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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

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KINETICS OF THE ACID-CATALYTIC DECARBONYLATION OF BENZOYLFORIC ACID

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An extensive literature is devoted to the question of the nature of the elementary act of acid-catalytic processes; however, the mechanisms most often proposed are based only on formal kinetic regularities. In the present work an attempt was made to detect the particles participating in the elementary act of acid processes and to correlate the rate constant with their concentration. As a model we chose the reaction of decarbonylation of benzoylformic acid $C_6H_5COCOOH \rightarrow CO + C_6H_5COOH$. Elliott and Hammick [1] investigated the kinetics of decarbonylation of $C_6H_5COCOOH$ by the rate of CO evolution.

Fig. 1. Dependence of the optical density of solutions of $C_6H_5COCOOH$ in H_2SO_4 on the concentration of H_2SO_4; $T = 15°$

Fig. 2. Kinetic curve of the decarbonylation reaction of $C_6H_5COCOOH$ in 99.94% H_2SO_4 and its logarithmic anamorphosis; $T = 15°$

They established that, with respect to $C_6H_5COCOOH$, the reaction is monomolecular, and that in the course of the process the rate constant K retains its constancy practically up to complete decomposition. They studied the catalytic action of H_2SO_4 in a narrow range of acid concentrations (from 94.05 to 98%). In this concentration interval the effective rate constant K is approximately proportional to the square of the acidity of the medium.

Solutions of benzoylformic acid in water and in dilute solutions of sulfuric acid do not absorb in the visible region of the spectrum. When $C_6H_5COCOOH$ is dissolved in concentrated H_2SO_4 (80-90%), absorption appears in the visible region of the spectrum; such a solution can be decolorized by diluting it with water. The absorption coefficient, for example ε^{400}, of a solution of benzoylformic acid in sulfuric acid increases strongly with increasing concentration of H_2SO_4 (see Fig. 1).

In the present work, the rate of decarbonylation of solutions of $C_6H_5COCOOH$ in H_2SO_4 was measured from the rate of decrease of the optical density of the solution at $\lambda = 400$ mμ. Measurements of optical density were carried out on an SF-4 spectrophotometer in quartz cuvettes.

Figure 2 presents one typical kinetic curve of the decarbonylation process (the dependence of the optical density of the solution D on time t) and its logarithmic anamorphosis.

The influence of the acidity of the medium h_0 on the magnitude of K was studied in the interval of H_2SO_4 concentrations from 85.46 to 99.94% at $T = 15°$. In Table 1 and in Fig. 3

these data are presented. In the acidity region from $h_0 = 10^{8.06}$ to $h_0 = 10^{9.4}$ there is a linear relationship between $\lg K$ and the acidity function

Table 1

No.	H_2SO_4, %	H_0	K, min^{-1}	C_φ	C_1	C_2	K/C_2
1	85.46	−8.06	$7.95 \cdot 10^{-6}$	0.97	$2.6 \cdot 10^{-2}$	$3.3 \cdot 10^{-5}$	0.24
2	89.77	−8.6	$8.32 \cdot 10^{-5}$	0.92	$8.5 \cdot 10^{-2}$	$3.7 \cdot 10^{-4}$	0.23
3	92.0	−8.9	$2.57 \cdot 10^{-4}$	0.84	0.16	$1.36 \cdot 10^{-3}$	0.2
4	94.34	−9.24	$1.17 \cdot 10^{-3}$	0.82	0.28	$5.4 \cdot 10^{-3}$	0.22
5	95.61	−9.43	$2.8 \cdot 10^{-3}$	0.61	0.38	$1.17 \cdot 10^{-2}$	0.24
6	96.2	−9.55	$3.75 \cdot 10^{-3}$	0.55	0.43	$1.62 \cdot 10^{-2}$	0.23
7	96.63	−9.60	$4.1 \cdot 10^{-3}$	0.51	0.47	$2.08 \cdot 10^{-2}$	0.2
8	96.74	−9.62	$5.2 \cdot 10^{-3}$	0.48	0.50	$2.24 \cdot 10^{-2}$	0.23
9	97.36	−9.74	$7.18 \cdot 10^{-3}$	0.42	0.54	$3.27 \cdot 10^{-2}$	0.22
10	97.39	−9.75	$7.57 \cdot 10^{-3}$	0.42	0.55	$3.38 \cdot 10^{-2}$	0.22
11	97.76	−9.83	$9.67 \cdot 10^{-3}$	0.38	0.58	$4.27 \cdot 10^{-2}$	0.23
12	97.82	−9.85	$11.5 \cdot 10^{-2}$	0.36	0.60	$4.6 \cdot 10^{-2}$	0.25

