Kinetic Studies of Catalytic Oxidation of Cyclohexene Using Chromium VI Oxide in Acetic Acid Medium

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ABSTRACT: Cyclohexene was oxidized using chromium (VI) oxide (CrO_3) in pure acetic acid medium. The products of oxidation were analysed using simple qualitative analysis, IR spectroscopy and Gas chromatography-Mass spectrometry (GC/MS). Kinetics studies were carried out to determine the order of reaction, rate constant and the activation energy with respect to the oxidant using pseudo-order approximation method. The influence of Cu^{2+}, Co^{2+} and Fe^{2+} as catalysts were also investigated. Qualitative analyses of the products revealed the presence alcohols and ketones while the GC/MS shows the presence of cyclohexanol (2.46%), cyclohexanone (5.05%), 2-cyclohexen-1-one (59.37%), 1,2-cyclohexanediol monoacetate (9.88%), 2-hydroxy-cyclohexanone (1.75%) and bi-2-cyclohexen-1-yl (5.16%). The reaction order was shown to be 2nd order with respect to the CrO_3 with activation energy of 45.32 kJ mol^{-1} while Co^{2+} and Fe^{2+} indicated some catalytic activity on the reaction.

INTRODUCTION

Catalysts are widely used in both organic and inorganic reactions. However their widest application, today, is in organic reactions in general and in the petrochemical industry in particular because hydrocarbons, which are the main raw materials for petrochemical industry, are mostly found naturally in reduced form therefore the only way to convert them into other substances is through oxidation (Matar and Hatch, 2001).

Generally, oxidation of hydrocarbons is unselective. The major reason being that the desired products (such as alcohols or carbonyls) are easier to oxidise than the hydrocarbons. Therefore as these reactive products are formed they get further oxidized resulting in a variety of oxidized products (Kouw, *et al,* 1993). Therefore, catalysts are commonly employed to confine reactions to the right products.

Unsaturated hydrocarbons, particularly olefins, are reactive nevertheless, catalyst are often employed in their oxidation principally to direct the oxidation to a particular product (Grasselli et al, 1997).

There are several reports of successful catalytic oxidation of cyclohexene (an olefin) such as that of Okad et al, 1968 where cyclohexene was selectively converted to cyclohexanone in the presence of palladium(II) catalyst. Likewise Kenneth et al, 1987, reported

oxidation of cyclohexene in the presence of manganese III porphyrin using perchlorate and periodate as oxidants. The products obtained were cyclohexane oxide, 2-cyclohexen-1-ol and 2-cyclohexen-1-one in the ratio of 6:1:2. Ziqiang (2000) reported selective oxidation of cyclohexene to 2-cyclohexen-1-ol and 2-cyclohexen-1-one by molecular oxygen at atmospheric pressure and a temperature of 70°C in the presence of ruthenium catalyst. N_2O was equally reported to effectively oxidize cyclohexene in gaseous phase to cyclohexanone with nearly 100% selectivity (Avdeev et al, 2003). The kinetics of the reaction by which thallium(III) acetate oxidizes cyclohexene in glacial acetic acid medium at 30°C, was studied and reported by Leon *et al*, (2004). The reaction was said to follow a second-order rate law exhibiting first-order dependence on each of thallium(III) acetate and cyclohexene. Another catalyst used in oxidation of cyclohexene is monosubstituted titanium polyoxometalate in actonitrile medium using aqueous H_2O_2 as oxidant. The main product is trans-cyclohexane-1,2-diol along with allylic oxidation products, 2-cyclohexene-1-ol and 2-cyclohexene-1-one, along with comparable amounts of the corresponding epoxide and diol (Kholdeeva et al 2005).

Some of the catalysts used in the literature cited above are noble and expensive metals that make the process uneconomical while some catalyst are active but not selective and hence bring about multiple products resulting in separation dilemma. In most of the reports kinetic studies were not included in spite of its importance in solving problems of selective transformation to the required products. In addition, it gives insight into the role of temperature, concentration/pressure, catalyst and solvents on the direction of a reaction (De Paula, 2009).

