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Kinetics of Conversion of Diacetylacetone in Aqueous Solution[1,2]

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The influence of pH on the conversion of diacetylacetone in aqueous solution and its mechanistic pathway were investigated in detail. And it was concluded that diacetylacetone converts completely to 2,6-dimethyl-4-pyrone in acidic region (pH —5), the main reaction in neutral region (pH 5—10), the intermolecular condensation of undissociated diacetylacetone, is catalyzed by specific base, general acid and base (buffer components), and diacetylacetone decomposes *via* a parallel reaction path involving acetylacetone and acetoacetate as the important intermediates in lower alkaline region. A kinetic approach was quite effective for investigation in alkaline region.

Previously, the degradation of dehydroacetic acid (DHA), one of the officially recognized food preservatives in Japan, in acidic aqueous solution was reported,[4] and it was shown that diacetylacetone (DAA) was identified by means of gas chromatography as the major intermediate of DHA degradation. In order to characterize the stability of DHA in aqueous solution, it seems first necessary to study the reactivity of DAA in aqueous solution in more detail. Moreover the kinetic study of DAA degradation has apparently not been reported to date.

The present work is aimed at extensively kinetic investigation on behavior of DAA in the whole pH region.

Experimental

Preparation of Diacetylacetone (DAA), 7-Acetyl-3,8-dihydroxy-3,6-dimethyl-1-tetralone (tetralone) and 2-Acetyl-3,6-dimethylnaphthalene-1,8-diol (naphthalenediol)——These compounds were prepared by the literature of Bethell, *et al.*[5]

2,6-Dimethyl-4-pyrone (DMP)——Dehydroacetic acid (40 g) and concentrated hydrochloric acid (400 ml) were boiled until the evolution of CO_2 ceased. The solution was neutralized with sodium carbonate, and extracted with chloroform. The solvent was removed. The residue was recrystallized from chloroform–ether; mp 132°, yield 20 g.

3-Acetonyl-2,6-diacetyl-5-methylphenol (benzene derivative)——The barium salt of DMP (2 g) was added to 20% acetic acid (10 ml) and then kept at room temperature for 4 days. The precipitate obtained was recrystallized from benzene; mp 113°, yield 0.7 g.

General Procedure for Kinetic Study——DAA was dissolved in hydrochloric acid, sodium hydroxide and various buffer solutions, respectively. And the pH values of buffer solutions were determined with a Hitachi–Horiba pH meter of the M-4 type using glass–saturated calomel electrodes. In the cases of hydrochloric acid and sodium hydroxide solutions, the pH values were calculated from Eq. (1) and (2):[6]

$$\mathrm{pH} = -\log f_{\mathrm{HCl}}[\mathrm{HCl}] \tag{1}$$

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{w}} + \log f_{\mathrm{NaOH}}[\mathrm{NaOH}] \tag{2}$$

where f_{HCl} and f_{NaOH} are the mean activity coefficients of hydrochloric acid and sodium hydroxide, and are given at various temperatures, and HCl and NaOH concentrations.[7] The $\mathrm{p}K_{\mathrm{w}}$ is obtained from the litera-

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[1] This forms Part III of "Kinetics of Reaction of Dehydroacetic acid."

[2] Part II: S. Goto, A. Kono and S. Iguchi, *J. Pharm. Sci.*, **57**, 791 (1968).

[3] Location: *Katakasu, Fukuoka.*

[4] T. Aoyama, S. Iguchi and M. Yamamoto, *Shokuhin Eiseigaku Zasshi*, **8**, 33 (1967).

[5] J.R. Bethell and P. Maitland, *J. Chem. Soc.*, **1962**, 3751.

[6] E.R. Garrett, *J. Pharm. Sci.*, **51**, 811 (1962).

[7] H.S. Harned and B.B. Owen, "The Physical Chemistry of Electrolytic Solutions" 3rd edition, Reinhold Publishing Co., New York, 1958, pp. 716 and 729.

ture.8) The ionic strength of solution was adjusted to a constant value by adding sodium chloride. The solution was transfered to a glass volumetric flask and placed in a constant temperature bath maintained at 60°. Aliquots were withdrawn at regular time intervals and diluted with adequate solvents in another volumetric flask. The progress of reaction was determined by measuring the amounts of residual DAA or products spectrophotometrically and gas chromatographically.

Gas Chromatographic Analysis——1) Apparatus and Condition: A Shimadzu Model GC-1B gas chromatograph equipped with a differential hydrogen flame ionization detection system type HFD-1 and a U-shaped stainless column, 75 cm in length and 4 mm in internal diameter, were used. A column packing was 30% DC–550 silicone oil/celeite 545 (80—100 mesh). The gas chromatography parameters for DAA and acetylacetone (AA) were as follows; Column temperature, 150°; detector temperature, 200°; nitrogen flow rate, 25 ml/min (inlet pressure 2 kg per cm^2).

2) Calibration Curve: The various amounts, 2—15 mg, of DAA were weighed and dissolved in 1 ml of 0.2% 3,4-dimethyl phenol (Internal standard) in acetone. Two μl of sample solution was injected with a 10.0 μl Hamilton microsyringe into a column. A straight line passing through origin was obtained for calibration curve by plotting the weight ratios against the peak height ratios of DAA to 3,4-dimethylphenol (Internal standard).

3) Sample Preparation: The sample solution that was carefully neutralized was added into 20 ml acetate buffer (pH 5). The above solution was then extracted by chloroform (30 ml) twice. The solvent was evaporated. The sample for gas chromatography was prepared by addition of 0.03 or 0.2% 3,4-dimethylphenol (Internal standard) in acetone.

