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THE EFFECT OF CHLOROBENZENE AND CATECHOL ON THE DECARBOXYLATION OF BENZOIC ACIDS

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Abstract. Kinetic study of the decarboxylation of substituted-benzoic acids have been made in catechol. The reaction is first order, chlorobenzene and dichlorobenzene have a retarding effect on the rate of reaction. No kinetic data has been reported in catechol.

The kinetics of the decomposition of benzoic acid in catechol is first order via an intermediate complex. The decomposition rate of benzoic acid[1] in resorcinol is faster than in catechol though catechol is more acidic in nature. It has been observed in our present investigations that the rate of decomposition of *o*-chloro-benzoic acid is slower than benzoic acid in catechol. Since the solvent catechol has never been the subject of kinetic study for the decarboxylation of benzoic acid and substituted-benzoic acids. It was thought important to carry out an investigation of the kinetics of these acids in catechol in order to ascertain whether or not it follows the same mechanism as in resorcinol[2] solvent reported earlier. The authors take up this problem to investigate the complexity forming between the substituted-benzoic acids such as chlorobenzoic acid and dichlorobenzoic acid. Like benzoic acid the reaction is of the first order for the above acids with observed Arrhenius parameters, $E = 23.6$ and 39.0 kcal mole-[1]. It has been reported earlier that these acids undergo thermal decarboxylation through a bimolecular mechanism involving the electrophilic replacement of ($COOH^+$) from the acid in resorcinol[2] solvent. But the investigations of halogenoacetic acid[3] and malonic acid[4] showed first order kinetics in resorcinol solvent. In view of the above discrepancy our results of substituted-benzoic acid in catechol further guided us to conduct several experiments in resorcinol[5] solvent other than catechol to study the validity of the reaction mechanism and our results support the view of Verhock[3] and Hall.[4]

Experimental

Reagents. Eastman Kodak analytical reagent materials were used. *o*-Chlorobenzoic acid and 2,4-dichlorobenzoic acid were stored over magnesium perchlorate in a desiccator. The resorcinol and catechol solvents used were BDH analytical reagents. They were white crystalline solids and changed 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 $\pm$ 0.05 in a closed system by measuring the volume of CO_2 produced at constant pressure. The evolved CO_2 was measured by observing its volume in the burette (calibrated by the Bureau of Standards at 20°). The apparatus and technique used in studying the decarboxylation is similar as described in our previous articles.[6,7] A weighed amount of *o*-chlorobenzoic acid (0.12–0.279 g) was dropped in 25 g molten solvent and CO_2 was collected at room temperature in a measuring burette filled with water which had been previously saturated with dry CO_2. Similarly 2,4-dichlorobenzoic acid (0.12–0.352 g) was used for each run at each temperature. Several experimental runs were made and the results are quite reproduciable for each sample of acid at a fixed temperature. The amount of the catechol was varied from 25–40 g, no change in rates have been recorded.

For every experiment the quantity of CO_2 evolved was plotted against time. For the experimental plots representative points were used for the preparation of graphs ($V\infty - Vt$) *Vs* t, where $V\infty$ represents the maximum yield of CO_2 (97–98%) of the theoretical yield in all experiments and Vt is the amount of gas at any time t. The apparent first order rate constant was in each case taken as the absolute slope of the logarithmic plot for the decarboxylation of these acids in catechol shown in Table 1.

Further additional experiments were conducted at the run temperatures by the addition of 0.02 cm^3 99% chlorobenzene to the catechol solvent, similar to our previous studies for the decarboxylation of oxalic acid[8] in glycerol in which formic acid was one of the product, and pure formic acid was added to study its effect, where formic acid accelerated the reaction. However, the values of rate constants observed in these experiments are definitely lower (Table 1, column 2) than that shown in column 1. This proves that the chlorobenzene formed as one of the product during the decarboxylation of *o*-chlorobenzoic acid has a retarding effect on the rate of reaction which might be having an association with the solvent. The various activation parameters of the Eyring[9] equation, based upon the data in Table 1 are collected in Table 2.

Results and Discussion

Our investigations for the decarboxylation of benzoic acid had shown that the decomposition rate of benzoic acid is higher in resorcinol than in catechol.[1] The decomposition rate of *o*-chlorobenzoic acid in catechol at 240°, $k = 42.5 \times 10^5$/sec and the rate of 2,4-dichlorobenzoic acid at 255°C is 10.9×10^5/sec but the priliminary experiments for the decarboxylation of 2,4-dichlorobenzoic acid at 255°C gave the rate 12.6×10^5/sec in resorcinol solvent (unpublished

TABLE 1. RATE OF DECOMPOSITION OF *o*-CHLOROBENZOIC ACID AND 2,4-DICHLOROBENZOIC ACID IN CATECHOL.

