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Kinetics of Decarboxylation of Ethylmalonic Acid: A Hundred-fold Reactivity of the Acid Molecule over its Mono-anion

R. GOPALAN
Department of Chemistry, Madras Christian College
Tambaram, Chennai-600 059, India

The kinetics of molten and aqueous ethylmalonic acid have been studied. The acid molecule is about 100 times more reactive than its carboxylate ion, while the dicarboxylate ion is unreactive. Increasing pH sharply impedes the reaction due to depletion of the concentration of the active species, *viz.*, the unionized acid molecule. Investigation of solvent effect with water-dioxane system indicates that the reaction is most facile in media containing 75–85% dioxane. This has been explained based on the degree of dissociation of ethylmalonic acid and also on a kinetic solvent effect. The Arrhenius parameters for reactions in molten and aqueous solution have been evaluated. These data fall well in line with those on other malonic acids, and suggest a mechanism involving a concerted-switch of electrons in the intra-molecularly hydrogen-bonded molecule.

INTRODUCTION

The ease of decarboxylation of acids depends on structural and experimental factors. Malonic acids are decarboxylated easily either by heating them in molten state or in solution[1]. The reaction might involve the undissociated acid, the monoanion, the dianion or all of these species. However, all of these species may not be equally reactive. The reaction may involve one of these species preferentially. The kinetics of decarboxylation of ethylmalonic acid were studied with a view to ascertaining the relative reactivities of the acid species and comparing the results with those on related acids.

EXPERIMENTAL

Ethylmalonic acid (BDH) was purified by repeated recrystallisation from benzene (m.p. 111.3°C). Its neutralization equivalent indicated a purity of 99.2%. Dioxane was purified by the usual procedure. All solutions were prepared in demineralized and previously boiled water.

The reaction was monitored by measuring the volume of carbon dioxide evolved with a manometer at a constant temperature and a constant pressure[2]. The reaction vessel was maintained at a fixed temperature correct to ± 0.05°C by a vapour bath.

RESULTS AND DISCUSSION

Decarboxylation in molten state: The decarboxylation of molten ethylmalonic acid has been followed at different temperatues and the results are given in Table-1. In Table-2 are given the activation parameters for this acid along with those for three other malonic acids[1]. The decarboxylation of molten malonic acid has been assumed to be bimolecular, the activated complex being formed by the interaction of two molecules of malonic acid-a polarized electrophilic carbonyl carbon atom of one molecule attracted by the lone pair of electrons of the nucleophilic hydroxyl oxygen atom of another. This mechanism is likely to operate in ethylmalonic acid also.

TABLE-1
DECARBOXYLATION OF MOLTEN ETHYLMALONIC ACID

Temperature (°C)	$k_1 \times 10^4/s^{-1}$
134.0	0.64
140.0	1.10
146.2	2.25
150.1	3.29

TABLE-2
ACTIVATION ENERGIES FOR THE DECARBOXYLATION OF MOLTEN MALONIC ACIDS

Acid	$\Delta H^{\neq}$/kJ mol	$\Delta G^{\neq}$/kJ mol	$\Delta S^{\neq}$/e.u.
Malonic Acid	150	130	12.0
Methylmalonic Acid	147	131	9.6
Ethylmalonic Acid	140	134	4.0
N-Butylmalonic Acid	135	130	3.0

The activation parameters for ethylmalonic acid are in accord with this mechanism. The ethyl-substituent, due to its $+I_s$ effect increases the nucleophilicity of the hydroxyl oxygen thereby decreasing the enthalpy of activation. The entropy of activation also decreases because of the bulky nature of the ethyl group compared to a hydrogen or a methyl group. Thus the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values for this acid fall between those for methyl- and *n*-butylmalonic acids.

