

## OXIDATION OF ALKYLPIRIDINES BY USING COBALT (III) ACETATE. Part III

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Oxidation of 2-picoline and 3-picoline was carried out by using cobalt (III) acetate to obtain the corresponding carboxylic acids. Effects of the variations in temperature and time period during such oxidation were also studied and tabulated. The picolinic carboxylic acids upto 52% yield were obtained.

*Key words:* Oxidation, Picoline, Cobalt acetate.

### INTRODUCTION

Cobalt belongs to the group of transition metals, and always exhibits one equivalent oxidation behaviour. The strong oxidising properties of cobalt have been utilized for quantitative determination of various organic, inorganic and pharmaceutical compounds. Kinetic studies [1-8] had been undertaken by various workers using trivalent cobalt for the oxidation of formaldehyde, amines, aliphatic alcohols, benzene, etc. Cobalt (III) acetate because of its strong oxidising properties and good stability in glacial acetic acid has been extensively used as a volumetric titrant by various workers [9-18]. However, the studies regarding its application as an oxidising agent for the various organic compounds are still to be carried out.

### RESULTS AND DISCUSSION

In this paper we submit the results which were obtained by the oxidation of alkylpyridines by cobalt (III) acetate under the varied conditions with respect to oxygen and temperature. Oxidation of alkylpyridines was also studied by changing the molar ratio of the reactants, i.e. cobalt (III) acetate and alkylpyridines. The reaction was carried out in the equimolar ratio and 2:1 ratio. It was found that higher yield of the pyridine carboxylic acid was obtained by using the double amount of the oxidising agent. Temperature was found to play an important role in this oxidation. No reaction seemed to occur at room temperature (30°). Appreciable yield was, however, obtained at 70°. It was also found that the presence of free oxygen resulted in a higher yield.

The explanation to the above mentioned fact that despite being a strong oxidant Co (III) does not oxidise the picolines to the corresponding acids at 30° even at the increased Co (III): C<sub>6</sub>H<sub>7</sub>N mole ratio, can be sought in the fact that Co (III) ion shows a particular affinity for N

donors. Picolines contain N donor and therefore, Co (III) forms various complex species with them [19]. Now in the light of this fact the results of the present study can be interpreted. Thus at 30° since no free Co (III) is available (because it has entered into complexation with the ligand C<sub>6</sub>H<sub>7</sub>N) the -CH<sub>3</sub> group in C<sub>6</sub>H<sub>7</sub>N is not oxidised to -COOH group. However at elevated temperatures the oxidation becomes possible owing to the dissociation of the complexes which results in the liberation of Co (III) ions. In the free state Co (III) ions are, however, susceptible to their reduction to Co (II) by water. In the presence of free oxygen these Co (II) ions are oxidised back to Co (III) ions. The accelerating role of free oxygen in the oxidation of alkylpyridines to the corresponding carboxylic acid might be accounted for this phenomenon.

The comparison of the rate of oxidation of 2-picoline with that of 3-picoline showed that under similar reaction conditions, the yield of nicotinic acid (pyridine - 3 - carboxylic acid) was more than that of the 2-picolinic acid. This had occurred, because 2-picolinic acid tends to decarboxylate at higher temperature.

Results of oxidation of 2-picoline with cobalt (III) acetate in the normal atmospheric conditions at different temperatures are tabulated in the Tables 1 - 3. The results obtained in the presence of free oxygen are given in the Table 4. The rate of flow of oxygen was maintained as 0.3 l/min. in these experiments. In the following tables the empirical formula (C<sub>6</sub>H<sub>7</sub>N) stands for 2-picoline while (Co III) denotes the cobalt (III) acetate. These reactants were taken in the molar ratios as given in the tables.

Results of oxidation of 3-picoline with cobalt (III) acetate in the normal atmospheric conditions at different temperatures are tabulated in the Tables 5 - 7. The results obtained in the presence of free oxygen are given in the Table 8. The rate of flow of oxygen was maintained as 0.3 l/min. in these experiments. In these tables the empirical formula (C<sub>6</sub>H<sub>7</sub>N) stands for 3-picoline while (Co III)

Table 1. Oxidation of 2-picoline at 30°C with cobalt (III) acetate.

S. No.	(Co III) Mol.	(C <sub>6</sub> H <sub>7</sub> N) Mol.	(Co III): (C <sub>6</sub> H <sub>7</sub> N) Mol. Ratio	Time (Hours)	Yield %
1.	0.05	0.05	1:1	6	—
2.	0.05	0.05	1:1	10	—
3.	0.05	0.025	2:1	10	—
4.	0.05	0.025	2:1	12	—
5.	0.05	0.025	2:1	16	—

Table 2. Oxidation of 2-picoline at 60°C with cobalt (III) acetate.