Thin-Layer Chromatographic Analysis——The thin–layer plates (5 × 20 cm) were coated with Kieselgel G (Merck). After a sample was spotted on the plates, the plates were developed with $\mathrm{CCl_4}$–$\mathrm{AcOC_2H_5}$ (5:1). For the detection of benzene derivative, tetralone and naphthalendiol, a $\mathrm{FeCl_3}$–$\mathrm{CH_3OH}$ reagent was used. The Dragendorff's reagent was used for detection of DMP. Moreover, when the developed plates were exposed to iodine vapor in a sealed box, a visible spot for orcinol was recognized.

Determination of Acetone in Alkaline Degraded DAA Solution——Twenty ml of sample solution was transfered in 150 ml water containing 4 ml of 10% phosphoric acid. The above solution was distilled during about 25 min. A trip of distiller put in water in a receiver which must be cooled with ice water. A distillate was added into a mixture of 30 ml of 40% KOH and 50 ml of 0.1N J_2. After 5 min standing, a concentrated hydrochloric acid was added in solution. The solution was titrated with 0.1N sodium thiosulfate.

Determination of Acetic Acid in Alkaline Degraded DAA Solution——The procedure is essentially similar to that of determination for acetone. However a concentrated phosphoric acid was used instead of 10% phosphoric acid and a steam–distillation was adopted instead of a distillation. A distillate was titrated with 0.01N NaOH.

Determination of Acetylacetone (AA) by Spectrophotometric Method——The sample solution was neutralized with a diluted hydrochloric acid and then an acetate buffer was added (pH 5). The solution was extracted with chloroform (20 ml) twice. The extract was diluted with chloroform adequately. And the chloroform solution was read at 280 mμ and 320 mμ. The concentrations of DAA and AA were calculated by following equations:

$$A_{280}=E_{280}^{\mathrm{DAA}}[\mathrm{DAA}]+E_{280}^{\mathrm{AA}}[\mathrm{AA}] \tag{3}$$

$$A_{320}=E_{320}^{\mathrm{DAA}}[\mathrm{DAA}] \tag{4}$$

where A_λ is the absorbance at wavelength λ in mμ, and [DAA] and [AA] are molar concentrations of DAA and AA. Molar absorptivity values are $E_{280}^{\mathrm{DAA}}=8940$, $E_{280}^{\mathrm{AA}}=8800$, $E_{320}^{\mathrm{DAA}}=6230$.

Results and Discussion

Conversion in Diluted Hydrochloric Acid Solution (pH -2)

It is well–known that DAA converts easily to DMP in hydrochloric acid, but a complete knowledge on the reaction rate and a pH dependency of this conversion have not been presented. The reaction was proceeded in the constant temperature bath maintained at 60°. The samples were drawn at timed intervals from a reaction solution and the reaction was quenched by cooling in ice water. The wavelengths of 250 mμ and 280 mμ were chosen for the kinetic study, and the concentrations of DAA and DMP were calculated by using the following simultaneous equations:

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8) A. Albert and E.P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co., London, 1962, p. 171.

$$A_{250}=E_{250}^{\mathrm{DMP}}[\mathrm{DMP}]+E_{250}^{\mathrm{DAA}}[\mathrm{DAA}] \tag{5}$$

$$A_{280}=E_{280}^{\mathrm{DMP}}[\mathrm{DMP}]+E_{280}^{\mathrm{DAA}}[\mathrm{DAA}] \tag{6}$$

Molar absorptivity values are $E_{250}^{\mathrm{DMP}}=15230$, $E_{280}^{\mathrm{DMP}}=310$, $E_{250}^{\mathrm{DAA}}=3040$, $E_{280}^{\mathrm{DAA}}=7800$, where [DMP] is molar concentration of DMP.

The apparent first-order rate constants in sec^{-1} for the disappearance of DAA and formation of DMP were calculated from the slopes of the plots of the logarithms of these absorbances against time. And these rate constants were completely identical. The conditions and the first-order rate constants for the reaction of DAA in hydrochloric acid solution are given in Table I.

Table I. Conditions and Observed First-order Rate Constants (k in sec^{-1}) for Acid Catalyzed Conversion of Diacetylacetone[a)]

[HCl]	pH[b)]	10^5k
0.01	2.01	0.600
0.05	1.35	2.36
0.10	1.06	4.69
0.20	0.77	11.1 (10.9[c)])
0.30	0.60	13.4

a) initial concentration, $1.41\times10^{-5}\,\mathrm{M}$

b) The pH values listed were calculated from the equation (1).

c) Determined from gas chromatographic data.

