J. Indian Chem. Soc.,
Vol. LIV, May 1977, pp. 521-523

The Kinetics of the Decarboxylation of *O*-Aminobenzoic Acid, *m*-Aminobenzoic Acid and *p*-Aminobenzoic Acid in Catechol.

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Manuscript received 19 April 1976 ; revised 1 December 1976 ; accepted 15 January 1977

Rate constants and activation parameters are reported for the decarboxylation of ortho-, meta- and para-aminobenzoic acids in catechol. The results of this investigations are compared with those of other substituted benzoic acids in this solvent.

KINETIC data have been reported previously on the decarboxylation of malonic acid[1] and oxamic acid[2] in the solvents resorcinol and catechol. The decarboxylation supported the mechanism for the reaction proposed by Fraenkel and his co-workers[3]—namely, that an electrophilic carbonyl atom of the malonic acid co-ordinates with a nucleophilic atom of a molecule of a solvent to form a transition complex. In our earlier investigations it has been reported that benzoic acid[4] and *o*-Chlorobenzoic acid[5] decarboxylate in catechol solvent via an intermediate complex mechanism. The behaviour of the solvents resorcinol and catechol for the decomposition of β-resorcylic acid[6], oxanilic acid[7], picolinic acid[8], malonanilic acid[9] and cinamalmalonic acid[10] is somewhat different from that of phenol. It was thought that valuable information on the mechanism of these reactions might be obtained by studying the effect on the rate of decomposition of ortho-meta and para-aminobenzoic acids. It has been observed in our earlier investigations that substituted acids decarboxylate at a lower speed than that of parent acids[11] and decompose faster in resorcinol than in catechol. The hydroxyl group of ortho-hydroxy phenol is more attractive than meta-hydroxyl phenol (resorcinol) in the formation of an intermediate complex. However, only oxanilic and malonanilic acids[9], in a certain range of temperature, gave higher velocity constant in catechol than in resorcinol ; above that range, the reaction behaviour was similar to that in other acids. These studies were made in order to know whether these acids decarboxylate in a fashion similar to that of benzoic acid or like oxanilic acid. We were rather interested in ortho-aminobenzoic acid, in which the amino group and carboxylic group are adjacent, as well as in the solvent catechol in which two hydroxyl groups are also adjacent For comparison the decomposition of meta-aninobenzoic and para-aminobenzoic acids have also been studied. The resultsof this investigation are reported herein.

Experimental

Materials : Ortho-aminobenzoic acid, meta-aminobenzoic acid and para-aminobenzoic acid were BDH, analar grade m.p., 145.7°, 173.4° and 187.6° respectively. The catechol used was BDH analytical reagent. It is white crystalline solid, m.p., 105° and changes its colour to dark red upon melting. No further purification of these chemicals was done.

Apparatus : The kinetic experiments were conducted, in a constant temperature oil-bath ± 0.05°, by measuring the volume of CO_2 produced at constant pressure. The apparatus and procedure are the same as described in our previous articles[12,13]. The aminobenzoic acids used yielded the theoretical amounts of CO_2 in each set of experiment on complete decomposition. The separate amount of the acids were taken in a glass capsule and dropped in the usual manner in 50.g of molten catechol. The CO_2 was collected at room temperature in a burette, filled with water and previously saturated with carbon dioxide. Several experimental runs were made at each temperature for each acid. No appreciable difference in the specific reaction velocity constant at constant temperature was detected when the amount of catechol was varied from 30-60g. Similar results have been reported earlier and no significant difference in the velocity constant was observed for the decarboxylation of *o*-chlorobenzoic acid and 2.4-dichlorobenzoic[5] acid in catechol solvent.

Results

Catechol, due to its acidic character, is a suitable solvent for studying the reaction mechanism. The rates of decarboxylation of these acids were measured in catechol at five temperatures in the range 160-190°. The plot of $\log (V_\infty - V_t)$ vs t was linear in all the experiments, indicating that the reactions were first order, where V_∞ is the volume of CO_2 after completion of the reaction and V_t is the volume at any time t. The average rate constant calculated from the slopes of the experimental logarithmic plots are shown in Table 1. A plot of $\log k$ vs $\frac{1}{T}$ gave a straight line from which the energy of activation, was computed for these three acids. The parameters of the Eyring equation, based upon the data

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of Table 1, are tabulated in Table 2 along with corresponding data for *o*-chlorobenzoic acid in catechol.

TABLE 1—APPARENT FIRST-ORDER RATE CONSTANTS FOR THE DECARBOXYLATION OF *m*-AMINOBENZOIC ACID, *p*-AMINOBENZOIC ACID AND *o*-AMINOBENZOIC ACID IN CATECHOL.