This work is aimed at studying the kinetics of cyclohexene oxidation with chromium (VI) oxide in acetic acid medium with and without catalyst in search of optimal condition of its cheap and exclusive conversion to cyclohexanone and/or cyclohexanone; precursors to adipic acid; the nylon raw material

EXPERIMENTAL

The reagents used in this work are AnalaR grades obtained from BDH except 2,4-dinitrophenylhydrazine which is LR grade (98%) from Merck

Oxidation reaction: Cyclohexene (10 cm^3) was added to 50 cm^3 of saturated solution of chromium (VI) oxide (CrO$_3$) in acetic acid in a round bottom flask to which a reflux condenser was fitted in order to condense any escaping vapour. When signs of reaction ceased (in about 10 minutes), 20 cm^3 of distilled water was added and the content was extracted with chloroform. The chloroform extract was washed with distilled water and then analysed (Pavia *et al,* 1982).

Qualitative analysis: The presence of alcohols was tested with Jone's reagent, that of ketones by Brady's test, unsaturation with permanganate solution and acids were tested with saturated solution of sodium hydrogen carbonate (Pavia *et al*, 1982).

Infrared: Infrared spectroscopy was carried out using BUCK500 instrument. The sample was analysed neat by placing a drop between two fused sodium chloride windows and the windows held together by capillary action.

GC/MS: The GC/MS analysis was carried out on Agilent Gas Chromatographic Instrument (model 6890) coupled to mass selective detector (MSD 5973N). The GC column used was Agilent 122-5532 of 30m nominal length, 0.25mm (250 μm) diameter with 0.25 μm film thickness. One microlitre of the sample was injected into the injection port (set at 250°C)

with the help of an Automatic Liquid Sampler (Agilent 7683B). The GC oven temperature was initially held at 80 ^{o}C for five minutes and allowed to rise at the rate of 10 ^{o}C/minute for the next 20 minutes to the final temperature of 280°C which was maintained for five minutes bringing the total running time to 30 minutes. The pressure of the carrier gas (helium) and its flow rate were set at 2.33 psi and 28.4 cm^3/min respectively. The data analysis was done with the ChemStation software. For each peak in the GC chromatogram, a corresponding mass spectrum was produced and each mass spectrum was compared with that of NIST[*] electronic library to bring out the compounds that match each of the products.

Kinetic measurements: The essence of this experiment was to determine the order of the reaction, and the rate constant with respect to the oxidant (CrO$_3$). To achieve that, Psuedo-first order approximation was applied by making the concentration of the cyclohexene in excess so that its concentration during the course of reaction is practically constant hence the rate depends solely on the concentration of the CrO$_3$.

An aqueous solution of CrO$_3$ (3 cm^3, 5 x 10^{-3} M) was transferred into a spectrometer cell and the cell was fitted into the sample hole of the sample compartment of the spectrophotometer (Shimadzu UV/VIS instrument, UV-1600 Series). The instrument was set to 339 nm which is the pH independent λ$_{max}$ for CrO$_3$ solution (Xia *et al*, 2000). The initial absorbance of the CrO$_3$ solution was then measured and recorded. Then 0.8 cm^3 of the 1 M cyclohexene (in n-hexane) was injected into the cell containing the 3 cm^3 of the CrO$_3$ solution and the absorbance readings were measured every five seconds for five consecutive minutes. The measurements were carried out at the prevailing laboratory temperature (about 35 ^{o}C). The absorbance was plotted against time and the rate constant was calculated from the slope.The data obtained was used to determine the reaction order and the rate constant as follows;

The integrated first order rate law is

$ln \dfrac{[A]}{[A]_o} = k_1 t$ where [A]$_o$ is the initial

absorbance (concentration) of the sample A and [A] is its absorbance at time *t*. Therefore a

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[*] NIST stands for National Institute of Standards and Technology, USA (www.nist.gov)

plot of $\ln\dfrac{[A]}{[A]_o}$ against t is expected to give a straight line with rate constant k_1 as a slope if the reaction is first order (Nakamura and Tsutsui 1980).