The apparent first-order rate constant (k) for the reaction of DAA can be written in terms of microscopic rate constants as:

$$\left.\begin{aligned} k=&(k_{\mathrm{H}^+}[\mathrm{H}^+]+k_0+k_{\mathrm{OH}^-}[\mathrm{OH}^-])\frac{[\mathrm{H}^+]^2}{[\mathrm{H}^+]^2+K_{\mathrm{a1}}K_{\mathrm{a2}}+K_{\mathrm{a1}}[\mathrm{H}^+]}\\ &+(k'_{\mathrm{H}^+}[\mathrm{H}^+]+k'_0+k'_{\mathrm{OH}^-}[\mathrm{OH}^-])\frac{K_{\mathrm{a1}}[\mathrm{H}^+]}{[\mathrm{H}^+]^2+K_{\mathrm{a1}}K_{\mathrm{a2}}+K_{\mathrm{a1}}[\mathrm{H}^+]}\\ &+(k''_{\mathrm{H}^+}[\mathrm{H}^+]+k''_0+k''_{\mathrm{OH}^-}[\mathrm{OH}^-])\frac{K_{\mathrm{a1}}K_{\mathrm{a2}}}{[\mathrm{H}^+]^2+K_{\mathrm{a1}}K_{\mathrm{a2}}+K_{\mathrm{a1}}[\mathrm{H}^+]} \end{aligned}\right\} \tag{7}$$

where K_{a1} and K_{a2} are the dissociation constants of DAA,[9,10] k_{H^+} and k_{OH^-} are the bimolecular rate constants for hydrogen and hydroxyl ions catalyzed conversion of undissociated DAA, k'_{H^+} and k'_{OH^-} are the bimolecular rate constants for hydrogen and hydroxyl ions catalyzed conversion of monoanionic DAA, k''_{H^+} and k''_{OH^-} are the bimolecular rate constants for hydrogen and hydroxyl ions catalyzed conversion of dianionic DAA, and k_0, k'_0 and k''_0 are the rate constants for solvent catalyzed conversion of the undissociated, monoanionic and dianionic DAA, respectively.

Since DAA presents as undissociatd form and the concentrations of hydroxyl ion is almost zero in acidic region, the equation (7) reduces to:

$$k=k_{\mathrm{H}^+}[\mathrm{H}^+]+k_0 \tag{8}$$

A plot of the apparent first-order rate constant (k) against the hydrogen ion activity estimates k_{H^+} from the slope and k_0 from the intercept. The values of k_{H^+} and k_0 were obtained to be $5.0\times10^{-4}\,\mathrm{M}^{-1}\mathrm{sec}^{-1}$, and $2.3\times10^{-6}\,\mathrm{sec}^{-1}$ at 60°, respectively.

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[9] G.K. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, **23**, 1162 (1940). According to the above literature, $\mathrm{p}K_{\mathrm{a1}}$ and $\mathrm{p}K_{\mathrm{a2}}$ of DAA determined by means of pH measurements were 7.4 and 13.5.

[10] J. Stuehr, *J. Am. Chem. Soc.*, **89**, 2826 (1967).

From the fact that the sum of molar concentrations of DAA and DMP during experimental period maintains a constant value (initial concentration of DAA), it may be concluded that DAA converts to DMP in hydrochloric acid solution completely. And single isosbestic point of absorption spectra in Fig. 1. suggests that the conversion reaction proceeds with no intermediates detectable by spectrophotometric means.

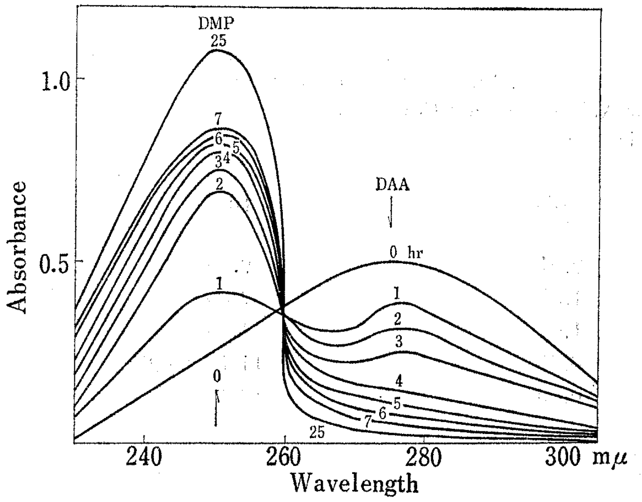

Fig. 1. Typical Spectrophotometric Change as a Function of Time in 0.2N Hydrochloric Acid of Diacetylacetone

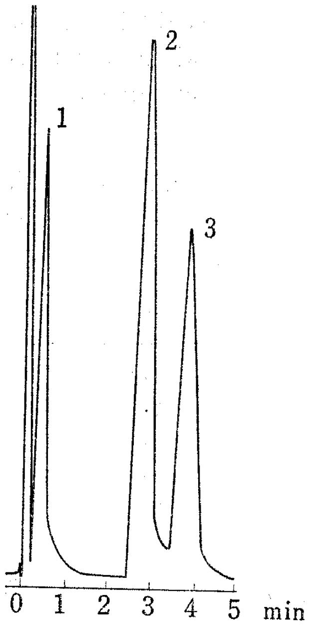

Fig. 2. Gas Chromatogram of Mixture of Acetylacetone, Diacetylacetone and 3,4-Dimethylphenol

peak 1, acetylacetone; peak 2, diacetylacetone; peak 3, 3,4-dimethylphenol (internal standard)

The gas chromatographic method was adopted for determination of the conversion rate of DAA. The gas chromatogram for DAA and AA is shown in Fig. 2. The rate constant obtained agrees approximately with the vlaue by spectrophotometric method. The result in 0.2N HCl is given in Table I.

Conversion in Acetate Buffer Solution (pH 3—5)

Diacetylacetone (DAA) transformed readily into DMP at acetate buffer region. Therefore, it will demonstrate that the conversion mechanism of DAA in an acetate buffer solution is analogous to that in a hydrochloric acid solution. This conversion reaction is graphic example of general acid catalyzed reaction. The apparent first-order rate constant (k) is plotted against the acetic acid concentration at constant pH and constant ionic strength.

