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Kinetics of the Decarboxylation of Benzylmalonic Acid, Ethylmalonic Acid, and Dimethylmalonic Acid in Hydroxylic Solvents

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Synopsis. Kinetics of the decarboxylation of benzylmalonic acid, ethylmalonic acid, and dimethylmalonic acid have been shown to follow first order rate equation in several solvents, namely alkanediols and diethylene glycol (DEG), polyethylene glycol (PEG), and polypropylene glycol (PPG). The enthalpy and entropy of activation for the decarboxylation reactions were determined and the plot of ΔH^{*} *vs.* ΔS^{*} was found to be linear through all the solvents.

In the present Note, we report the results of our investigations into the kinetics of the decarboxylation of substituted malonic acids in hydroxylic solvents. The experimental set up is the same as was described previoulsy.[1,3,6] The decarboxylation was carried out in a thermostated bath controlled to within ±0.2 °C. The decarboxylation rates were measured by collecting the evolved carbon dioxide gas at atmospheric pressure at various time intervals. The solvents used are: ethylene glycol (Pfizer, India), 1,2-propanediol (B.D.H., L.R.), 1,3-butanediol (B.D.H., England), diethylene glycol (B.D.H., England), polyethylene glycol-400 (B.D.H., England), and polypropylene glycol-425 (Koch-Light, England). Benzylmalonic acid, ethylmalonic acid, and dimethylmalonic acid used were of Fluka, Switzerland. Ethylene glycol and 1,2-propanediol were distilled under reduced pressure before use. The solvents were previously saturated at the reaction temperature by passing a stream of pure and dry carbon dioxide gas. Stoichiometry was checked in all the solvents by collecting carbon dioxide gas when the reaction was complete. In each kinetic run, the amount of acid taken was about 0.17—0.18 g in 25 ml of the solvent.

Results and Discussion

The first order rate constants *k* given in Table 1 are mean values over at least four kinetic runs. We also observed that the decarboxylation of these acids obeys rate theory equation of Eyring. The thermodynamic parameters, enthalpy and entropy of activation, ΔH^{*} and ΔS^{*} have been evaluated and these are given in Table 2.

Figure 1 shows the enthalpy-entropy plot for the decarboxylation reaction of these acids in these solvents as well as in the molten state. Decarboxylation kinetics of benzylmalonic acid in the molten state have been reported by Clark.[7] We have also measured the decarboxylation rate in the molten state of these three acids at several temperatures.[8] It is seen that a straight line can be drawn through all the solvents including the melting point. The data for dimethylmalonic acid, however, is off as will be evident in Fig. 1. This is not unexpected because dimethylmalonic acid was seen to decarboxylate very fast in the molten state and there was some uncertainty in the values of the rate constant.[8] The linearity of $\Delta H^{*}-\Delta S^{*}$ plot implies one reaction series for each of these acids in these solvents. The slope of the enthalpy-entropy plot of Fig. 1 gives the isokinetic temperatures, which are very close to the respective melting points of the acids (Table 3). This is in harmony with the conclusions reached by Clark on the decarboxylation kinetics of alkyl-substituted malo-

Table 1. First order rate constants for the decarboxylation of substituted malonic acids in hydroxylic solvents

Temp/°C	Rate constant, $k\times10^{4}$/s^{-1}					
	Ethylene glycol	1,2-Propanediol	1,3-Butanediol	Diethylene glycol	Polyethylene glycol	Polypropylene glycol
			Benzylmalonic acid			
120	7.85±0.38	11.40±0.36	7.75±0.85	6.64±0.36	5.42±0.32	6.16±0.06
130	10.90±0.14	14.10±0.02	16.80±0.15	14.32±0.46	8.89±0.25	9.59±0.05
140	22.50±0.23	19.67±0.23	26.20±0.90	18.06±0.14	15.99±0.19	18.30±0.08
			Ethylmalonic acid			
120	2.89±0.11	2.57±0.17	3.01±0.34	3.67±0.18	2.14±0.04	2.04±0.03
130	7.13±0.01	6.24±0.01	7.78±0.15	5.70±0.22	3.68±0.12	4.51±0.15
140	15.12±0.01	9.07±0.21	14.88±0.05	10.75±0.25	7.57±0.28	9.23±0.29
145	20.09±0.12	15.44±0.09	—	—	13.30±0.54	14.08±0.22
			Dimethylmalonic acid			
130	3.53±0.05	3.41±0.11	2.99±0.45	3.33±0.05	3.43±0.02	2.07±0.05
140	7.37±0.07	8.03±0.21	7.61±0.08	7.05±0.18	6.07±0.05	4.63±0.22
145	14.79±0.77	13.33±0.12	12.71±0.01	8.84±0.08	7.54±0.12	9.82±0.91

