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The epoxidation of cyclohexene by dioxiranes over ketone catalysts

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Abstract

In this work, the dioxirane system has been applied to the epoxidation of cyclohexene. The catalytic activity of acetone, butan-2-one and pentan-2-one presented as homogeneous catalysts or supported on inorganic and polymer materials was investigated. It was found that the rate of cyclohexene oxide formation increased in proportion to increasing ketone concentrations using acetone and butan-2-one. Because of the advantages of supported catalysts, ketones were chemisorbed or grafted onto a range of different supports including different forms of silica and various polymers. The presence of carbonyl groups on the surface of the supports was confirmed and their catalytic activity was evaluated. The turnover frequency of the grafted ketones were compared with that of the homogeneous catalysts and design criteria for the further development of supported ketone catalysts were established.

Keywords: Epoxidation; Cyclohexene; Dioxiranes; Ketone; Catalysts; Oxone

1. Introduction

Dioxiranes, first isolated in 1972 [1], are remarkably reactive, efficient and versatile oxidizing agents. They have been used in the epoxidation of alkenes [2], oxidation of amines [3], oxidation of sulphides [4] and the conversion of saturated hydrocarbons into alcohols and ketones [5]. Dioxiranes can be prepared by a variety of methods including the oxidation of geminal dialkoxides by fluorine [1], the oxidation of diazo compounds [6] and the oxidation of ketones [7]. In this work potassium peroxymonosulphate ($KHSO_5$), a peracid, available in the form of oxone, $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was used to generate dioxiranes at pH 7.5. The catalytic cycle usually drawn for dioxiranes, as shown in Scheme 1, indicates that $KHSO_5$ is the oxidizing agent and the ketone acts as a catalyst.

The traditional epoxidation methods have served the chemical industry well over the last 30 years since epoxides have gained commercial importance. However, certain results have shown that the ketone/oxone process has certain key advantages over more established methods. The most striking advantages are the high yields obtained and the high reactivity of the system. For example phenanthrene, traditionally found to be difficult to oxidise, was epoxidised by isolated dimethyldioxirane to give phenanthrene-9,10-oxide in 50% yield over 20 h at 22°C [8].

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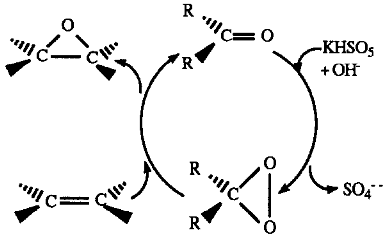


Scheme 1. Catalytic cycle of the ketone/oxone system.

In this work the advantages and limitations of dioxiranes acting as discrete species in solution or attached to an inorganic or polymer support are investigated for the epoxidation of cyclohexene to cyclohexene oxide in mild conditions at ambient temperature.

2. Experimental

2.1. Description of reaction system

The oxidation of cyclohexene was carried out in a batch reactor operating at a fixed temperature between 6 and 20°C. The pH of the reaction medium was maintained to within 0.01 of a pH unit with a Radiometer Copenhagen pH stat. Consumption of cyclohexene and formation of cyclohexene oxide was monitored using a HP 5890 series II gas chromatograph fitted with a HP-1 capillary column and an FID detector. $KHSO_5$ consumption was monitored by following the amount of KOH added by the pH stat.

Oxone (3.69 g, 11.18 mmol $KHSO_5$) and Na_2EDTA (0.1 g, 0.27 mmol) were dissolved in phosphate buffer (10 ml, 0.2 M, pH 7.5). The total volume was brought up to 30 ml by adding distilled water. THF (3.3 ml) was added and the mixture was stirred magnetically at 2200 rpm. 0.5 M KOH made up in a THF/water (10/90) mixture, was used to maintain the reaction mixture at the desired pH, then cyclohexene (9.7 mmol, 1 ml), n-octane (0.5 ml) (internal standard) and the ketone were added. This was taken as $t = 0$ for analysis of reaction kinetics. Samples were taken at set time intervals for GC analysis.

