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Solvent Effect on the Reaction of Decarboxylation of Malonic Acid. Correlation Analysis

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Abstract—Correlation analysis of the kinetics of thermal decarboxylation of dicarboxylic acids in various media has shown that adequate description requires taking into account the basicity, polarity, and molar volume of the solvent. The rate of the process increases with increase in these parameters, the effect of the basicity of the medium being the determining one, apparently, because of formation of the bond with the carboxylic carbon atom, facilitating the elimination of CO_2.

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Unsubstituted carboxylic acids are relatively thermally stable, although the presence of electron-acceptor groups in their molecules facilitates decarboxylation due to the assistance in the formation of the intermediate carbanion, as exemplified by rather high rate of decomposition of α-nitro- or trihaloacetates. The same is true for β-ketocarboxylic acids [1].

$$RCOOH \rightleftarrows RCOO^- + H^+; RCOO^- \rightleftarrows R^- + CO_2. \quad (1)$$

Similar to β-ketoacids, malonic acid and its substituted derivatives are decomposed, although at higher temperatures [2]. In aqueous medium the reaction follows the first order by two independent mechanisms: decomposition of non-dissociated acid and of the malonate ion [3], the rate of the former process being by an order of magnitude larger than that of the carboxylate ion. Therefore, the rate of decomposition in aqueous medium depends on the pH, the maximum rate being achieved at pH < 2. In organic media, the decomposition is accelerated with the growing dielectric constant of the medium, as well as at the addition of tertiary amines [4]. At 100°C the rate of decomposition of malonic acid in dioxane is comparable with that in water, in aniline and dimethylaniline it is tenfold higher, and in quinoline and pyridine, fifteen fold higher [5]. In binary mixtures of dioxane and quinoline the rate of decomposition increases linearly with the concentration of the latter. The IR spectroscopy data snow that in the solution of malonic acid in quinoline strong interaction of the components takes place leading to the shift of the C=O group frequencies. It was assumed that, unlike aqueous solutions, in which malonic acid forms with alkalies the slowly decomposing anion, in amines the interaction between the carboxylic carbon atom and the nitrogen atom of amine occurs promoting the decarboxylation.

The decomposition of malonic acid in different media was studied in detail in [6–9], where it was shown that the rate constants of decomposition substantially (by two orders of magnitude) vary depending on the nature of the solvent. In spite of a large number of the studied solvents (~30), Clark did not find any clear relationship between their properties and the rate of decomposition of malonic acid, or with the enthalpy of activation of the process. The obtained data allow only a conclusion that the increase of the negative charge on the nucleophilic atom of the solvent decreases the enthalpy of activation of the reaction. Steric effects can also play a significant role. Thus, the rate constant of decomposition in *o*-nitrotoluene is almost 1.5 times lower than in *m*-nitrotoluene [7], and in 8–methylquinoline it is substantially lower than in unsubstituted quinoline [8].

An attampt of a quantitative description of the reaction rate as a function of the solvent by means of

four-parameter equation was made in [10]. For 11 solvents at 120°C the equation was obtained with the multiple regression coefficient R 0.992:

$$\log (k\times10^5) = -(0.734\pm0.275) + (2.99\pm0.60)f(\varepsilon) + (0.0112\pm0.0005)B. \quad (2)$$

Here, e is dielectric constant, B is the basicity of the solvent by Palm [10]. The main factor affecting the rate of the reaction is the basicity of the medium, that is in compliance with the conclusion made in [5, 6].

We have recalculated the data from the above references using an extended equation:

$$\log k = a_0 + a_1(n^2-1)/(n^2+2) + a_2(\varepsilon-1)/(2\varepsilon+1) + a_3E_T + a_4B + a_5\delta^2 + a_6V_M, \quad (3)$$

where n is refraction index of the solvent, E_T its electrophilicity by Reichardt, B is basicity by Palm, δ is the Hildebrand solubility parameter proportional to cohesive energy of the medium, V_M is molar volume characterizing the structure of the solvent molecules and, hence, possible steric hindrances.

The data from [6, 8–11] on the first order rate constants for the reaction of decomposition of malonic acid at 140°C are given in Table 1. Unfortunately, only 15 solvents of the 29 studied can be used for analysis since for the others there are no data in the literature [12, 13] on the values of B or ε. These data are described by Eq. (4) with the value of R = 0.976:

$$\log (k\times10^5) = -2.764 + (1.166\pm1.800)f(n^2) + (5.336\pm1.196)f(\varepsilon) + (0.0046\pm0.0003)B + (0.0145\pm0.0110)E_T - (0.0003\pm0.0004)\times10^{-3}\delta^2 + (0.0057\pm0.0021)V_M,\ s\ \pm0.152. \quad (4)$$

The determining effect on the rate of the process is produced by the basicity of the medium, as indicated by the maximum value of the pair correlation coefficient between log k and B: r 0.934. This quantitatively proves the conclusion made in [5, 6] on the major role of the basicity of organic media in the process of decarboxylation of of malonic acid as a result of interaction between the components of the system. Other terms are insignificant (r within 0.2–0.3) or negligible since the standard deviations of their coefficients in the regression are larger than the coefficients themselves. To assess the significance of specific terms, they were excluded one by one, each time calculating the value of R for the obtained equations with smaller number of terms [14]. Finally, the data of Table 1 are satisfactorily described by Eq. (5):

$$\log (k\times10^5) = -1.543 + (4.832\pm1.119)f(\varepsilon) + (0.0045\pm0.0003)B + (0.0047\pm0.0018)V_M, \quad (5)$$

R 0.972; s ±0.163.

