oxalacetate. The following procedure uses the sodium salt of the ester, thus making the isolation of the ester unnecessary. Sodium ethyl oxalacetate, 210 g. (1 mole), was suspended in 1500 ml. of boiling alcohol. Phenylhydrazine, 119 g. (1.1 moles), was added and, after 2 minutes, all the salt was dissolved and 100 ml. of acetic acid was added. This solution was boiled for one-half hour, being concentrated thereby to one-half of its original volume. Water (30 ml.) was added and the solution was cooled. The precipitate was collected and washed with 1 l. of 40% alcohol (300 ml. on filter, 600 ml. by trituration, and then 100 ml. on filter). This was crystallized from 2 l. of xylene to give 173 g. (75%) of the pyrazolone melting at 182–184°.

1-Phenyl-4-carbethoxy-5-pyrazolone.—This intermediate, used in the preparation of the pyrazolone for Dye 3, was prepared formerly by the cyclization of diethylphenylhydrazonomethylene malonate at 170–175°. The cyclization can be effected more easily. The hydrazono compound (110 g.) was suspended in a solution of 25 g. of Na_2CO_3 in 1.3 l. of water and refluxed for 2 hours. The solution was treated with 5 g. of Darco, filtered, and acidified with HCl. The product was washed on the filter with water and dried. The yield was 90 g. (98%) of crude material, melting at 113–114°.

Preparation of Azomethine Dyes.—The azomethine dyes were prepared by the method previously described[15] for the preparation of indoanilines, an alkaline solution of the pyrazolone and 2-amino-5-diethylaminotoluene being oxidized with freshly precipitated, finely divided silver chloride. Each of the crude dyes, except No. 11 which was too insoluble, was first subjected to a preliminary purification by chromatographic adsorption. For this purpose, the crude dye (from 0.025 mole of pyrazolone) was dissolved in 50 to 100 ml. of acetone. The resulting solution was brought to a volume of 200 ml. with benzene and passed through a column, approximately 4 cm. in diameter and 45 cm. in length, packed with Doucil.[16] The chromatogram was developed and the main magenta band was finally eluted with a mixture of acetone and benzene in the same proportions used for dissolving the dye. In all cases, a small amount of yellow dye[17] passed rapidly through the column, followed by the main heavy magenta band. A dark-colored, tarry residue was retained in the upper half of the column after all of the magenta dye had been eluted. The solution of the magenta dye was then evaporated to dryness and the dye was brought to analytical purity by repeated recrystallization. The yields of purified dyes were 25 to 50% in most cases, no special precautions having been taken to avoid losses, since the main interest was in obtaining highly pure samples.

Spectrophotometric Measurements.—All the spectrophotometric measurements were made on 3.0×10^{-5} *M* solutions in 1-cm. cells, using the General Electric Automatic Recording Spectrophotometer. The solvents used were checked for purity by ultraviolet absorption measurements.

Acknowledgment.—The authors are grateful to Mr. E. E. Richardson for preparing the many spectrophotometric curves required in this work.

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[15] P. W. Vittum and G. H. Brown, THIS JOURNAL, **68**, 2235 (1946).

[16] Sodium aluminum silicate, obtained from the Philadelphia Quartz Co.

[17] Identified in earlier unpublished work as 4,4'-bis-(diethylamino)-2,2'-dimethylazobenzene. Gerbaux[7] also isolated *p,p'*-bis-(dialkylamino)-azobenzene derivatives from the pyrazolone-coupling reaction mixtures.

ROCHESTER, N. Y. RECEIVED AUGUST 23, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

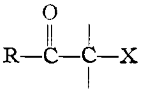
Mechanism of the Hydrolytic Cleavage of Carbon–Carbon Bonds. I. Alkaline Hydrolysis of β-Diketones[1]

BY RALPH G. PEARSON AND EVAN A. MAYERLE

The rates of alkaline hydrolysis of acetylacetone, methylacetylacetone and dimethylacetylacetone have been studied over a wide range of concentrations, and the "true" rate constants for the reactions have been calculated.