S. No.	(Co III) Mol.	(C <sub>6</sub> H <sub>7</sub> N) Mol.	(Co III): (C <sub>6</sub> H <sub>7</sub> N) Mol. Ratio	Time (Hours)	Yield %
1.	0.05	0.05	1:1	6	5
2.	0.05	0.05	1:1	8	8
3.	0.05	0.025	2:1	8	12
4.	0.05	0.025	2:1	10	18
5.	0.05	0.025	2:1	12	18

Table 3. Oxidation of 2-picoline at 70°C with cobalt (III) acetate.

S. No.	(Co III) Mol.	(C <sub>6</sub> H <sub>7</sub> N) Mol.	(Co III): (C <sub>6</sub> H <sub>7</sub> N) Mol. Ratio	Time (Hours)	Yield %
1.	0.05	0.05	1:1	6	10
2.	0.05	0.05	1:1	8	15
3.	0.05	0.025	2:1	8	23
4.	0.05	0.025	2:1	10	28
5.	0.05	0.025	2:1	12	28

Table 4. Oxidation of 2-picoline in the presence of free oxygen with cobalt (III) acetate.

S. No.	(Co III) Mol.	(C <sub>6</sub> H <sub>7</sub> N) Mol.	(Co III):C <sub>6</sub> H <sub>7</sub> N Mol. Ratio	Time (Hours)	Temp. (°C)	Yield %
1.	.05	.05	1:1	6	50	9
2.	.05	.05	1:1	8	60	23
3.	.05	.025	2:1	8	60	30
4.	.05	.025	2:1	10	70	45
5.	.05	.025	2:1	12	70	45
6.	.05	.025	2:1	12	80	45

Table 5. Oxidation of 3-picoline at 30°C with cobalt (III) acetate.

S. No.	(Co III) Mol.	(C <sub>6</sub> H <sub>7</sub> N) Mol.	(Co III): (C <sub>6</sub> H <sub>7</sub> N) Mol. Ratio	Time (Hours)	Yield %
1.	0.05	0.05	1:1	6	—
2.	0.05	0.05	1:1	10	—
3.	0.05	0.025	2:1	10	—
4.	0.05	0.025	2:1	12	—
5.	0.05	0.025	2:1	16	—

Table 6. Oxidation of 3-picoline at 60°C with cobalt (III) acetate.

S. No.	(Co III) Mol.	(C <sub>6</sub> H <sub>7</sub> N) Mol.	(Co III): (C <sub>6</sub> H <sub>7</sub> N) Mol. Ratio	Time (Hours)	Yield %
1.	0.05	0.05	1:1	6	7
2.	0.05	0.05	1:1	10	10
3.	0.05	0.025	2:1	10	19
4.	0.05	0.025	2:1	12	25
5.	0.05	0.025	2:1	16	25

Table 7. Oxidation of 3-picoline at 70°C with cobalt (III) acetate.

S. No.	(Co III) Mol.	(C <sub>6</sub> H <sub>7</sub> N) Mol.	(Co III): (C <sub>6</sub> H <sub>7</sub> N) Mol. Ratio	Time (Hours)	Yield %
1.	0.05	0.05	1:1	6	12
2.	0.05	0.05	1:1	10	17
3.	0.05	0.025	2:1	10	23
4.	0.05	0.025	2:1	12	32
5.	0.05	0.025	2:1	16	32

Table 8. Oxidation of 3-picoline in the presence of free oxygen with cobalt (III) acetate.

S. No.	(Co III) Mol.	(C <sub>6</sub> H <sub>7</sub> N) Mol.	(Co III):C <sub>6</sub> H <sub>7</sub> N Mol. Ratio	Time (Hours)	Temp. (°C)	Yield %
1.	0.05	0.05	1:1	6	50	12
2.	0.05	0.05	1:1	8	60	26
3.	0.05	0.025	1:2	8	60	38
4.	0.05	0.025	1:2	10	70	52
5.	0.05	0.025	1:2	12	70	52
6.	0.05	0.025	1:2	12	80	52

denotes the cobalt (III) acetate. These reactants were taken in the molar ratio as given in the tables.

#### EXPERIMENTAL

Cobalt (III) acetate solution was prepared in glacial acetic acid by anodic oxidation and it was standardised potentiometrically against standard ferrous sulphate solution [9].

Picoline was taken in three necked flask which was fitted with a thermometer, condenser and oxygen supply when required. It was heated and stirred at temperatures mentioned in the given tables. The rate of flow of oxygen was adjusted by a flow meter.

After the completion of time period the unreacted picoline was distilled off under reduced pressure. The pH of the solution was adjusted at 3.5 and was allowed to cool at 20°. The product (pyridine carboxylic acid) crystallised out which was then separated by filtration and dried. For recrystallisation it was dissolved in hot water and filtered. The pH of the filtrate was again adjusted at 3.5 and then cooled to obtain the crystals.

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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