Run temp. (°C)	No. of data pairs of *o*-chlorobenzoic acid	Av. $k1 \times 10^5$/sec o-chlorobenzoic acid	No. of data pairs	Av. $k_1 \times 10^5$/sec effect of chlorobenzene
220	8	17·0±0·04	3	15·3±0·02
230	7	27·5±0·05	2	25·3±0·01
240	8	42·5±0·09	2	40·6±0·03
250	9	70·1±0·18	4	67·3±0·03
	No. of data pairs of 2,4-dichlorobenzoic acid	Av. $k_1 \times 10^5$/sec 2,4-dichlorobenzoic acid	No. of data pairs	Av $k_1 \times 10^5$ sec effect of chlorobenzene
240	11	10·9±0·07	3	8·2±0·11
250	9	22·3±0·04	2	19·0±0·08
255	8	31·6±0·08	5	29·5±0·31
260	9	44·8±0·21	2	42·6±0·27
265	5	63·1±0·26	3	60·5±0·27

TABLE 2. COMPARISON OF ACTIVATION PARAMETERS IN CATECHOL.

Acids	$k \times 10^5$/sec	E* (kcal mole)	*A*/sec	△H≠ (kcal/mole)	△F≠ (kcal/mole)	△S≠ (cal/mol deg)
Benzoic acid[1] at 265°C	55·81	52·20	$8·7 \times 10^{17}$	51·13	40·28	+20·35
o-Chlorobenzoic acid at 240°C	42·5	23·61	$4·25 \times 10^6$	22·58	38·91	—29·8
2,4-dichlorobenzoic acid at 255°C	31·6	39·01	$4·07 \times 10^{12}$	37·10	41·36	— 4·47

*E** is the experimental energy of activation

results). However, catechol is more acidic than resorcinol but the decomposition rate of substituted-benzoic acids is much slower than in resorcinol. Similar results have been reported earlier for the decarboxylation of malonic,[10] oxalic[11] and benzoic acids in these solvents.

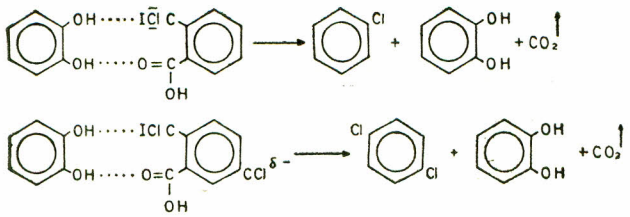
The decarboxylation of *o*-chlorobenzoic acid and dichlorobenzoic acid are first order at the run temperatures of this investigation. The rate determining steps are the intermediate complexes between these acids and the solvent catechol. All the activation parameters derived from this research are in good agreement with our previous investigations from experiments at temperatures where normal yields of CO_2 were observed. The entropy of activation decreases (Table 2, column 6) and the rates are also in a decreasing order for the substituted-acids at the same temperature (Table 1).

The entropy of activation decreases with respect to benzoic acid which indicates that the catechol molecules associated with that of the chlorobenzoic acid and dichlorobenzoic acid. The association of chlorobenzoic acid is more stable than that of dichlorobenzoic acid and the rate of decarboxylation of dichlorobenzoic acid is also more slow than chlorobenzoic acid. Similar results of lower entropy of activation for the decarboxylation of chlorobenzoic acid have been reported earlier[2] in resorcinol and more negative in comparison to dichlorobenzoic acid. If the decarboxylation involves intramolecular transfer, the entropies of activation should be more negative in the case of free acid decomposition and the other activation parameters should be little changed as we have observed in our investigations.[12] But the authors have not studied the effect of chlorobenzene formed as one of the product. In our present investigations it is evident that the rate of decomposition of these acids decreased in the presence of chlorobenzene (Table 1, column 2). This may be attributed to the increase of complexity and it can be concluded that the complex formed between these acids become relatively stable with the increase of the chlorobenzene. The lower rates for both the substituted—acids in these experiments with the addition of chlorobenzene also indicate for the stability of the the complexes beetween the solute and the solvent.

The energy of activation for dichlorobenzoic acid is higher than chlorobenzoic acid, it can be assumed that the solvent molecule is associating with the chlorine atoms of dichlorobenzene whereas chlorobenzoic acid forms the product, chlorobenzene which might be associating with a single chlorine atom, hence the distribution of energy among the bonds of stable complexes.

The higher steric factor of dichlorobenzoic acid may be due to the various complexes between solute and solvent, chlorobenzene and solvent and the product dichlorobenzene and the solvent.

The substituted-chlorine atom in the benzene ring has more electron density than carbon atom. The hydrogen of the hydroxyl group has an affinity towards chlorine forming hydrogen bonding, the hydroxyl group of catechol forms hydrogen bonding with the carboxyl group of the acid. This type of association may exist and a stable intermediate complex forms as shown in the structure in which rate determining step is the breakdown of the complex. The structures of the complexes between solute and solvent can be formulated as:



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