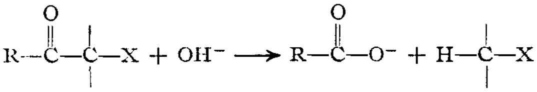
The mechanism appears to involve reactions of the neutral diketone molecule with either one or two hydroxide ions for acetylacetone and methylacetylacetone, but with only one hydroxide ion for dimethylacetylacetone. The "acid" and "ketone" cleavages of acetoacetic ester are commented upon.

Substances of the general formula



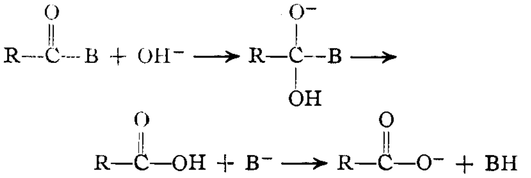
$R-\overset{\overset{O}{\|}}{C}-\underset{|}{\overset{|}{C}}-X$

where X is a suitable activating group are readily cleaved by aqueous alkali to give salts of carboxylic acids.



$$R-\overset{\overset{O}{\|}}{C}-\underset{|}{\overset{|}{C}}-X + OH^- \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^- + H-\underset{|}{\overset{|}{C}}-X \quad (1)$$

The group X must be a strong electron-attracting group such as nitro, carbonyl, carbalkoxyl or, in some cases, quaternary nitrogen. Halogen is effective if three atoms are alpha to the carbonyl.[2] It is reasonable to expect that the mechanism of this hydrolysis is analogous to that of the similar saponification of esters. Hauser and his co-workers[3] have written for example



$$R-\overset{\overset{O}{\|}}{C}-B + OH^- \longrightarrow R-\underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{C}}-B \longrightarrow$$

$$R-\overset{\overset{O}{\|}}{C}-OH + B^- \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^- + BH \quad (2)$$

for the mechanism of both reactions, B^- being either an alkoxyl ion or a displaceable carbanion such as $^-CH_2COCH_3$. An investigation, however, of the kinetics of alkaline hydrolysis of some 2-ketoalkylpyridinium salts[4] and of chloral hydrate[5] showed that the variation of the rate of cleavage with hydroxide ion concentration did not correspond to the demands of mechanism (2).

These compounds (and two of the β-diketones reported here) are acids capable of being ionized by alkali, the quaternary salts because of the α-hydrogen, and chloral hydrate because of the acidic hydroxyl. Furthermore, their acid strengths are such that the reaction

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[1] Abstracted from the M.S. thesis of Evan A. Mayerle, Northwestern University, 1950.

[2] For general reviews see Fuson and Bull, *Chem. Revs.*, **15**, 275 (1934), and Kröhnke and Heffe, *Ber.*, **70**, 864 (1937).

[3] Hauser, Swamer and Ringler, THIS JOURNAL, **70**, 4023 (1948).

[4] Pearson and Dillon, *ibid.*, **70**, 1933 (1948).

[5] Gustafsson and Johanson, *Acta Chem. Scand.*, **2**, 42 (1948).

$$\mathrm{HA} + \mathrm{OH}^- \rightleftharpoons \mathrm{A}^- + \mathrm{H_2O} \qquad (3)$$

where HA is the acid form, goes essentially to completion. If the mechanism of equation (2) held, the rate expression for cleavage would be

$$\mathrm{d}x/\mathrm{d}t = k_1[\mathrm{HA}][\mathrm{OH}^-] = (k_1/K_{\mathrm{eq}})[\mathrm{A}^-] = k_1'[\mathrm{A}^-] \qquad (4)$$

where K_{eq} is the equilibrium constant for the neutralization (3). If (3) goes to completion then $[\mathrm{A}^-] = (a - x)$ where a is the initial concentration of either HA or OH^- whichever one is present in smallest amount and x is the concentration reacted. The rate expression is then

$$\mathrm{d}x/\mathrm{d}t = k_1'(a - x) \qquad (5)$$

so that the reaction is pseudo-first order regardless of the relative amounts of the two reactants and with an apparent pseudo-first order rate constant k_1' equal to k_1/K_{eq}.[6]

