Studies of Chemical Kinetics by Means of the Velocity of Sound. II. The Condensation of Acetaldehyde to Aldol

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Bell[1,2] and Matsuyama[3] have investigated the kinetics of the condensation of acetaldehyde to aldol. In his earlier work Bell concluded, from his dilatometric study, that this reaction is of the first order with respect to acetaldehyde concentration and that the reaction velocity is proportional to the concentration of the OH^- catalyst. A major drawback in his experimental setup was that the scale of the dilatometer was not corrected for the increase in temperature in the reaction system at the initial state of this reaction. In his report in 1960, on the other hand, he concluded, from the ultraviolet absorption study, that the reaction is of the second order. With his method it is difficult to measure the time and to control the temperature accurately without disturbing the reaction system, because a part of the solution has to be removed. Matsuyama has also studied the same reaction system with a calorimetric method and has concluded that it is of the second order and that the relation between the velocity constant and the concentration of OH^- is linear. It is objectionable, however, to use, as in his study, a Beckmann thermometer with such a large heat capacity in order to measure the change in temperature in the reaction system. As has been described in a previous paper,[4] we measured the velocity of sound by means of a sing-around velocimeter in order to study the change in the chemical reaction with time. In this work we will attempt to study the condensation of acetaldehyde to aldol by the same method as has been used previously.

Theoretical

It is highly likely that the change in the velocity of sound is in proportion to the concentration of acetaldehyde, provided that the change in the concentration is comparatively small. Therefore,

$$C_1-C_\infty=\alpha(f_1-f_\infty) \tag{1}$$

$$C_i-C_\infty=\alpha(f_i-f_\infty) \tag{2}$$

where C_1, C_i, C_∞, f_1, f_i, and f_∞ are the concentrations of acetaldehyde and the pulse repetition frequencies at times t_1, t_i and t_∞ respectively, t_1 being the starting time for the measurement, and where α is a proportionality constant. By subtraction,

$$C_1-C_i=\alpha(f_1-f_i) \tag{3}$$

If this reaction is of the second order with respect to the acetaldehyde concentration and if no product reacts consecutively during the measurement, the reaction may be expressed by:

$$1/(a-x)=kt+1/a \tag{4}$$

where a is the initial concentration of acetaldehyde; x, the decrease in the concentration of acetaldehyde after the lapse of time, t, and k, the velocity constant. Equation 4 can be expressed with C in place of a and x:

$$1/(C_i-C_\infty)=k\Delta t_i+1/(C_1-C_\infty) \tag{5}$$

Thus:

$$(C_1-C_i)/\{(C_1-C_\infty)(C_i-C_\infty)\Delta t_i\}=k \tag{6}$$

or $$(C_1-C'_i)/\{(C_1-C_\infty)(C'_i-C_\infty)\Delta t'_i\}=k \tag{7}$$

where $\Delta t_i=t_i-t_1$, $\Delta t'_i=t'_i-t_1$, and C'_i is the concentration of acetaldehyde at $t=t'_i$. From Eqs. 6 and 7,

$$(C_1-C_i)/\{(C_1-C_\infty)(C_i-C_\infty)\Delta t_i\} \\ =(C_1-C'_i)/\{(C_1-C_\infty)(C'_i-C_\infty)\Delta t'_i\} \tag{8}$$

From Eqs. 1, 2, 3 and 8,

$$f_1-f_\infty=\{(f_1-f_i)(f_1-f'_i)(\Delta t'_i-\Delta t_i)\}/ \\ \{(f_1-f_i)\Delta t'_i-(f_1-f'_i)\Delta t_i\} \tag{9}$$

where f'_i is the pulse repetition frequency at $t=t'_i$. Equation 5 may also be rewritten as follows:

$$1/(f-f_\infty)=1/\{(f_1-f_\infty)-(f_1-f)\}= \\ \alpha k\Delta t+1/(f_1-f_\infty) \tag{10}$$

Therefore, if a plot of $1/(f-f_\infty)$ obtained from Eqs. 9 and 10 against Δt is linear, the reaction must be of the second order. On the other hand, if this reaction is of the first order, the reaction is given as follows:

$$\ln(f-f_\infty)=\ln\{(f_1-f_\infty)-(f_1-f)\}= \\ -k\Delta t+\ln(f_1-f_\infty) \tag{11}$$

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[1] R. P. Bell, *J. Chem. Soc.*, **1937**, 1636.

