

# Extended Kinetic Studies on the Decarboxylation of $\alpha$ -Picolinic Acid in Organic Solvents

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The kinetics of decarboxylation of  $\alpha$ -picolinic acid in eight additional organic solvents has been studied under inert atmosphere of nitrogen. The activation parameters of the reaction are calculated. The solvent effect on the kinetics of the reaction is discussed. The possibility of chelated picolinic acid molecule rather than zwitterion to act as an initial reactant is favoured. An isokinetic temperature of 149° is obtained.

CANTWELL and Brown<sup>1,2</sup>, in their studies on the decarboxylation of  $\alpha$ -picolinic acid in *p*-dimethoxybenzene and in polar solvents, proposed a unimolecular mechanism but failed to decide definitely whether the zwitterion form or the cyclic form of the acid molecule acts as the predominant initial reactant. However, subsequent work of Clark<sup>3,4</sup> revealed a bimolecular mechanism for the reaction. It was realised that more kinetic data were needed to establish the correct mechanism of the reaction, beyond dispute, and the solvent effect, based on the calculated activation parameters. With this in view, further kinetic studies were carried out on the decarboxylation of  $\alpha$ -picolinic acid in eight additional solvents under inert atmosphere of nitrogen. The results of this investigation are reported in this paper.

## Experimental

Picolinic acid supplied by Koch Light Laboratories, England was used after recrystallisation and drying in vacuum. The purity of the acid was demonstrated by the fact that the volume of carbon dioxide evolved from every quantitative sample in a decarboxylation experiment was invariably stoichiometric.

The organic solvents used were analytical grade BDH reagents. A fresh sample of each solvent was taken to run a kinetic experiment after distilling under reduced pressure immediately before use.

**Apparatus and Technique :** The apparatus essentially consisted of (a) a round bottom 200 ml reaction vessel fitted with a thermometer, a condenser, a movable probe with a glass spoon at the inner end through a mercury seal and an inlet for the passage of dry nitrogen gas, dipped in a constant temperature oil bath fitted with a magnetic stirrer ; (b) a glass spiral immersed in a water bath to maintain the temperature of the gas coming out of the reaction vessel through a condenser at room temperature and (c) a calibrated burette vertically held in a water jacket, (length 80 cm, diameter 4.5 cm) containing the entraining liquid (aqueous

solution of sodium sulfate, 20% w/v, sulfuric acid, 5% v/v and a few drops of methyl orange).

The technique adopted to study the reaction rate was essentially to measure the volume of carbon dioxide evolved during the decarboxylation process. About 60 g of a solvent and 0.2212 g of picolinic acid (corresponding to exactly 40 ml of carbon dioxide at STP on complete decarboxylation) were taken to run an experiment. After the entire assembly had been saturated with dry nitrogen gas and the thermal equilibrium attained, the reading of the burette was noted as the zero reading,  $V_0$ . The reaction was then started by tipping the picolinic acid sample into the solvent and the volume of the carbon dioxide evolved was noted at frequent intervals of time by equalising the levels of the entraining liquid in the burette and the water jacket. A constant stirring of the reaction mixture was maintained throughout the reaction. A Fortein's barometer was used to note the atmospheric pressure. The final reading in the measuring burette on completion of the reaction, after converting it into STP value, was taken as the volume of carbon dioxide at infinite time,  $V_\infty$ .  $(V_\infty - V_0)$  gave the concentration at zero time and  $(V_\infty - V_t)$  the concentration at time,  $t$ , where  $V_t$  is the volume of carbon dioxide at time  $t$ . The pseudo first order rate constants were then calculated using the integrated first order rate expression

$$k = \frac{2.303}{t} \log \frac{(V_\infty - V_0)}{(V_\infty - V_t)}$$

and expressed in  $\text{min}^{-1}$ .

## Results and Discussion

The values of pseudo first order rate constant as well as linear plots (for one solvent shown in Fig. 1) of  $\log (V_\infty - V_t)$  vs time show that about eighty percent of the reaction follows a first order kinetic. In earlier investigations<sup>3,5</sup>, the decarboxylation was carried out in carbon dioxide atmosphere. The present experiments show that the reaction rate becomes faster in an inert atmosphere of nitrogen as shown in Table 1. The carbon

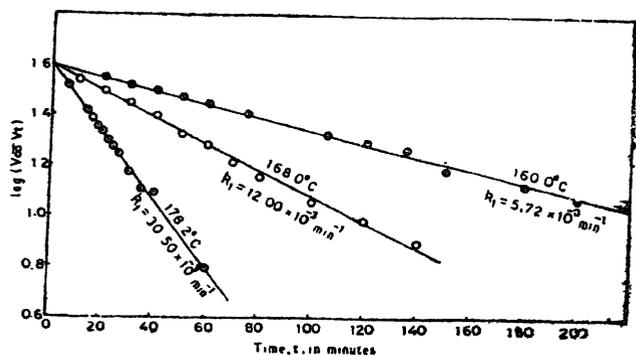


Fig. 1. Decarboxylation of  $\alpha$ -picolinic acid in diphenylamine.