In contrast to this expectation it was found that the rate of cleavage of chloral hydrate obeyed the rate equation

$$\mathrm{d}x/\mathrm{d}t = k_1'(a - x) + k_2'(a - x)[\mathrm{OH}^-] + k_3'(a - x)^2 \qquad (6)$$

and the rate of cleavage of the 2-ketoalkyl-pyridinium salts followed the rate equation

$$\mathrm{d}x/\mathrm{d}t = k_2'(a - x)[\mathrm{OH}^-] \qquad (7)$$

Accordingly it was decided to study the rate of cleavage of acetylacetone, methylacetylacetone and dimethylacetylacetone with aqueous barium hydroxide to get more information on the mechanism of hydrolysis of activated carbonyl compounds. The choice of compounds was intended to show the effect of diminishing ability to be ionized by alkali.

Experimental

Preparation of Materials.—Acetylacetone was purified from Eastman Kodak Co. White Label material by fractionation as described by Eidinoff,[7] $n^{25}\mathrm{D}$ 1.4500. Methylacetylacetone was made from acetylacetone and methyl iodide and purified as previously described.[8]

Dimethylacetylacetone was made in the same manner but starting with methylacetylacetone. After fractionating the crude product and collecting the material boiling between 170–173°, this fraction was washed with an excess of an aqueous solution of copper sulfate. By adjusting the *p*H to the neutral point of congo red (6–8) the blue-gray copper enolate of the unreacted methylacetylacetone would precipitate and could be removed by filtration. The remaining organic layer was washed and dried and fractionated through a ten-plate column. A middle fraction boiling within a 0.2° range at 172° (uncorrected) was taken; $n^{25}\mathrm{D}$ 1.4330. This material became colored on standing and was redistilled before each use.

Procedure.—Solutions of known concentration of the diketone and barium hydroxide were thermostated to ±0.05° for a half-hour and then mixed. From time to time samples (10 ml.) were withdrawn and discharged into a known excess of standard acid to quench the reaction. The acid was then back-titrated with alkali from a microburet graduated directly to 0.01 ml. The success of the method depends upon not titrating the diketone which is an acid of pK_a 9 or 11 (except for the dimethyl derivative) and upon titrating the acetic acid formed by cleavage. Calculations and checks with blanks indicated that this could best be done by taking a neutral *p*H as the end-point. Accordingly brom thymol blue was selected as an indicator. The greatest error lay in selecting the end-point which was not very sharp.

Calculations and Results

If V is the volume of base needed to back-titrate a sample at time t and V_∞ is the calculated volume of base at time equal to infinity,[9] then $(V_\infty - V)$ is proportional to $(a - x)$ and $(V_\infty - V_0)$ is proportional to a. Figures 1 and 2 show the results of plotting log $(V_\infty - V)$ against the time for acetylacetone and methylacetylacetone. From the slopes the observed rate constants were calculated in the usual way. Tables I and II give the data collected. It is seen that the observed rate constants vary with the concentration of hydroxide ion in solution.

TABLE I

ACETYLACETONE + BARIUM HYDROXIDE AT 35°

Initial concentration Base	Ketone	Excess base	k_{obs}, min.$^{-1}$ × 10^2
0.0423	0.0196	0.0227	0.745
.0423	.0196	.0227	.790
.0571	.0196	.0375	1.115
.0571	.0196	.0375	1.115
.0711	.0264	.0447	1.175
.0711	.0264	.0447	1.199
.0355	.0242	.0113	0.573
.0355[a]	.0175	.0180	.724
.1422	.0264	.1158	2.574
.1422	.0264	.1158	2.479
.0577	.0577	0	0.444
.0353	.0353	0	.449
.0284	.0350	−.0660	.468
.0386[b]	.0478	−.0092	.169

[a] Also 0.1069 *M* in KCl. [b] At 25.3°.