No.	H_2SO_4, %	H_0	K, min^{-1}	C_φ	C_1	C_2	K/C_2
13	98.18	−9.92	$1.46 \cdot 10^{-2}$	0.32	0.62	$5.7 \cdot 10^{-2}$	0.26
14	98.80	−10.02	$2.64 \cdot 10^{-2}$	0.24	0.67	$9 \cdot 10^{-2}$	0.29
15	99.18	−10.21	$3.93 \cdot 10^{-2}$	0.19	0.69	0.12	0.33
16	99.47	−10.38	$7.09 \cdot 10^{-2}$	0.12	0.7	0.18	0.39
17	99.90	−10.83	$14.4 \cdot 10^{-2}$	0.03	0.56	0.41	0.35
18	99.94	−10.93	0.16	0.03	0.52	0.45	0.36

Note. The values of K for 85.46, 89.77, and 92% H_2SO_4 were obtained by extrapolation from rates at high temperatures.

of acidity H_0: $\lg K + 1.8H_0 = \text{const}$. At higher acidities a deviation from this dependence is observed, and in the region close to 100% H_2SO_4 the rate constant increases even more slowly than would be expected with proportionality between $\lg K$ and H_0.

Fig. 3

Fig. 4

Fig. 3. Dependence of $\lg K$ on the acidity function H_0 at $T = 15°$.

Fig. 4. Temperature dependence of the rate constant for decarbonylation of benzoylformic acid at various concentrations of H_2SO_4. 1 $-C = 98.56\%$, $E =$ 22.1 kcal/mol; 2 $-C = 96.2\%$, $E = 22.7$ kcal/mol; 3 $-C = 92\%$, $E = 25.2$ kcal/mol; 4 $-C = 89.77\%$, $E = 25$ kcal/mol; 5 $-C = 85.46\%$, $E = 25$ kcal/mol.

The temperature dependence of K was determined for solutions of $C_6H_5COCOOH$ in 98.80, 96.2, 92, 89.77, and 85.46% H_2SO_4, but over a narrow temperature range. As can be seen from Fig. 4, these data fit the Arrhenius equation, but the activation energy determined in this way proves to depend on the acid concentration.

From the fact that solutions of $C_6H_5COCOOH$ in concentrated and dilute H_2SO_4 differ in color, it may be concluded that, in these media, benzoylformic acid exists in different forms. There is reason to believe that $C_6H_5COCOOH$ dissolved in dilute H_2SO_4 is in the nonionized state, whereas with increasing acidity of the medium (acid concentration) it undergoes ionization (protonation). In 72% and more dilute solutions

at $\lambda = 400$ mμ, $\varepsilon = 7.0$. We take this value as the absorption coefficient of the nonionized form of benzoylformic acid.

To determine the basicity constant, in addition to ε_0 it is necessary to know the absorption coefficient of the ionized form ε_1 and the acidity function of the medium H_0. The values of H_0 for solutions of H_2SO_4 at 15° were measured by us. If the optical densities $D = \varepsilon_0 C_0 + \varepsilon_1 C_1$ in solutions of different acidity are known, then ε_1 is determined from the equation

$$\Delta H_0 = \lg \frac{D_1 - \varepsilon_1}{D_2 - \varepsilon_2} + \lg \frac{D_2 - \varepsilon_0}{D_1 - \varepsilon_0}, \tag{1}$$

where ΔH_0 is the difference of the acidity functions of the solutions with optical densities D_1 and D_2. Having determined ε_1, one can calculate the value of pK_1 of the reagent.

