Anal. Calcd. for $C_{13}H_9O_4NS$: C, 56.73; H, 3.27. Found: C, 56.52; H, 3.56.

6-Aminoacridine-2-sulfonic Acid.—To the hot solution of 6-aminoacridone-2-sulfonic acid (6 g.) in sodium hydroxide (10%, 9 g.) and water (120 cc.), sodium amalgam (5%, 60 g.) was added. The mixture was shaken gently at 80° for two hours. The filtered hot solution on acidifying with hydrochloric acid deposited prismatic needles of pink color; yield 5.5 g. It forms brownish-orange rods from water, being unaltered at 360° and soluble in hot water and hot alcohol with green fluorescence. The almost colorless solution in concentrated sulfuric acid shows intense greenish-blue fluorescence. This compound is rather sensitive to heat especially in alkaline solution.

Anal. Calcd. for $C_{13}H_{10}O_3N_2S$: C, 56.93; H, 3.65. Found: C, 56.95; H, 3.77.

The sodium salt gives yellow thick plates from water. It is soluble in water and alcohol with green fluorescence.

Anal. Calcd. for $C_{13}H_9O_3N_2SNa$: Na, 7.77. Found: Na, 7.15.

6-Carboxymethylaminoacridine-2-sulfonic Acid.—A solution of 6-aminoacridine-2-sulfonic acid (0.55 g.), monochloroacetic acid (0.2 g.) and hydrated sodium carbonate (0.6 g.) in water (8 cc.) was refluxed for two hours and gave, on acidifying with hydrochloric acid, aggregates of violet-red fibrous needles (0.4 g.) which turned to tar at 345–360°.

Anal. Calcd. for $C_{15}H_{12}O_5N_2S$: C, 54.22; H, 3.61. Found: C, 54.32; H, 4.08.

***p*-Chloroacetylaminophenyl-arsinic Acid.**—A mixture of *p*-aminophenyl-arsinic acid (1.1 g.) and chloroacetyl chloride (0.9 g.) was warmed at 70° for a few minutes and poured on cooling into water. The reaction product was dissolved in sodium carbonate and precipitated with hydrochloric acid in colorless plates, m. p. 295–296° (dec.). It is readily soluble in methanol but insoluble in water.

Anal. Calcd. for $C_8H_9O_4NClAs$: C, 32.72; H, 3.07. Found: C, 33.00; H, 3.38.

6-Arsacetinylaminoacridine-2-sulfonic Acid.—A solution of 6-aminoacridine-2-sulfonic acid (0.5480 g.) and *p*-chloroacetylaminophenyl-arsinic acid (0.5720 g.) in sodium hydroxide (10%, 1.6 g.) was warmed at 70–80° for three hours and acidified with hydrochloric acid on cooling. The solid was digested with warm water, washed with water and then with methanol; yield 0.75 g.

The substance crystallizes in dark red prisms, turning to tar at 340–360°. It is soluble in dilute sodium carbonate and insoluble in alcohol and acetone. The yellow solution in concd. sulfuric acid exhibits green fluorescence.

Anal. Calcd. for $C_{21}H_{18}O_7N_3SAs$: C, 47.46; H, 3.39. Found: C, 47.33; H, 4.02.

I hereby thank Professor Hata for his interest in the work.

Summary

Fuming sulfuric acid acts upon 6-nitroacridone as well as 5-nitrodiphenylamine-2-carboxylic acid to give 6-nitroacridone-2-sulfonic acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ROYAL VETERINARY AND AGRICULTURAL COLLEGE]

Amine Catalysis of the Ketonic Decomposition of α,α-Dimethylacetoacetic Acid

BY KAI JULIUS PEDERSEN

It has been found by Widmark and Jeppsson[1] and by Ljunggren[2] that the ketonic decomposition of acetoacetic acid

$$CH_3COCH_2COOH \longrightarrow CH_3COCH_3 + CO_2$$

is catalyzed by primary amines when the *p*H of the solution is kept within certain limits. In more acid and in more alkaline solution the amines do not catalyze. The influence of the acidity of the medium is explained by assuming that the reaction takes place either between the neutral amine and the undissociated acetoacetic acid, or between the positive aminium ion and the acetoacetate ion.

It is the object of this paper to examine more closely the amine catalysis of the decomposition of β-keto carboxylic acids. Instead of acetoacetic acid there was used α,α-dimethylacetoacetic acid, whose uncatalyzed decomposition has been studied in earlier papers.[3,4] The two amines aniline and *o*-chloroaniline were chosen as catalysts. Experiments were carried out at 24.97 and 34.93° in aniline–anilinium chloride buffer solutions and in *o*-chloroaniline–*o*-chloroanilinium chloride buffer solutions. To all the solutions had been added enough sodium chloride to make the total salt concentration 0.150 *N*.