TABLE II

METHYLACETYLACETONE + BARIUM HYDROXIDE AT 35°

Initial concentration Base	Ketone	Excess base	k_{obs}, min.$^{-1}$ × 10^2
0.0671	0.0272	0.0399	4.30
.0671[a]	.0272	.0399	4.17
.0824	.0264	.0560	4.64
.0549	.0264	.0285	3.63
.0732	.0353	.0379	3.97
.0732	.0353	.0379	3.98
.0549	.0317	.0232	3.71
.0549	.0148	.0401	4.23
.0366	.0165	.0201	3.86
.0142	.0264	−.0122	3.08
.0362	.0447	−.0085	3.35
.0362	.0447	−.0085	3.21
.0274	.0529	−.0255	3.25
.0137[b]	.0371	−.0324	1.37

[a] Also 0.0525 *M* in KCl. [b] At 25.0°.

Figures 3 and 4 show the results of plotting k_{obs} against the concentration of hydroxide ion. The linearity indicates a rate equation of the form

$$\mathrm{d}x/\mathrm{d}t = k_1'(a - x) + k_2'(a - x)[\mathrm{OH}^-] \qquad (8)$$

Values of $k_1' = 0.00044$ and $k_2' = 0.0169$ for acetylacetone and $k_1' = 0.0308$ and $k_2' = 0.279$ for methylacetylacetone gave the best fit to the data.[10] The points for zero concentration of hydroxide ion in

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[6] For a similar case see Goldschmidt and Oslan, *Ber.*, **32**, 2390 (1899); **33**, 1140 (1900).

[7] Eidinoff, THIS JOURNAL, **67**, 2072 (1945).

[8] Mills and Pearson, *ibid.*, **72**, 1692 (1950).

[9] In a few runs V_∞ was checked experimentally and good agreement with the theory was observed. In view of the slowness of most of the runs, it was more convenient to use a theoretical value of V_∞.

[10] The values of k_2' are probably a little too high because of the poor choice of barium hydroxide as a cleaving agent. Barium ion probably increases the rate of reaction of two negative ions both by the ionic strength effect and by a specific effect.

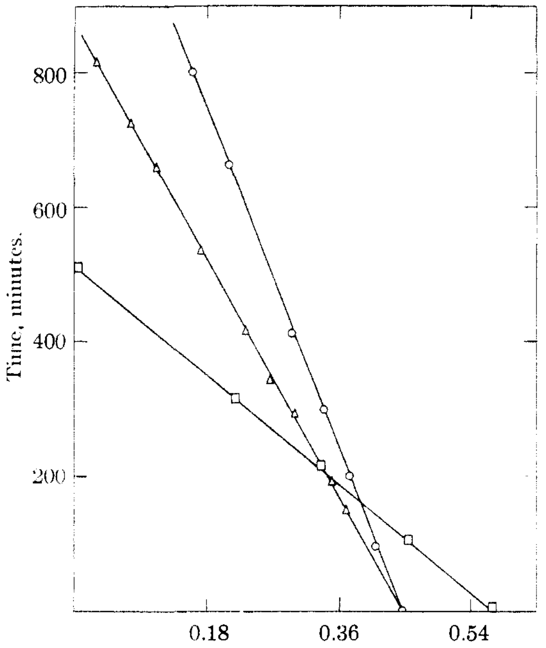


Fig. 1.—Acetylacetone + $Ba(OH)_2$ at 35°: ○, 0.0423 *M* base + 0.0196 *M* ketone; △, 0.0571 *M* base + 0.0196 *M* ketone; □, 0.1422 *M* base + 0.0264 *M* ketone.