Table 2. Thermodynamic parameters of the decarboxylation reaction in solvents

Solvents	Benzylmalonic acid			Ethylmalonic acid			Dimethylmalonic acid		
	ΔH^{*}/kcal mol^{-1}	ΔS^{*}/e.u.	ΔF^{*} m.p./kcal mol^{-1}	ΔH^{*}/kcal mol^{-1}	ΔS^{*}/e.u.	ΔF^{*} m.p./kcal mol^{-1}	ΔH^{*}/kcal mol^{-1}	ΔS^{*}/e.u.	ΔF^{*} m.p./kcal mol^{-1}
Ethylene glycol	16.93	−30.39	28.90	27.09	−6.46	29.56	30.02	−0.52	30.26
1,3-Butanediol	20.40	−21.38	28.82	24.43	−12.90	29.37	30.07	−0.59	30.34
1,2-Propanediol	8.61	−50.72	28.59	23.12	−16.74	29.53	32.17	4.66	30.00
Diethylene glycol	15.52	−33.97	28.90	16.41	−33.11	29.09	21.08	−22.66	31.60
Polyethylene glycol	17.39	−29.87	29.19	22.19	−19.51	29.66	16.62	−33,73	32.27
Polypropylene glycol	18.26	−27.46	29.08	23.55	−16.00	29.68	31.79	2.85	30.46

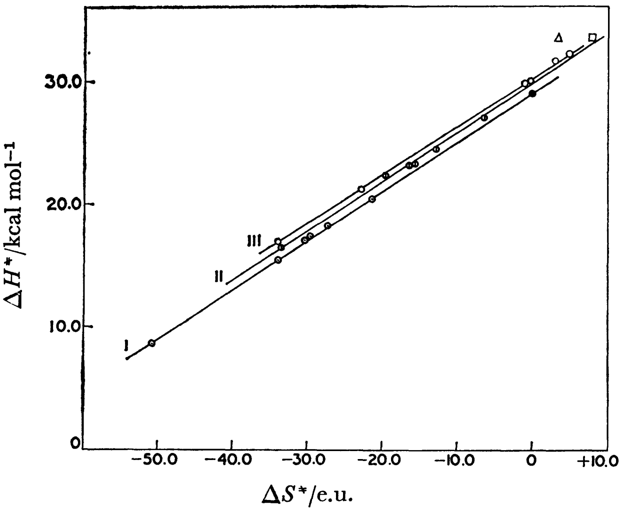

Fig. 1. Enthalpy-entropy plot for the decarboxylation of: benzylmalonic acid[line-I; solvents (⊙); molten state (●)], ethylmalonic acid[line-II; solvents (⦶); molten state (□)], dimethylmalonic acid[line-III; solvents (○); molten state (△)].

Table 3. Analysis of the effect of errors in the $\Delta H^*-\Delta S^*$ relationship for the decarboxylation reaction in alkanediols, DEG, PEG, and PPG

Acids	$\frac{2\delta}{\text{kcal mol}^{-1}}$	$\frac{\mathrm{d}(\Delta H^*)}{\text{kcal mol}^{-1}}$	$\mathrm{d}(\Delta H^*/2\delta)$	Isokinetic temp
Benzylmalonic	3.25	11.79	3.6	120°C
Ethylmalonic	2.89	10.70	3.7	111°C
Dimethylmalonic	4.04	16.94	4.2	192°C

nic acids in alkanols and carboxylic acids. Peterson and coworkers,[5)] however, suggested the criterion which must be satisfied for any valid conclusions from the linearity of ΔH^* *vs.* ΔS^* plot.

