

MECHANISM FOR PARTIAL OXIDATION OF CYCLOHEXENE BY CHROMIUM (VI) OXIDE IN ACETIC ACID

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ABSTRACT

The oxidation of cyclohexene by chromium (VI) oxide in aqueous and acetic media has been studied. The reaction products were analysed using classical method, IR and GC/MS analyses. The major products of the oxidation reaction in acetic acid medium are cyclohexanol, cyclohexanone, cyclohex-2-en-1-one, cyclohexan-1,2-diol monoacetate and Bi-2-cyclohexen-1-yl. However, no reaction was observed between cyclohexene and chromium (VI) oxide in aqueous medium. Based on the result a mechanism for the oxidation reactions has been proposed involving dissociation of acetic acid to form an acetate anion which attacks the chromium (VI) oxide to form an acetochromate ion. The latter then attacks cyclohexene to form an acetochromate cyclohexenyl ion intermediate which undergoes electron shift and rearrangement to produce cyclohexanone and chromium (IV) oxide, thereby regenerating the acid. The proposed mechanism suggests that the acetic acid serves both as homogeneous catalyst as well as medium for the reaction.

KEY WORDS: Cyclohexene, oxidation, acetic acid, mechanism

INTRODUCTION

Oxidation of hydrocarbons is one of the main goals of petroleum chemistry because of its potential to provide a wide range of useful products (Speight 1999). Like many other hydrocarbons, oxidation products of cyclohexene find several applications as intermediates for the manufacture of useful chemicals. The common products of uncatalysed oxidation of cyclohexene are, cyclohexene hydroperoxide, cyclohexenol, cyclohexanone and cyclohexene oxide. Selective catalysts are often employed to direct the reaction to the required products (Mahajani et al, 1999).

Chromium (VI) oxide (CrO_3), which forms chromic acid in aqueous solution, is one of the versatile oxidising agents, and reacts with most of the oxidisable organic groups (Carruthers, 2004). Chromium (VI) oxide, in the presence of mineral acids such as H_2SO_4 , cleaves olefinic bonds to produce acids. This reaction competes with oxidation of allylic C-H bonds (Murry, 1977).

The objective of this work is to study the products of chromium (VI) oxidation of cyclohexene and to propose a plausible mechanism for the reaction.

PROCEDURES

The oxidation reaction was carried out by separately mixing cyclohexene with aqueous and acetic acid solutions of chromium (VI) oxide (CrO_3) and the products in each case were extracted with chloroform using separatory funnel. The chloroform extracts were analysed using classical qualitative analytical methods, infrared spectroscopy (IR) and gas chromatography coupled with mass spectrometry (GC/MS).

Qualitative analysis

The presence of alcohols was tested with Jones' reagent, that of ketones with 2,4-dinitrophenylhydrazine reagent, 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

For the GC/MS, Agilent Gas Chromatographic Instrument (model 6890) coupled to mass selective detector (MSD 5973N) was used. The GC column was Agilent 122-5532 of 30m nominal length, 0.25mm (250 μm) diameter with 0.25 μm film thickness of dimethylpolysiloxane coating. The temperature programming of the GC oven involved holding the initial temperature of 80 °C for five minutes, followed by raising the temperature to 280°C at the rate of 10 °C/minute and then holding the final column temperature of 280°C for five minutes bringing the total running time to 30 minutes. The injection port temperature and pressure were set at 250°C, and 2.33 psi respectively. The total flow rate of 28.4 cm^3/min was achieved using helium as the carrier gas. In a typical GC analysis, one microlitre of the sample was injected into the injection port by an Automatic Liquid Sampler (Agilent 7683B). The analysis of the chromatogram was done with the ChemStation software. For each peak in the mass 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.

RESULTS AND DISCUSSION

Results of classical qualitative and infrared analyses
Result of the qualitative and the infrared spectroscopic analyses of the products are shown in Table I below and

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Table I: Result of qualitative and infrared analysis

Test	Products obtained			
	Alcohols	Ketones	Acids	Unsat
Qualitative test on products of oxidation by aqueous CrO ₃	-	-	-	-
Qualitative test on products of oxidation by saturated CrO ₃ in Acetic acid	+ve	+ve	-	+ve
IR spectrum of Chloroform extract of the reaction products in acetic acid medium	+ve (3414, 728.4 & 1149.37 cm ⁻¹)	+ve (1714.3 cm ⁻¹)		

When cyclohexene was added to the aqueous solution of chromium (VI) oxide, the content separated into two phases; the upper organic (cyclohexene) and the lower aqueous (CrO₃ solution). In spite of the continuous stirring that provided proper contact between the two phases, no reaction was observed. Likewise heating and stirring did not bring about reaction. Therefore further

analysis was only carried on the chloroform extract of the reaction carried out in acetic acid.

