

OXIDATION OF ALKYL PYRIDINES BY METAL NAPHTHENATES PART-I

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Cobalt and manganese naphthenates were studied as catalysts for the oxidation of alkylpyridines. They were found to be inactive at room temperature. The catalytic activity of these naphthenates was observed at high temperature and conversion of alkylpyridines to the corresponding carboxylic acids was observed in moderate yield (24-28%).

INTRODUCTION

Pyridine carboxylic acids and their derivatives have acquired considerable significance in recent years. Nicotinic acid (3-pyridine carboxylic acid) and its amides like nicotinamide and nikethamide are well known in pharmaceuticals. INH, which is a derivative of isonicotinic acid, is a known drug for tuberculosis. Alkylpyridines can be isolated from coaltar or they can be synthesised by ammonia-aldehyde condensation [1-5]. The oxidation of alkylpyridines to corresponding carboxylic acids has been carried out with a wide variety of oxidising agents. Different oxidation methods, however, have also been used e.g.

- (i) Catalytic vapour-phase oxidation [6-8]
- (ii) Catalytic liquid-phase oxidation [9-12]
- (iii) Photochemical oxidation [13]
- (iv) Electrolytic oxidation [14]

In view of the importance of pyridine carboxylic acids it is felt that there is still a scope for much further work in the field of oxidation of alkylpyridines both from academic and industrial view points.

RESULTS AND DISCUSSION

In this paper we submit the results which were obtained by the study of the catalytic effects of metal naphthenates for the oxidation of alkylpyridines at atmospheric pressure. Certain salts of cobalt, manganese, iron, aluminium, etc. have been used in the oxidation of alkylpyridines at elevated temperatures and under high pressure in autoclaves which give a fairly good yield of the product [15]. This led us to explore the catalytic activity of such salts which could carry out oxidation at atmospheric pressure. In this respect cobalt and manganese naphthenates were studied for the oxidation of alkylpyridines at different

temperatures in the liquid phase by variation of the time period at atmospheric pressure.

At room temperature (25^o) no oxidation was observed even in the presence of oxygen. At 100^o oxidation to the corresponding carboxylic acids occurred in poor yields. The yield increased with increase in temperature. The maximum yield was obtained at the reflux temperatures. It was 24-28%.

A comparison of the rates of oxidation of 2-picoline with 3-picoline showed that under similar reaction conditions, the yield of nicotinic acid was more than 2-picolinic acid. The tendency of decarboxylation 2- and 4- carboxyl groups on pyridine nucleus at higher temperature has also been stated by Mueller [16] and other workers.

Results of the oxidation of 2-picoline using cobalt naphthenate and manganese naphthenate at different temperatures and time intervals under oxygen at atmospheric pressure are given in Tables 1-2 respectively.



Table 1. Oxidation of 2-picoline using cobalt naphthenates as catalyst

S. No.	Time hr.	Temperature (°C)	Rate of flow of oxygen	Yield (%)
1.	20	24	0.3 l/min	Nil
2.	20	110	0.3 "	7
3.	30	110	0.3 "	9
4.	40	110	0.3 "	10
5.	40	128	0.3 "	20
6.	50	128	0.3 "	21

Table 2. Oxidation of 2-picoline using manganese naphthenates as catalyst

S. No.	Time hr.	Temperature (°C)	Rate of flow of oxygen	Yield (%)
1.	20	24	0.3 l/min	Nil
2.	20	110	0.3 "	6
3.	30	110	0.3 "	8
4.	40	110	0.3 "	9
5.	40	128	0.3 "	18
6.	50	128	0.3 "	19

Results of the oxidation of 3-picoline using cobalt naphthenate and manganese naphthenate as a catalyst at different temperatures and time intervals under oxygen at atmospheric pressure are given in Tables 3-4.



Table 3. Oxidation of 3-picoline using cobalt naphthenate as catalyst

S. No.	Time hr.	Temperature (°C)	Rate of flow of oxygen	Yield (%)
1.	20	24	0.3 l/min	Nil
2.	20	110	0.3 "	14
3.	30	110	0.3 "	22
4.	40	110	0.3 "	22
5.	40	144	0.3 "	27
6.	50	144	0.3 "	28

Table 4. Oxidation of 3-picoline using cobalt naphthenate as catalyst

S. No.	Time hr.	Temperature (°C)	Rate of flow of oxygen	Yield (%)
1.	20	24	0.3 l/min	Nil
2.	20	110	0.3 "	12
3.	20	110	0.3 "	20
4.	40	110	0.3 "	21
5.	40	144	0.3 "	24
6.	50	144	0.3 "	25

EXPERIMENTAL

A general experimental procedure which has been carried out for the oxidation of picolines is given below.

Picoline (50.00 g) was taken in a three-necked flask. The catalyst (cobalt naphthenate or manganese naphthenate 2.00 g) which was used 4% by weight of the picoline was added. The reaction mixture was stirred for the given time period, maintaining the temperature as detailed in the tables. Oxygen was passed through the reaction mixture using a flow meter to measure the oxygen flow.

After completion of the time the unreacted picoline was separated by distillation under reduced pressure. The residue was boiled with water and filtered. The catalyst and other water insoluble materials were isolated as residue. The filtrate was evaporated on a steam bath. When the PH of the remaining solution was about 3.5, it was allowed to cool. The product (pyridine carboxylic acid) crystallised out and was separated by filtration and dried. The product was recrystallised in distilled water.

M.P. of Picolinic acid, 119° (120°)
M.P. of Nicotinic acid, 215° (216°)

The IR spectra of nicotinic and picolinic acids were identical with those of authentic samples.

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