[2] R. P. Bell and P. T. McTigue, ibid., **1960**, 2983.

[3] H. Matsuyama, *Proc. Japan Acad.*, **27**, 552 (1951).

[4] T. Yasunaga, N. Tatsumoto and M. Miura, This Bulletin, **37**, 1655 (1964).

Therefore, f_1-f_∞ is given in Eq. 12 under the condition that $2\Delta t_i=\Delta t'_i$:

$$f_1-f_\infty=(f_1-f_i)^2/(f_1+f'_i-2f_i) \qquad (12)$$

If the experimental values of $\ln(f-f_\infty)$ plotted against Δt satisfy Eq. 11, giving a linear curve, then the reaction is probably of the first order.

Experimental

The condensation of acetaldehyde to aldol has been investigated in a dilute aqueous solution of sodium hydroxide (0.0050—0.0145 M). The reagent was extra pure grade acetaldehyde in an ampoule and used without further purification. The acetaldehyde was diluted with air-free water in order to prepare about 0.57 mol./l. of an aqueous solution. The concentration of acetic acid contained in this solution was found to be 0.002 mol./l. by titration.

The sample and the catalyst solution were then mixed in a flask and transferred from it into a cell. Before each measurement, air was replaced with nitrogen. The measurements were carried out in a water bath at 25°C. The temperature was observed in the water bath with a Beckmann thermometer and inside the cell with a thermistor thermometer. (A detailed description of our sing-around velocimeter was given in the previous paper.[4]) As a result of the mixing of the sample solution with the catalyst, the temperature in the reacting system began to rise in seven to ten minutes and reached an equilibrium with the bath temperature, 25°C, in thirty minutes. The correction for the velocity of sound, therefore, should be made for the temperature rise in the initial stage of the reaction. Measurement over a long period is not desirable in this study, for subsequent reactions would probably occur in this system.

Results

The changes in the velocity of sound, corrected for the temperature change with time, are shown in Fig. 1 for a dilute aqueous solution of sodium hydroxide (0.0050—0.0145 M). The changes in the values for $1/(f-f_\infty)$ and $\ln(f-f_\infty)$ with time are plotted in Figs. 2 and 3 respectively. A comparison of the two curves shows that the results from the former give a better linearity than those from the latter. That is, all of the curves for the former are linear, but those for the latter deviate from the linear line, passing through three points, $\log(f_1-f_\infty)$, $\log(f_i-f_\infty)$ and $\log(f'_i-f_\infty)$. Hence, this reaction is probably of the second order within the period studied here.

Discussion

The above experimental results can be explained on the basis of a reaction scheme[5] of

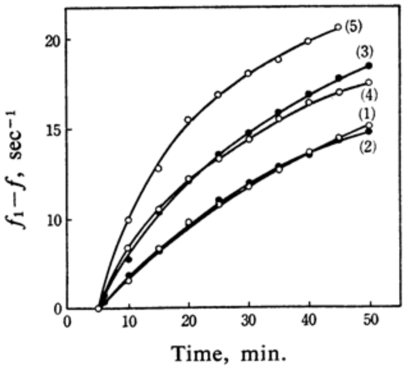

Fig. 1. Change in the repetition frequency with time.

	a, M	Concn. of NaOH M
(1)	0.4339	0.0015
(2)	0.4339	0.0019
(3)	0.3978	0.0040
(4)	0.3409	0'0080
(5)	0.4009	0.0145

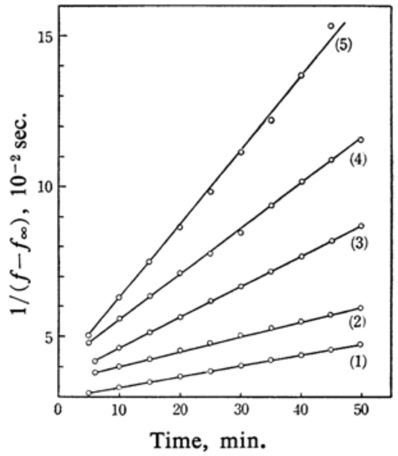

Fig. 2. Change in reciprocal of the difference between f and f_∞ with time.