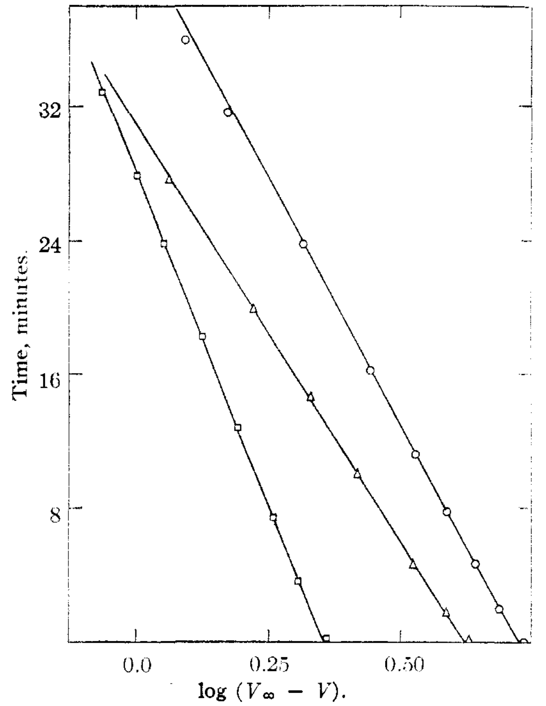


Fig. 2.—Methylacetylacetone + $Ba(OH)_2$ at 35°: ○, 0.0549 *M* base + 0.0317 *M* ketone; △, 0.0824 *M* base + 0.0264 *M* ketone; □, 0.0142 *M* base + 0.0264 *M* ketone.

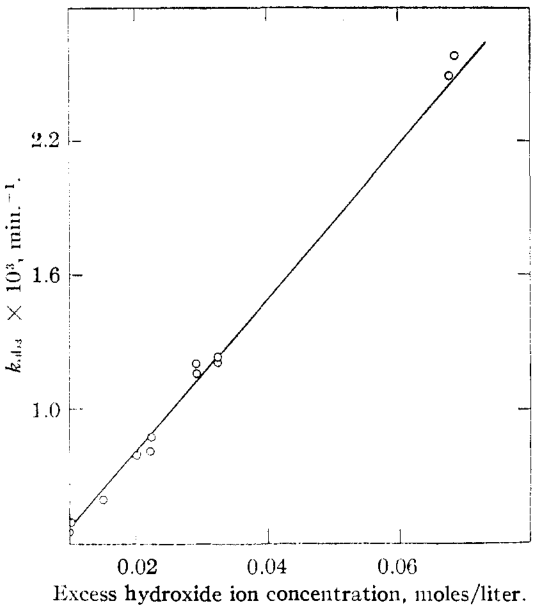


Fig. 3.—Acetylacetone.

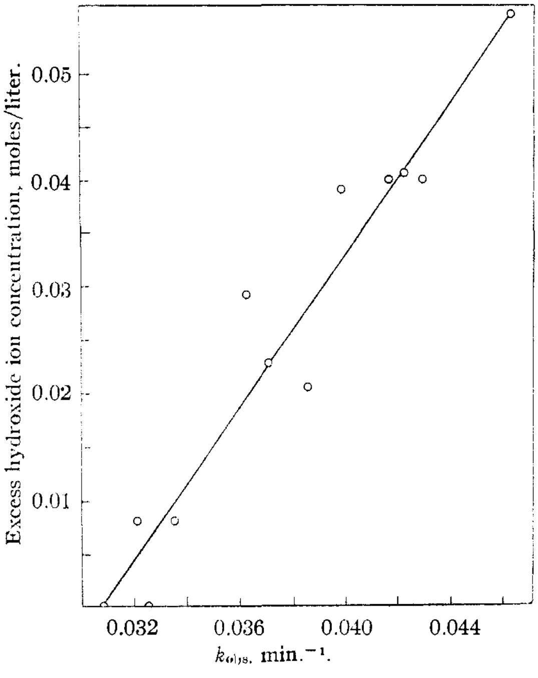


Fig. 4.—Methylacetylacetone.

Figs. 3 and 4 are for solutions where the diketone was either equivalent to the base or in greater concentration. This reduces the hydroxide concentration to a very low value (10^{-4} to 10^{-5} molar.)