Temperature °C.	No. of data pairs.	$k \times 10^4$ sec^{-1} *m*-Aminobenzoic Acid.	No. of data pairs.	$k \times 10^4$ sec^{-1} *p*-Aminobenzoic Acid.	No. of data pairs.	$k \times 10^4$ sec^{-1} *o*-Aminobenzoic Acid.
160	2	1.82	3	1.74	4	1.66
170	1	3.47	2	3.09	3	2.82
180	1	6.17	3	5.50	2	4.79
190	2	11.51	2	9.12	2	7.76

TABLE 2—CALCULATED COMPARISON ACTIVATION PARAMETERS IN CATECHOL

Acids.	E k cal $mole^{-1}$	log A (Sec^{-1})	$\Delta H^{\neq}$ Kcal $mole^{-1}$	$\Delta F^{\neq}$ Kcal $mole^{-1}$	$\Delta S^{\neq}$ cal $mole^{-1}$ deg^{-1}
m-Aminobenzoic Acid.	24.35	8.52	23.45	33.42	−22 00
p-Aminobenzoic Acid.	2?.03	7.22	21.17	33.58	−28.68
o-Aminobenzoic Acid.	20.27	6.43	19.41	33.42	−32.35
o-Chlorobenzoic Acid[5]	23.61	6.26	22.58	38.91	−29.80

Discussion

It is a well-known fact that carboxylic acids decarboxylate with different velocities in various non-aqueous solvents. The results of Table 1 show that *m*-aminobenzoic acid decarboxylates at a faster speed than para and ortho-aminobenzoic acid. Clark[14] has reported that the rates of malonic acid decarboxylation in phenolic solvents are in the order *m*-cresol, *p*-creasol *o*-cresol. The velocity of reaction of solutes in catechol is in the order *m* aminobenzoic acid, *p*-aminobenzoic acid *o*-aminobenzoic acid (Table 1). The results of various investigators showed that the energy of activation for the decarboxylation of malonic acid is higher than for substituted acids and is also high for the solvents resorcinol and catechol. The energy of activation for the decomposition of benzoic acid in resorcinol and catechol was higher than that of ortho-chlorobenzoic acid and 2,4-dichlorobenzoic acid[5], but the entropy of activation was more negative for substituted acids in almost all the solvents than it was for the parent acids. This clearly indicates that the intermediate complexes formed between the substituted acids and the solvents are more stable than the complexes of solvents and parent acids. The high energy of activation may be attributed to the fact that the energy was distributed among the bonds, as the C-C bond of the acid ruptures. The benzene ring assumes a negative charge, and the proton of the carboxylic group is immediately attracted by the carbon atom. The weaker association of hydrogen bonds breaks with the transfer of an electron to benzene nucleus, and the resulting electrophile is partially stabilized by resonance. In this process, a large amount of energy is induced and breaks the bonds.

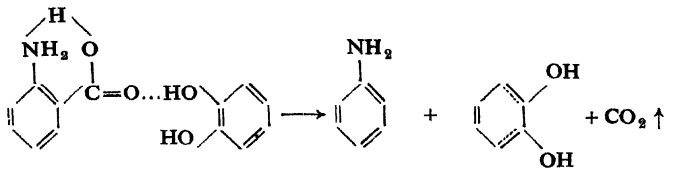
The higher rates of decarboxylation of m-aminobenzoic acid, as compared to that of *p*-and *o*-aminobenzoic acids, may be explained by the fact that one of the hydroxyl solvent groups associates with the carbonyl group of the acid and the other remains isolated, and that the latter might be having an accelerative effect. As against this the two hydroxyl groups of catechol associates with *p*-aminobenzoic acid & this accounts for the slower rate of reaction.

Amino group and carboxylic groups are adjacent in *o*-aminobenzoic acid. The single hydroxyl group of catechol associates with the acid but the amino group has a greater attraction in forming NH_3^+. The resulting hydrogen bonds are strong and the complex is bulkier than that of the *p*-and *m*-aminobenzoic acids. The bulkier the complex is, the more stable it is and more negative is its entropy of activation. Similar findings have been reported earlier[15]. The large negative value of the entropy of activation (Table 2, column 6, line 3) is an indication of a corresponding low steric factor. The amino group of *o*-aminobenzoic acid is likely to inhibit the velocity of reaction. Thus accounting for low frequency factor and low entropy of activation. The lower enthalpy of activation is definitely due to greater attraction of OH group which later might have formed NH_3^+ which attracts electrons and increases positive charge on the carbonyl atom of carbyxylate ion, thus causing the low value of ΔH.

The free energy of activation of these acids is comparable with one another, and the value is almost the same (Table 2. column 4). This should cause the reaction to proceed with the same velocity but the difference may be due to the presence of carboxylic group in different positions.

The structures of the intermediate complexes may be in the following form.

1-



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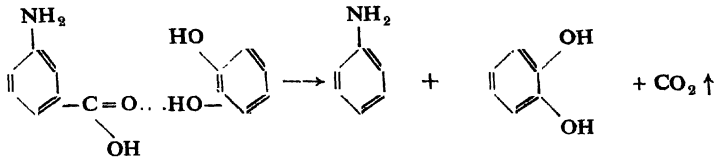

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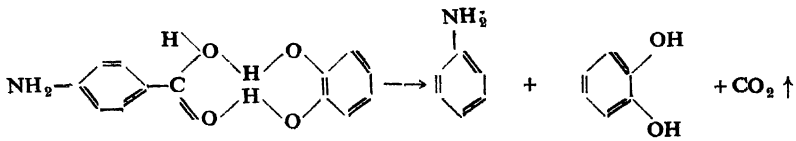

Acknowledgement

The authors thank Dr. H. Siddiqui and Dr. C. Balasubramaniam for valuable suggestions. We also thank Mrs. R. Rehana for reading this manuscript. The help given by the University is acknowledged with gratitude.

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