We denote the undissociated dimethylacetoacetic acid by HA, the uncharged amine by B, and the total concentration of the reacting substance by $x \equiv (\text{HA}) + (\text{A}^-)$. According to the Swedish investigators[1,2] we may interpret the decomposition in the amine buffer solutions as

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(1) E. M. P. Widmark and C. A. Jeppsson, *Skand. Arch. Physiol.*, **42**, 43 (1922).

(2) G. Ljunggren, "Katalytisk Kolsyreavspjälkning ur Ketokarbonsyror," Dissertation, Lund, 1925.

(3) K. J. Pedersen, THIS JOURNAL, **51**, 2098 (1929).

(4) K. J. Pedersen, *ibid.*, **58**, 240 (1936).

the result of three simultaneous reactions, namely, the unimolecular decompositions of HA and A^-, and a bimolecular reaction between B and HA

$$-\mathrm{d}x/\mathrm{d}t = k_0(\mathrm{HA}) + k_1(\mathrm{A}^-) + k_2(\mathrm{B})(\mathrm{HA}) \qquad (1)$$

k_0 and k_1 have been determined separately in the earlier paper.[4] Expression 1 holds only very roughly for the experiments in this paper. For the aniline buffers we must add a term of the form $k_3(\mathrm{B})^2(\mathrm{HA})$, and for the *o*-chloroaniline buffers one of the form $k_4(\mathrm{BH}^+)(\mathrm{HA})$. Thus the velocity in these buffer solutions may be expressed as

$$-\mathrm{d}x/\mathrm{d}t = k_0(\mathrm{HA}) + k_1(\mathrm{A}^-) + k_2(\mathrm{B})(\mathrm{HA}) + k_3(\mathrm{B})^2(\mathrm{HA}) + k_4(\mathrm{BH}^+)(\mathrm{HA}) \qquad (2)$$

For the experiments in aniline buffers the term containing k_4, and for those in *o*-chloroaniline buffers the terms containing k_1 and k_3 are negligibly small.

The solutions of sodium dimethylacetoacetate were prepared from the same sample of purified ethyl ester ("fraction 2") as was used in the earlier paper,[4] and in the same way as described there. The decomposition was followed by measuring the carbon dioxide pressure above the solution in an apparatus described earlier.[5] Before an experiment was begun the apparatus was evacuated with the water pump, filled with carbon dioxide, and evacuated again.

Experiments in *o*-Chloroaniline Buffers.—The *o*-chloroaniline buffers were prepared from *o*-chloroanilinium chloride and sodium hydroxide solution. The *o*-chloroanilinium chloride used was prepared by dissolving *o*-chloroaniline (British Drug Houses, Ltd.) in boiling 10% hydrochloric acid. The crystals obtained by cooling in ice were recrystallized from 10% hydrochloric acid. The preparation was analyzed by titration with sodium hydroxide and by determination of the amount of bromine which it could take up.[6] One mole of pure *o*-chloroanilinium chloride needs four equivalents of bromine. The results of both titrations agreed with those calculated from the formula within less than 0.5%.

We use the following symbols. Initial and final values are indicated by the subscripts 0 and ∞ respectively; $P \equiv p_\infty - p$, difference between the final pressure readings and the reading t minutes after the start; $\varphi \equiv P_0/x_0$, proportionality factor of the equation $P = \varphi x$; $\alpha = (\mathrm{A}^-)/x$, degree of dissociation of dimethylacetoacetic acid. Analytical concentration of the solution at the start of the experiment: a molar *o*-chloroanilinium chloride, b molar *o*-chloroaniline, x_0 molar dimethylacetoacetic acid, $(0.150 - a)$ molar sodium chloride. $L \equiv K_{\mathrm{BH}^+}/K_{\mathrm{HA}}$, ratio between the dissociation constants of the acids BH^+ and HA.

The values of (B), (BH^+), α, and (H^+), corresponding to each of the readings are first calculated by successive approximations from the four equations

$$(\mathrm{B}) = b + (\mathrm{H}^+) - \alpha P/\varphi \qquad (3)$$

$$(\mathrm{BH}^+) = a - (\mathrm{H}^+) + \alpha P/\varphi \qquad (4)$$

$$\alpha = (\mathrm{B})/[(\mathrm{B}) + L(\mathrm{BH}^+)] \qquad (5)$$

$$(\mathrm{H}^+) = K_{\mathrm{BH}^+}(\mathrm{BH}^+)/(\mathrm{B}) \qquad (6)$$

For the dissociation constants of dimethylacetoacetic acid and the *o*-chloroanilinium ion are used the values found in 0.150 *N* sodium chloride solution in earlier publications.[4,7] They are given at the top of Tables I and II. In order to show that the rate of decomposition found in the experiments may be expressed by equation 2 we transform this equation as explained below. For k_0 and k_1 we use the values found earlier[4] and given at the top of Tables I and II. The solutions are so acid that $k_1(\mathrm{A}^-)$ is always negligibly small. As we shall see we get agreement with the experiments when we leave out also the term with k_3. Equation 2 may then be written

$$-\mathrm{d}x/\mathrm{d}t = [k_0 + k_2(\mathrm{B}) + k_4(\mathrm{BH}^+)](1 - \alpha)x \qquad (7)$$