In Fig 3 the curves for the conversion reaction of DAA at pH 3.2 and 4.1 have the same slope, and thus only general acid catalyzed reaction is concluded.

The above fact is considered as follows: the apparent first-order rate constant can be dis-

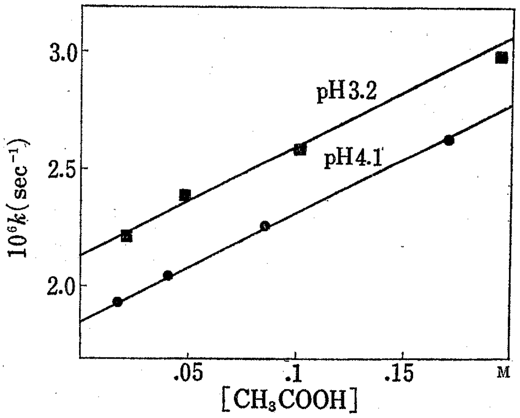

Fig. 3. Effect of Varying Acetic Acid Concentration at Constant Ionic Strength on Apparent First-order Rate Constants of Reaction of Diacetylacetone at 60°

sected into the component contributions of acid (k_{HAc}) and base (k_{Ac}) catalyzed rate constants:

$$k=\left(k_{\mathrm{HAc}}\frac{[\mathrm{H}^+]}{[\mathrm{H}^+]+K_{\mathrm{a}}'}+k_{\mathrm{Ac}}\frac{K_{\mathrm{a}}'}{[\mathrm{H}^+]+K_{\mathrm{a}}'}\right)[\mathrm{HAc}]_T+k'$$

$$=\left(k_{\mathrm{HAc}}+k_{\mathrm{Ac}}\frac{K_{\mathrm{a}}'}{[\mathrm{H}^+]}\right)[\mathrm{HAc}]+k' \qquad (9)$$

where K'_{a} is the dissociation constant of acetic acid (1.54×10^{-5} at 60°),[11] $[\mathrm{HAc}]_T$ represents the total concentration of acetic acid and acetate ion and k' is the sum of the rate constants for the specifc acid catalyzed reaction and solvent catalyzed reaction of DAA.

In equation (9), a coefficient $\left(k_{\mathrm{HAc}}+k_{\mathrm{Ac}}\frac{K'_{\mathrm{a}}}{[\mathrm{H}^+]}\right)$ represents the slopes in Fig. 3 and $k_{\mathrm{Ac}}\frac{K'_{\mathrm{a}}}{[\mathrm{H}^+]}$ is variable with pH changes. Therefore, it will be concluded that the general base catalyzed rate constant (k_{Ac}) must be zero from the fact that the curves in Fig. 3 have a same slope. The acetic acid catalyzed rate constant (k_{HAc}) was calculated to be 4.5×10^{-6} $\mathrm{sec}^{-1}\mathrm{M}^{-1}$ at 60°.

Conversion in Neutral Region (pH 5—10)

The self-condensation involved intermolecular reaction of two DAA units occurs in neutral region. Already several authors[5,12,13] have shown that the condensation of DAA proceeds through benzene derivative and tetralone to naphthalenediol finally (Chart 1). The constitution of these reaction products has been rigorously proved by Bathell, *et al.*[5]

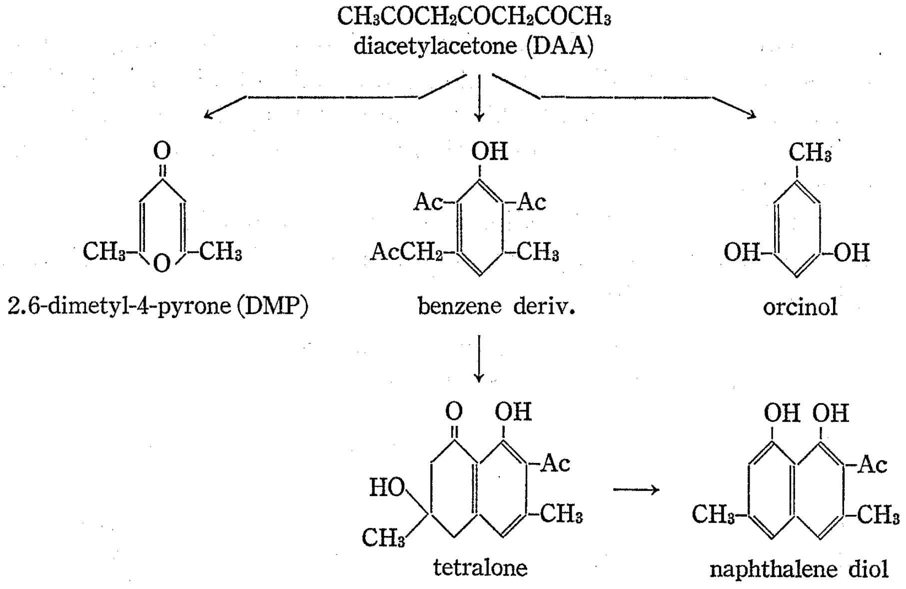

Chart 1. Possible Routes for Reactions of Diacetylacetone in Neutral Region (pH 5—10)

However, no quantitative rate measurements were obtained in either of these studies. In this section, we wish to present the kinetic investigation for the self-condensation of DAA in detail.

