

CATALYTIC OXIDATION OF ALKYL PYRIDINES BY METAL ROSINATES. PART II.

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Catalytic oxidation of alkylpyridines was studied using cobalt and manganese rosinate. These catalysts were found to be inactive at room temperature. The catalytic activity of these rosinate was, however, observed at high temperatures. Alkylpyridines were converted to the corresponding carboxylic acids in moderate yields (24-25%).

INTRODUCTION

The significant importance of pyridinecarboxylic acids and their derivatives has already been discussed in the Part I of these studies. The availability [1-5] of alkylpyridines and the various methods for their oxidation [6-14] were also discussed in the same paper. The encouraging results obtained by using cobalt and manganese naphthenates as catalysts induced us to carry out such work and explore some more catalysts in this field.

RESULTS AND DISCUSSION

The catalytic activities of cobalt and manganese rosinate have been studied at different temperatures in liquid phase by variation of the time period at atmospheric pressure.

No oxidation of the alkylpyridines was observed at room temperature (25°) even in the presence of oxygen. At 100° oxidation to the corresponding carboxylic acids occurred in poor yields. The yield increased with increase in temperature. The maximum yield obtained at the reflux temperatures was 24-25%. It was observed that the catalytic behaviour of cobalt and manganese rosinate was almost the same as that of cobalt and manganese naphthenates which was discussed in the last paper.

A comparison of the rates of oxidation of 2-picoline with that of 3-picoline showed that under similar reaction conditions, the yield of nicotinic acid was more than that of 2-picolinic acid. This tendency had also been indicated in our previous paper (Part I). Mueller [15] and other workers had also stated the tendency of decarboxylation of 2- and 4- carboxyl groups on the pyridine nucleus at higher temperature. Hence, it substantiates the assumption that 2-picolinic acid tends to decarboxylate at high temperature and this results in low yield.

Results of the oxidation of 2-picoline using cobalt rosinate and manganese rosinate as catalysts at different

temperatures and time intervals under oxygen, at atmospheric pressure, are given in Table 1 and 2 respectively.



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

S. No.	Time period (hr)	Temperature (°C)	Rate of flow of oxygen 1/min	Yield
1.	20	24	0.3	Nil
2.	20	110	0.3	6%
3.	30	110	0.3	8%
4.	40	110	0.3	12%
5.	40	128	0.3	18%
6.	50	128	0.3	20%
7.	60	128	0.3	20%

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

S. No.	Time period (hr)	Temperature (°C)	Rate of flow of oxygen 1/min	Yield
1.	20	24	0.3	Nil
2.	20	110	0.3	7%
3.	30	110	0.3	9%
4.	40	110	0.3	11%
5.	40	128	0.3	17%
6.	50	128	0.3	20%
7.	60	128	0.3	20%

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

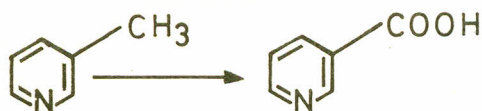


Table 3. Oxidation of 3-picoline using cobalt rosinate as catalyst.

S. No.	Time period (hr)	Temperature (°C)	Rate of flow of oxygen 1/min	Yield
1.	20	24	0.3	Nil
2.	20	110	0.3	6%
3.	30	110	0.3	10%
4.	40	110	0.3	14%
5.	40	144	0.3	18%
6.	50	144	0.3	24%
7.	60	144	0.3	25%

Table 4. Oxidation of 3-picoline using manganese rosinate as catalyst.

S. No.	Time period (hr)	Temperature (°C)	Rate of flow of oxygen 1/min	Yield
1.	20	24	0.3	Nil
2.	20	110	0.3	7%
3.	30	110	0.3	10%
4.	40	110	0.3	13%
5.	40	144	0.3	19%
6.	50	144	0.3	24%
7.	60	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 rosinate or manganese rosinate) (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 period 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 acid were identical with those of authentic samples.

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