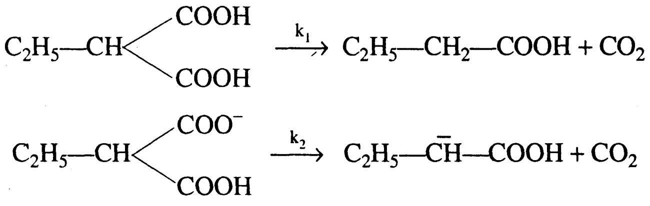
Decarboxylation in aqueous medium: Effect of concentration of the substrate: The rate of decarboxylation of ethylmalonic acid in water has been followed at 93.6°C for a set of acid concentrations in the range 0.01 to 0.05 M. The reaction in all cases follows first order kinetics (Table-3).

In aqueous solution, there can be three species of ethylmalonic acid, *viz.*, the unionised molecule, the monoanion and the dianion. The reaction may take place preferentially through one or two of these species or all the species may decompose simultaneously. But, disodium ethylmalonate did not decompose when refluxed in

TABLE-3
DECARBOXYLATION OF AQUEOUS ETHYLMALONIC ACID AT 93.6°C

Acid	pH	$k_{obs} \times 10^6/s^{-1}$	x/a
0.0483	2.41	5.52	0.027
0.0453	2.47	5.48	0.031
0.0394	2.60	5.42	0.042
0.0340	2.62	5.39	0.048
0.0301	2.71	5.28	0.053
0.0217	2.75	5.26	0.059
0.0150	2.88	5.21	0.077
0.0108	2.91	5.17	0.082

aqueous solution even for 10 h. The dianion can therefore be considered stable. The stability of the doubly-charged anion has to be attributed to the high electron-density in the carbon-carbon bond and the difficulty of accommodating the negative charge in the fission process. The reaction may then occur either through the free acid or through the monoanion or through both. The simultaneous decarboxylation of the free acid and the anion may be represented as



$$C_2H_5\text{—}CH(COOH)_2 \xrightarrow{k_1} C_2H_5\text{—}CH_2\text{—}COOH + CO_2$$

$$C_2H_5\text{—}CH(COO^-)(COOH) \xrightarrow{k_2} C_2H_5\text{—}\bar{C}H\text{—}COOH + CO_2$$

Then, the overall rate,

$$k_{obs}(a) = k_1(a - x) + k_2(x) \quad \text{or} \quad k_{obs} = k_1 + (k_2 - k_1)(x/a)$$

where 'x' is the concentration of the monoanion in equilibrium and 'a' the total stoichiometric concentration of all species. The quantity (x/a) represents the degree of primary dissociation and can be obtained from the known values of 'a', the measured value of pH and the first dissociation constant of the acid ($pK_a = 3.96$). The data should give a linear graph when the rate constants are plotted against the quantity (x/a) with an intercept equal to k_1 and a slope equal to $(k_2 - k_1)$. Fig. 1 represents such a plot from which k_1 is calculated to be 5.67×10^{-6} and k_2, 0.005×10^{-6} s^{-1}. Thus, k_2 is only about one-hundredth of k_1. The undissociated ethylmalonic acid decomposes about hundred times as fast as the monoanion and completely masks the reaction of the latter. The observed rate is, therefore, almost due to the decarboxylation of the free acid. The relative values of k_1 and k_2 for the decarboxylation of substituted malonic acid[3] are given in Table-4. An electron-attracting substituent on malonic acid favours the decomposition through the anion while an electron-releasing one aids decomposition through the free acid. The proportion of anionic and acid[3] decompositions should closely be related to the type and amount of substitution on the methylene group of the acid.

TABLE-4
RELATIVE RATES OF DECARBOXYLATION OF MALONIC ACID SPECIES

Acid	Relative rate	
	Acid	Anion
Ethylmalonic Acid	100	1
Malonic Acid	10	1
Phenylmalonic Acid	1	3–4
Dibromomalonic Acid	1	Very large

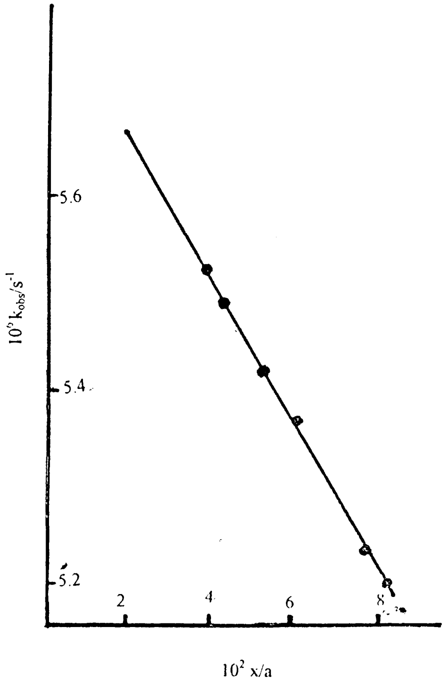


Fig. 1.