The influences of pH on the self-condensation were examined at first. The products in the recation solution which was maintained in the constant temperature bath during about 200 hours period at 60°, were separated by thin-layer chromatogarphic technique. Figure 4 is a com-

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[11] "Kagakubinran" New ed., Maruzen, Tokyo, 1958, p. 869.
[12] N. Collie and W.S. Myers, *J. Chem. Soc.*, **63**, 122 (1893).
[13] J.N. Collie, *J. Chem. Soc.*, **91**, 1806 (1907).

posite representation of the chromatographs obtained from degraded samples at various pH's together with spots from known compounds.

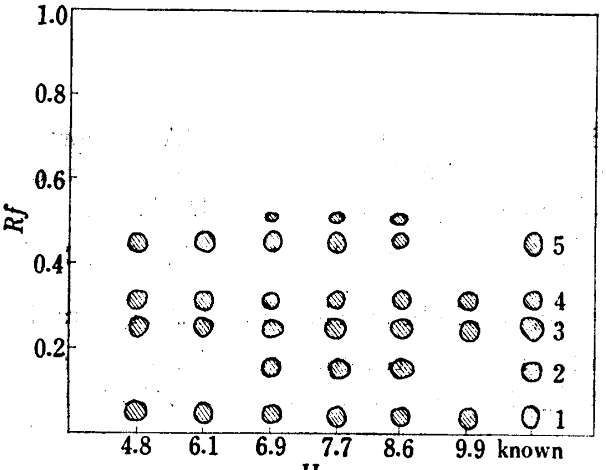

Fig. 4. Result of Thin-Layer Chromatograms from Reaction Solution of Diacetylacetone at 60°

solvent: $CH_3COOC_2H_5:CCl_4=1:5$
1: 2,6-dimethyl-4-pyrone 2: tetralone
3: orcinol 4: benzene deriv.5 : naphthalene diol

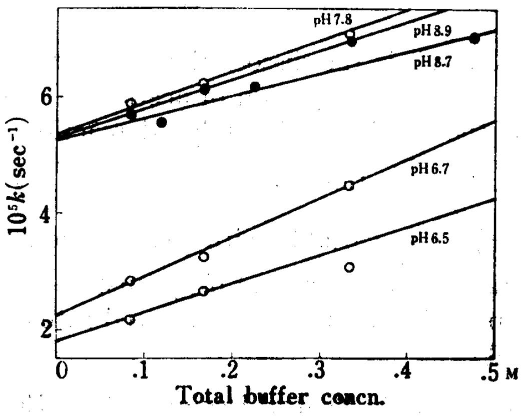

Fig. 5. Effect of Buffer Concentrations for Conversion of Diacetylacetone

—○—: phosphate buffer
—●—: carbonate buffer

The benzene derivative which is the first intermediate could be recognized in all experimental pH's. The second intermediate, tetralone, was only obtained in pH's 6.9, 7.7 and 8.6. And the final product except for pH 9.9 was naphthalendiol. Based on these findings, it was easily conceivable that the self-condensation process to naphthalenediol was extremely depressed in above pH 9.9.

The sum of amounts of naphthalenediol which precipitated in nearly pure state after 200 hours and the its solubility at each pH are shown in Table II as a total yield of naphthalenediol over the pH range of 5 to 10.

Table II. Amount of Naphthalenediol Formed When Diacetylacetone[a] Reacts in 100 ml Buffer Solution at 60° for 200 Hours

Final pH	Precipitated amount mg	Solubility mg	Total amount mg
4.8	90.0	4.1	94.1
6.1	151.1	8.4	159.5
6.9	144.0	10.4	154.5
7.7	105.0	15.4	120.4
8.6	45.4	47.2	92.6
9.9[b]	0.0	(50∼)	0.0

a) initial concentration, 500 mg/100 ml
b) Naphthalenediol was not detected in solution by thin-layer chromatography

As the traces of the intramolecular condensation products for DAA, orcinol and DMP were obtained by thin-layer chromatographic technique but it was indicated that the amounts formed were almost negligible compared with the intermolecular condensation products. A reaction solution which had 500 mg DAA in 100 ml as initial concentration was extracted by ether after 24 hours experimental period. The obtained white crystal, mp 128—130°, showed intense color by Dragendorff's reagent and ultraviolet spectrum of the substance was completely identical with DMP.

The rate of disappearance of DAA from solution was found to be first-order with respect to DAA. There was a linear relationship between time and logarithm of residual DAA concentration. The initial concentration of DAA was changed at four fold ranges, no significant difference in the apparent first-order rate constants was observed.

The catalytic effects of phosphate and carbonate buffers were checked by making runs with each buffer, varying the total buffer concentration but keeping the constant pH and constant ionic strength ($\mu=1.0$). Except the case of pH 10.3, the rate of DAA conversion increased with increasing buffer strength at constant pH as shown in Fig. 5. So the catalytic effects of general acid and base on the conversion of DAA were expected.

The catalytic constants for phosphate and carbonate buffers, measured over the pH range 6.5—10.3, are given in Table III.

