

Chlorine Dioxide Oxidation of Cyclohexene

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The following compounds have been isolated from the chlorine dioxide oxidation of cyclohexene: Cyclohex-1-en-3-one, 3-chlorocyclohex-1-ene, *trans*-2-chlorocyclohexan-1-ol, 2-chlorocyclohexan-1-one, *trans*-1,2-dichlorocyclohexane, 1,2-epoxycyclohexane, adipic acid and 2-chlorocyclohexan-1,3-dione.

Few studies of the reactions of chlorine dioxide with organic compounds have been reported in spite of their technical importance, for example, in the pulping industry.^{1,2} Fürst³ as early as 1881 obtained monochloroacetic acid by oxidation of ethylene with this reagent, and Bhaduri⁴ oxidised ethanol to acetic acid. Schmidt and Braunsdorf⁵ found that chlorine dioxide reacts with olefines. Somsen⁶ has examined the reaction with model substances for carbohydrates, and Sarkanen *et al.*⁷⁻⁹ with aromatic compounds as models for lignin. Recently Rosenblatt *et al.*¹⁰ published a report concerning the oxidation of triethylamine with chlorine dioxide.

Leopold and Mutton² studied the reaction between chlorine dioxide and triolein and found that the reaction product contained equimolar amounts of chlorine and carbonyl groups, and small amounts of epoxy and hydroxyl groups as well as traces of free carboxyl groups.

RESULTS

The following paper reports a study of the reaction between chlorine dioxide and cyclohexene. The reaction was carried out in two ways, one by passing dry chlorine dioxide gas through pure cyclohexene, and the other by stirring an aqueous solution of the gas with cyclohexene. The chlorine dioxide used was free from chlorine.

For the non-aqueous experiment the following compounds were isolated from the reaction product: 1,2-epoxycyclohexane, 3-chlorocyclohex-1-ene, cyclohex-1-en-3-one, *trans*-1,2-dichlorocyclohexane, *trans*-2-chlorocyclohexan-

1-ol, 2-chlorocyclohexan-1-one and adipic acid. Adipic aldehyde and cyclohexan-1,2-dione were not present. When using larger amounts of chlorine dioxide (molar ratio cyclohexene/chlorine dioxide about 5:1) 2-chlorocyclohexan-1,3-dione was obtained, and gas phase chromatography showed the presence of traces of glutaric acid.

Adipic acid and 2-chlorocyclohexan-1,3-dione precipitated out during the reaction and were separated from each other by benzene extraction. The structure of 2-chlorocyclohexan-1,3-dione was proved by its synthesis from cyclohexan-1,3-dione and chlorine. The location of the chloro group followed from the fact that the product yielded glutaric acid on oxidation. The other reaction products obtained were isolated by preparative gas phase chromatography and their IR-spectra shown to be identical with those of authentic samples. Table 1 gives the relative retention times of the cyclohexane derivatives, that of *trans*-1,2-dichlorocyclohexane being taken as unity.

The yields of the products are reported in Table 2 for two experiments which differed in the amount of chlorine dioxide used. The total amount of isolated cyclohexane derivatives was 0.6 moles per mole of chlorine dioxide consumed.

For the aqueous experiment, gas phase and thin layer chromatography showed that the reaction product contained all the compounds in Table 2

Table 1. Relative retention times of cyclohexane derivatives.

