THE DECARBOXYLATION OF OXALIC ACID IN RESORCINOL AND CATECHOL

M.A. Haleem and M. Azeem

College of Engineering, University of Riyadh, Riyadh, Saudi Arabia

Abstract. Kinetic study of the decarboxylation of oxalic acid in resorcinol and catechol has been made for the first time. The reaction is of first order. The observations support the view that all the five decompositions proceed through an intermediate complex.

Kinetic studies have been reported on the decarboxylation of oxalic acid in various solvents including dioxane,[1] glycerol,[2] quinoline[3] and cresol.[4] Clark studied the decarboxylation of oxalic acid in a number of solvents and supported the mechanism of the formation of transition complex proposed by Fraenkel *et al.*[5] The authors suggested a simple intramolecular mechanism for the decarboxylation of oxalic acid in glycerine[6] and the study of C^{12}—C^{13} isotopes[7] supported the above mechanism of first order reaction. Since the kinetic study on the decarboxylation of oxalic acid in resorcinol and catechol has not been made so far, therefore, the kinetic was studied and the results are discussed in the present article, with the previously reported data for the other solvents.

Experimental

Reagents. Anhydrous oxalic acid (BDH) grade was used without further purification. It was heated in an electric oven at 100°C for about 6 hr and then stored over H_2SO_4 (concd). White crystalline solids of resorcinol and catechol (BDH, Analar grade), were used as solvents. The colour of the molten solvents were found to be dark red.

Procedure. The progress of the reaction was studied by measuring the volume of CO_2 evolved. The experimental set up and the procedure used in this study are the same described in previous papers.[8,9] About 50 g resorcinol and 50 g catechol were separately taken in each run and 0.1606 g oxalic acid was allowed to decomposed in a constant temperature oil-bath ($\pm 0.05°C$). The CO_2 was collected at room temperature in a measuring burette filled with water which had been previously saturated with CO_2. Duplicate runs were made in each set of experiment and the deviation in the results were within $\pm 0.166\%$.

Results and Discussion

The decarboxylation of oxalic acid was studied at five different temperatures in resorcinol and catechol. The plot of $\log(V_\infty - V_t)$ vs t, was linear in almost all the experiments indicating that the reaction is of first order where V_∞ is the volume of CO_2 after complete decomposition and V_t is the volume at time t. The average rate constants calculated from the slopes of the logarithmic plots are tabulated in Table 1. The thermodynamic quantities for the activation were calculated using the Eyring equation, based upon the data in Table 1, and are tabulated in Table 3 along-

with those for the reactions in several other solvents previously investigated. The values of entropy and enthalpy of activation for the decarboxylation of oxalic acid in different solvents other than resorcinol and catechol, reported by Clark and others are collected and presented in Table 4 for comparative study.

The decarboxylation of oxalic acid is kinetically first order at the run temperatures of this investigation. The rate determining step is an intermediate complex between oxalic acid and resorcinol. The energy of activation obtained for the decarboxylation of oxalic acid in resorcinol solvent is 28.99 kcal mole–; which is very close to 28.44 ± 2.0 kcal mole^{-1} reported by the author in glycerol.[6] It indicates that the distribution of energy among the bonds of activated complex is almost the same; though the rate of reaction is faster in resorcinol than that of glycerol. Hence the association might be responsible for the formation of a transition complex which decomposes faster in resorcinol solvent and one of the byproducts, formic acid might be acting only as a simple acid catalyst.

It has been reported that the hydroxyl group of phenol[13] is associated with malonic acid, since phenol and resorcinol and catechol have similar structures, one can expect similar association in the case of still stronger acid (oxalic acid) in these solvents. The intermediate complex may be in the following form:
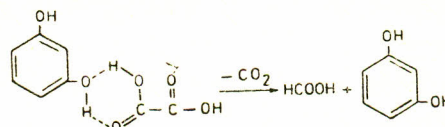

TABLE 1. RATE OF DECOMPOSITION OF OXALIC ACID IN RESORCINOL AND CATECHOL.

Run temperature (°C)	125	130	140	150	160
Av.k_1 (sec^{-1}×10^4) (resorcinol)	3·36	5·28	21·4	70·8	100·0
Av. k_1 (sec^{-1}) 10^4 (catechol)	2·82	4·08	8·32	17·1	17·78

TABLE 2. COMPARISON OF ACTIVATION PARAMETERS OF MALONIC AND OXALIC ACIDS IN RESORCINOL.