In determining ε_1 we encountered the following fact. If one uses the values of D in the concentration interval from 90 to 96% H_2SO_4, then the average value of ε_1, calculated from equation (1), is equal to $2.95 \cdot 10^2$ and $pK_1 = -9.63$. In reality, however, at concentrations of H_2SO_4 close to 100%, the optical densities of $C_6H_5COCOOH$ are higher than would be expected by extrapolation from the value of pK_1 calculated in the interval from 90 to 96% H_2SO_4 (for example, at $C_{H_2SO_4} = 99.94\%$, $D = 4.7 \cdot 10^2$). If ε_1 is determined from values of D in the interval $C_{H_2SO_4}$ from 95 to 99.94%, then $\varepsilon^{400} = 53$. Such a discrepancy in the values of ε_1 cannot be explained by measurement error. We assume that the appearance of excess optical density at $\lambda = 400$ mμ of solutions of $C_6H_5COCOOH$ in H_2SO_4 at concentrations above 95% is connected with the appearance, at appreciable concentrations, of a new form—doubly protonated benzoylformic acid. Ionization of the type

$$\mathrm{RCOCOOH + H^+ \rightleftarrows RCOCO^+ + H_2O} \tag{2}$$

cannot be accepted for the first protonation of $C_6H_5COCOOH$. If scheme (2) is accepted, values of ε that are too small are obtained for the ionized form, and the large values of ε observed experimentally at high acidities cannot be explained. The second protonation may proceed either according to the scheme

$$\mathrm{C_6H_5C(^{+}OH) - C(=O) - OH + H^+ \rightleftarrows C_6H_5C(^{+}OH) - C(^{+}OH) - OH}, \tag{3}$$

or according to the scheme

$$\mathrm{C_6H_5C(^{+}OH) - C(=O) - OH + H^+ \rightleftarrows C_6H_5C(^{+}OH) - CO^+ + H_2O} \tag{4}$$

Taking into account the decrease in the concentration of the singly ionized form, with increasing h_0, $\lg K$ will be a rectilinear function of H_0 in the case of ionization according to scheme (3), and of J_0 in the case of ionization according to scheme (4). According to our experimental data, $\lg K$ is a rectilinear function of H_0 when the change in C_1 is taken into account. The value $pK_1 = -9.63$, determined in the concentration interval of H_2SO_4 from 90 to 96%, we ascribe to the singly protonated form. The absorption coefficient ε_2 and pK_2 of the doubly ionized form can be calculated from the equations

$$D = \varepsilon_0 C_0 + \varepsilon_1 C_1 + \varepsilon_2 C_2; \qquad H_0 = pK_2 + \lg \frac{C_1}{C_2}, \tag{5}$$

where the singly ionized form is the base.

Using equations (5), from the values of D in the concentration interval of H_2SO_4 from 97 to 99.94%, $\varepsilon_2 = 0.95 \cdot 10^3$ and $pK_2 = -10.96$ were calculated.

Thus, in our opinion, in sulfuric acid $C_6H_5COCOOH$ exists in three forms: as the nonionized form (C_0), the singly protonated form (C_1), and the doubly protonated form (C_2).