Compound	Synthes. ^a	Column			
		Polyglycol ^b	Polyester 1 ^c	2 ^d	Carbowax ^e
1,2-Epoxycyclohexane	11	0.26	0.30	0.24	0.34
3-Chlorocyclohex-1-ene	12	0.35	0.33	0.30	0.43
Cyclohexanol		0.58	0.69	0.61	
Cyclohex-1-en-3-one	13	0.62	1.36	1.20	0.91
Cyclohex-1-en-3-ol				0.88	
<i>trans</i> -1,2-Dichlorocyclohexane	14	1.00	1.00	1.00	1.00
Cyclohexan-1,2-dione	15	1.24			
<i>trans</i> -2-Chlorocyclohexan-1-ol	16	1.58	2.55	2.24	1.85
2-Chlorocyclohexan-1-one	17	1.36	3.10	2.72	1.78
Adipic aldehyde	18	1.81			

P-E = Perkin Elmer

a) Reference number.

b) Polypropylene glycol (Ucon-oil LB-550-X) on Chromosorb W (P-E column R). The nitrogen flow rate was 40 ml/min, and column temperature 105°C. P-E fractometer 116e with flame ionization detector.

c) Succinate polyester of ethylene glycol (25 wt %) on Chromosorb W. The helium flow rate was 65 ml/min, and column temperature 112°C. P-E fractometer 116e with hot wire detector.

d) Succinate polyester of butanediol (15 wt %) on Chromosorb W (80–100 mesh) (P-E column BDS). The nitrogen flow rate was 25 ml/min, and column temperature 100°C. P-E model 800.

e) Carbowax 20 M (20 wt %) on Chromosorb W (60–80 mesh, treated with hexamethyldisilazane). Column length 20', inner diameter 3/8". The helium flow rate was 200 ml/min, and column temperature 165°C. Aerograph Autoprep A-700.

Table 2. The yields of the products from the oxidation of cyclohexene with chlorine dioxide.

Reaction products	Yields ^a	
	Ratio ^b = 35:1	Ratio ^b = 7:1
Cyclohex-1-en-3-one	16	13
3-Chlorocyclohex-1-ene	13	14
<i>trans</i> -2-Chlorocyclohexan-1-ol	11	15
2-Chlorocyclohexan-1-one	11	7
<i>trans</i> -1,2-Dichlorocyclohexane	5	7
1,2-Epoxy cyclohexane	3	0
Adipic acid	3 ^c	4 ^d
Total	62	60

a) In mole % of the product per one mole of chlorine dioxide consumed.

b) Molar ratio cyclohexene/chlorine dioxide.

c) The yield of precipitate, which contains almost pure adipic acid.

d) The yield of precipitate, which contains adipic acid plus 2-chlorocyclohexan-1,3-dione and traces of glutaric acid.

Table 3. Acids formed from cyclohexene on oxidation in aqueous suspension.

pH	Reactant ratio ^a	Acids ^b		
		Succinic	Glutaric	Adipic
7	1.5:1	<1	<1	100
	15:1	<1	<1	100
4	1.5:1	5	11	100
	15:1	7	25	100
2	1.5:1	19	37	100
	15:1		86	100
<i>c</i>	5.5:1		575	100
<i>d</i>	5:1	0	<1	100

a) The cyclohexene/chlorine dioxide ratio.

b) Determined by gas phase chromatography of the dimethyl esters. Succinate polyester of ethylene glycol on Chromosorb W (P-E column P). The nitrogen flow rate was 55–80 ml/min and column temperature 155°C. P-E fractometer 116e with flame ionisation detector. The relative retention times for the esters are 0.45, 0.65, and 1.00, respectively. The figures give the relative peak areas taking that of dimethyl adipate as 100.

c) No buffering, which yielded a very acidic solution.

d) The results obtained under non-aqueous condition given for comparison.

but 2-chlorocyclohexan-1,3-dione. In addition cyclohex-1-en-3-ol was detected when the reaction was carried out at pH 4–7 but not under more acidic conditions. At lower pH considerable amounts of glutaric and succinic acids were formed together with adipic acid (Table 3).

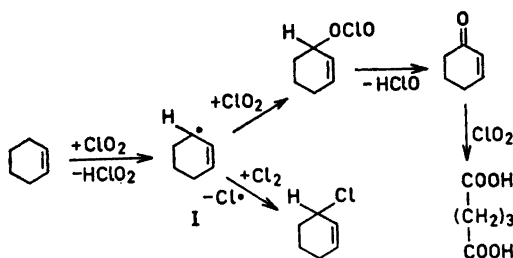


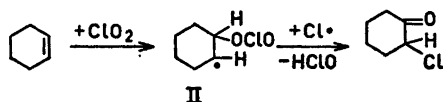
Fig. 1.