The turnover frequency (TOF) was measured for each catalyst and is defined as follows:

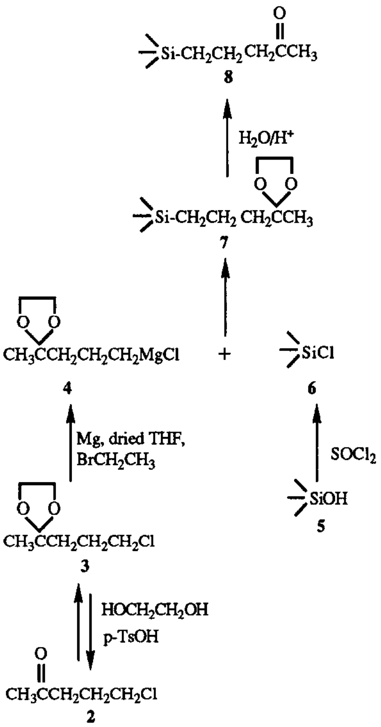
$$\mathrm{TOF}\ (/\mathrm{h}) = \frac{\text{Initial rate (mmol/h)}}{\text{Amount of ketone present (mmol)}}$$

2.2. Preparation of supported ketones

2.2.1. Silica / silica gel supported ketones

Silica and silica gel supported ketones were prepared according to the route outlined in Scheme 2. 2-(3-chloropropyl)-2-methyl-1,3-dioxolane **3** was prepared from 5-chloro-2-pentanone [9,10].

To prepare silica chloride **6**, a 500 ml round-bottomed flask equipped with a reflux condenser and a magnetic pellet was charged with $SOCl_2$ (80 ml, 1.1 mol) and toluene (160 ml, 1.5 mol). To the vigorously stirred solution, silica (10 g) which had previously been activated by heating at 150°C for 3 h, was added.



Scheme 2. Synthesis of pentan-2-one derivatised silica.

The mixture was heated to reflux for 24 h with constant stirring. The mixture was allowed to cool and once the silica had settled the supernatant liquid was decanted. The remaining thionyl chloride and toluene were removed under reduced pressure using a rotary evaporator. Silica chloride **6**, a deep purple coloured powder was collected, and stored in a dessicator.

A 250 ml round-bottomed flask fitted with a magnetic stirrer, a pressure equalising dropping funnel and a double-faced condenser, was purged with dry oxygen-free N_2. Mg turnings (1.85 g, 0.077 mol) and dried THF (60 ml) were charged into the flask. The mixture was vigorously stirred for 15 min. A few drops of bromoethane and 1 ml of **3** were added. The solution was heated gently. After the reaction had initiated, the heat was removed and moderate reflux was maintained by addition of the remainder of **3** in THF (30 ml) giving a total of 0.066 mol of **3** added. The solution was heated to reflux for 30 to 45 min after the addition and then cooled to room temperature. The resulting solution of Grignard was centrifuged to remove suspended solids.

To freshly made silica chloride (7.5 g), the Grignard solution was added dropwise at room temperature under an inert (N_2) atmosphere. The dark red reaction mixture was stirred for 1 h at room temperature and for a further hour at 40°C. The solution was centrifuged, and the supernatant liquid was decanted. The silica material was filtered and washed with 1 M CH_3COOH (100 ml). It was further washed with ethanol, ether and chloroform and then extracted with chloroform for 24 h in a soxhlet extractor to remove all traces of non-bonded organics.

The following polymer supported ketones were prepared:

2.2.2. Methyl vinyl ketone / divinylbenzene

2.2.2.1. (MVK / DVB) copolymers. A range of copolymers was prepared with varying levels of DVB, from 0 to 50% in weight. In each case the total weight of monomer used was 8.4 g. Toluene (16 ml) and azo-*iso*-butyronitrile (0.4 g), were added to the monomers and the mixture was divided between 4 test tubes equipped with magnetic pellets to allow constant stirring. The test tubes were placed in a water bath at 50°C for 10 min. The temperature was allowed to rise to 80°C over 20 min. Reaction was allowed to continue at this temperature for 30–60 min until polymerisation was complete, giving a white solid or a gel depending on the level of DVB present. The polymer was removed from the test tubes, crushed and washed with methanol to remove the toluene. The filtered product was dried in a vacuum oven at 60°C for 2 h.