Acids	E (kcal/mole)	$\log A$ (sec^{-1})	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (cal/mole) (deg)	$\Delta F^{\ddagger}$ (kcal/mole)	k(sec^{-1}) ×10^5 at 140°C
Malonic[10]	32·31	13·87	13·49	+1·95	30·68	63·83
Oxalic	28·99	12·66	28·07	—5·85	31·39	213·80

TABLE 3. COMPARISON OF ACTIVATION PARAMETERS FOR OXALIC ACID IN VARIOUS SOLVENTS WITH THAT OF RESORCINOL AND CATECHOL.

Solvents	Glycerine[6]	Quinoline[3]	Resor-cinol	Catechol
E (kcal/mole)	$28\cdot4\pm0\cdot2$	$40\cdot13$	$28\cdot99$	$23\cdot80$
$\log A$ (sec^{-1})	$12\cdot3\pm0\cdot01$	$17\cdot10$	$12\cdot66$	$9\cdot50$
$\triangle H^{\ddagger}$ (kcal/mole)	$27\cdot6\pm0\cdot2$	$38\cdot90$	$28\cdot07$	$22\cdot89$
$\triangle S^{\ddagger}$ (cal/mole) (deg)	$-4\cdot9\pm0\cdot4$	$-15\cdot75$	$-5\cdot85$	$-17\cdot93$
$\triangle F^{\ddagger}$ (kcal/mole)	$29\cdot6\pm0\cdot3$	$45\cdot40$	$31\cdot37$	$31\cdot21$
k_1 (sec^{-1}) $\times10^5$	$197\cdot0$	$5\cdot0$	$213\cdot00$	$83\cdot1$

TABLE 4. ENTHALPY AND ENTROPY OF ACTIVATION FOR THE DECARBOXYLATION OF OXALIC ACID IN COMPARISON OF SEVERAL OTHER SOLVENTS.

	$\triangle H^{\ddagger}$ (kcal/mole)	($\triangle S^{\ddagger}$ cal/mole) (deg)
Dioxane[1]	29.20	-5.5
o-Cresol[4]	32.10	$+0.9$
p-Cresol[4]	31.20	-1.9
Ethylene glycol[11]	17.60	-30.0
Methylaniline[11]	35.50	$+8.3$
Dimethylaniline[11]	32.40	$+1.3$
Resorcinol	28.07	-5.85
Catechol	22.89	-17.93

The results of Table 2 show that the malonic acid–resorcinol[9] complex is more stabler than oxalic acid, the negative entropy of activation is in confirmity and hence the 3.3 times faster rate is obtained.

It is very interesting to note that though catechol is more acidic in nature than resorcinol; the rate of decarboxylation of oxalic acid in catechol is much slower than in resorcinol (Table 3). In the earlier study with the glycerol[14] solvent it was observed that the velocity of the reaction was accelerated by increasing the amount of formic acid in accordance with the theory that most of the carboxylic acids decompose faster in more acidic solvents than in basic solvents. The slow rates observed in the present study suggests that more stable complex might be forming between catechol and oxalic acid. The association may be in the following form:
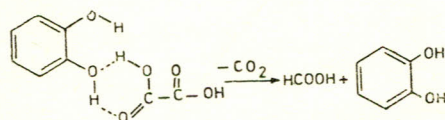
From the structure suggested the H—H bond between the free hydroxyl group of the solvent and the carboxylic group is not possible and hence there will not be much difference between the intermediate complex structures of oxalic acid–resorcinol and

oxalic acid–catechol. During the decarboxylation of oxalic acid, the resulting product (formic acid) might be associated with the hydroxyl group of catechol and forming a complicated complex. There is every possibility that the free hydroxyl solvent group might be reacting with the carbonyl double bond of the formic acid converting the acid into a stable ortho formic acid derivative. This may probably be the cause for the slow decomposition of oxalic acid. Again the more negative entropy of activation (Table 4), also shows less stability of the complex which is in confirmity with the results obtained by Clark[15] for other solvents.

The entropy and enthalpy of activation collected from the literature are given in Tables 3 and 4 for the decarboxylation of oxalic acid in several solvents, the values of enthalpy and entropy of activation obtained by the authors are also found to be lying in the same line. The enthalpy–entropy of activation plot gives a straight line. The isokinetic temperature reported by Clark is 467°K corresponding to a temperature 194°C, which is very close to the melting point of oxalic acid. Present work also supports the above conclusion arrived at by Clark.[11]

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