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 A-E

Table II: Result of the GC/MS analysis

Sample	RT (mins)	Peak area (%)	Compound Matching	Correlation (%)
Chloroform extract of the reaction in acetic acid medium	4.29	2.46	Cyclohexanol	95
	4.51	5.05	Cyclohexanone	93
	5.36	59.37	Cyclohex-2-en-1-one	91
	11.13	9.88	Cyclohexan-1,2-diol, monoacetate	72
	13.12	5.16	Bi-2-cyclohexen-1-yl	78

Key: RT = Retention time

DISCUSSION

Qualitative test on the chloroform phase of the oxidation in acetic acid medium indicated the presence of ketone and unsaturation but not acids. Likewise the IR spectrum did not indicate any peak for acids. Unsaturation was also not detected but there was an absorption band at 1714.3 cm⁻¹ which can be assigned to carbonyl group for ketones, there were also other bands at 3414 and 728.4 cm⁻¹ which fall within the range of hydrogen bonded OH and O-H bending vibrations respectively. There was still another absorption at 1149.7 cm⁻¹ that indicate C-O stretching vibration. These indicated the presence of ketones and alcohol in the fraction. However the IR spectrum did not show any peak assignable to carbon-carbon double bond. Both the qualitative test and the IR spectra indicated the presence of ketone therefore it was confirmed. But the difficulty here is with alcohol and unsaturation. Only the IR spectra indicated the presence of alcohol. This may mean that the amount of alcohol present was below the detection limit of the classical test but was detected by the IR spectroscopic test. The unsaturation detected by decolourisation of the permanganate may be from the allylic ketone.

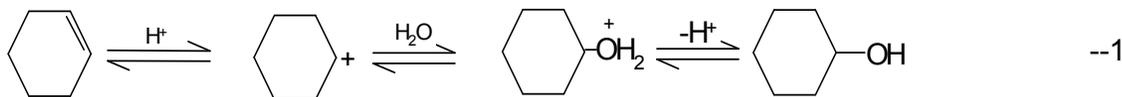
GC/MS Analysis of Cyclohexene Oxidation Products

The chromatogram gave eleven (11) distinct peaks. On comparing the MS spectrum of each peak with the NIST electronic library, it was revealed that one of the peaks had no matching at all while other five have a correlation of less than 70. The remaining five that constitute 81%

of the total peak area were cyclohexanol (2.46%), cyclohexanone (5.05%), cyclohex-2-en-1-one (59.37%), cyclohexan-1,2-diol 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 effort was made to see how the yield of the needed product can be enhanced. This can be done in one of two ways; one of them is to find active and selective catalyst that would make the target compound the major or sole product. (Magee and Dolbear, 1998). Another way is to explore the favourable conditions and pathways of each of the products and employ that to enhance production of the target product(s). This latter option was resorted to in this work.

Proposed Mechanism of Oxidation of Cyclohexene by CrO₃

The products of interest in this work were the cyclohexanol and cyclohexanone and emphasis was given to them. However, cyclohex-2-en-1-one (allylic ketone) cannot be ignored since it happened to be the major product in the system. The mechanism of formation of the 2-cyclohexen-1-one (allylic ketone) from cyclohexene was reported by Tsuda et al 2006. The formation of cyclohexanol has also been reported to come by acid catalysed nucleophilic addition on the double bond (Skyles, 1991).