When x is sufficiently small the reaction will follow the unimolecular law with the constant

$$k = [k_0 + k_2(\mathrm{B})_\infty + k_4(\mathrm{BH}^+)_\infty](1 - \alpha_\infty) \qquad (8)$$

From equations 3 and 4 we find

$$(\mathrm{B})_\infty - (\mathrm{B}) = (\mathrm{BH}^+) - (\mathrm{BH}^+)_\infty = \alpha P/\varphi - (\mathrm{H}^+) + (\mathrm{H}^+)_\infty$$

By means of this equation and $P = \varphi x$ we transform equation 7 into

$$-\mathrm{d}P/P\mathrm{d}t = [k_0 + k_2(\mathrm{B})_\infty + k_4(\mathrm{BH}^+)_\infty]\,(1 - \alpha) - (k_2 - k_4)(1 - \alpha)\,(\alpha P/\varphi - (\mathrm{H}^+) + (\mathrm{H}^+)_\infty)$$

If we use the abbreviation (8) it may be written

$$-\mathrm{d}P/P\mathrm{d}t = k + \left[k\frac{\alpha_\infty - \alpha}{1 - \alpha_\infty} - (k_2 - k_4)(1 - \alpha)(\alpha P/\varphi - (\mathrm{H}^+) + (\mathrm{H}^+)_\infty)\right]$$

By integration we find

$$-k^*t = \log P + \Delta - \log P_0 \qquad (9)$$

where the small correction Δ is

$$\Delta = \int_0^t \left[k^*\frac{\alpha_\infty - \alpha}{1 - \alpha_\infty} - (k_2^* - k_4^*)(1 - \alpha)(\alpha P/\varphi - (\mathrm{H}^+) + (\mathrm{H}^+)_\infty\right)\mathrm{d}t$$

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(5) K. J. Pedersen, THIS JOURNAL, **53**, 18 (1931).

(6) K. J. Pedersen, *ibid.*, **56**, 2615 (1934).

(7) K. J. Pedersen, *Kgl. Danske Vid. Selsk., Math.-fys. Medd.*, **15** No. 3 (1937).

TABLE I

KETONIC DECOMPOSITION OF α,α-DIMETHYLACETOACETIC ACID IN *o*-CHLOROANILINE BUFFER SOLUTIONS AT 24.97°

$K_{\mathrm{BH}^+} = 2.12 \times 10^{-3}$. $K_{\mathrm{HA}} = 5.11 \times 10^{-4}$. $L = 4.15$. $k_0^* = 1.822 \times 10^{-3}$. $k_1^* = 3.99 \times 10^{-6}$. x_0 was always about 0.019.

$a \times 10^3$	$b \times 10^3$	$(\mathrm{H}^+)_\infty \times 10^3$	$(\mathrm{BH}^+)_\infty \times 10^3$	$(\mathrm{B})_\infty \times 10^3$	α first read.	α_∞	$k^* \times 10^3$		$k_0^* \times 10^3 \times (1-\alpha_\infty)$	$k_2^* \times 10^3 \times (1-\alpha_\infty) \times (\mathrm{B})_\infty$	$k_4^* \times 10^3 \times (1-\alpha_\infty) \times (\mathrm{BH}^+)_\infty$
							Exptl.	Calcd.			
13.56	36.41	0.73	12.83	37.14	0.3074	0.4109	1.808	1.807	1.073	0.710	0.024
21.58	28.40	1.43	20.15	29.83	.2122	.2629	2.103	2.103	1.343	.713	.047
38.55	36.44	2.01	36.54	38.45	.1792	.2023	2.534	2.540	1.453	.995	.092
46.68	28.3	2.96	43.72	31.27	.1334	.1470	2.540	2.537	1.554	.865	.118
63.65	36.31	3.24	60.41	39.54	.1268	.1362	2.832	2.847	1.574	1.108	.165
71.56	28.30	4.35	67.21	32.74	.0988	.1051	2.785	2.771	1.631	0.950	.190
88.7	36.49	4.39	84.31	40.79	.0994	.1044	3.071	3.056	1.632	1.185	.239
113.6	36.41	5.47	108.1	41.88	.0822	.0854	3.198	3.221	1.666	1.243	.312

From the experiments are found: $k_2^* = 0.03244$, $k_4^* = 0.00316$.

TABLE II

KETONIC DECOMPOSITION OF α,α-DIMETHYLACETOACETIC ACID IN *o*-CHLOROANILINE BUFFER SOLUTIONS AT 34.93°

$K_{\mathrm{BH}^+} = 2.93 \times 10^{-3}$. $K_{\mathrm{HA}} = 4.62 \times 10^{-4}$. $L = 6.34$. $k_0^* = 6.36 \times 10^{-3}$. $k_1^* = 17.5 \times 10^{-6}$. x_0 was always about 0.019.