Effect of pH on the rate: In addition to the range of pH obtainable from the dissociation of the acid in aqueous solution, experiments have been carried out with calculated amounts of HCl and NaOH giving a total pH range of 1.65 to 4.91. The results so obtained are given in Table-5 and represented graphically in Fig. 2. The data confirm that the free acid undergoes decarboxylation at a rate very much faster than that of monoanion ($k_1 \gg k_2$). Thus the curve approaches a maximum for k_{obs}(5.6×10^{-6} s^{-1} at pH value= 2.0). At this pH region, ethylmalonic acid will exist mostly as the undissociated species thus accounting for the maximum rate. At higher pH values, the amount of the monoanion in equilibrium will increase and since the monoanion undergoes decomposition much slowly compared to the free acid, the effect of increasing pH is reduce the overall rate, which is indeed observed. At pH = 4.91, $k_{obs} = 1.60 \times 10^{-6}$ s^{-1}.

TABLE-5
EFFECT OF pH ON DECARBOXYLATION OF ETHYLMALONIC ACID

[Acid]/M	pH	$k_{obs} \times 10^6/s^{-1}$
0.0378	1.90	5.55
0.0380	1.65	5.57
0.0395	3.12	4.91
0.0390	3.44	4.40
0.0379	4.91	1.60

which indicates the presence of considerable amount of the slowly decomposing monoanion in equilibrium. Calculations based on the pK_a value of the acid show that at $pH = 4.91$, the fraction of monoanion in equilibrium is about 0.84, *i.e.*, 84% of the overall species. At still higher pH values, the rate should fall further. It has been noticed that the reaction becomes immeasurably slow as the pH is increased beyond 5.0.

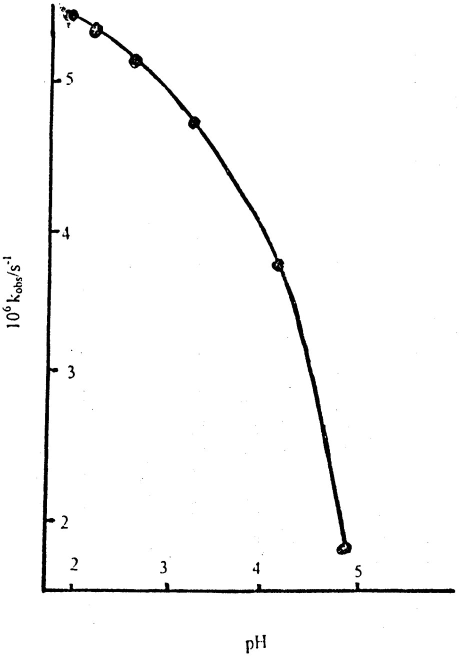


Fig. 2.

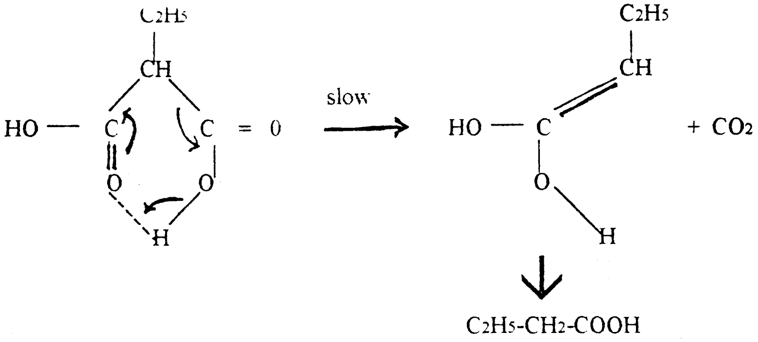
Effect of Dioxane on the rate: Experiments were performed keeping the substrate concentration constant at 0.040 M in various dioxane-water mixtures at 91.2°C. These values are given in Table-6. In all cases, no extraneous acid like HCl has been added and the pH would be in the vicinity of 2.60 due to the substrate concentration of 0.04 M. The variation of rate with changes in the