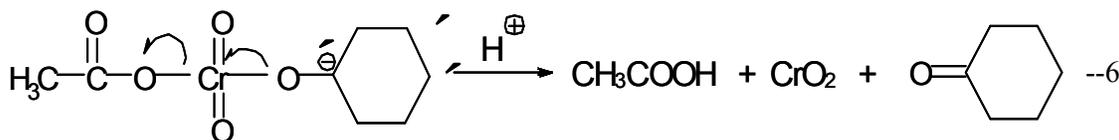
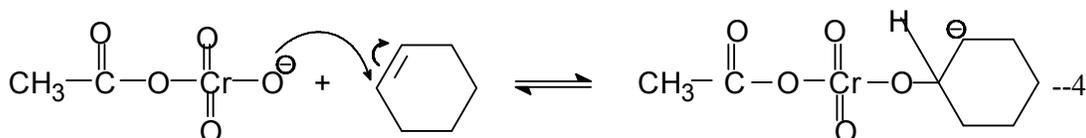
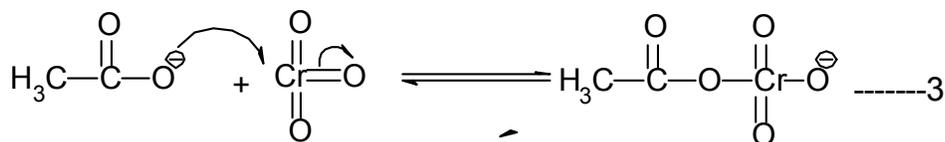
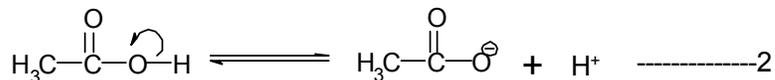


Since the reaction medium is acid, this reaction can readily take place. Considering that acid catalysed

hydration of alkenes to alcohols takes place readily, one would expect the cyclohexanol to be the predominant

product in such acidic medium. To the contrary cyclohexanol constitutes only about 2.5% of the total products. This can be explained by the fact that hydration of alkenes to alcohol depends on the water content in the system, however, water was avoided in this reaction in order to prevent phase separation. Therefore, the quantity of the cyclohexanol formed was limited to the amount of moisture in the system which was very small.

Formation of Cyclohexanone: The species present in the reaction system were acetic acid (solvent), chromium (VI) oxide (oxidant) and cyclohexene (substrate). Therefore the reaction was expected to be initiated by a metal complex-hydrocarbon or metal complex — oxygen — hydrocarbon interaction (Józef and Witold, 1980). Thus, for the production of cyclohexanone the following scheme is proposed;



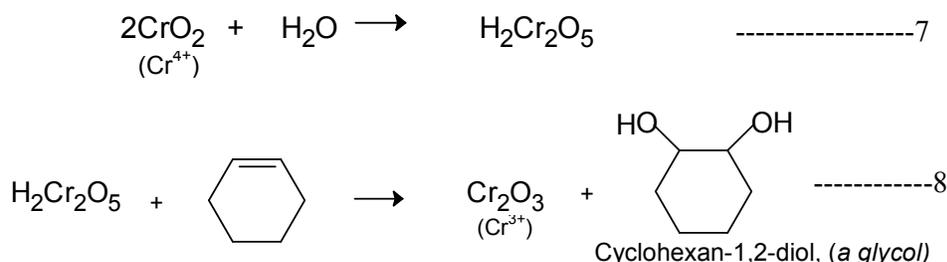
The reaction starts with dissociation of the acetic acid to give the acetate ion. The acetate ion reacts with the chromium (VI) oxide molecule to produce acetochromate ion (eqn. 3). The acetochromate ion then

attacks the cyclohexene to produce an acetochromate cyclohexenyl ion as an intermediate (eqn 4). This later intermediate undergoes electron shift and rearrangement (eqn. 5) and finally decompose to

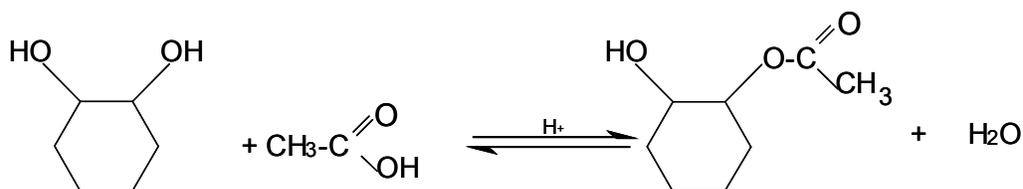
produce cyclohexanone and chromium (IV) oxide thereby regenerating the acetic acid molecule (eqn. 6). If this mechanism holds then acetic acid acts as a catalyst since it participated at the intermediate stage of the reaction and was regenerated at the end of the reaction. This is supported by the fact that the reaction did not take place in the absence of the acid. By this electron-pair shift, chromium has gone from an oxidation state of +6 to +4, but it is not stable in the latter state (Brown, 1995).