Further exclusion of the relatively insignificant term with V_M substantially worsens the correlation: R 0.958.

Table 1. Rate constants of decomposition of malonic acid at 140°C ($k\times10^5$ s^{-1}), experimental and calculated by Eq. (3) values of log ($k\times10^5$)

Run no.	Solvent	$k\times10^5$	log ($k\times10^5$)		
			experiment	calculated	Δlog k
1	Aniline	500.0 [7]	2.6990	2.3491	–0.3499
2	*N*-Methylaniline	440.0 [7]	2.6435	2.8309	0.1874
3	Dimethylaniline	418.0 [7]	2.6212	2.6168	–0.0044
4	Triethyl phosphate	520.0 [7]	2.7160	2.7369	0.0209
5	Pyridine	1110.0 [7]	3.0453	3.0679	0.0226
6	Diethylaniline	440.0 [7]	2.6435	2.3912	–0.2523
7	Glycerol	130.0 [7]	2.1139	2.1517	0.0378
8	Dimethylsulfoxide	920.0 [7]	2.9638	2.7451	–0.2187
9	α-Picoline	1080.0 [7]	3.0334	3.2144	0.1810
10	Nitrobenzene	28.3 [8]	1.4518	1.5490	0.0972
11	Quinoline	1607.0 [9]	3.2060	3.2341	0.0281
12	Anisole	13.5 [2]	1.1303	1.3357	0.2054
13	Phenol	33.7 [2]	1.5276	1.4412	–0.0864
14	4-Picoline	1517.0 [7]	3.1810	3.2514	0.0704
15	*o*-Nitrotoluene	33.6 [8]	1.5263	1.5872	0.0609

Table 2. Rate constants of decomposition of oxalic acid at 140°C ($k\times10^5$ s^{-1}), experimental and calculated by Eq. (6) values of log ($k\times10^5$)

Run no.	Solvent	$k\times10^5$	log ($k\times10^5$)		
			experiment	calculated	Δlog *k*
1	Aniline	14.5	1.1614	1.1147	–0.0467
2	*N*-Methylaniline	5.8	0.7634	0.8017	0.0383
3	Dimethylaniline	9.5	0.9777	0.9485	–0.0292
4	Quinoline	5.0	0.6990	0.6846	–0.0144
5	Triethyl phosphate	22.0	1.3424	1.3605	0.0181
6	Dimethylsulfoxide	9.5	0.9777	1.0116	0.0339

Table 1 includes the values of log ($k\times10^5$) calculated by Eq. (5) and their deviation from the experimental values, Δlog *k*. As can be seen, the deviations mainly fall within the limits $s = \pm0.163$ and, except for aniline, do not exceed $\pm2s$.

In the majority of the cited works the values of the enthalpy of activation of the reaction are also given, but we failed to clearly define the solvent effect on these values since all parameters of Eq. (3) are significant; the maximum values of the pair correlation coefficients *r* of ~0.5 are observed for $f(n^2)$ and *B*.

Decarboxylation of oxalic acid in solutions is more difficult; stoichiometric decomposition is observed only above 150°C [15, 16]; correspondingly, the energy of activation of the process is on the average by 16 kcal mol^{-1} higher, and the rate constants extrapolated to 140°C are 1.5–2 times lower than those for malonic acid. Nevertheless, the mechanism of the reaction is the same, as proved by the same pattern of the solvent effect on the reaction. The data from [16] on the first order rate constants for decarboxylation of oxalic acid in six solvents are given in Table 2.

Since the number of the solvents studied (six) is insufficient for their description by the use of the six-parameter Eq. (3), we tried to describe them using Eq. (6), taking into account only three factors, which turned out to be significant in the case of malonic acid, namely, basicity, polarity, and molar volume of the solvent.

$$\log (k\times10^5) = 33.001 - (2.884\pm0.031)f(\varepsilon) - (0.083\pm0.007)B + (0.085\pm0.015)V_M, \quad (6)$$
$$R\ 0.990;\ s\ \pm0.875.$$

The experimental and the calculated by Eq. (6) values of log ($k\times10^5$) are given in Table 2. However, the two-parameter Eq. (7) is also quite adequate:

$$\log (k\times10^5) = 32.540 - (0.080\pm0.006)B + (0.094\pm0.013)V_M, \quad (7)$$
$$R\ 0.989;\ s\ \pm0.947.$$

The value of the pair correlation coefficient *r* between log *k* and *B* is substantially lower, only 0.851. Therefore, unlike malonic acid, the effect of the solvent polarity on the rate is insignificant, and the increase of the basicity of the solvent slows down the reaction rather than accelerates it. Apparently, this is due to higher acidity of oxalic acid relative to malonic acid; as a result, both carboxylic groups are solvated in more basic solvents and the molecule is relatively stabilized. Oxalic acid is known to form the dihydrate.

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