On the other hand the integrated second order rate law is given by $\dfrac{1}{[A]}$ = $k_2 t$ + $\dfrac{1}{[A]_o}$, and a plot of $\dfrac{1}{[A]}$ against t is expected to give a straight line and the constant k_2 as the slope if the reaction is second order (Nakamura and Tsutsui 1980).

Kinetic studies using Cu^{2+}, Co^{2+} and Fe^{3+} as catalyst: The above procedure was repeated with 5×10^{-5} M aqueous solutions of each of Cu^{2+}, Co^{2+} and Fe^{3+} solution as catalysts.

Determination of activation energy: This experiment was carried out using a thermostated Water-bath and Shimadzu UV/VIS instrument, UV-1600 Series set at 339 nm. The water bath was thermostated at 35 °C and allowed to equilibrate at that temperature for 10 minutes. Then, 90 cm³ of 5 mM aqueous solution of CrO_3 was transferred into a 250 cm³ conical flask and 10 cm³ of 1M cyclohexene solution (in n-hexane) was transferred into a 100 cm³ volumetric flask. The two flasks were placed in the water bath and a thermometer was inserted into each of the flasks to measure its temperature. When the two solutions attained the temperature of the water bath, 4 cm³ of the CrO_3 solution was transferred into the spectrometer cell and its absorbance (initial absorbance) was immediately measured at the set wavelength (339 nm). Then, the cyclohexene solution was transferred to the CrO_3 solution and stirred continuously. Every 10 seconds, 4 cm³ aliquots of the mixture was transferred into the single cell of the spectrophotometer and the absorbance was measured immediately and recorded for 4 consecutive minutes. This procedure was repeated at 40, 45, 50 and 55 °C.

The activation energy (*Ea*) was determined from Arrhenius equation ($\ln k = \ln A(-\dfrac{Ea}{RT}$) by plotting *ln k* determined at different temperatures against $\dfrac{1}{T}$. The pre-exponential factor (A) was determined from the y-intercept of the plot.

RESULT AND DISCUSSIONS

Qualitative analysis: The result of the qualitative analysis test for the products indicated the presence of alcohols, ketones and unsaturation but acids were absent. This indicated partial oxidation of the substrate and absence of over oxidation to acid. However, this result cannot determine whether the functional groups identified are on one or different molecules.

IR Analysis: Important IR absorption peaks obtained on the spectrum is given in Table I below. (See appendix I for the spectrum)

The IR spectrum showed strong absorption at 1714.3 cm⁻¹ which indicated presence of ketonic group. It also indicated the presence of hydroxyl group by showing peaks at 3414, 1272 and 1149.37 cm⁻¹ that correspond to hydrogen bonded OH, –O-H bending vibrations and C-O stretching respectively. Still the spectrum gave peaks at the three regions for alkenes that is 302.1, 1655 and 728.4 cm⁻¹. The peak at 1655 cm⁻¹ particularly falls within the range for unconjugated C=C stretching (Stuart, 2004).

Table I: Important IR absorption peaks of the oxidation product solution

Sample	Important peaks (cm⁻¹)	**Inference**
Oxidized cyclohexene	1714.3	R-CO-R Present
	3414, 1272, & 1149.37	-OH Present
	3021.1, 1655 & 728.4	C=C Present

The two tests (qualitative and IR) complemented one another in confirming the presence of ketonic and hydroxyl groups in the products of this reaction. However, the nature of the compounds present could not be ascertained at this stage.

Result of the GC/MS analysis: Summary of the GC/MS data is given in Table II below and the GC and MS spectra are given in Appendix II and III respectively.

The GC chromatogram of the sample gave eleven (11) distinct peaks. The five prominent ones that constitute 81% of the total peak area were identified as cyclohexanol (2.46%), cyclohexanone (5.05%), 2-cyclohexen-1-one (59.37%), 1,2-cyclohexanediol monoacetate (9.88%), 2-hydroxy-cyclohexanone (1.75%) and bi-2-cyclohexen-1-yl (5.16%). Having multiple products in this kind of reaction

where versatile oxidant is used is not surprising. The prime information that such reactions furnish is the obtainable products. Therefore further kinetics studies were carried out to understand the reaction better as a prelude towards confining the reaction to a single target product.

