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## THE KINETICS OF THE DECARBOXYLATION OF METHYLETHYLMALONIC ACID IN CATECHOL

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Kinetic data reveal decarboxylation of methylethylmalonic acid in resorcinol and catechol. The activation parameters are calculated and compared with those earlier reported for the decarboxylation of methylmalonic acid and ethylmalonic acid. The isokinetic temperature corresponds to the exact melting point of methylethylmalonic acid.

### INTRODUCTION

In our earlier investigations on the decarboxylation of methylmalonic acid (MMA) [1] and ethylmalonic acid (EMA)[2] it has been shown that the carbonyl carbon atom of the reactant coordinates with a pair of unshared electrons on the nucleophilic atom of the solvent molecule and in the transition state these interactions between the reagents lowered the enthalpy of activation. This principle has been tested for the decarboxylation of cinnamylidene-malonic acid [3], catechuric acid [4], oxamic acid [5], oxanilic acid [6], malonanilic acid [7], and benzylmalonic acid [8]. The decarboxylation of MMA and EMA were reported in resorcinol and catechol and the effect of methyl group and ethyl group of the acids were discussed. It has also been shown that the mono and dicarboxylic acids decarboxylate at a faster rate in resorcinol [9] than in catechol[10]. Consequently, a kinetic study on the decarboxylation of methylethylmalonic acid (MEMA), in resorcinol and catechol was carried out to ascertain any exception from that reported earlier for MMA [1] and EMA[2]. The results of this investigations are reported in this paper.

### EXPERIMENTAL

*Reagents.* Methylethylmalonic acid (MEMA), analytical grade, melted at 122.3°, reported m.p in the literature is 122.0° used without purification. The resorcinol and catechol used as solvents were chemically pure BDH analytical reagent grade.

*Apparatus and Technique.* The kinetic experiments were made in a constant temperature oil-bath  $\pm 0.05^\circ$  in a closed system by measuring the volume of CO<sub>2</sub> produced at constant pressure as described earlier [11,12]. In each experiment 0.216 g of MEMA sample was dropped in the usual manner in the reactor at the run temperatures, containing 30 g of the solvent.

### RESULTS

The rate of decarboxylation of MEMA was measured in resorcinol and catechol at four temperatures. The plot of  $\log(v - v_t)$  against  $t$ , was linear over the entire experiment indicating the first-order reaction. The average rate constant calculated in the usual manner from the slopes of the experimental logarithmic plots, are cited in Table 1, while thermodynamic parameters based thereon are tabulated in Table 2 alongwith the corresponding data of MMA and EMA.

### DISCUSSION

The rates of decarboxylation of MEMA in resorcinol and catechol were exactly the same at 130° (Table 1). The decomposition rates of MMA and EMA though not the same, they were very close at this temperature, which may be attributed to the hydroxyl group of resorcinol isolated alongwith the methyl and ethyl group of the solute. It has been reported earlier that the velocity of a reaction for the decarboxylation of MMA and EMA at 130° was the same in resorcinol as well as in catechol

Table 1. First-order rate constants for the decarboxylation of methylethylmalonic acid in resorcinol and catechol.

Run temp. °C	No. of data pairs	Catechol $k_1 \times 10^5$ (sec <sup>-1</sup> )	No. of data pairs	Resorcinol $K_1 \times 10^5$ (sec <sup>-1</sup> )
130	3	10.72	2	10.72
140	3	22.65	2	25.12
145	2	30.55	2	36.73
150	2	44.67	3	55.59

acids.

A plot of H vs S gave a fairly straight line, parallel to the line of EMA with a slope of 395.0 K° corresponding to 122° which is the melting point of MEMA. The m.p. obtained by the graphical method for MMA and EMA was 8° lower than the correct experimental m.p. This meant that the rate of reaction of MMA and EMA may be falling in the range from 122 to 130° in these solvents. The experimental results have so far shown that at 130° the velocity of the reaction for each of these acids was the same in resorcinol and catechol.

Table 2. Comparative thermodynamic parameters.

	Resorcinol			Catechol		
	MEM acid	MM acid <sup>4</sup>	EM acid <sup>4</sup>	MEM acid	MM acid <sup>5</sup>	EM acid <sup>5</sup>
E	29.07	32.92	30.45	23.60	30.34	25.69
Log A (sec <sup>-1</sup> )	12.75	13.86	12.51	8.81	10.50	9.94
$\Delta H^\ddagger$	28.25	32.10	29.63	22.78	29.50	24.87
$\Delta S^\ddagger$	-8.8	+2.3	-4.0	-20.89	-4.0	-15.66
$\Delta F^\ddagger$	31.33	31.14	31.27	31.41	31.18	31.24

E,  $\Delta H^\ddagger$  &  $\Delta F^\ddagger$  Units, Kcal mole<sup>-1</sup>  
 $\Delta S^\ddagger$ , cal mole<sup>-1</sup> deg<sup>-1</sup>  
 MEM = Methylethylmalonic acid,

MM = Methylmalonic acid,  
 EM = Ethylmalonic acid,

though different from resorcinol. It was, therefore, concluded that the isolated hydroxyl group might have accelerated the reaction, and at higher temperature this effect was more pronounced. Such a normal behaviour was also shown by other carboxylic acids as well; MEMA also gave higher rates in resorcinol above 130° than that in catechol.

The thermodynamic parameters were lower for the decarboxylation of MEMA in catechol than in resorcinol (Table 2 column 1 and 4). It was expected due to adjacent groups of catechol as lowering the enthalpy and entropy of activation. The data of MMA and EMA also fell in line due to the two carboxylic groups having a greater tendency of linear polymerization compared to the monocarboxylic acids. Further, the enthalpy as well as the entropy of activation decreased in both the solvents in the order of MMA, EMA, MEMA which is the order of complexity in the solvents of this investigation. The acids in this investigation behaved like electrophilic agents similar to malonic acid and oxalic acid, in which a pair of unshared electrons on the nucleophilic atom of the solvent coordinated with the electrophilic carbonyl atom of the

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