TABLE III. Catalytic Constants for General Acid and Base Catalysis of Undissociated Diacetylacetone Conversion at 60°[a)]

Buffer	Catalytic species	Catalytic constant ($sec^{-1}M^{-1}$)
Phosphate	$H_2PO_4^-$	5.4×10^{-7}
	$HPO_4^=$	2.5×10^{-5}
Carbonate	HCO_3^-	1.8×10^{-5}
	$CO_3^=$	2.7×10^{-3}

a) ionic strength maintained at 1.0 by the addition of NaCl

At the pH range of 9.5 to 11.5, it is easy to calculate the general acid and base catalytic rate constants of carbonate buffer ($k_{HCO_3^-}$ and $k_{CO_3^=}$) for monoanionic DAA because there are almost no undissociated and dianionic forms present. And the apparent rate constant (k) for DAA should follow the rate equation (10):

$$k=\left(k_{HCO_3^-}\frac{[H^+]}{([H^+]+K_a'')}+k_{CO_3^=}\frac{K_a''}{([H^+]+K_a'')}\right)([HCO_3^-]+[CO_3^=])+k_0 \qquad (10)$$

where k_0 is the sum of specific base and uncatalyzed (solvent catalyzed) rate constants for monoanionic DAA, and K''_a is the dissociation constant for HCO_3^- (5.61×10^{-11}).14) But the slope of line representing the run at pH 10.3 is zero. This indicates the fact that both HCO_3^- and $CO_3^=$ are noncatalytic with respect to monoanionic DAA. The slope of line on phosphate buffer in Fig. 5 is represented by equation (11):

$$\text{Slope}=\frac{k_{H_2PO_4^-}[H^+]^2+k'_{H_2PO_4^-}K_{a1}[H^+]+k_{HPO_4^=}K_a'''[H^+]+k_{HPO_4^=}K_a'''K_{a1}}{([H^+]+K_{a1})([H^+]+K_a''')} \qquad (11)$$

where K'''_a is the dissociation constant for $H_2PO_4^-$ (6.23×10^{-8}).14) $k_{H_2PO_4^-}$ and $k_{HPO_4^=}$ are the general acid and base catalytic rate constants of phosphate buffer for undissociated DAA, respectively. $k'_{H_2PO_4^-}$ and $k'_{HPO_4^=}$ are the general acid and base catalytic rate constants of phosphate buffer monoanionic DAA, respectively. These catalytic rate contants could be calculated by the simultaneous eqautions (11) obtained from the experiments at different pH's. From the result of calculation, it was found that $k'_{H_2PO_4^-}$ and $k'_{HPO_4^=}$ were approximately zero, that is, it appeared that the reaction rate of monoanionic DAA was extremely small as compared to that of undissociated DAA. Thus equation (11) reduces to:

$$\text{Slope}=\frac{k_{H_2PO_4^-}[H^+]^2+k_{HPO_4^=}K_a'''[H^+]}{([H^+]+K_{a1})([H^+]+K_a''')} \qquad (12)$$

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14) "Kagakubinran" New ed., Maruzen, Tokyo, 1958, p. 868.

The rate constant at each pH is obtained by extending to zero buffer concentration as shown in Fig. 5. The rate constants are shown in Fig. 6 as a function of pH. It appears to be quite similar to the shape of pH-rate profile obtained in aspirin. The pH-independent region exists in the pH range 8—10.5. According to Edwards[15] the horizontal portion of the profile may be controlled by either the reaction between undissociated molecule and OH^- or the reaction between dissociated molecule and H_2O. Since these two conversion rates, $k[OH^-][DAA]$ and $k'[DAA^-]$, are kinetically equivalent, it is difficult to distinguish the reactive spieces related to the conversion. But it must be expected that if OH^- acts as the catalyst, another catalytic species that can act as bases with catalytic activity exist. Fortunately, general base catalytic reaction for undissociated DAA was observed in phosphate and carbonate buffers as mentioned above. Therefore it can be considered that the reaction between undissociated DAA and OH^- is a rate limiting and the self-condensation of DAA is a suitable example of aldol condensation for ketones.

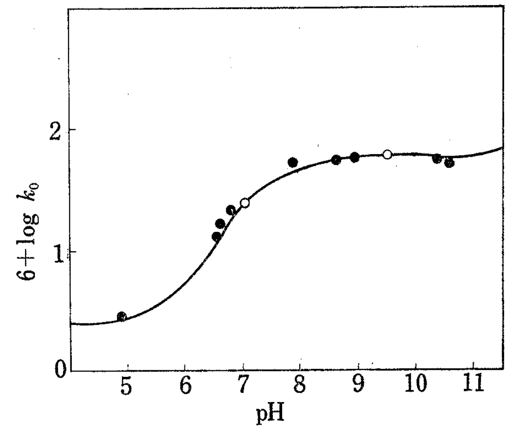

Fig. 6. log k_0-pH Profile for Reaction of Diacetylacetone in Neutral Region (pH 5—10)

●: experimental value (spectrophotometric method)
○: experimental value (gas chromatographic method)
—: calculated line

Conversion in Sodium Hydroxide Solution (pH 11-)

The alkaline decomposition of DAA was proceeded in sodium hydroxide of concentrations, 0.1, 0.25, 0.5 and 1.0 N. The condition and the apparent first-order rate constants for disappearance of DAA are shown in Table IV. It was demonstrated that acetone and acetic acid were ultimately produced in this reaction. And the molar ratio of acetone to acetic acid became almost unity in such alkaline concentrations studied.

Table IV. Summary of Conditions, Observed First-order Rate Constants for DAA[a] and AA,[b] and Amounts of Degraded Products in Sodium Hydroxide Solution

Concentration NaOH, (N)	pH[c]	Rate constant (hr^{-1})			Amount of product Experimental		(10^3 mole/100 ml) Calculated	
		k	k_{AA}	k'_{AA}	Acetone	Acetic acid	Acetone	Acetic acid
1.0	12.86	3.22	2.22	5.24	2.00	1.80	2.00	1.84
0.5	12.61	1.46	—	—	1.92	1.78	—	—
0.25	12.32	0.81	0.50	1.36	1.80	1.62	1.94	1.75
0.1	11.96	0.39 (0.38)[d]	—	—	1.44	1.49	—	—

[a] initial amount, 1.41×10^{-3} mole in 100 ml
[b] initial amount, 1.83×10^{-4} mole in 100 ml
[c] Calculated from eq. (2).
[d] Determined from gas chromatographic data.

