Synthese of Nitoro-compounds by Means of Oxidation of Acylamino-compounds. (VI)

The Catalytic Action of the Stabilizung Agents of Hydrogen Peroxid And the Mechanism of these Catalytic Action.

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In this paper, we describe the catalytic actions of carboxilic acids on the oxidation of acetylamino-compounds.

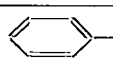
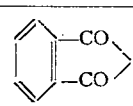
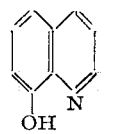
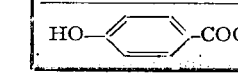
In one of this series, we reported that carboxylic acids have the catalictic actions on the oxidation of acetylamino-compounds.

In this papaer, we report the catalytic action of stabilizing agents of hydrogen peroxide.

In the experiments, p-nitro-toluene was employed as oxidized material and stabilizing agents were added by one-thirds mol. of the acylanilide in each reaction.

Results are shown in the following tablel.

Table I

Stabilizing agent	Increasing rate of yield
H_3PO_4	— 4%
SnO_2	— 7%
H_2SO_4	— 7%
H_3ASO_4	— 8%
Glucose	1 %
	2 %
	5 %
	6 %
	7.5%

In the next place, we report further studies on the mechanism of the catalytic action of these compounds.

In order to show that the ctalytic action results from stabilizing power of these compounds of hydrogen peroxide, the influence of reaction times on the yield were examined, when these agants were added.

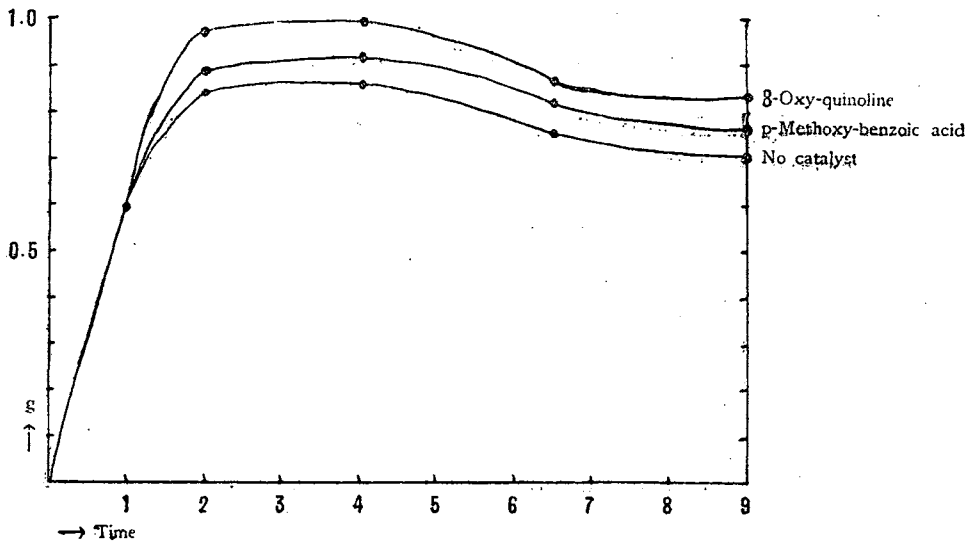
p-acetylamino-toluene was used as oxidized material and one-sirds Mol. ratio of 8-oxy-quinoline and p-methoxy benzoic acid were employed as the stabilizing agants.

The influence of the reaction times on the yield were studied and results are shown in the following table II and figure.

Table II

	1 hr	2hrs.	4hrs.	6.5hrs.	9hrs.
8-Oxy-quinoline 0.67g.	0.70g.	0.98g.	0.99g.	0.86g.	0.84g.
p-Methoxy-benzoic acid 0.7g.	0.69g.	0.89g.	0.92g.	0.82g.	0.77g.
No catalyst	0.69g.	0.86g.	0.87g.	0.76g.	0.71g.

Fig. I



From the results obtained above, it is found that at the point of one hour after adding, neither 8-oxy-quinoline nor p-methoxy benzoic acid increased the yield, but after 2 hours both catalysts increased the yields. then after four, six, and nine horse the increasing ratio did not vary. From the facts mentioned above, it is concluded that the catalytic actions of these compounds are due to stabilising effect of hydrogen peroxide during one to two house.

As shown in the figure, the yield decreased with the time. It seems probable that p-nitro toluene produced was further oxidized with hydrogen peroxide.

In order to determine the structure oxidized products of p-ntrotoluene, we oxidized p-nitro-tolune in the similar procedure mentioned above and obtained p-nitro benzoic acid in 18% yield after 9 hours reaction.

Summary

1) It was found that organic stabilizing agents of hydrogen peroxide especially 8-quinoline has catalytic action on the oyxdation.

2) The mechanism of these catalytic action consists in stabiliszing of hydrogen peroxide.

3) p-Nitro-toluene was oxideized to p-nitro-benzoic acid in 18% yield in this oxidation.

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1) A mixture of 4.1g of p-acettoluidide, 1.34g. of 8-oxy-quinoline, 60cc. of hydrogebn peroxide and 40cc. of glacial acetic acid was heated on the water bath for 9 hours. Neutralization with ammoniak and steam destillation yielded 0.92g. (24.3%) of p-nitro touene. The similar procedure was employed when other stabilizing agents were used.

Stabilizing agent	(g)	Hydrogen peroxide	Glacial acetic acid	Reaction time	Yield g.	Yield %
H_3PO_4	0.9 g.	60cc.	40cc.	9 hrs	0.55g.	14.5%
SnO_2	1.4	〃	〃	〃	0.44	11.6
H_2SO_8	0.9	〃	〃	〃	0.45	11.9
H_3ASO_4	0.9	〃	〃	〃	4.4	10.6
Glucose	1.83	〃	〃	〃	0.74	19.5
Benzene sulfonamide	1.45	〃	〃	〃	0.79	20.9
phtalic acid imide	0.95	〃	〃	〃	0.90	23.8
8-Oxy-quinoline	1.43	〃	〃	〃	0.92	24.3
p-Oxy-Benzoic acid butylester	1.8	〃	〃	〃	0.98	26

2) A mixture of 5.g. of p-nitrotoluene, 60cc. of 30% hydrogen peroxide, and 40cc. of glacial acetic acid was heated on the water bath for 9 house. Neutralization with ammoniak and stea destillation produced 60% (3 g.) of p-nitro toluene. The reaction soltuion was destilled under steam to remove p-ntitro toluene and acetic acid. The solution, removed of acetic acid and p-nitro toluene, was neutralized with sodium hydroxide and evaporated to almost dryness.

Neutralization of the residue with acid yielded p-nitro benzoic acid.

Recrystallization from water produced 18% (0.9g.) of p-nitro benzoic acid (m. p. 235°). This did not lower the melting point of an authentic material.

(Received March, 31, 1952)
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