Determination of Order of Reaction and Rate Constants: To test the order of the

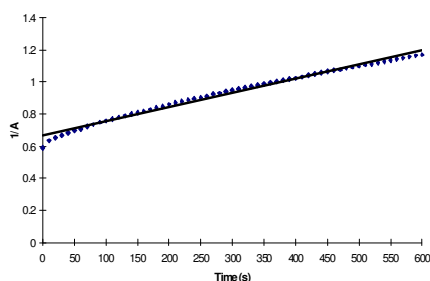reaction, each of $ln \frac{[A]}{[A]_o}$ and $\frac{1}{[A]}$ was plotted against t for both the uncatalysed and catalysed reactions. The second order plots gave a straight line indicating that the reaction is 2nd order with respect to the CrO_3 as shown in the figures below
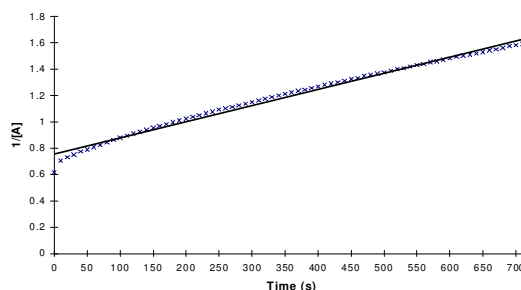
Table II: Result of the GC/MS analysis

| RT (mins)	% Peak area	Compound Matching	Correlation (%)
4.29	2.46	Cyclohexanol	95
4.51	5.05	Cyclohexanone	93
5.36	59.37	2-cyclohexen-1-one	91
11.13	9.88	1,2-cyclohexanediol, monoacetate	72
13.12	5.16	Bi-2-cyclohexen-1-yl	78

Key: RT = Retention time

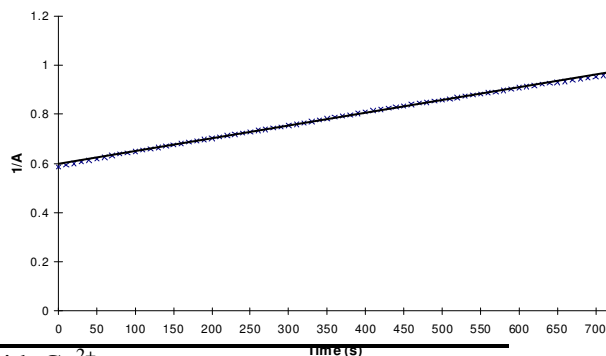1: Plot for 2nd order plot of the uncatalysed reaction

2: Plot for 2nd order plot of the Cu catalysed reaction

3: Plot for 2nd order plot of the Co catalysed reaction
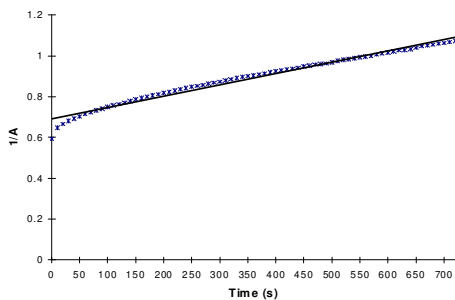
4: Plot for 2nd order plot of the Fe catalysed reaction

The rate constants determined from the plots are summarised in Table III.

Table III: Rate Constants for the reactions at 35°C

Title	Rate constant, k (dm³mol⁻¹ s⁻¹)
Uncatalysed reaction	8.05×10^{-4}
Reaction with Cu^{2+} catalyst	4.85×10^{-4}
Reaction with Co^{2+} catalyst	1.435×10^{-3}
Reaction with Fe^{2+} catalyst	4.04×10^{-3}

It can be seen from the table that the there was a decrease in the rate of the reaction in the presence of Cu^{2+} indicating some inhibitory activity whereas there was an increase in the rate with respect to Co^{2+} and Fe^{2+} which shows evidence of catalytic activity. therefore the work was taken further to determine the activation energy of the uncatalysed reaction.