If the total maximum possible error in ΔH^* is 2δ and the range of ΔH^* values is designated as $\mathrm{d}\Delta H^*$, then the ratio, $\mathrm{d}\Delta H^*/2\delta \gg 1$. The maximum possible error in ΔH^*, may be calculated from the relation,[5,6)]

$$\delta = 2R\frac{T'T}{T'-T}\alpha \quad \text{if } \alpha \ll 1.$$

Using this relation, we have given in Table 3 the maximum possible error 2δ in ΔH^*, the range of $\mathrm{d}\Delta H^*$ values for a reaction series and the ratio, $\mathrm{d}\Delta H^*/2\delta$.

It will be seen that the ratio $\mathrm{d}\Delta H^*/2\delta$ is always greater than 1. So the observed linearity of ΔH^* *vs.* ΔS^* plot (Fig. 1) may be regarded as valid. Therefore at the isokinetic temperature, the rate constant is the same for a reaction series in all the solvents.

Diethylene glycol (DEG), polyethylene glycol (PEG), and polypropylene glycol (PPG) differ from the alkanediols in having oxygen in the middle of the chain in addition to having two hydroxyl groups at the ends. Therefore in the solvents, namely, DEG, PEG, and PPG, the activated complex may form either with the ether oxygen or the hydroxyl oxygen and the polarised carbonyl carbon of the acid. Accordingly the enthalpy-entropy plot for malonic acid and methylmalonic acid[4)] shows two parallel straight lines-one passing through the alkanediols and the other through DEG, PEG, and PPG. The nature of the activated complex thus significantly differs in the two types of solvents. With benzylmalonic acid, ethylmalonic acid, and dimethylmalonic acid, the bulky substituents are likely to hinder coordination with the lone pair of electrons on ether oxygen of the solvents buried deep in the middle of the chain, so that effective participation of hydroxylic oxygen is only permitted. Thus in the decarboxylation of benzylmalonic acid, ethylmalonic acid, and dimethylmalonic acid the nature of the activated complex will be similar in alkanediols and DEG, PEG, and PPG. So it is natural to expect one straight line passing through all the solvents in respect of decarboxylation of a given acid in the series.

Now it is further noticed that the decarboxylation rate constant in these solvents decreases in the following order:

Benzylmalonic acid, ethylmalonic acid, dimethylmalonic acid. This is also the order in which the electron donating ability of alkyl group namely ethyl- and dimethyl-, decreases. If the Fraenkel[2)] mechanism is accepted, then the C–C bond will be broken more easily, when the substituent is an electron attracting group. On the other hand, if the substituent is an electron donating group such as alkyl, the excess negative charge on the carbonyl carbon atom will hinder the process of C–C bond breaking and thus retard the rate of decarboxylation reaction. It is thus expected that the rate of decarboxylation should decrease as the electron donating ability of the substituent increases. The electron donating ability of two methyl-being greater than the ethyl, it is easy to understand the decreasing value of the rate constant as we go from ethylmalonic acid to dimethylmalonic acid. The benzyl group, on the other hand, may act either as an electron sink or as an electron donor; so it is difficult to locate its position in the inductivity scale. However, our kinetic studies suggest that the benzyl group has a low electron donating ability in the decarboxylation reactions-much less than the alkyl substituents. On these considerations we may place them in the following order of decreasing electron donating ability: benzylmalonic acid ethylmalonic acid and dimethylmalonic acid, and this is exactly the order in which the decarboxylation rate constant decreases.

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References

1) L. W. Clark, "The chemistry of carboxylic acids and esters," ed by S. Patai, Interscience (1969), p. 589.
2) G. Fraenkel, R. L. Belford, and P. E. Yankwich, *J. Am. Chem. Soc.*, **76**, 15 (1954).
3) M. K. Biswas and D. K. Majumdar, *J. Ind. Chem. Soc.*, **56**, 280 (1979).
4) M. K. Biswas and D. K. Majumdar, *J. Ind. Chem. Soc.*, **56**, 874 (1979).
5) R. C. Peterson, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).
6) L. W. Clark, *J. Phys. Chem.*, **67**, 1481 (1963).
7) L. W. Clark, *J. Phys. Chem.*, **67**, 138 (1963).
8) M. K. Biswas and D. K. Majumdar, *J. Ind. Chem. Soc.*, (communicated).