$a \times 10^3$	$b \times 10^3$	$(\mathrm{H}^+)_\infty \times 10^3$	$(\mathrm{BH}^+)_\infty \times 10^3$	$(\mathrm{B})_\infty \times 10^3$	α first read.	α_∞	$k^* \times 10^3$		$k_0^* \times 10^3 \times (1-\alpha_\infty)$	$k_2^* \times 10^3 \times (1-\alpha_\infty) \times (\mathrm{B})_\infty$	$k_4^* \times 10^3 \times (1-\alpha_\infty) \times (\mathrm{BH}^+)_\infty$
							Exptl.	Calcd.			
15.84	40.07	1.05	14.79	41.12	0.2446	0.3048	6.33	6.33	4.42	1.84	0.07
31.43	40.12	2.06	29.37	42.18	.1656	.1847	7.52	7.56	5.19	2.21	.16
47.51	40.04	3.06	44.45	43.10	.1239	.1327	8.22	8.18	5.52	2.40	.26
79.2	40.04	4.91	74.3	44.95	.0841	.0871	8.95	8.91	5.81	2.64	.46
110.7	40.06	6.63	104.1	46.69	.0645	.0661	9.36	9.40	5.94	2.80	.66

From the experiments are found: $k_2^* = 0.0643$, $k_4^* = 0.0068$.

and $k^* = 0.4343\ k$. Δ is found by rough graphical integration, preliminary values of the constants being used. When $\log P + \Delta$ is plotted against t the points fall along a straight line whose slope determines k^* of the experiment. The agreement with equation 9 was always very satisfactory. The values of the velocity constants k^* computed in this way are given in the eighth column of Tables I and II.

In order to find k_2^* and k_4^* we introduce the known values of k_0^* and α_∞ into equation 8, and calculate $k_2^*\ (\mathrm{B})_\infty + k_4^*\ (\mathrm{BH}^+)_\infty$ for each of the experiments. From the values of this expression for the whole series of experiments at the same temperature we compute k_2^* and k_4^* by the method of least squares. The results are given at the bottom of the tables. The agreement is tested by calculation of k^* for each of the experiments from the values of k_2^* and k_4^*. The results of this calculation are given in the ninth column of Tables I and II. A comparison of the values in the eighth and ninth columns will show that the agreement is good. This good agreement confirms that it was permissible to leave out the term with k_3 in equation 2. The last three columns of Tables I and II have been computed in order to show how much each of the three simultaneous reactions contributes to the total reaction.

Experiments in Solutions of *o*-Chloroanilinium Chloride and Hydrochloric Acid.—For the explanation of the results of the kinetic measurements in *o*-chloroaniline buffer solutions it has been necessary to assume that a bimolecular reaction between the undissociated keto acid and the aminium ion contributed to the catalysis. This effect is expressed in equation 7 by the term containing k_4, and its importance is seen clearly from the last column of Tables I and II. We may expect that this reaction also will take place in strongly acid solution, and, consequently, that the catalysis by *o*-chloroaniline is not confined to a limited *p*H interval. In order to test this directly experiments were carried out at 24.97° in solutions containing hydrochloric acid (*c* molar) *o*-chloroanilinium chloride (*a* molar), and sodium chloride (*s*-*c*-*a* molar). Within each series of experiments *c* and the total salt concentration *s* were kept constant, while *a* was varied.

If equation 7 holds the unimolecular velocity constant is given by the equation

$$k = [k_0 + k_2(\mathrm{B}) + k_4(\mathrm{BH}^+)](1 - \alpha) \qquad (10)$$

α was always smaller than 0.01 and was calculated with sufficient accuracy from a rough estimate of K_{HA}. By means of equation 6 and the abbreviations

$$\lambda \equiv \lambda_2 + \lambda_4 \qquad (11)$$

$$\lambda_2 \equiv k_2 K_{BH^+}/[(H^+) + K_{BH^+}] \qquad (12)$$

$$\lambda_4 \equiv k_4(H^+)/[(H^+) + K_{BH^+}] \qquad (13)$$

equation 10 may be written as

$$k/(1 - \alpha) = k_0 + \lambda a \qquad (14)$$

Within a series of experiments at constant hydrogen ion concentration λ is constant. It was determined graphically by plotting $k/(1-\alpha)$ against a, and drawing a straight line through the points. In order to separate the catalytic effects of BH^+ and B, λ_2^* was calculated by means of equation 12 from the known values of k_2^* and K_{BH^+}. $k_2^* = 0.03244$ was taken from Table I. For the solutions where $s = 0.15$ was used $K_{BH^+} = 2.12 \times 10^{-3}$. For the more concentrated solutions it was considered sufficiently accurate to use the value $K_{BH^+} = 1.5 \times 10^{-3}$, obtained by extrapolation to $s = 0.75$ of the formula given in an earlier paper.[7]

λ_4^* was found by subtracting λ_2^* from λ^*. Finally, k_4^* was calculated from λ_4^* by means of equation 13. The results are summarized in Table III. The last column but one gives the values of k_4^* determined from the experiments as just explained. For comparison k_4^* found for the buffer solutions is given in the last line of the table.

