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HYDROGEN PEROXIDE OXIDATION OF CYCLOHEXANONE AND CYCLOHEXANONE PEROXIDE IN THE PRESENCE OF SOME METAL OXIDES

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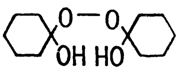
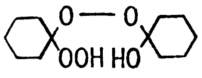
Cyclohexanone was oxidized to 1-hydroxy-1'-hydroperoxydicyclohexyl peroxide(HHP) by TeO_2 and to adipic acid by H_2MoO_4 and H_2WO_4. The oxidation products from cyclohexanone peroxide were the same as those of cyclohexanone. 1-Hydroxy-1-hydroperoxycyclohexane(HHC) was proposed as a reaction intermediate.

In general, the reaction of cyclohexanone with hydrogen peroxide gives 1, 1'-dihydroxydicyclohexyl peroxide(DHP) via 1-hydroxy-1-hydroperoxycyclohexane(HHC), and also, in the presence of mineral acid, DHP is further oxidized by additional one mole of hydrogen peroxide to HHP.1)


(DHP)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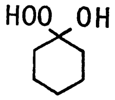
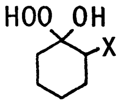

(HHC)


(halo-HHC)

(X = Cl, Br)

HHC, which has not been isolated and may be in an equilibrium with cyclohexanone and hydrogen peroxide or DHP and water in solution, is a presumed intermediate, but the corresponding halo-HHC derived from 2-halocyclohexanone was isolated and characterized.1) Payne2) has reported that the oxidation of cyclohexanone with hydrogen peroxide catalyzed by SeO_2 gave ring-contracted cyclopentanecarboxylic acid.

In the present work, the oxidations of cyclohexanone and cyclohexanone peroxide3) catalyzed by SeO_2, TeO_2, V_2O_5, H_2MoO_4, and H_2WO_4 were investigated.

Table 1 shows the principal products and their yields in the oxidation by a variety of catalysts. The reaction was carried out by using a mixture of cyclohexanone(0.1 mol), 35% hydrogen peroxide(0.1 mol) and the catalyst(2 mmol) at refluxing temperature for 10 h. The oxidation products from cyclohexanone varied depending on the catalyst, i.e., HHP, which was prepared from cyclohexanone with hydrogen peroxide in the presence of mineral acid, was obtained by TeO_2, and adipic acid was by V_2O_5, H_2MoO_4 and H_2WO_4. It is interesting to note that only HHP is formed by TeO_2 without the formation of cyclopentanecarboxylic acid or adipic acid. This is probably due to less catalytic activity of TeO_2 comparing with those of SeO_2, H_2MoO_4 and H_2WO_4. Consequently, HHP may be considered as a precursor to cyclopentanecarboxylic acid or adipic acid.

Table 1. Oxidation of cyclohexanone by various catalysts

Catalyst	Product	Yield(%)[a]
-	DHP	90.0[b]
SeO_2	Cyclo-C_5H_9COOH	32.0[b]
TeO_2	HHP	42.7
V_2O_5	$HOOC(CH_2)_4COOH$	2.3
H_2MoO_4	$HOOC(CH_2)_4COOH$	15.4
H_2WO_4	$HOOC(CH_2)_4COOH$	10.3

a) Isolated yield based on cyclohexanone.

b) These values from references 1) and 2).

To obtain more detailed information about the behaviour of HHP in the oxidation of cyclohexanone, the oxidation of cyclohexanone peroxides, DHP and HHP, was carried out. Table 2 summarizes the reaction products and their yields obtained by various catalysts.

Table 2. Oxidation of DHP and HHP by various catalysts[a]

Catalyst	Product	Yield(%)[b]	
		from DHP	from HHP
SeO_2	Cyclo-C_5H_9COOH	60.5	33.7[c]
H_2MoO_4	$HOOC(CH_2)_4COOH$	32.3	40.0
H_2WO_4	$HOOC(CH_2)_4COOH$	19.2	29.5

a) DHP(0.1 mol) was allowed to react with hydrogen peroxide(0.1 mol) and catalyst(2 mmol) in t-BuOH at 82°C for 10 h.

b) Isolated yield based on DHP and HHP, respectively.

c) A small amount of adipic acid was isolated.

