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Further Studies on the Decarboxylation of Cinnamylidenemalonic Acid in Resorcinol and Catechol

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Synopsis. Kinetic data are reported for the decarboxylation of cinnamylidenemalonic acid in resorcinol and catechol. The activation parameters are culculated and compared with those previously reported for the decarboxylation of unsubstituted and substituted malonic acids.

The kinetics for decarboxylation of the derivatives of malonic acid[1] have been reported in our earlier investigations in resorcinol and catechol solvents. Bernoulli and Jakubowicz[2] studied the decarboxylation of malonic acid derivatives in aqueous solution in the range of 76—110 °C, including disubstituted malonic acids. Muus[3] reported the kinetic data of dibromomalonic acid in water at 45 °C. Clark[4] studied the decarboxylation of cinnamylidenemalonic and malonic acids in phenol, *m*-cresol, *p*-cresol and several aromatic amines. In the transition state of decarboxylation, it is considered that the carbonyl carbon atom of the reactant coordinates with a pair of unshared electrons on the nucleophilic atom of the solvent molecule and that these interactions between the reagents lower the enthalpy of activation ($\Delta H^{\neq}$) of the reaction. This principle has been tested on a number of compounds and it was thought to be worth-while to carry out the decarboxylation of cinnamylidenemalonic acid to see whether or not any exception could be found. For this purpose a kinetics study of the decarboxylation of cinnamylidenemalonic acid was carried out in resorcinol and catechol.

Experimental

Reagents. The cinnamylidenemalonic acid was prepared by Riaz Ahmed and Das Gupta in Sirohi College by condensation of cinnamaldehyde with malonic acid and purified several times with ethanol, mp 201 °C. Resorcinol and catechol were of analar reagent grade.

Apparatus and Technique. The reaction was usually followed by measuring the volume of carbon dioxide evolved. The apparatus and technique are similar to those described in previous articles.[5-7] About 20 g of resorcinol were separately taken in each run and 0.394 g of cinnamylidenemalonic acid weighed in a sample tube was placed on the movable probe inside the reactor. The set-up was then placed in a constant temperature oil-bath (±0.05 °C) and, when thermal equilibrium was established, the reaction was started by dropping the acid in the solvent. The evolved CO_2 was determined with a measuring burette filled with water saturated with carbon dioxide.

Results and Discussion

Plots of $\log(V_\infty - V_t)$ *vs.* t (where V_∞ is the volume of CO_2 after completion of the reaction and V_t is the volume at time t) showed straight lines, indicating a first order reaction. The rate constant at each temperature was calculated from the slope of the line and these values are tabulated in Table 1. The activation parameters calculated are tabulated in Table 2, along with the results of Clark in other solvents.

TABLE 1. APPARENT FIRST-ORDER RATE CONSTANTS FOR THE DECARBOXYLATION OF CINNAMYLIDENEMALONIC ACID IN RESORCINOL AND CATECHOL

Temp (°C)	No. of data pairs	$k_1 \times 10^5$ (s^{-1}) Catechol	Av. dev.	$k_1 \times 10^5$ (s^{-1}) Resorcinol	Av. dev.
140	5	3.63	±0.02	5.13	±0.01
145	3	5.37	±0.03	8.13	±0.02
150	2	7.76	±0.04	10.96	±0.02
155	3	12.02	±0.02	15.85	±0.02
160	4	16.60	±0.03	21.88	±0.03

In the same solvent, the $\Delta H^{\neq}$ was less for the decarboxylation of cinnamylidenemalonic acid that for malonic acid (see Table 2). Hall[8] found that the mono-anion and the free acid of malonic acid have different rates of decarboxylation in aqueous solution. In non-aqueous solvents the mono-ions may be few and a change is not expected to increase the rate of the process. However, carbon isotope effect studies on hydrogen malonate ions suggest that CO_2 originates from the COOH group and not from the COO^- group, in the decarboxylation in quinoline[9] or dioxane.[10]

As seen in Table 2 (lines 4 and 5) the entropy of activation ($\Delta S^{\neq}$) for the decarboxylation of cinnamylidenemalonic acid in catechol is more negative than in resorcinol, indicating that the activated complex is more stable in catechol than in resorcinol; this result is similar to that in 2,4-dihydroxybenzoic acid, xalic acid,[12] benzoic acid,[13] substituted benzoic acids,[14] oxanilic acid,[15] picolinic acid,[16] and hexylmalinic acid.[1] This proves that the adjacent hydroxyl groups of catechol are mainly responsible for forming the hydrogen bonding and for stabilizing the complex. The methyl and hydroxyl groups in *o*-cresol are adjacent and the entropy of activation is expected to be somewhat more negetive than in *p* and *m*-cresols. Unfortunately, no data is available. However, the comparative entropy of activation of malonic acid and butylmalonic acid[17] (Table 2, line 1) is in support of our conclusion. The decrease in entropy of activation in catechol is an indication of greater interaction towards the acid that in resorcinol. On the contrary, the malonic acid has almost the same enthalpy of activation, probaly due to a super-molecule cluster as proposed by Clark.[18] Substituted malonic acids gave less enthalpy of activation than malonic acid in most of the solvents.

Table 2. Comparative thermodynamic parameters

Solvents	Malonic acid		Cinnamylidenemalonic acid		Butylmalonic acid	
	$\Delta H^{\ddagger}$ a)	$\Delta S^{\ddagger}$ b)	$\Delta H^{\ddagger}$ a)	$\Delta S^{\ddagger}$ b)	$\Delta H^{\ddagger}$ a)	$\Delta S^{\ddagger}$ b)
o-Cresol[17]	24.2	−16.5	—	—	21.3	−22.8
m-Cresol[17]	32.3	+ 3.2	22.0	−25.2	29.7	− 2.3
p-Cresol[17]	29.8	− 2.4	27.1	−14.2	24.0	−15.8
Resorcinol	32.3	+ 1.95	27.08	−11.4	—	—
Catechol	32.2	+ 1.82	22.09	24.2	—	—

a) kcal/mol. b) kcal/mol K.

A plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ for cinnamylidenemalonic acid is approximately linear. Such a linear relationship is evidence that the reaction mechanism in different phenolic solvents is almost the same.

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