TABLE III

KETONIC DECOMPOSITION OF α,α-DIMETHYLACETOACETIC ACID AT 24.97° IN SOLUTIONS CONTAINING a MOLAR o-CHLOROANILINIUM CHLORIDE, c MOLAR HYDROCHLORIC ACID, AND (s-a-c) MOLAR SODIUM CHLORIDE

Each line gives a summary of n experiments where c was kept constant while a was varied from 0 to $a_{max.}$

c	s	$a_{max.}$	n	Prep. no.	λ^*10^3	$\lambda_2^*10^3$	$\lambda_4^*10^3$	$k_4^*10^3$ Exptl.	$k_4^*10^3$ Calcd.
1.98	2.15	0.150	4	2	0.32	0.02	0.30	0.30	0.31
0.478	0.75	.256	4	2	.60	.10	.50	.50	.49
.228	.75	.256	4	2	.95	.21	.74	.75	.72
.121	.75	.256	4	2	1.42	.40	1.02	1.03	1.03
.057	.15	.075	4	1	2.58	1.19	1.39	1.44	1.55
.057	.15	.075	4	2	2.68	1.19	1.49	1.55	1.55
.057	.15	.075	2	3a	2.65	1.19	1.46	1.51	1.55
.057	.15	.075	2	3b	2.60	1.19	1.41	1.46	1.55
~ .004[a]	.15		8	1				3.16	3.11

[a] Experiments in buffer solutions (Table I), $(H^+) \sim 0.004$.

It is seen from the table that k_4^* is far from being independent of the hydrogen ion concentration. k_4^* decreases with increasing hydrogen ion concentration as if the catalyzing molecule were gradually being transformed into a less active form by taking up a hydrogen ion. Thus, the variation of k_4^* with (H^+) agrees with the assumption that the form stable in strongly acid solution has the acid strength 0.040 and the catalytic constant 0.25×10^{-3}, while the form stable in weakly acid solution has the catalytic constant 3.40×10^{-3}. This is seen from the last column of Table III, which gives k_4^* calculated from the formula

$$(H^+)\frac{k_4^* - 0.25 \times 10^{-3}}{3.40 \times 10^{-3} - k_4^*} = 0.040 \qquad (15)$$

The formula contains three arbitrary constants. The agreement may therefore be accidental. It is not surprising that a constant value of k_4^* was found for the buffer solutions (Table I). It follows from formula 15 that the relative variation of k_4^* in the buffer solutions examined is not considerable. If the results are recalculated using k_4^* from formula 15 instead of the constant value 3.16×10^{-3}, exactly the same value of k_2^* is obtained.

It has not been possible to give a satisfactory explanation of the variation of k_4. It is very improbable that the o-chloroanilinium ion takes up another proton in the solutions of hydrochloric acid used for the experiments, and if this were the case the decrease of the hydrogen ion concentration would be so great that it, especially in the solutions where $a > c$, could hardly escape detection. Another possibility is that the o-chloroanilinium chloride used for the experiments has contained a catalyzing basic impurity whose corresponding acid has the strength about 0.04. The assumed impurity can only be present in small amount because it has not been detected by the analyses of the substance, and it must therefore be a very powerful catalyst. However, this explanation also is very improbable, because the experiments have been carried out with preparations of different origin, and which have been purified in different ways. In Table III prepn. 1 refers to the preparation which was also used for the buffer solutions. It was made from o-chloroaniline (British Drug Houses) as already described. Preparation 2 was from o-chloroaniline (Kahlbaum, "reinst"). The chloride was recrystallized five times from 10% hydrochloric acid and, finally, once from water. Preparations 3a and 3b were different fractions obtained by distilling Kahlbaum o-chloroaniline ***in vacuo*** in an all-glass still fitted with a Widmer column. As seen especially from the experiments in 0.057 molar hydrochloric acid the four preparations all gave the same catalytic effect.