Formation of diol: Literature has established that the commonest product of alkene oxidation is a glycol

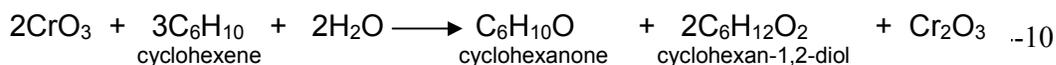
(ethan-1,2-diol). A glycol is the product of alkene oxidation with permanganate (MnO_4^-), osmium tetroxide (OsO_4), hydrogen peroxide (H_2O_2), peracids etc (Morgan and Robinson, 1975). However, this product was not among those identified in our study. Instead, cyclohexan-1,2-diol monoacetate (acetate ester of the cyclohexan-1,2-diol), that constituted about 10% of the total product, was found. This compound is most likely a product of esterification of the glycol. The glycol might have been formed in the process and reduced the unstable chromium (IV) ions (CrO_2) produced as a by-product of ketone formation.



The glycol formed can then undergo mono-esterification with acetic acid to produce the cyclohexan-1,2-diol monoacetate in the presence of chromic acid as catalyst.



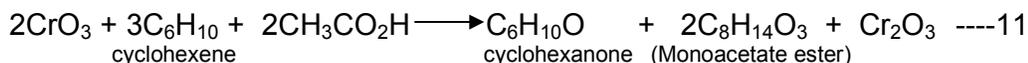
If this transition holds then the overall equation that produced the green coloured Cr_2O_3 , cyclohexanone and the glycol (cyclohexan-1,2-diol) from the CrO_3 can be written as:



This equation indicates that the ratio of the cyclohexanone to cyclohexan-1,2-diol and hence the subsequent ester (cyclohexan-1,2-diol monoacetate) is 1:2. These correspond closely with the ratio of the two compounds as indicated by their percentage peak areas (that is $5.05:9.88 \approx 5:10 = 1:2$). The closeness of the figures provides a strong support for the proposed equation and hence the proposed synthetic pathway of the two compounds.

Earlier, we argued that the quantity of the alcohol (cyclohexanol) produced was limited by the amount of water in the reaction mixture. This means that the production of the cyclohexan-1,2-diol (another alcohol) a

precursor to the ester (cyclohexan-1,2-diol monoacetate) should also be limited by the same factor. By implication, the two reactions (production of cyclohexanol and that of cyclohexan-1,2-diol) should compete with one another for the little water available in the system. But, this doesn't seem to have happened because the esterification reaction eliminates one molecule of water for every molecule of the ester produced and these water molecules formed were available for continuous glycol formation. Therefore, if equation 10 is rewritten in terms of production of the ester, the two molecules of water on the reactants side will disappear.



Thus, the glycol was formed as an intermediate, after all it is said to be unstable (Morrison and Boyd, 2002).

At this juncture it can be conveniently stated that the reaction pathways for the production of the cyclohexanol (2.46%), cyclohexanone (5.05%), and cyclohexan-1,2-diol monoacetate (9.88%), depends on the presence of acetic acid as a catalyst in the former two and as reactant in the ester formation. However, since formation of the cyclohexanol depends on the presence of water, then it can either be enhanced or suppressed by addition or removal of water from the system as the case may be. In the same vein, glycol formation requires water for its initiation, that is for conversion of the CrO_2 to $\text{H}_2\text{Cr}_2\text{O}_5$ that produce the glycol as ester precursor. Consequently, production of the ester is also dependent on the presence of some water in the system. Thus, carrying out the reaction in absolutely dry acetic acid would suppress production of both the alcohol and the ester and in effect boost that of cyclohexanone and its allylic counterpart.

CONCLUSION

It can be concluded that cyclohexene can be oxidized by chromium (VI) oxide in acetic acid to produce a number of oxygenated compounds. The acetic acid serves both as a necessary medium and to some extent as catalyst. It can also be asserted that elimination of water from the reaction medium can suppress production of alcohols and enhance that of ketones.

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