Already the decomposition of DAA at higher concentration of sodium hydroxide has been described by Birch, *et al.*[16] The values, moles of acetic acid formed divided by that of acetone formed, were calculated on the basis of their data. The obtained values were 1.8 at 10 N, 1.4 at 5 N and 0.9 at 1 N sodium hydroxide, respectively. Because DAA converts to acetone

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[15] L.J. Edwards, *Trans. Faraday Soc.*, **46**, 723 (1950).
[16] A.J. Birch, P. Fitton, D.C.C Smith, D.E. Steere and A.R. Stelfox, *J. Chem. Soc.*, **1963**, 2209.

considerably and the formation of acetic acid is depressed at lower alkaline concentration, it may be expected that the above values gradually decrease with decreasing in concentration of alkali.

The plausible intermediates in alkaline decomposition of DAA are acetylacetone (AA) and acetoacetate (AT). The presence of AA in the reaction solution could be recognized by both thin-layer and gas chromatographic means.

The rate of the alkaline hydrolysis of AA has been expressed as[17]:

$$v=k[\mathrm{AA}]_T[\mathrm{OH}^-] \qquad (13)$$

where v is the reaction rate, k is the observed rate constant and $[\mathrm{AA}]_\mathrm{T}$ represents the total concentration of AA.

Acetylacetone is an acid capable of being ionized by alkali.

$$\mathrm{HA}+\mathrm{OH}^- \rightleftharpoons \mathrm{A}^-+\mathrm{H_2O}$$

Therefore, the apparent equilibrium constant (K_eq) for the neutralization mentioned above can be defined as:

$$K_\mathrm{eq}=\frac{[\mathrm{A}^-]}{[\mathrm{HA}][\mathrm{OH}^-]} \qquad (14)$$

where $[\mathrm{HA}]$, $[\mathrm{A}^-]$ and $[\mathrm{OH}^-]$ are the concentration of undissociated, dissociated AA and hydroxide ion, respectively.

The rate of decrease of the total concentration AA by hydrolytic process is equivalent to the sum of the rates of decrease of the undissociated form (HA) and the dissociated form (A^-). The rate expressions would be:

$$\begin{aligned} v&=k[\mathrm{AA}]_T[\mathrm{OH}^-]=k([\mathrm{HA}]+[\mathrm{A}^-])[\mathrm{OH}^-] \\ &=k\left(\frac{[\mathrm{A}^-]}{K_\mathrm{eq}[\mathrm{OH}^-]}+[\mathrm{A}^-]\right)[\mathrm{OH}^-] \\ &=\frac{k}{K_\mathrm{eq}}[\mathrm{A}^-]+k[\mathrm{A}^-][\mathrm{OH}^-] \\ &=k'[\mathrm{A}^-]+k[\mathrm{A}^-][\mathrm{OH}^-] \qquad (15) \end{aligned}$$

and similarly

$$v=k[\mathrm{AA}]_T[\mathrm{OH}^-]=k[\mathrm{HA}][\mathrm{OH}^-]+k''[\mathrm{HA}][\mathrm{OH}^-]^2 \qquad (16)$$

Namely, the observed reaction rate and the dependency on alkali concentration can be interpreted as due either to the reaction of the dissociated form with zero or one hydroxide ion (eq. (15)) or to the reaction of the undissociated form with one or two hydroxide ions (eq. (16)). These two possibilities are kinetically indistinguishable. But the first rate expression (eq. (15)) involving the dissociated form is improbable for several reasons.[18,19] The example will be given to clarify the explanation done. Dimethylacetylacetone which is one of the acetylacetone derivatives and does not form a dissociated form are readily cleaved in alkaline solution. It means that only undissociated form is hydrolyzed by alkali. In the possible rate equation (16), the first term is consistent with the mechanism analogous to the alkaline hydrolysis of an ester. The second term is most reasonably explained as an addition of one hydroxide ion to a carbonyl followed by a reaction with another hydroxide ion.