Experiments in Aniline Buffer Solutions.—The solutions were prepared from aniline and hydrochloric acid. The aniline used was the middle fraction obtained by distillation *in vacuo* of Kahlbaum aniline for analytical purposes. In the aniline buffers the hydrogen ion concentration was so small that it was necessary to make a correction for the hydrocarbonate ion present in the solution. If the carbon dioxide pressure is p_{CO_2} cm. above a solution with the hydrogen ion concentration (H^+) the hydrocarbonate concentration is

$$(HCO_3^-) = \frac{K_{CO_2} f p_{CO_2}}{(H^+) 76RT}$$

where K_{CO_2} is the ordinary dissociation constant of carbonic acid, f the Ostwald absorption coefficient for carbon dioxide, R the gas constant in liter atm./degree mole, and T the absolute temperature. For the buffer solutions the correction will therefore be

$$\Delta p = \varphi(HCO_3^-) = \left(\frac{K_{CO_2}}{K_{BH^+}} \frac{f\varphi}{76RT}\right)\frac{(B)}{(BH^+)}\, p_{CO_2} \qquad (16)$$

For K_{BH^+}, the dissociation constant of the anilinium ion, was used the values found earlier[8] for 0.150 N sodium chloride solution. They are given at the top of Tables IV and V. For K_{CO_2} the values 7.8×10^{-7} at 25° and 8.5×10^{-7} at 35° were estimated from the measurements of Shedlovsky and MacInnes,[9] and Güntelberg and Schiödt.[10] For f we have used the values 0.821 at 25° and 0.59 at 35° from the measurements of Geffcken[11] (the latter value by extrapolation).

P is here the difference between the corrected pressure readings at the times ∞ and t

$$P = p_\infty + \Delta p_\infty - p - \Delta p \qquad (17)$$

The meaning of the other symbols is the same as or analogous to that in the treatment of the *o*-chloroaniline buffers. Instead of equations 3 and 4 we have

$$(B) = b + (H^+) - \Delta p/\varphi - \alpha P/\varphi \qquad (18)$$

$$(BH^+) = a - (H^+) + \Delta p/\varphi + \alpha P/\varphi \qquad (19)$$

From the equations 16, 17, 18, 19, 5, and 6, we find by successive approximations the values of Δp, P, (B), (BH^+), α, and (H^+), corresponding to each of the readings.

We shall now show that expression 2 holds for the aniline buffers when we set $k_4 = 0$. The expression is transformed into

$$-dx/dt = k_0(HA) + k_1(A^-) + k_2L(BH^+)(A^-) + k_3L(B)(BH^+)(A^-) = [k_0(1 - \alpha) + k_1\alpha + k_2L\alpha(BH^+) + k_3L\alpha(B)(BH^+)]x \qquad (20)$$

When x is sufficiently small the reaction will follow the unimolecular law with the constant

$$k \equiv k_0(1 - \alpha_\infty) + k_1\alpha_\infty + k_2L\alpha_\infty(BH^+)_\infty + k_3L\alpha_\infty(B)_\infty(BH^+)_\infty \qquad (21)$$

We further use the abbreviation

$$\beta \equiv (k_2L + (B)_\infty k_3L)\alpha^2_\infty/\varphi k \qquad (22)$$

By means of the equations 18, 19, 21, and 22, equation 20 may be written as

$$k = -\frac{dP}{P(1 + \beta P)dt} + f(P) \qquad (23)$$

where

$$f(P) \equiv \frac{\alpha_\infty - \alpha}{\alpha_\infty}\left[k - k_0 + \frac{\beta}{\frac{1}{P} + \beta}\left(k\frac{\alpha}{\alpha_\infty} + k_0\right)\right] + \frac{\alpha^2 k_3L[(BH^+)_\infty\varphi + \alpha P]}{\varphi^2\left(\frac{1}{P} + \beta\right)} + \frac{\alpha[k_2L - k_3L((BH^+)_\infty - (B)_\infty + 2\alpha P/\varphi)]}{\varphi P\left(\frac{1}{P} + \beta\right)} \times [\Delta p_\infty - \Delta p + \varphi(H^+) - \varphi(H^+)_\infty]$$

By integration of equation 23 we find

$$k^*t = \log\left(\frac{1}{P} + \beta\right) - \log\left(\frac{1}{P_0} + \beta\right) + \int_0^t f^*(P)dt \qquad (24)$$

The small correction $\int_0^t f^*(P)dt$, where * denotes that all velocity constants should be expressed by means of decadic logarithms, is found by rough graphical integration. Before we can carry out the computation we must know approximate values of the constants in order to estimate β and $\int_0^t f^*(P)dt$. We therefore make a preliminary computation of k^* setting $\beta = 0$ and $\int_0^t f^*(P)dt = 0$. From the values of k^* thus determined we find by means of equation 21 preliminary values of k_2^*L and k_3^*L which we use for the final computation. For k_0^* and k_1^* we have used the values found in an earlier paper,[4] and given at the top of Tables IV and V. When

$$\log\left(\frac{1}{P} + \beta\right) + \int_0^t f^*(P)dt$$

is plotted against t the points fall along a straight line whose slope determines k^* of the experiment. The agreement with equation 24 was always very

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[8] K. J. Pedersen, *Kgl. Danske Vid. Selsk., Math.-fys. Medd.*, **14**, no. 9 (1937).

