# Electrochemical Reduction of Pyridine 2,6-Dicarboxylic Acid and pyridine 2,6-Dialdehyde.

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Controlled potential electrolysis of pyridine 2,6-dicarboxylic acid in buffer solution of different pH values at amalgamated rotating disc electrode indicated non-quantitative reduction of the acid to pyridine 2,6-dialdehyde. No reduction was observed at tin, graphite and lead electrodes in these media. The acid was electro inactive at Cd in acidic solution but gave a reduction wave in neutral phosphate buffer. The second reduction step (aldehyde to alcohol) in the overall reduction process, was found to be quantitative in neutral phosphate buffer but non-quantitative in acidic phosphate and acetate buffers. Votammetric studies of pyridine 2,6-dialdehyde were undertaken to explore the mechanism of reduction.

An earlier paper(1) presented coulometric and voltammetric results on pyridine mono-carboxylic acids and the corresponding aldehydes, in buffer solution of different pH values at mercury cathodes. Picolinic acid was found to be reduced to aldehyde in almost quantitative yields in acidic media.

Dipicolinic acid has been the subject of polarographic studies(2,4) but the results are inconclusive and are mainly of analytical nature. In acidic solution, two polarographic waves have been observed. But at pH 4.5, a single wave was reported, the limiting height of single wave decreases with increasing pH(4). Companelea et al(2) have observed more than one wave in different media, but these waves were erroneously assigned to be reversible process due to reduction of proton to hydrogen. However, Tisser and Agontin(3) have ascribed these waves to a 2e transfer process according to coulometry carried out on pyridine 2,3-dicarboxylic acid. Brown et al(5) have investigated the reduction of dipicolinic acid to dialcohol, in buffer solutions of different pH values, using a large mercury pool, as cathode. In aqueous phosphate buffer (pH 6.1) at -1.3 V (vs SCE), the chemical yield of dialcohol was 10% and current efficiency was 15%.

However, in acetate buffer (pH 4.8) and at 65°C the chemical yield increased to 26% and current efficiency to 30%.

This article reports controlled potential electrolysis results on pyridine 2,6-dicarboxylic acid, and pyridine 2,6-dialdehyde at rotating disc electrodes in buffer solution of different pH values. Dipicolinic acid reduction was undertaken to synthesise pyridine 2,6-dialdehyde which is a starting material for a drug.

## EXPERIMENTAL

Dipicolinic acid and dialdehyde obtained from "Synthetic Chemicals Ltd" were used as received without any further purification. The supporting electrolytes were prepared from BDH AnalaR chemical dissolved in thrice distilled water. pH was measured with "Electronic pH meter 2320".

In this work all glass cells divided by glass sinters were used. The catholytes were purged with nitrogen presaturated by passing through a buffer containing cathodic solution. The cells were thermostated by means of an air thermostat.

All potentials are refered to SCE. Acquisition and treatment of voltammetric data has been described previously(1,7).

In controlled potential electrolysis, the currents were recorded on a "TOA model EPE-2 T" pen recorder. The total charge passed during the elecrolysis was calculated from current-time chart, and was also obtained simultaneously by a charge integrator.

Coulometric determination of number of electrons involved, controlled potential electrolysis (CPE) and in Situ electroanalysis of the product were carried out simultaneously in a single run. This was achieved using a large amalgamated copper cathode (4.9 $cm^2$). The electrolysis was performed at constant potential with the exception that at regular interval (3 minutes) the potential was pulsed for 3 seconds to a more positive values corresponding to the potential plateau of the aldehyde reduction wave. The total charge passed was obtained from current-time chart as well as from the integrating section of the current recording module. Dialdehyde was not separated for chemical analysis but analyzed voltammetrically, the half wave potentials of the wave which appeared at positive potential was compared with $E_{1/2}$ value obtained after adding the standard sample

to the same catholyte.

