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A NEW METHOD FOR SYNTHESIS OF HYDROPEROXIDES

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A new method of synthesizing hydroperoxides with high selectivities from such hydrocarbons as cyclohexane, p-xylene, ethylbenzene and cumene is described.

We found a new method of synthesizing hydroperoxides from several hydrocarbons in better yields than by the conventional autoxidation. By adding a nitrile compound to the reaction system of autoxidation a great increase in the hydroperoxide selectivity was obtained, and simultaneously an increase in the oxidation rate was observed. We found its action was effective for preparing hydroperoxides by autoxidation of hydrocarbons having primary or secondary carbon-hydrogen bond which was usually autoxidized with difficulty.

Figure 1 shows the results of cyclohexane autoxidation in the presence or absence of acetonitrile. It indicates that the presence of the nitrile enabled an increase in the cyclohexyl hydroperoxide selectivity of more than 40 to 50 % at the cyclohexane conversion of 6 to 7 % as compared with autoxidation which we traced experimentally in the absence of the nitrile.

In other experiments we observed that the presence of nitrile compounds retarded the catalytic decomposition of cyclohexyl hydroperoxide by metal salts. On the other hand, Kharasch$^{1)}$ and Denny$^{2)}$ reported that the decomposition of t-butyl hydroperoxide in the presence of sodium hydroxide was accelerated by addition of a nitrile.

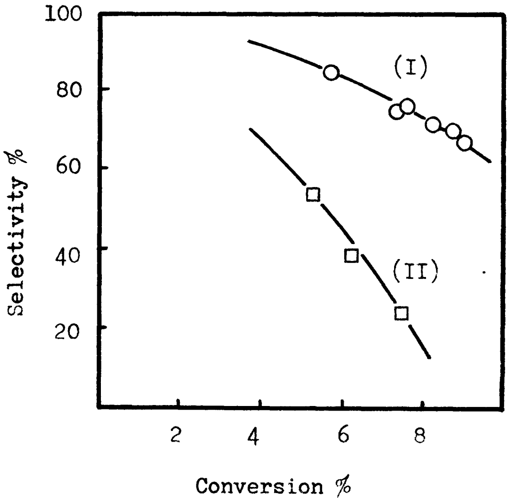


Figure 1. Autoxidation of Cyclohexane in the Presence or Absence of Acetonitrile

reaction temperature:150°C,
acetonitrile/cyclohexane:0.2,
reactor:stainless steel coated with sodium pyrophosphate,
(I):in the presence of acetonitrile,
(II):in the absence of acetonitrile

Also, Howard$^{3)}$ indicated that acetonitrile used as a solvent increased $k_3/k_5^{1/2}$ (k_3 and k_5 are the propagation and termination rate constant) in autoxidation of tetralin, cumene and styrene.
We think our results indicate that the nitriles added depress the decomposition of the hydroperoxide by metallic wall of a reactor and promote the propagation reaction without increase of the termination reaction, and this is the reason for the good results.

Figure 2 shows the result of p-xylene autoxidation in the presence of benzonitrile. In this case we did not add any initiator. It also indicates an increase in the hydroperoxide selectivity by adding the nitrile. Usually, its hydroperoxide cannot be synthesized without a large amount of initiator such as di-t-butyl peroxide of more than 20 % based on the reactant.$^{4)}$ However, our method enabled the synthesis of the hydroperoxide with good selectivity without any initiator and catalyst.

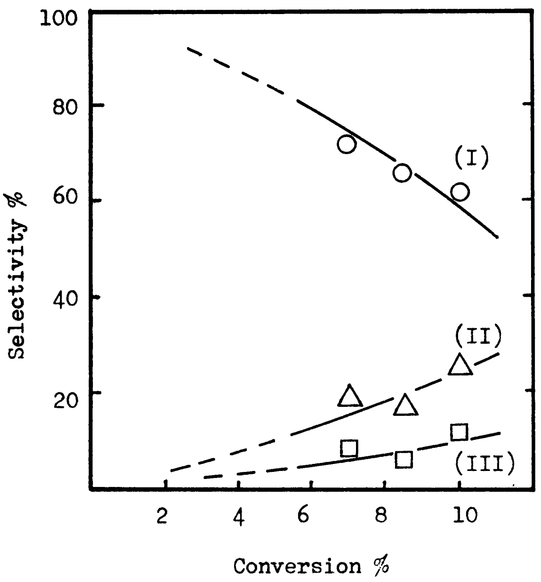
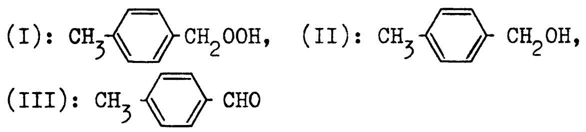


Figure 2. Autoxidation of p-Xylene in the Presence of Benzonitrile

reaction temperature:155°C, p-xylene/benzonitrile:1,



We observed our method is suitable for the synthesis of other hydroperoxides such as ethylbenzene hydroperoxide and cumene hydroperoxide (Table 1).

Table 1. Autoxidation of Ethylbenzene and Cumene in the Presence of a Nitrile

initiator:AIBN 500ppm, O_2 pressure:20 kg/cm^2 abs.
RCN:propionitrile(a), benzonitrile(b)

Hydrocarbon	Reaction temperature	Reaction time	RH/RCN	RH conversion	ROOH selec.
	°C	hr		%	%
Ethylbenzene	150	6.0	--	23.5	46.4
"	150	5.0	2^b	20.7	75.6
Cumene	125	7.3	--	32.2	86.4
"	125	5.5	5^b	24.0	99.2
"	120	8.0	10^a	36.6	91.5

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