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TABLE IV

KETONIC DECOMPOSITION OF α,α-DIMETHYLACETOACETIC ACID IN ANILINE BUFFER SOLUTIONS AT 24.97°

$K_{BH^+} = 2.35 \times 10^{-5}$. $K_{HA} = 5.11 \times 10^{-4}$. $L = 0.0460$. $k_0^* = 1.822 \times 10^{-3}$. $k_1^* = 3.99 \times 10^{-6}$. x_0 was always about 0.019.

$(BH^+)_\infty$	$(B)_\infty$	α first read.	α_∞	$k^* \times 10^3$ Exptl.	$k^* \times 10^3$ Calcd.	$[k_0^*(1-\alpha_\infty) + k_1\alpha_\infty] \times 10^3$	$k_2^*L\alpha_\infty \times (BH^+)_\infty \times 10^3$	$k_3^*L\alpha_\infty \times (B)_\infty(BH^+)_\infty \times 10^3$
0.0525	0.0368	0.872	0.9385	1.242	1.240	0.116	1.088	0.036
.0528	.0867	.951	.9727	1.276	1.276	.054	1.134	.088
.0532	.1890	.982	.9872	1.386	1.383	.027	1.160	.196
.0536	.2884	.987	.9915	1.493	1.495	.019	1.174	.302
.1279	.0646	.871	.9165	2.889	2.894	.156	2.589	.149
.1281	.0930	.922	.9403	2.985	2.994	.113	2.661	.220
.1282	.2412	.967	.9761	3.396	3.406	.047	2.764	.595
.1284	.2950	.974	.9803	3.557	3.552	.040	2.780	.732

From the experiments are found: $k_2^*L = 0.02209$, $k_3^*L = 0.0197$.

TABLE V

KETONIC DECOMPOSITION OF α,α-DIMETHYLACETOACETIC ACID IN ANILINE BUFFER SOLUTIONS AT 34.93°

$K_{BH^+} = 3.48 \times 10^{-5}$. $K_{HA} = 4.62 \times 10^{-4}$. $L = 0.0754$. $k_0^* = 6.36 \times 10^{-3}$. $k_1^* = 17.5 \times 10^{-6}$. x_0 was always about 0.019.

$(BH^+)_\infty$	$(B)_\infty$	α first read.	α_∞	$k^* \times 10^3$ Exptl.	$k^* \times 10^3$ Calcd.	$[k_0^*(1-\alpha_\infty) + k_1^*\alpha_\infty] \times 10^3$	$k_2^*L\alpha_\infty \times (BH^+)_\infty \times 10^3$	$k_3^*L\alpha_\infty \times (B)_\infty(BH^+)_\infty \times 10^3$
0.05453	0.0425	0.858	0.9118	3.89	3.90	0.58	3.21	0.11
.05377	.1016	.945	.9616	3.89	3.88	.26	3.35	.27
.05430	.1949	.972	.9794	4.12	4.12	.15	3.44	.53
.05423	.2670	.980	.9849	4.31	4.30	.11	3.46	.73
.0790	.0474	.829	.8884	5.46	5.44	.73	4.54	.17
.0794	.0467	.826	.8866	5.47	5.46	.74	4.55	.17
.0792	.1420	.946	.9597	5.73	5.74	.27	4.92	.55
.0792	.1420	.948	.9597	5.72	5.74	.27	4.92	.55
.0788	.2455	.971	.9770	6.12	6.11	.16	4.98	.97
.0792	.2417	.970	.9759	6.14	6.13	.17	5.00	.96
.1293	.0436	.756	.8165	8.26	8.25	1.18	6.83	.24
.1304	.1009	.888	.9111	8.82	8.88	0.58	7.69	.61
.1295	.1941	.942	.9520	9.52	9.52	.32	7.97	1.23
.1311	.2633	.959	.9638	10.11	10.12	.25	8.17	1.70

From the experiments are found: $k_2^*L = 0.0647$, $k_3^*L = 0.0512$.

satisfactory. The values of the velocity constants computed in this way are given in the fifth column of Tables IV and V.

In order to find k_2^*L and k_3^*L we introduce the known values of k_0^*, k_1^*, and α_∞ into equation 21, and calculate $k_2^*L(BH^+)_\infty + k_3^*L(B)_\infty(BH^+)_\infty$ for each of the experiments. From the values of this expression for the whole series of experiments at the same temperature we compute k_2^*L and k_3^*L by the method of least squares. The results are given at the bottom of the tables. The four last columns have been computed from the constants k_2^*L and k_3^*L in order to show the agreement with the formula, and to give an impression of how much the uncatalyzed and each of the two catalyzed reactions contribute to the total reaction.