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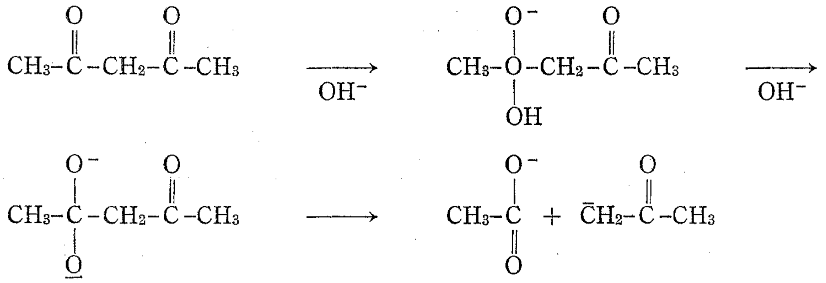
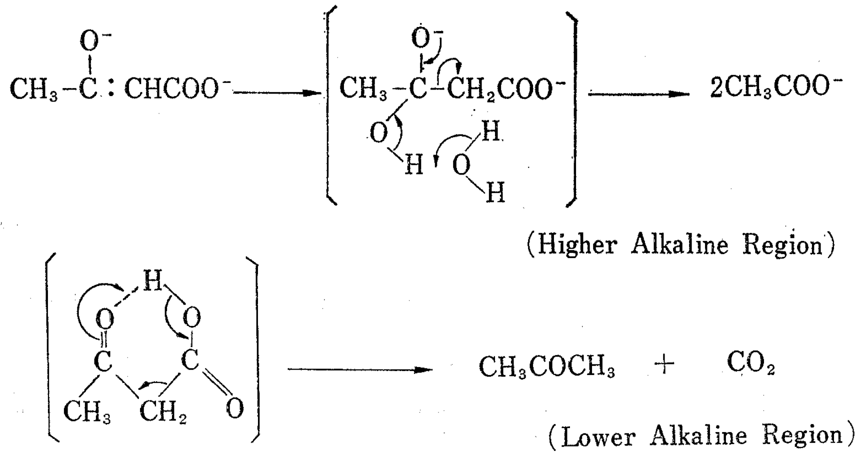
17) R.G. Pearson and E.A. Mayerle, *J. Am. Chem. Soc.*, **73**, 926 (1951).
18) C.R. Hauser, F.W. Swamer and B.I. Ringler, *J. Am. Chem. Soc.*, **70**, 4023 (1948).
19) C.J. Pierre and M. Pierre, *Bull. Soc. Chim. Fr.*, **1968**, 3761.

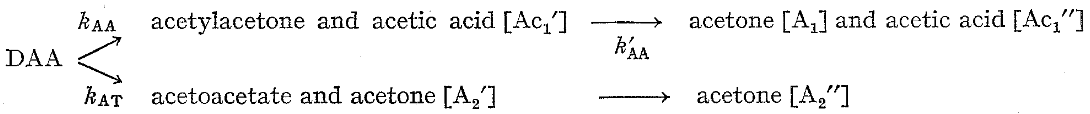


Moreover, it has been observed[16] that AT decomposes to acetic acid at higher pH region which the most of AT exists as the dianion. On the other hand, AT converts to acetone and dicarboxide at lower alkaline concentrations completely.



Based on the mentioned above, it is expected that if AT is an only intermediate in the conversion of DAA at the range of 0.1 to 1.0N alkaline concentration, one mole DAA converts to two moles acetone, and secondly if AA is considered as an intermediate, one mole acetone and two moles acetic acid are produced ultimately. Therefore the experimental result that the concentrations of acetone and acetic acid in a final reaction solution are almost equivalent may propose the following: both AT and AA must be considered in DAA conversion as the intermediates simultaneously.

In order to obtain a suitable explanation for experimental results, the kinetic procedure was adopted. We considered the mechanism for DAA conversion as shown in Chart 2.



$$[Ac_1']+[Ac_1'']=[Ac_1],\quad [A_2']+[A_2'']=[A_2]$$

Chart 2. Proposed Route for Conversion of Diacetylacetone in Alkaline Region

The differential equations for the route mentioned above are

$$-\frac{d[\mathrm{DAA}]}{dt}=(k_{\mathrm{AA}}+k_{\mathrm{AT}})[\mathrm{DAA}]=k[\mathrm{DAA}] \tag{17}$$

$$\frac{d[\mathrm{AA}]}{dt}=k_{\mathrm{AA}}[\mathrm{DAA}]-k'_{\mathrm{AA}}[\mathrm{AA}] \tag{18}$$

From equations (17) and (18), we obtain the following equation (19) for AA:

$$[\mathrm{AA}]=\frac{k_{\mathrm{AA}}[\mathrm{DAA}]_0}{k'_{\mathrm{AA}}-(k_{\mathrm{AA}}+k_{\mathrm{AT}})}(e^{-kt}-e^{-k'_{\mathrm{AA}}t}) \tag{19}$$

and

$$k_{AA}=\frac{[AA]}{[DAA]_0}\cdot\frac{k'_{AA}-k}{e^{-kt}-e^{-k'_{AA}t}} \tag{20}$$

where $[DAA]_0$ represents the initial concentration of DAA, and [AA] is the concentration of AA in the experimental period. The each value was put in the equation (20), and then k_{AA} and k_{AT} could be estimated. The k'_{AA} could be obtained from the kinetics of the degradation of AA in alkaline medium. In Chart 2, $[A_1]$ represents acetone which yielded from AA, and $[Ac_1]$ and $[A_2]$ indicate the cumulative amounts of acetic acid and that of acetone which produced in the routes *via* AA and AT, respectively. The final amounts of acetone formed and that of acetic acid formed in the reaction solution can be expressed by means of the ratios k_{AA}/k and k_{AT}/k, and initial amount of DAA. Assignment made, for example, are $k=3.22\ hr^{-1}$ and $k_{AA}=2.25\ hr^{-1}$ for the degradation of DAA in 1N NaOH solution, and the initial amount of DAA is equal to 1.41×10^{-3} mole in 100 ml. And then $k_{AA}/k=0.7$ and $k_{AT}/k=0.3$ are obtained, and the values of $[A_1]$, $[Ac_1]$ and $[A_2]$ are calculated to be 1.0×10^{-3} mole in 100 ml, 2.0×10^{-3} mole in 100 ml and 0.84×10^{-3} mole in 100 ml, respectively. The experimental results are quite identical with the calculated values as shown in Table IV. Therfore it may be suggested that the degradation of DAA in lower alkaline region proceeds *via* a parallel reaction path involving AA and AT as the intermediates.