TABLE-6
EFFECT OF DIOXANE ON DECARBOXYLATION OF ETHYLMALONIC ACID

Dioxane % (v/v)	$k_{obs} \times 10^6/s^{-1}$
0	4.01
20	4.09
40	4.38
60	4.82
80	5.50
90	4.96

composition of the solvent indicates a maximum in the region 75–85% dioxane composition. A similar trend with a maximum rate in the region of 60–80% dioxane has been observed in the decarboxylation of phenylmalonic acid[4]. In this case, it is the monoanion which undergoes faster decomposition than the free acid and this trend has been explained as due to the increase in the rate of decarboxylation of the monoanion with increasing dioxane content of the solvent, *i.e.*, a kinetic solvent effect.

With ethylmalonic acid, since it is the free acid which decarboxylates faster, the observed increase in the rate may be explained as follows. The mechanism involving a transition state with an intra-molecular hydrogen bonding proposed for the decarboxylation of malonic acid may be assumed to operate in the present reaction, also. The mechanism can then be represented as below:



Two contributing factors appear to suggest possible explanations:

(i) With the increase in dioxane content of the solvent and the corresponding decrease in dielectric constant, the degree of dissociation of the free acid decreases, *i.e.*, in solvent mixture of low dielectric constant there is very little monoanion in equilibrium and hence more of the free acid available for reaction. This will enhance the rate which is cumulative of the simultaneous decarboxylation of the free acid and the monoanion. However, in view of k_1 being 100 times greater than k_2, the contribution to the enhanced rate by this factor should be small.

(ii) A kinetic solvent effect may operate, the dioxane molecule interacting with the acid molecule in the transition state, thereby favouring the decarboxylation of the free acid. Perhaps, both these factors are simultaneously operating. It will be difficult to resolve their respective contributions to the overall rate unless more is known about the exact dielectric nature of the mixture and also the relevance of dissociation constants as applied to mixed solvents.

Yet another explanation may lie in the relative 'availabilities' of the solvent molecules to facilitate the reaction. Water is highly associated. This association is broken down to some degree by the addition of a second solvent which is capable of hydrogen bonding with water.

On adding more and more dioxane, more and more water molecules would be pulled out of their association and forced to be associated with dioxane molecules. Dioxane itself is not associated in this fashion as there can be no hydrogen bonding involving dioxane molecules alone. Remembering that bulk water is represented as $(H_2O)_5$, *i.e.*, each water molecule is tetrahedrally surrounded by four other water molecules, on adding increasing amounts of dioxane, water molecules will be drawn apart to hydrogen-bond with the new species, breaking down the associated structure. Dioxane has a molecular weight of 88 while water, 18. The densities are nearly the same (density of dioxane at 20°C = 1.034). Therefore, in 82% dioxane, the mole fractions of water and of dioxane are nearly equal, *i.e.*, for each molecule of water in the mixture there is one molecule of dioxane present. In solvents of higher dioxane content more of its molecule will be present than water molecules; under these conditions, water molecules are more likely to coordinate with dioxane molecules than with each other (assuming, of course, that the hydrogen bond formed between water and dioxane is nearly of the same strength as that between two water molecules). This sudden change in the orientation (coordination) between solvent molecules in mixtures of >80% dioxane content will necessarily affect the rates of reactions taking place in their environment. This can explain the observed decrease in rate in this region.

The decrease in rate with higher percentage of dioxane may also be due to the fact that the intra-molecularly hydrogen-bonded structure, the precursor for the reaction is more favourable in water than in a solvent of the dioxane type. It is shown that the acid maleate ion contains an intramolecular hydrogen bond, which is stable in water, but not in dioxane. Such a situation may be analogous with ethylmalonic acid, too low a water content of the medium not favouring the hydrogen bonded intermediate.