The good agreement confirms that it was permissible to leave out the term with k_4, corresponding to a reaction between the anilinium ion and the undissociated dimethylacetoacetic acid. In the anilinium buffers $1-\alpha$ is small, which naturally makes the part played by this reaction less important. In order to see if the reaction takes place to an appreciable extent in more acid solution some experiments were carried out in 0.018 and 0.056 M hydrochloric acid containing anilinium chloride. For these solutions (B) and the terms with k_1 and k_3 are negligibly small. We therefore apply the equation

$$k = k_0(1-\alpha) + k_2L\alpha(BH^+) + k_4(1-\alpha)(BH^+)$$

to the unimolecular velocity constant k found in the experiments (Table VI). All the constants except k_4 are known. We find $k_4^* = 0.00056$ independently of the hydrogen ion concentration. We see that the effect exists, but it is too small to be detected in the aniline buffer solutions.

In an earlier paper[4] it was shown that aniline, in agreement with formula 2, has no appreciable effect in sufficiently alkaline solution.

TABLE VI

KETONIC DECOMPOSITION OF α,α-DIMETHYLACETOACETIC ACID AT 24.97° IN SOLUTIONS CONTAINING c MOLAR HYDROCHLORIC ACID, a MOLAR ANILINIUM CHLORIDE, AND (0.150-c-a) MOLAR SODIUM CHLORIDE. THE CONSTANTS GIVEN AT THE TOP AND BOTTOM OF TABLE IV HAVE BEEN USED

$c \times 10^3$	$a \times 10^3$	α	$k^* \times 10^3$ Exptl.	$k^* \times 10^3$ Calcd.	$k_0 \times 10^3 (1-\alpha)$	$k_2^*L \times 10^3 (BH^+)\alpha$	$k_4 \times 10^3 (BH^+)(1-\alpha)$
55.5	37.7	0.0091	1.833	1.835	1.807	0.007	0.021
18.26	56.4	.0271	1.844	1.837	1.772	.034	.031
55.7	75.4	.0091	1.860	1.864	1.807	.015	.042
18.40	112.7	.0268	1.901	1.901	1.773	.067	.061

From the experiments is found: $k_4^* = 0.00056$.

The results of the experiments both in *o*-chloroaniline and in aniline buffer solutions have been summarized in Table VII. It is impossible on the basis of the kinetic experiments to distinguish between the two possibilities mentioned in the introduction, namely, that B reacts with HA (corresponding to the velocity constants k_2 and k_3), or that BH^+ reacts with A^- (corresponding to the velocity constants k_2L and k_3L). In Table VII the velocity constants have therefore been given in both ways. If we assume that the Arrhenius equation $k = Ae^{-Q/RT}$ holds for the velocity constants, we may calculate the constants A and Q for each of the simultaneous reactions. Table VIII gives the values of A and Q, when the time unit is the second.

TABLE VII

THE DECOMPOSITION OF α,α-DIMETHYLACETOACETIC ACID IN *o*-CHLOROANILINE AND ANILINE BUFFER SOLUTIONS

The experimental data agree with the following expressions for the velocity, where HA denotes the undissociated keto acid, B the amine, and L the ratio between the dissociation constants of the acids BH^+ and HA: (1) $k_0(HA) + k_1(A^-) + k_2(B)(HA) + k_3(B)^2(HA) + k_4(BH^+)(HA)$ and (2) $k_0(HA) + k_1(A^-) + k_2L(BH^+)(A^-) + k_3L(B)(BH^+)(A^-) + k_4(BH^+)(HA)$. The velocity constants have the following values ($k^* = 0.4343\,k$, time in minutes)

		24.97°	34.93°
	k_0^*	0.001822	0.00636
	k_1^*	3.99×10^{-6}	17.5×10^{-6}
o-Chloroaniline	k_2^*	0.03244	0.0643
	k_3^*	0	0
	k_4^*	.00316	.0068
	k_2^*L	.1346	.408
Aniline	k_2^*	.480	.858
	k_3^*	.429	.680
	k_4^*	0	
	k_2^*L	.02209	.0647
	k_3^*L	.0197	.0512

TABLE VIII

THE CONSTANTS A AND Q OF THE FORMULA $k = Ae^{-Q/RT}$ TIME IN SECONDS

		A	Q (cal./mole)
	k_0	4.76×10^{12}	23.0×10^3
	k_1	1.09×10^{13}	27.1×10^3
o-Chloroaniline	k_2	1.921×10^6	12.53×10^3
	k_4	2.24×10^6	14.0×10^3
	k_2L	4.044×10^{12}	20.31×10^3
Aniline	k_2	1.165×10^6	10.64×10^3
	k_3	2.503×10^4	8.43×10^3
	k_2L	2.291×10^{11}	19.68×10^3
	k_3L	5.06×10^9	17.49×10^3

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Summary

The ketonic decomposition of α,α-dimethylacetoacetic acid has been investigated at the temperatures 24.97 and 34.93° in *o*-chloroaniline and aniline buffer solutions. Several reactions take place simultaneously. Tables VII and VIII give a summary of the experimental results.

The decomposition was also studied in solutions of *o*-chloroanilinium chloride (and anilinium chloride) containing hydrochloric acid. The influence of the hydrogen ion concentration seems to be more complicated than it appears from the experiments in the buffer solutions.

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