2.2.2.2. Acylated styrene / DVB. A range of copolymers of styrene and DVB was prepared by varying levels of DVB present from 0% to 8% by weight. The general method used was as follows [11,12]:

A 1 l reactor flask equipped with a mechanical stirrer and a reflux condenser, was purged with N_2. Polyvinylalcohol (0.675 g) was added to the flask and dissolved at 50°C in distilled water (375 ml). To the vigorously stirred solution, benzoyl peroxide (0.675 g) was added. Styrene and divinylbenzene with varying ratios, (giving a total weight of 58.1 g of monomer), were added along with heptane (39 ml) and *iso*-amyl acetate (39 ml) which were added as precipitants. An emulsion of fine polymer droplets was obtained which was heated to 90°C in a water bath, while maintaining a constant rate of stirring and passing a slow stream of N_2 through the reaction vessel. The mixture was stirred for 8 h at 90°C thereupon heating was discontinued and the contents of the flask was allowed to cool to room temperature. Stirring was then stopped and the supernatant liquid decanted. The resulting polymer was filtered and washed several times with methanol and reslurried in methanol (500 ml) for 2 h. The product was filtered and dried at 50°C in a vacuum oven for 4 h.

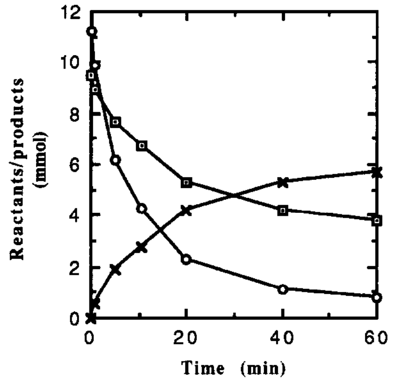


Fig. 1. Typical reaction profile in the presence of acetone (41 mmol). ○, $KHSO_5$; dotted square, cyclohexene, ×, cyclohexene oxide.

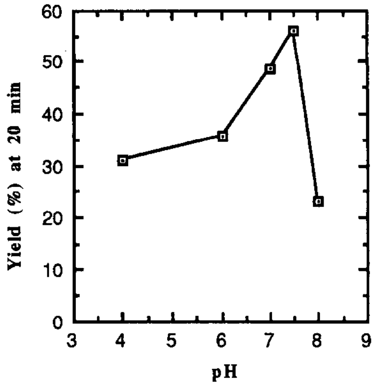


Fig. 3. Yield of cyclohexene oxide at 20 min over a range of pH values. At pH 4 and 5 water was substituted for buffer.

The procedure used for the acylation of styrene/DVB copolymers was as follows. In a 100 ml 3-necked round-bottomed flask equipped with a thermometer and reflux condenser, polymer beads (5.0 g) were suspended in nitrobenzene (40 ml) for 30 min to allow the beads to swell. To this mixture acetyl chloride (1.6 g, 0.02 mol) was added with constant stirring. Anhydrous $AlCl_3$ (3 g, 0.02 mol) was slowly added and the mixture was stirred for 1 h at 25°C. The mixture was heated to 70°C for 1 h and allowed to cool to room temperature. The product was filtered and washed successively with distilled water (100 ml), THF (100 ml), HCl (0.5 M, 100 ml), THF/water (50/50, 100 ml) and methanol (100 ml). The product was dried in a vacuum oven at 50°C for 4 h.

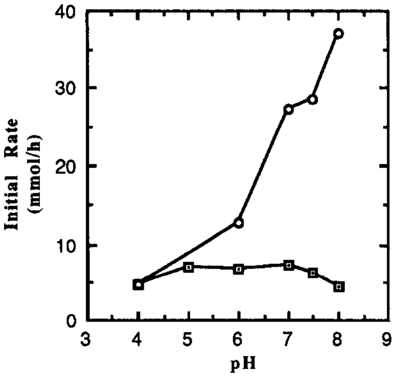


Fig. 2. Initial rate of cyclohexene oxide formation as a function of pH. Dotted square, in the absence of ketone; ○, in the presence of acetone (68 mmol). At pH 4 and 5 water was substituted for buffer.

2.2.3. Alkylation of 3-methyl-2,4-pentanedione with the Merrifield resin

The Merrifield resin which is commercially available, is a copolymer of styrene and divinylbenzene with CH_2Cl groups (1 mmol/g) on the surface. 1% crosslinked Merrifield resin (5 g) was swollen in THF (50 ml) for 2 h. The slurry was then charged to a 100 ml round-bottomed flask fitted with a reflux condenser. 3-methyl-2,4-pentanedione (1.4 g, 0.012 mol), anhydrous K_2CO_3 (2.76 g, 0.02 mol) and tetrabutylammonium hydrogen sulphate (0.4 g, 1.18 mmol) were added. The mixture was heated to reflux overnight with vigorous stirring. During the course of the reflux the colour of the reaction mixture changed from clear to brown. The solution was filtered and the solid material was added to a beaker containing water (100 ml) and stirred for 2 h. The solution was filtered and washed with water (50 ml), THF (50 ml), ethanol