TABLE 1—RATE DATA OF DECARBOXYLATION OF  $\alpha$ -PICOLINIC ACID IN ANILINE IN DIFFERENT GAS ATMOSPHERES

Temperature (°C)	$k_1 \times 10^4 \cdot \text{sec}^{-1}$ ( $\text{CO}_2$ atmosphere)	$k_1 \times 10^4 \cdot \text{sec}^{-1}$ ( $\text{N}_2$ atmosphere)
160.2	1.15	1.49
168.2	1.60	2.75
178.2	3.82	6.98

dioxide being a product of the reaction, the effect of the presence of excess carbon dioxide to reduce the rate constant is obviously due to the setting up of the dynamic equilibrium



The variation of the pseudo first order rate constants with temperature in all the solvents studied are shown in Table 2. These data were

TABLE 2—PSEUDO FIRST ORDER RATE CONSTANT FOR THE DECARBOXYLATION OF  $\alpha$ -PICOLINIC ACID IN DIFFERENT SOLVENTS

Solvent	Temperature (°C)	$k \times 10^3$ ( $\text{min}^{-1}$ )
Aniline	160.2	8.94
	168.2	16.58
	178.2	41.90
<i>m</i> -Toluidine	160.2	7.46
	168.2	16.97
	175.0	32.99
<i>p</i> -Toluidine	160.2	7.40
	168.0	18.52
	178.2	42.93
<i>o</i> -Toluidine	160.2	7.19
	168.2	18.47
	178.2	36.23
<i>m</i> -Cresol	170.0	8.48
	177.2	14.18
	183.2	31.37
<i>o</i> -Cresol	170.0	11.38
	177.0	22.73
	183.2	36.85
<i>m</i> -Chloroaniline	160.4	4.74
	168.2	11.66
	178.2	26.03
<i>o</i> -Chloroaniline	160.2	6.17
	168.4	13.16
	178.2	30.75
Diphenylamine	160.2	5.75
	168.0	12.00
	178.2	30.45

used to calculate the values of Eyring parameters of the reaction by the least square method.

The data in Table 3 indicate that the enthalpy of activation for the reaction is not affected strongly by the acidity or basicity of the solvent. The largest value of  $\Delta H^\ddagger$  observed occurs both in *m*-toluidine ( $pK_b=9.3$ ) and *m*-cresol ( $pK_a=10.01$ ) whereas the lowest value occurs both in aniline ( $pK_b=9.3$ ) and *o*-chloroaniline ( $pK_b=12.05$ ). Furthermore, the observed rate constants do not show any mathematical regularity with the dielectric constants of the solvents used. This result supports that the zwitterion of the picolinic acid may not be acting as the predominant initial reactant in the decarboxylation reaction.

TABLE 3—ACTIVATION PARAMETERS FOR THE DECARBOXYLATION OF  $\alpha$ -PICOLINIC ACID IN ORGANIC SOLVENTS

Solvent	$\Delta H^\ddagger$ (k cal mole <sup>-1</sup> )	$\Delta F^\ddagger$ (k cal mole <sup>-1</sup> )	$\Delta S^\ddagger$ (eu mole <sup>-1</sup> )
<i>m</i> -Toluidine	40.30	33.41	+15.57
<i>p</i> -Toluidine	37.29	33.53	+ 8.51
<i>o</i> -Toluidine	33.99	33.74	+ 0.58
<i>m</i> -Cresol	38.59	34.08	+10.02
<i>p</i> -Cresol	35.80	—	+ 3.40
<i>o</i> -Cresol	33.67	33.83	+ 0.00
<i>m</i> -Chloroaniline	35.93	33.65	+ 5.16
<i>o</i> -Chloroaniline	32.33	33.55	- 2.75
Aniline	32.46	33.55	- 2.01
Diphenylamine	34.55	33.63	+ 2.08

The enthalpy of activation,  $\Delta H^\ddagger$ , for the reaction decreases in the order *o*-toluidine < *p*-toluidine < *m*-toluidine. It is because the presence of a methyl group in toluidines has two effects (i) positive inductive (+I) effect which increases the electron density on the nitrogen atom of the amine making it more nucleophilic and giving rise to a decrease in  $\Delta H^\ddagger$  and (ii) a steric effect which hinders the approach of picolinic acid molecule to the nitrogen atom of the amine resulting in a decrease in the entropy of activation,  $\Delta S^\ddagger$ . Thus, the increasing nucleophilicity of the solvents decreases both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ .