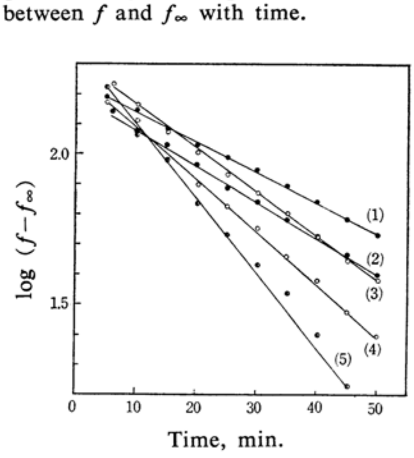

Fig. 3. Change in logarithm of the difference between f and f_∞ with time.

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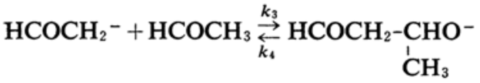
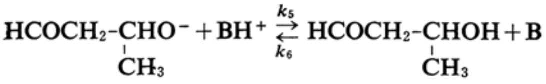
5) A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons Inc., New York, London (1961), p. 335.

the following condensation of acetaldehyde:

$$HCOCH_3 + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} HCOCH_2^- + BH^+ \tag{13}$$



$$HCOCH_2^- + HCOCH_3 \underset{k_4}{\overset{k_3}{\rightleftarrows}} HCOCH_2\text{-}\underset{\substack{| \\ CH_3}}{C}HO^- \tag{14}$$



$$HCOCH_2\text{-}\underset{\substack{| \\ CH_3}}{C}HO^- + BH^+ \underset{k_6}{\overset{k_5}{\rightleftarrows}} HCOCH_2\text{-}\underset{\substack{| \\ CH_3}}{C}HOH + B \tag{15}$$

where B is a base and k is the velocity constant. The last step being very fast, the above scheme can be reduced to:

$$HCOCH_3 + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} HCOCH_2^- + BH^+ \tag{16}$$

$$HCOCH_2^- + HCOCH_3 \xrightarrow{k_3} \text{Product} \tag{17}$$

Thus,

$$[HCOCH_2^-] = \{k_1[HCOCH_3][B]\}/\{k_3[HCOCH_3] + k_2[BH^+]\} \tag{18}$$

$$d[\text{product}]/dt = \{k_1k_3[HCOCH_3]^2[B]\}/\{k_3[HCOCH_3] + k_2[BH^+]\} \tag{19}$$

Two limiting cases, in which $k_3[HCOCH_3]$ is much greater or much smaller than $k_2[BH^+]$, are of interest. The first case leads to:

$$\text{rate} = k_1[HCOCH_3][B] \tag{20}$$

and the second to:

$$\begin{aligned}\text{rate} &= k_1k_3[HCOCH_3]^2[B]/k_2[BH^+] \\ &= k_1k_3[HCOCH_3]^2[S^-]/k_2K_B\end{aligned} \tag{21}$$

where K_B is the ionization constant of the base and S^- is the anion of the solvent, SH. If $k_3[HCOCH_3]$ is greater than $k_2[BH^+]$, the reaction is of the first order. As $[HCOCH_3]$ approaches zero, the rate must become second order with respect to the concentration of acetaldehyde. The concentration of acetaldehyde is so dilute in this study that these reactions would be second order.

The above consideration leads to the conclusion that the measurement of the velocity of sound is a useful method for the study of the chemical kinetics of simple reactions as in our present and previous papers. Further, considering the advantageous characteristics of the sing-around velocimeter, we expect that this method can be extended to the study of the kinetics of the fast reaction, which is difficult to measure with other methods.

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