Table 1
Influence of ketone structure on TOF

Ketone	TOF (h^{-1})
Acetone	0.39
Butan-2-one	0.20
Pentan-2-one	0.01

Table 2
The quantity of ketone on the supports

Material	Ketone on surface (mmol/g)
Pentan-2-one derivatised silica	0.07
Pentan-2-one derivatised silica gel	0.35
(98/2) MVK/DVB copolymer	14
3-methyl-2,4-pentanedione on Merrifield resin	≤ 1

(50 ml), ether (50 ml) and chloroform (50 ml). It was then dried in a vacuum oven at 50°C for 4 h.

3. Results and discussion

A typical reaction profile is shown in Fig. 1 for the oxidation by $KHSO_5$ of cyclohexene to cyclohexene oxide catalysed by acetone in the THF/water system. In addition, it should be noted that there was a significant background contribution to this reaction, because cyclohexene also reacted with $KHSO_5$ in the absence of the ketone. Relative sizes of the background and ketone catalysed reaction was strongly pH dependent, as shown in Fig. 2. The optimum yield of cyclohexene oxide was obtained at pH 7.5 as shown in Fig. 3.

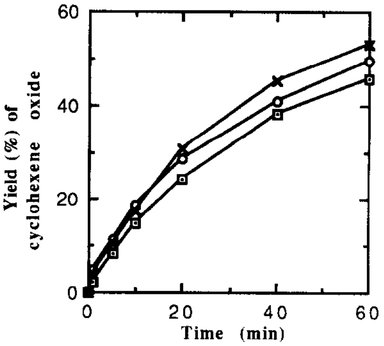


Fig. 4. Yield of cyclohexene oxide versus time. Dotted square, background reaction; O, 0.125 g (98/2) MVK/DVB; ×, 0.5 g (98/2) MVK/DVB.

The reactivity of the system was strongly dependent on the structure of the ketone used as catalyst. Table 1 shows the TOF, based on initial reaction rates, for cyclohexene oxide formation from cyclohexene with acetone, butan-2-one and pentan-2-one as catalysts. Clearly acetone, with the shortest chain length, was the most effective. The solubility of the ketones was not a factor in determining order of reactivity since all the ketones listed above were fully soluble in the THF–water system used.

The pentan-2-one derivatised silica and silica gel materials each displayed infra-red bands at 1710 cm^{-1}, characteristic of carbonyl compounds. This band remained intact when the samples were heated up to 220°C but disappeared above this temperature. Correspondingly, a weight loss was recorded in thermogravimetric analysis at this temperature and was taken as a measure of the amount of chemically grafted pentan-2-one present in the system. The amounts of grafted ketones measured in this way are presented in Table 2 for silica and silica gel. The presence of carbonyl groups on the polymers was also confirmed by infra-red spectroscopy. For the MVK/DVB copolymers, the quantity of ketone present was estimated by determining the amount of monomer used (Table 2). For the alkylated Merrifield resin, the amount of ketone supported was known not to be greater than 1 mmol/g as this was the level of CH_2Cl groups on the surface originally (Table 2).

Table 3
Reactivity of some supported ketones

Supported ketone	TOF of free ketone (h^{-1})	Ketone present (mmol)	Expected init. rate (mmol/h)
Pentan-2-one derivatised silica	0.01	0.14	0.0014
Pentan-2-one derivatised silica gel	0.01	0.7	0.007
(98/2) MVK/DVK copolymer	0.2	7	1.4
(90/10) MVK/DVB copolymer	0.2	6.45	1.29

All the supported ketones were tested as catalysts for the epoxidation of cyclohexene and the only one to show activity above the background level was the (98/2) MVK/DVB copolymer (Fig. 4).

In Table 3, the expected initial rate of epoxidation was calculated knowing the TOF and the quantity of supported ketone used. As this figure is small relative to that for the uncatalysed background reaction (5.8 mmol/h), the apparently poor catalytic activity of the supported ketones is not surprising.

4. Conclusions

The low concentration of the supported ketone in the reaction system coupled with low reactivity explains in part the poor catalytic ability of the supported ketone. Since there is a physical limit to the amount of solid that can be introduced, in order to generate a more active catalyst it would be necessary to support a more active ketone.

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