The reduction of chlorine dioxide can proceed to varying valency states. The formation of hypochlorous acid and chlorine is evident from the isolation of *trans*-1,2-dichlorocyclohexane and *trans*-2-chlorocyclohexan-1-ol. The presence of chlorous acid and hydrogen chloride in the reaction mixture was proved by paper chromatography and titration (see experimental section).

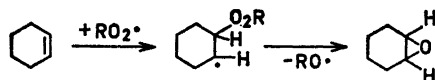
DISCUSSION

Since chlorine dioxide has an unpaired electron the primary reaction products from cyclohexene and the dioxide are radicals. Cyclohex-1-en-3-one and 3-chlorocyclohex-1-ene are probably formed *via* the radical (I) according to the sequence given in Fig. 1.

2-Chlorocyclohexan-1-one may be an oxidation product of *trans*-2-chlorocyclohexan-1-ol. The chloro-ketone is, however, present in a higher proportion at the beginning than at the end of the reaction (Table 2) and the reverse is true for the chlorohydrin. We therefore believe it more probable that the chloro-ketone is synthesised by a radical mechanism involving chlorine dioxide, for example:



1,2-Epoxy-cyclohexane may also be formed from the radical (II) by separation of the radical monochlorine monoxide (ClO). This compound is stable at low temperatures and is formed for example by UV irradiation of chlorine dioxide.¹⁹ The reaction is similar to that suggested by Walling²⁰ for the formation of epoxides from unsaturated compounds during autoxidation:



The epoxide is not present in the final stages of the reaction, evidently having been destroyed by acids formed during the oxidation.

The yield figures in Table 2 show that the attack of chlorine dioxide in the 3-position giving the radical (I) is more important than attack directly on the double bond.

Glutaric acid is formed when cyclohex-1-en-3-one and 2-chlorocyclohexan-1,3-dione are treated with chlorine dioxide, which probably explains its presence as a reaction product from the cyclohexene oxidation. 2-Chlorocyclohexan-1,3-dione is not formed when cyclohex-1-en-3-one reacts with chlorine dioxide, and therefore does not seem to be an intermediate in the oxidation of the cyclohexenone to glutaric acid.

EXPERIMENTAL

Chlorine dioxide

Preparation. Chlorine was passed into a 3 % solution of sodium chlorite until the colour of the solution changed from brown to yellow. The chlorine and chlorine dioxide present in the solution were flushed out by a flow of nitrogen. The gaseous mixture was allowed to pass through a column filled with glass beads over which water flowed. The water dissolved chlorine dioxide preferentially and the solution obtained (the stock solution) from the bottom of the column contained 4–12 g of chlorine dioxide and 0.01–0.2 g of chlorine per litre.

For reaction, the chlorine and the chlorine dioxide in the stock solution were flushed out with nitrogen, and the chlorine and the water vapour were removed by passing the gaseous mixture through a tube (length 1 m, diameter 1.5 cm) containing dried sodium chlorite (9–24 mesh).

Analysis. The determinations of chlorine and chlorine dioxide in aqueous solution were carried out according to Bonn.²¹ The solution (25 ml) is added to a potassium iodide solution (25 ml, 25 %) buffered to pH 8 with a phosphate-borate solution (50 ml, 13.8 mM solution of sodium tetraborate and 22.5 mM solution of potassium dihydrogen phosphate). The iodine formed by the reduction of chlorine dioxide to chlorite and of chlorine or hypochlorite to chloride is titrated with 0.1 N sodium thiosulphate. The solution is then acidified (0.2 N sulphuric acid, 100 ml) which causes the chlorite to react with the potassium iodide giving chloride and iodine. The iodine is titrated with sodium thiosulphate 5 min after acidification. From the two titrations the contents of chlorine and of chlorine dioxide are calculated.