Pyridine 2,6-dialdehyde was reduced at amalgamated copper RDE, in different buffer solution of varying pH values. Reduction was carried out at a constant rotation speed (150 rad. $S^{-1}$) and at temperature 20 ± 2°C.

The percentage consumption of the aldehyde was calculated from the ratio of initial to the final current. The number of electrons transferred during electrolysis was calculated from the relationship.

$$Q = n F V (C_o - C) \quad \ldots (1)$$

Where Q is the total charge passed, $C_o$ is the initial concentration of the dialdehyde and C is the final concentration of the dialdehyde. V = Volume of the solution.

## RESULTS AND DISCUSSION

### REDUCTION OF DIPICOLINIC ACID

Dipicolinic acid gave well-defined waves when reduced at an amalgamated copper RDE, in neutral phosphate (0.1M $NaH_2PO_4$, 0.1M $Na_2HPO_4$; pH 6.65), acetate (0.1M NaOAc, 0.1M HOAc; pH 4.65) and acidic phosphate (0.1M $NaH_2PO_4$, 0.1M $H_3PO_4$; pH 2.1) buffers. Results of Controlled potential electrolysis and $E_{1/2}$ values in different buffer solution are tabulated in Table 1. In calculating $Q_{ald}$, the number of electrons transferred were taken as 4. Quantitative reduction of aldehyde to alcohol was assumed.

In this table $E_2$ is the potential on the plateau of the acid reduction wave and $E_1$ is the potential on the plateau of the corresponding aldehyde reduction wave. $di_{total}/dt$ & $di_{ald}/dt$ are each proportional to the total rate of consumption of electroactive material and to the rate at which concentration of dialdehyde is built up in solution. $i_{acid}$ is $i_{total} - i_{ald}$ The percentage reduction is the fraction of acid consumed and is based on the limiting current density for the acid at the begining of the electrolysis ($i_{2,o}$) and at the termination of electrolysis ($i_2 - i_1$) where $i_2$ is the current density at $E_2$ and $i_1$ is the current density at $E_1$, ($i_{2,0}$) is the initial value of $i_2$.

The number of electrons $n_{acid}$ is obtained by dividing the measured charge passed ($Q_{exp}$) by the amount of acid consumed. However $n_{acid}$ is not a very meaningful quantity because not all of the acid reduced has reached the form of the final product (alcohol). In order to asses the total charge involved in the complete reduction of the same amount of acid, it is necessary to add to the measured charge $Q_{exp}$ the charge $Q_{ald}$ which would be passed in the reduction of the aldehyde that has accamulated in the solution:

$$Q_{total} = Q_{exp} + Q_{ald} \quad \ldots (2)$$

$$Q = nFVC_k \frac{i_1}{i_3} \quad \ldots (3)$$

Here $i_3$ is the current density measured when in a separate experiment, a solution of aldehyde at a stoichimetric concentration $C_k$ in the same background electrolyte is reduced at the same rotational speed as is used in here) to obtain $i_1$. In calculating $Q_{ald}$, the value of n was taken to be 4; dialdehyde to dialcohol reduction was assumed to be quantitative.

Dipicolinic acid reduction at an amalgamated copper or at a cadmium cathode was non-quantitative both in neutral and acidic media. In Situ voltammetry of the dialdehyde in the neutral phosphate buffer (pH 6.65) gives a small wave, whereas in acidic phosphate and acetate buffers, the dialdehyde wave did rise to a steady value, as electrolysis proceeded, indicating the production of dialdehyde. This was proved by a comparison of the $E_{1/2}$ values for the intermediate (electrogenerated) and an authentic sample of the dialdehyde. The values of $di_{ald}/dt$ in the initial stages indicates that the aldehyde is escaping to the bulk of the solution and is strongly hydrated there. At higher temperature, the aldehyde wave did not rise indicating rapid dehydration of the hydrated aldehyde at higher temperatures. Although at higher temperatures, the number of faraday per mole consumed increased, the reduction process remained non-quantitative (< 8 F $mol^{-1}$).