Thermodynamic parameters: The reaction has been carried out at different temperatures in aqueous solution at a constant initial concentration of the acid.

Since the monoanion decarboxylates at a negligible rate compared to the free acid, these rate values may be taken to be due more or less entirely to that of the free acid. These values give a satisfactory Arrhenius plot and the activation parameters are given in Table-7. To examine the significance of these results, comparisons can be made with those of malonic and phenylmalonic acids.

Comparing the enthalpies of activation (computed error limit 2 units), one can notice the conspicuous trend, as expected. The $\Delta H^{\neq}$ value for ethylmalonic acid is higher than that for malonic acid, which can be explained on the basis of the strong $+I_s$ effect of the ethyl substituent. This results in a *diminished attraction* between the carbonyl carbon of the substrate and the solvent. The effect is opposite for phenylmalonic acid and accordingly, $\Delta H^{\neq}$ is minimum in this case.

TABLE-7
ACTIVATION ENERGIES FOR THE DECARBOXYLATION OF AQUEOUS MALONIC ACIDS

Acid	$\Delta H^{\neq}$/ kJ mol	$\Delta G^{\neq}$/ kJ mol	$\Delta S^{\neq}$/ e.u.
Ethylmalonic Acid	130	128	+ 3.4
Malonic Acid	126	127	- 0.4
Phenylmalonic Acid	100	113	- 8.2

The $\Delta S^{\neq}$ value for phenylmalonic acid is lower than that for malonic acid due to the bulky nature of the phenyl group. The ethyl group is bulkier than a hydrogen atom and it is reasonable to expect a more negative $\Delta S^{\neq}$ value for ethylmalonic acid, compared to malonic acid. A value in the region of –3 to –5 e.u., inbetween the values for malonic acid and phenylmalonic acid will be appropriate; but the actual value is +3.4 e.u. Barring experimental errors, this may be attributed to the steric factors operating in the *actual species*, which are involved in the activated complex formation. It has been suggested by Huckel that diacids exist as 'supermolecular clusters' of four or more molecules[7, 8]. The entropy values for the decarboxylation of diacids in the molten state concur well with this concept. Huckel's view has been extended by Clark to non-aqueous solutions as well, *i.e.*, in non-aqueous media also, he visualized the reacting entity of malonic acid to be a 'super-molecular cluster'. But, it is a moot point whether malonic acid and other diacids can exist as 'super-molecular clusters' in aqueous solution; the high hydrogen bonding capacity of water coupled with its dielectric properties is bound to break down the larger aggregates to varying degree, depending on the nature and identity of the substituted malonic acid. In aqueous solution, they may still exist as 'clusters', but perhaps, made of less than 4 units. And the size of this unit may vary with different substituted malonic acids.

Perhaps, though ethylmalonic acid itself is a larger molecule than malonic acid, the actual aggregate of the ethyl acid existing and reacting with water to form the activated complex may be, in effect, smaller than the aggregate cluster of malonic acid that exists in similar conditions. In other words, the smaller cluster of ethylmalonic acid leads to a greater probability of formation of the activated complex. This may account for the higher $\Delta S^{\neq}$ value. The lower $\Delta S^{\neq}$ value of phenylmalonic acid can be explained by the possibility that the aggregate of this species, whatever it be, is larger in size than those of both malonic and ethylmalonic acids. The free energy of activation at 100°C for ethylmalonic acid is higher than the value for malonic acid; thus, ethylmalonic acid undergoes slower decarboxylation than malonic acid. This can be attributed to the strengthening of the carbon-carbon bond by $+I_s$ effect of the ethyl substituent impeding the heterolytic cleavage. Bernoulli and Wege[9], while studying the decomposition of substituted malonic acids noticed that simple alkyl-substitution on the methylene group of malonic acid leads to decrease in reaction rates.

The activation parameters show that phenylmalonic acid falls apart from the other two acids—it has a low $\Delta G^{\neq}$ value. In this case, one is dealing with too powerful an electron-withdrawing substituent, so much so, the mechanism itself is shifted in favour of the anion decarboxylation.

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