Activation energy determination: The data obtained for the reactions at different temperatures is given in Table IV below.

The slope obtained from the plot was -5451.218, which corresponds to activation energy of 45.32 kJ mol^{-1}. This activation energy is relatively small but it is higher than the 17.4 kJ mol^{-1} reported for oxidation of cyclohexene with Acetylperoxyl Radicals at 373 - 433 K, (Smith *et al*, 1999).

Conclusion: The results of the present study shows that

i. Cyclohexene is oxidized by chromium (VI) oxide in acetic acid to produce Cyclohexanol, Cyclohexanone, 2-cyclohexen-1-one, 1,2-cyclohexanediol, monoacetate and Bi-2-cyclohexen-1-yl.

ii. The reaction is second order with respect to the oxidant with rate constant of 8.05 x 10^{-4} dm^{3}mol^{-1} s^{-1} and activation energy of 45.32 kJ mol^{-1}

iii. The reaction can be homogeneously catalysed, to some extent, by Co^{2+} and Fe^{2+} while Cu^{2+} appears to inhibit the reaction.

Table IV: Kinetic data for determination of activation data

T(^{o}C)	T(K)	1/T(K) [x 10^{-3}]	Rate coefficient (k) [x 10^{-2}]	ln k
35	308	3.25	8.07	-2.5167
40	313	3.19	8.54	-2.4598
45	318	3.14	11.23	-2.1863
50	323	3.10	15.65	-1.8549
55	328	3.05	23.13	-1.4640

The rate constants obtained at various temperatures (Table IV above) are consistent with the kinetic rule of thumb which states that the reaction rates near room/ambient temperature doubles or triples for every 10-degree rise in temperature (De Paula, 2009). On moving from 313 to 323 K, the rate increased from 8.54 x 10^{-2} to 15.65 x 10^{-2} that

is by a factor of 1.8. Likewise from 318 to 328 K the rate moved from 11.23 x 10^{-2} to 23.13 x 10^{-2} that is by a factor of 2.05. This indicates that the reaction shows typical Arrhenius behaviour (De Paula 2009).The data above was used to make the Arrhenius plot; *ln k* vs *1/T* as shown below.
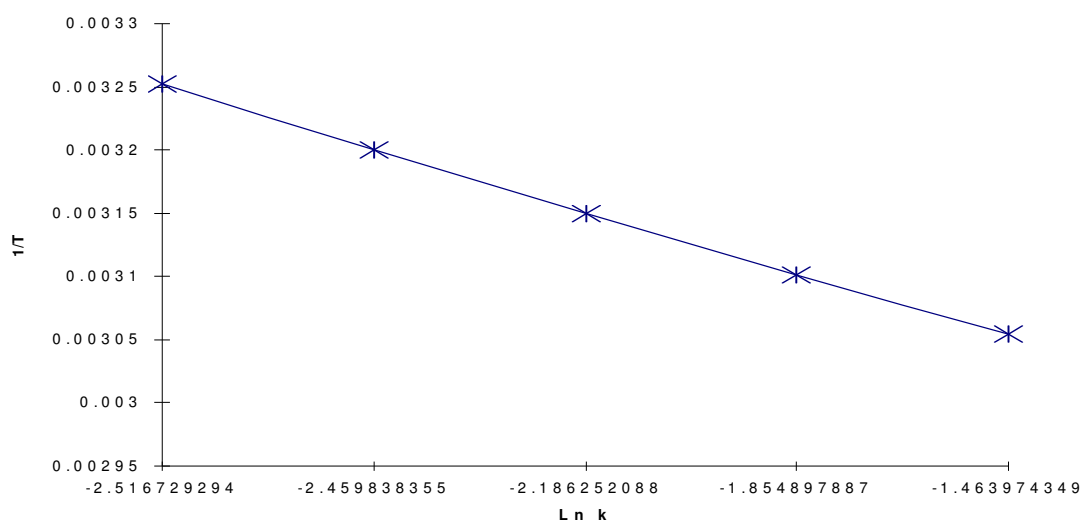

Figure 3.15: Plot of lnk against 1/T for determination of activation energy

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