The values of pK_1 and pK_2 were used to calculate the relative concentrations C_0, C_1, and C_2 as functions of the acidity of the medium. Which of these forms of $C_6H_5COCOOH$ is reactive? Naturally—

but that the unprotonated form is not reactive. However, the singly protonated form is also not reactive, since no direct proportionality is observed between the rate constant K and C_1. As is seen from Table 1, over the range of variation of K from $8 \cdot 10^{-6}$ to 0.16 min^{-1}, K/C_2 is almost constant. On this basis we believe that in the rate-limiting step of the decarbonylation of benzoylformic acid the doubly ionized form participates

$$\begin{array}{c} \quad\;\; {}^{+}\mathrm{OH} \;\; {}^{+}\mathrm{OH} \\ \mathrm{C_6H_5C - C - OH.} \end{array}$$

To derive the rate equation of the process, let us denote the equilibrium constant of the first protonation $B + H^+ \rightleftharpoons BH^+$ by

$$K_1 = \frac{a_{BH^+}}{a_B a_{H^+}} = \frac{C_{BH^+}}{C_B a_{H^+}} \frac{f_{BH^+}}{f_B} = \frac{C_{BH^+}}{C_B} \frac{1}{h_0} \tag{6}$$

and the equilibrium constant of the second protonation $BH^+ + H^+ \rightleftharpoons BH_2^{++}$ by

$$K_2 = \frac{a_{BH2^{++}}}{a_{BH^+} a_{H^+}} = \frac{C_{BH2^{++}}}{C_{BH^+} a_{H^+}} \frac{f_{BH2^{++}}}{f_{BH^+}} = \frac{C_{BH2^{++}}}{C_{BH^+}} \frac{1}{h_+}. \tag{7}$$

Using the balance equation $C_0 + C_1 + C_2 = C$ and relations (6) and (7), we obtain the general expression for the concentration of the doubly ionized form

$$C_{\mathrm{BH2}^{++}} = \frac{K_1 K_2 h_0 h_+}{1 + K_1 h_0 + K_1 K_2 h_0 h_+} C.$$

Assuming that the molecules BH_2^{++} are in equilibrium with the activated complex $(BH_2^{++})^*$, the rate equation of the process can be expressed as follows:

$$-\frac{dC}{dt} = W = K'_{\mathrm{ist}} \frac{a_{(\mathrm{BH2}^{++})^*}}{f_{(\mathrm{BH2}^{++})^*}} = K_{\mathrm{ist}} \frac{C_{\mathrm{BH2}^{++}} f_{\mathrm{BH2}^{++}}}{f_{(\mathrm{BH2}^{++})^*}}. \tag{8}$$

In this process the composition of the activated complex $(BH_2^{++})^*$ is the same as that of the doubly protonated molecule BH_2^{++}. Therefore there is every reason to assume that the activity coefficients of the activated complex $f_{(\mathrm{BH2}^{++})^*}$ and of the doubly protonated molecule $f_{(\mathrm{BH2}^{++})}$ are equal. Taking $f_{\mathrm{BH2}^{++}} = f_{(\mathrm{BH2}^{++})^*}$, we obtain

$$-\frac{dC}{dt} = K_{\mathrm{ist}} C_{\mathrm{BH2}^{++}} = K_{\mathrm{ist}} \frac{K_1 K_2 h_0 h_+}{1 + K_1 h_0 + K_1 K_2 h_0 h_+} C = KC; \tag{9}$$

K_{ist} is the true rate constant.

As is seen from equation (9), in the presence of several equilibrium forms of the reacting substance, in the case of a monomolecular process the rate constant K determined experimentally is an effective one. The effective constant is the product of the true rate constant and the fraction of reactive molecules among the total number of molecules of the reacting substance. Only in the case when all molecules of the reacting substance are in the reactive form (in our case, as BH_2^{++}) is the rate constant determined the true one. Since at H_2SO_4 concentrations of about 99.94% high concentrations of $C_{\mathrm{BH2}^{++}}$ ($0.4C$) are reached, the activation energy at such acidities ($E = 21.8$ kcal/mol) may be taken as the true one.

Taking $E_{\mathrm{ist}} = 21.8$ kcal/mol, we calculated the preexponential factor of the process; this value is $1.5 \cdot 10^{14}$, which is close to normal values of preexponential factors for monomolecular processes.

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CITED LITERATURE

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