For cresols, the observed order of decreasing  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values is *m*-cresol < *p*-cresol < *o*-cresol which may likewise be attributed to the inductive and steric effects of the methyl group. In this case the +I effect increases electron density on the oxygen of the cresol.

The halogens exhibit a negative inductive (-I) effect which withdraws electrons from the nitrogen and are also capable of a positive electrometric (+E) effect furnishing electrons to the nitrogen atom of the amine. In the present data,  $\Delta H^\ddagger$  for *o*-chloroaniline and *m*-chloroaniline are higher than that for aniline indicating that a -I effect is operating. However, the value of  $\Delta H^\ddagger$  for *o*-chloroaniline was found to be lower than that for *m*-chloroaniline showing exactly an opposite relationship to what would be expected on the basis of -I effect alone.

This result is not too surprising if both  $-I$  and  $+E$  effects are taken into consideration. The larger steric hindrance of chlorine atom in *ortho* position is revealed by a lower  $\Delta S^\ddagger$  value in *o*-chloroaniline than it is in *m*-chloroaniline.

The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  in diphenylamine and aniline can well be compared in the manner of the foregoing discussion.

The isokinetic temperature is the temperature at which the rates of decarboxylation of certain acid are the same in a number of solvents and is arrived at by determining the slope of a line obtained by plotting  $\Delta H^\ddagger$  vs  $\Delta S^\ddagger$  for the decarboxylation in these solvents. The isokinetic temperature obtained from the slope of line I (Fig. 2) comes out to be  $149^\circ$ . On examining with Petersen's<sup>6</sup> critical

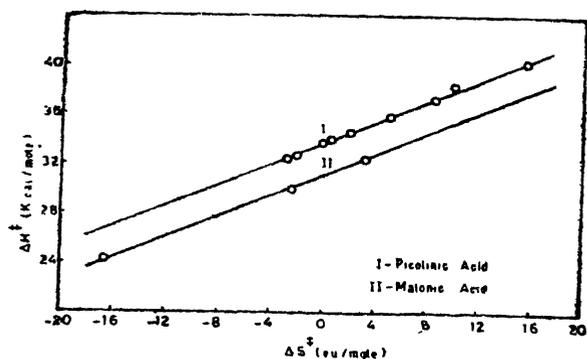


Fig. 2. Enthalpy-Entropy of activation plot for the decarboxylation of picolinic acid in solution.

analysis the range of  $\Delta H^\ddagger$  values (from 32.33 to 40.30 K cal/mole) is found to be 7.97 K cal/mole whereas the maximum possible error in  $\Delta H^\ddagger$  (assuming a maximum fractional error in the rate constant to be 0.05) turns out to be 2.0 K cal/mole. Thus the range of  $\Delta H^\ddagger$  values is more than three times the maximum possible error in  $\Delta H^\ddagger$ . Hence

line I is a valid relationship and not due to experimental error.

For a given reaction, a change in the nature of the reactant often results in the formation of a new isokinetic temperature line parallel to the original line<sup>7-9</sup> and it is of interest to find that the lines I and II of Fig. 2 are parallel. On this basis also it may be inferred that the mechanism of decarboxylation of picolinic acid in the solvents studied is the same or similar to that of malonic acid<sup>6</sup> involving the electrophilic, polarised, carbonyl carbon atom of the carboxyl group of the acid uniting with the unshared pair of electrons on a nucleophilic atom of the solvent.

The intercept of the isokinetic temperature line on the zero entropy of activation axis yields the free energy of activation at the isokinetic temperature,  $\Delta F_0^\ddagger$ , for all the reactions conferring to the line I, equal to 33.64 K cal/mole. On substituting the value of  $\Delta F_0^\ddagger$  in the absolute reaction rate equation

$$k = \frac{KT}{h} e^{-\Delta F_0^\ddagger/RT}$$

the pseudo first order rate constant of the present reaction at the isokinetic temperature of  $149^\circ$  comes out to be  $0.000033 \text{ sec}^{-1}$ .

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