCrO}_4^-] \\ &= k_2 K [\text{enol}] [\text{HCrO}_4^-] \\ &= k_2 K [\text{cyclohexanone}] [\text{H}^+] [\text{HCrO}_4^-] \end{aligned}$$

#### 4. CONCLUSION

The oxidation reaction of cyclohexanone to adipic acid by dichromate is very smooth in aqueous acetic acid phase and thus this can be extended to study the oxidation reactions of other substrates. Kinetic studies helps to propose the mechanism of such oxidation reactions.

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