The conversion of dialdehyde to dialcohol in neutral solution was almost quantitative (vide infra), therefore the poor yield of dialcohol obtained must be due to ineffective converstion of acid to aldehyde.

In acetate (pH 4.65) and acidic phosphate (pH 2.1) buffers, the slight increase in the number of Faraday per mol consumed could be an indication that the process R COOH ⟶ R $CH(OH)_2$ might be efficient, but the aldehyde to alcohol process is not as the aldehyde hydrates are favoured in acidic media(6).

To look into the possibility of a quantitiative reduction, other cathode metals were also investigated; lead and cadmium gave an ill defined wave but the currents fell very sharply with time making it difficult to measure $E_{1/2}$ or a limiting current values acurately. However, the $E_{1/2}$ value given in Table 1, are the values obtained from the first voltamograms recorded. Tin and graphite were found inactive in neutral media, however, graphite gave a wave in acidic phosphate buffer (pH 2.1). The limiting currents in acidic media were essentially kinetically controlled and were too low to carry our electrolysis at large RDE within reasonable time.

Brown et al(5) have reported the poor yield of dialcohol in acetate buffer (pH 4.8) when they reduced dipicolic acid using a mercury pool cathode. They have also reported the formation of polymetric byproducts. It is likely that the electrode surface is covered with polymeric film and thus cause the current to fall sharply.

REDUCTION OF PYRIDINE 2,6-DIALDEHYDE

Pyridine 2,6-dialdehyde gave reduction wave in the three media studies i.e. pH 6.65, 4.65 and 2.1. The wave analysis was precluded as a result of formation of a polymetric film, which inhibits the electrode surface. However, in buffer of pH 6.65, the log plot gave a slope equal to 4 RT/F. The inhibition of the reduction process was observed in all the three solutions but was least in neutral phosphates buffer (pH 6.65). However the $E_{1/2}$ values (vs SCE) for the dialdehyde in solutions of pH 6.65, 4.65 and 2.1 were -0.90, -0.80 and -0.48 V, respectively. The limiting currents were predominantly diffusion controlled in neutral phosphates buffers and mainly

TABLE 1

REDUCTION OF DIPICOLINIC ACID AT ROTATING DISC ELECTRODES (AT CONSTANT ROTATION SPEED 150 RAD $S^{-1}$ IN DIFFERENT BUFFERS, AT DIFFERENT CATHODES AND DEPOLARIZE CONCENTRATIONS

| S. No. | Buffer (pH) | Cathode | t °C | conc. # | $E_{1/2}$ V | $E_2^*$ V | $E_1^{**}$ V | $-di_{total}$ $^{\$}$ / dt | $-di_{acid}$ @ / dt | $di_{ald}$ (~) / dt | $(1-\frac{i_2-i_1}{i_{2,0}})100$ | $Q_{expt}$ | $n_{acid}$ | $n_{total}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Phosphate buffer (0.65) | Amalgamated Cu | 25 | 1 | -1.26 | -1.4 | -1.1 | 8.5 | 10 | 1.6 | 69 | 19 | 2.45 | 2.6 |
| 2 | " | " | " | " | - | - | " | 12.7 | 14.3 | 1.6 | 73 | 23 | 2.7 | 2.9 |
| 3 | " | " | " | " | - | -1.4 | -1.05 | 11.7 | 14.4 | 2.7 | 81 | 29 | 2.9 | 2.9 |
| 4 | " | " | 50 | " | -1.28 | -1.4 | -1.1 | -- | -- | - | 86 | 28 | 2.9 | 3.0 |
| 5 | " | " | " | " | -- | -1.5 | -1.0 | -- | -- | - | 74 | 28 | 3.1 | 3.3 |
| 6 | " | " | " | 10 | -1.28 | -1.4 | -1.05 | -- | -- | - | 86 | 300 | 3.3 | 3.5 |
| 7 | " | Cd | 25 | 1 | -1.25 | - | -- | -- | -- | - | -- | | | |
| 8 | " | " | " | 10 | -1.26 | -1.3 | -1.0 | -- | -- | - | 72 | 180 | 2 | - |
| 9 | acetate buffer (4.65) | Amalgamated Cu | 25 | 1 | -- | -1.3 | -0.9 | -14.6 | 23.2 | 8.6 | 79 | 40 | 3.95 | 4.2 |
| 10 | Phosphate buffer (2.1) | " | " | " | -0.842 | -1.05 | -0.65 | 15.3 | 23.2 | 7.9 | 78 | 31 | 3.5 | 3.7 |
| 11 | " | " | " | " | -- | -1.0 | -0.6 | 12.6 | 20.5 | 7.97 | 85 | 35 | 3.5 | 4.4 |
| 12 | " | Pb | " | " | -0.960 | -- | -- | -- | -- | -- | -- | | | |
| 13 | " | graphite | " | " | -0.940 | | | | | | | | | |
| 14 | " | Cd | " | " | -0.90 | -- | -- | -- | -- | -- | -- | | | |