The same method was also used for determining chlorite and hypochlorite when no chlorine dioxide was present.

The reaction between cyclohexene and chlorine dioxide in the absence of water

Organic reaction products. The mixture of chlorine dioxide and nitrogen was passed into gas chromatographically pure cyclohexene which was obtained by dehydration of cyclohexanol²² followed by careful purification.²³ The temperature during the reaction rose to about 40°C. The flow time varied from 1 to 10 h depending on the amount of dioxide desired and on the dioxide concentration in the stock solution. The weight of dioxide consumed was calculated from the decrease during the experiment in the dioxide content of the stock solution minus the small amount of dioxide which passed through the reaction flask and was collected by water washing of the gas leaving the flask. The flask was provided with a condenser to decrease the evaporation of cyclohexene.

After reaction the precipitate formed was collected and weighed (see Table 2). Thin layer chromatography²⁴ revealed the presence of adipic acid and an acidic ketone moving faster than adipic acid. A part of the precipitate was heated with refluxing methanolic hydrogen chloride for 1 h. The neutral fraction obtained was analysed on a gas chromatograph. Dimethyl adipate and traces of dimethyl glutarate were found (see Table 3, the last line).

The adipic acid was isolated by preparative thin layer chromatography followed by sublimation and identified by its m.p. (152–154°C), mixed m.p. and IR-spectrum. When using small amounts of chlorine dioxide the precipitate was almost pure adipic acid.

The acidic ketone was isolated by extraction of the precipitate with hot benzene. The crystals obtained on cooling were recrystallised twice from dioxan. The ketone was

identified as 2-chlorocyclohexan-1,3-dione (synthesised as described below) from its m.p. (175–178°C decomp.), mixed m.p., IR and UV-spectra, and elemental analysis.

The solution obtained after removing the precipitate was analysed by gas phase chromatography. Table 1 gives the relative retention times for the cyclohexane derivatives of current interest taking that of *trans*-1,2-dichlorocyclohexane as unity.

The substances in Table 2 except adipic acid were found in the solution and isolated by preparative gas chromatography on an Aerograph Autoprep A-700. For *trans*-2-chlorocyclohexan-1-ol and 2-chlorocyclohexan-1-one a preparative polyester column [coated as column (c), Table 1] at 170° was used and for the rest, the carbowax column (e), Table 1. The IR-spectra of the isolated substances in carbon tetrachloride solution were identical with those of authentic samples, which were synthesised according to references given in Table 1.

For the quantitative determination (Table 2) cyclohexanol was used as internal standard. The peak areas were determined by triangulation.

Inorganic reaction products. Chlorine dioxide (4.65 mmole) diluted with nitrogen was passed into a stirred mixture of cyclohexene (148 mmole) and sodium hydrogen carbonate (6.0 mmole) during 8 h. The salts were then removed and examined by paper chromatography.¹⁰ The presence of chlorite, chloride and traces of chlorate was indicated. Titration according to Bonn (see above) showed that the salt mixture contained 0.16 mmole of chlorite.

The reaction between cyclohexene and chlorine dioxide in the presence of water

Cyclohexene was stirred with an aqueous solution (70 ml) of chlorine dioxide (5.3 mmole). During the reaction acids were formed. The pH was kept constant at 2, 4 and 7 by automatic addition of 0.1 N sodium hydroxide solution. Two runs were carried out at each pH value; one with 8.0 mmole of cyclohexene for a reaction time of 48 h; the other with 80 mmole for 24 h. The cyclohexene was smoothly suspended in the aqueous solution after a short time of reaction.

The reaction mixture was extracted with isopropyl ether. A gas phase chromatogram of the ether solution showed peaks for all of the compounds in Table 2 except adipic acid. A peak for cyclohex-1-en-3-ol was also observed at pH 4 and 7 but not at pH 2.