Interestingly, DHP and HHP were oxidized in the same manner as that of cyclohexanone to give cyclopentanecarboxylic acid by SeO_2 and adipic acid by H_2MoO_4 and H_2WO_4. This fact may suggest that the oxidation of DHP and HHP proceeds through a reaction intermediate similar to that of cyclohexanone.

Furthermore, 2-chloro-HHC corresponding to HHC, which was an intermediate to DHP or HHP, was prepared from 2-chlorocyclohexanone[1)] and was oxidized under similar conditions. Their results are shown in Table 3. Both 2-chlorocyclopentanecarboxylic acid and α-chloroadipic acid were formed in every oxidation.

Table 3. Oxidation of 2-chloro-HHC by various catalysts[a)]

Catalyst	Yield(%)[b)]	
	2-chlorocyclopentane-carboxylic acid	α-chloroadipic acid
SeO_2	20.7	6.7
H_2MoO_4	4.8	23.3
H_2WO_4	trace	14.6

a) 2-Chloro-HHC(0.1 mol) was allowed to react with hydrogen peroxide (0.1 mol) and catalyst(2 mmol) in t-BuOH at 82°C for 10 h.

b) Isolated yield based on 2-chloro-HHC.

In order to estimate stoichiometric quantities of hydrogen peroxide to cyclohexanone for the formation of cyclopentanecarboxylic acid or adipic acid, the reaction was carried out with a variety of molar ratios of reactants. These results are shown in Table 4.

Table 4. Relationship between H_2O_2/cyclohexanone ratios and the yield[a)]

Catalyst	H_2O_2/cyclohexanone	Product	Yield(%)[b)]
SeO_2	1	Cyclo-C_5H_9COOH	32.0
	2	Cyclo-C_5H_9COOH	29.9
	3	Cyclo-C_5H_9COOH	23.6
H_2MoO_4	1	$HOOC(CH_2)_4COOH$	15.4
	2	$HOOC(CH_2)_4COOH$	34.9
	3	$HOOC(CH_2)_4COOH$	47.9
	4	$HOOC(CH_2)_4COOH$	50.8
	5	$HOOC(CH_2)_4COOH$	51.3
H_2WO_4	1	$HOOC(CH_2)_4COOH$	10.3
	2	$HOOC(CH_2)_4COOH$	20.5
	3	$HOOC(CH_2)_4COOH$	29.5
	4	$HOOC(CH_2)_4COOH$	30.8
	5	$HOOC(CH_2)_4COOH$	31.4

a) Cyclohexanone(0.1 mol) was allowed to react with various amounts of hydrogen peroxide and catalyst(2 mmol) in t-BuOH at 82°C for 10 h.

b) Isolated yield based on cyclohexanone.

In the oxidation by SeO_2, the yield of cyclopentanecarboxylic acid decreased with increasing molar ratio of hydrogen peroxide to cyclohexanone. On the contrary, the yield of adipic acid, which was formed in higher yield by H_2MoO_4 than H_2WO_4, increased with increasing amount of hydrogen peroxide. These observations indicate that cyclohexanone reacts with one or three moles of hydrogen peroxide to give cyclopentanecarboxylic acid or adipic acid, respectively.

Several investigators[4,5,6)] have demonstrated the reaction mechanisms for the oxidation of aliphatic and cyclic ketones with hydrogen peroxide by SeO_2, but their proposed mechanisms were different from each other.

In the oxidations of both cyclohexanone and cyclohexanone peroxide, the same product was obtained when the same catalyst was used, i.e., cyclopentanecarboxylic acid by SeO_2 and adipic acid by H_2MoO_4 and H_2WO_4. These results show that both cyclohexanone peroxides, DHP and HHP, are probably oxidized to cyclopentanecarboxylic acid or adipic acid through the same reaction intermediate as that of cyclohexanone.

As mentioned above, a presumed intermediate HHC are a hydrolysis product in an equilibrium with DHP or HHP in solution, and moreover, 2-chlorocyclopentanecarboxylic acid and α-chloroadipic acid were obtained by the oxidation of 2-chloro-HHC. Consequently, we proposed that HHC may be an important intermediate for the hydrogen peroxide oxidation of cyclohexanone.

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References and Notes

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