# Depolariser concentration in millimoles $dm^{-3}$

* $E_2$ is the potential on the plateau of the reduction wave of acid

** $E_1$ is the potential on the plateau on the reduction wave of aldehyde

$ $-di_{total}/dt$ rate of consumption of dipicolinic acid in mA $cm^{-2}$ $sec^{-1}$ $x10^5$

@ $-di_{acid}/dt$ in mA $cm^{-2}$ $sec^{-1}$ $x10^5$

(~) $+di_{ald}/dt$ rate of build up of dialdehyde in solution in mA $cm^{-2}$ $sec^{-1}$ $x10^5$

kinetically controlled in acidic phophate buffer pH 2.1). The limiting current vary linearly with the square root of rotation speed.

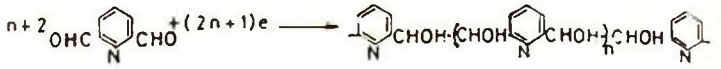
Controlled potential electrolysis was performed at the plateau of the wave in each buffer. The electrolysis were carried out at a constant rotational speed (150 rad $S^{-1}$ ) and at room temperature. The results are tabulated in Table 2.

**TABLE 2**

CATHODIC REDUCTION OF PYRIDINE 2,6-DIALDEHYDE ($1 \times 10^{-3}$ M) AT THE AMALGAMATED RDE

| S. No. | Buffer | pH | E V | $(1-\frac{i_{final}}{i_{initial}})\times 100$ % | $Q_{expt}$ | Charge passed F $mol^{-1}$ |
|---|---|---|---|---|---|---|
| 1. | $NaH_2PO_4$ 0.1 M $Na_2HPO_4$ 0.1 M | 6.65 | -1.3 | 76 | 35 | 4.1 |
| 2. | HOAC 0.1 M NaOAC 0.1 M | 4.65 | -1.3 | 47 | 11.3 | 2.3 |
| 3. | $NaH_2PO_4$ 1.0 M $H_3PO_4$ 0.1 M | 2.1 | -0.7 | 49 | 15.5 | 2.8 |

In view of the charge passed, the tendencies towards polymerisation and the familiarity of pinacolisation reaction in aldehyde reductions, it is probable that the process occuring in acidic media is of the type:



Clearly n will vary over a range of values and cyclic oligomers might also be possible in neutral buffers. However, this result is likely to be affected by the polymerisation process diminishing currents at more negative potential. The predominantly kinetically controlled limiting currents in the acidic media indicate the hydration - dehydration process being the rate determining process.

## ACKNOWLEDGEMENT

Author is thankful to Dr. Brown for useful suggestions.

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