The extracted aqueous solutions contained chlorous acid, chloric acid (a weak spot) and hydrogen chloride, as shown by paper chromatography.¹⁰

Aliquots of the solutions were titrated for chlorous acid according to Bonn.²¹ From the experiments with 80 mmole of cyclohexene at pH 7 the amount of this acid was 1.7 mmole; at pH 4, 1.5 mmole, and at pH 2, 0.3 mmole. If 8 mmole of cyclohexene were used the solutions contained unreacted chlorine dioxide which invalidated the analysis.

Sulphur dioxide was passed into another portion of the aqueous solution to reduce the chlorine compounds. The solutions were then evaporated to dryness and the residue was analysed by gas phase chromatography for succinic, adipic, and glutaric acids as described above. The relative peak areas of dimethyl succinate, dimethyl adipate and dimethyl glutarate are shown in Table 3. Some slow moving compounds, whose peaks were also observed, may be esters of chlorinated acids.

The experiment was also carried out by passing a mixture of chlorine dioxide (103 mmole) and nitrogen into a stirred mixture of cyclohexene (493 mmole) and water (50 mmole) (no buffering). The organic compounds obtained were analysed as above. The ratio glutaric acid/adipic acid is shown in Table 3.

The reactions between chlorine dioxide and three of the reaction products

1,2-Epoxy-cyclohexane. Chlorine dioxide (59 mmole) was passed into 1,2-epoxycyclohexane (100 mmole) during 18 hours. The complex reaction product contained *trans*-2-chlorocyclohexan-1-ol (shown by gas phase chromatography) and adipic acid (by thin layer chromatography).

Cyclohex-1-en-3-one. Chlorine dioxide (27 mmole) was passed into cyclohex-1-en-3-one (51 mmole) during 21 hours. The complex reaction product contained glutaric, succinic

and oxalic acids (shown by gas phase chromatography). No 2-chlorocyclohexan-1,3-dione was formed as shown by thin layer chromatography and the absence of a carbonyl peak at 1570–1580 cm^{-1} , which could be due to the diketone. A similar result was obtained when the reaction was carried out in a dilute carbon tetrachloride solution.

2-Chlorocyclohexan-1,3-dione. An aqueous solution of chlorine dioxide (0.108 M, 20 ml) was added to a vigorously stirred mixture of 2-chlorocyclohexan-1,3-dione (2.0 mmole) in water (3 ml). After 4.5 h, the resulting colourless solution was evaporated to dryness. The residue was heated under reflux with methanolic hydrogen chloride and the amount of dimethyl glutarate formed was determined (0.36 mmole, yield 18 %) by gas phase chromatography using dimethyl adipate as an internal standard. The peak areas were determined by triangulation.

Synthesis of 2-chlorocyclohexan-1,3-dione

Chlorine (43 mmole) dissolved in glacial acetic acid (65 ml) was added during one hour to a stirred solution of cyclohexan-1,3-dione (41 mmole) and sodium acetate (42 mmole) in glacial acetic acid (60 ml), the temperature being maintained at 15–20°C. After an additional hour at the same temperature the precipitate was removed and the filtrate evaporated. The residue was recrystallised first from benzene and then from dioxan giving colourless crystals, m.p. 176–179°C (decomp.). A further small crop could be isolated from the precipitate by benzene extraction. The total yield was 0.60 g (10 %). (Found: C 48.95; H 4.96; Cl 24.08 and O 21.91. Calc. for $\text{C}_6\text{H}_9\text{ClO}_2$: C 49.17; H 4.81; Cl 24.19 and O 21.83). Its UV-spectrum shows a maximum at 266 μ (5×10^{-5} moles in ethanol plus a trace of hydrogen chloride). It absorbs strongly in the IR at 1570–1580, 1655 and 2600 cm^{-1} in a potassium bromide pellet.

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