Dimethylacetylacetone which is not an acid did not give first order kinetics. For equal concentrations of base and diketone plots of $1/(V_\infty - V)$ *versus* the time were linear showing second order kinetics as Fig. 5 illustrates. The second order rate constants were calculated from

$$k_1 = [(V_\infty - V_0)/a]\,(\text{slope}) \qquad (9)$$

As a check some runs were made with different initial concentrations *a* and *b* of base and diketone. log $[(V_\infty - V_0) - (a/b)(V - V_0)]/(V_\infty - V)$ was linear with the time showing the reaction to be truly first order in each component. Table III gives the data for dimethylacetylacetone. The rate constants are seen to be substantially constant for a fivefold variation in the hydroxide ion concentration. To check the influence of ionic strength on the rate constant one run was made for each diketone with KCl added to increase the ionic strength to a high value. The effect of ionic strength is seen to be small from Tables I, II and III.

TABLE III

DIMETHYLACETYLACETONE + $Ba(OH)_2$

Initial concentration Base	Ketone	Temp., °C.	k_1, l./mole-min.
0.0340	0.0340	0	1.96
.0340	.0340	0	2.15
.0253	.0253	0	2.09
.0104	.0104	0	2.08
.0366	.0220	0	2.04
.0366	.0550	0	1.88
.0549	.0197	0	2.10
.0275	.0492	0	1.94
.0104	.0104	13	3.88
.0131[a]	.0131	13	3.65
.0131	.0131	13	3.87

[a] Also 0.1570 *M* in KCl.

Discussion

Acetylacetone and methylacetylacetone are acids whose k_a's are known to be 1.2×10^{-9},[7] and 2.8×10^{-11},[11] respectively, at 35°. Consequently the value of K_{eq} is 10^5 to 10^3 for reaction (5) which goes substantially to completion. Hence the observed first order kinetics and the dependence on base

$$[A^-]/[HA][OH^-] = K_{eq} = Ka/Kw \qquad (10)$$

concentration can be interpreted as due either to the reaction of the carbanion with zero or one hydroxide ion or to the reaction of the neutral diketone with one or two hydroxide ions. The rate expressions would be

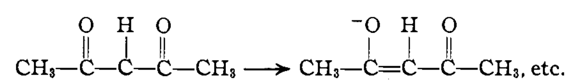
$$dx/dt = k_1[A^-] + k_2[A^-][OH^-] \qquad (11)$$

or

$$dx/dt = k_1[HA][OH^-] + k_2[HA][OH^-]^2 \qquad (12)$$

These two possibilities are kinetically indistinguishable because of the equilibrium shown in (10). Actually the rate expression could also be a combination of (11) and (12).

The first rate expression involving the carbanion is improbable for several reasons. First of all dimethylacetylacetone which does not form a carbanion and chloral hydrate, which forms an oxy-anion, are readily cleaved by alkali. Secondly, the resonance forms of the carbanion give the bond to be cleaved a considerable fraction of double bond



$$CH_3-\overset{\overset{O}{\|}}{C}-\underset{-}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\overset{\overset{^-O}{|}}{C}=\overset{\overset{H}{|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3\text{, etc.}$$

character which must strengthen it. Hauser[3] also cites organic evidence for believing that it is the keto form of the neutral molecule which cleaves rather than the carbanion or the enol form.

The second rate expression involving the neutral diketone is consistent with several detailed mechanisms. The first term is consistent with Hauser's mechanism analogous to the alkaline hydrolysis of an ester. The second term is most reasonably explained as a reversible addition of one hydroxide ion to a carbonyl followed by a reaction of the complex with another hydroxide ion. Since it is shown in another communication[12] that alkaline alcoholysis of activated carbonyl compounds does not involve two moles of ethoxide ion, it seems reasonable that the hydrogen of the first hydroxide ion is involved. There may be a slow formation of a doubly charged anion which then spontaneously cleaves

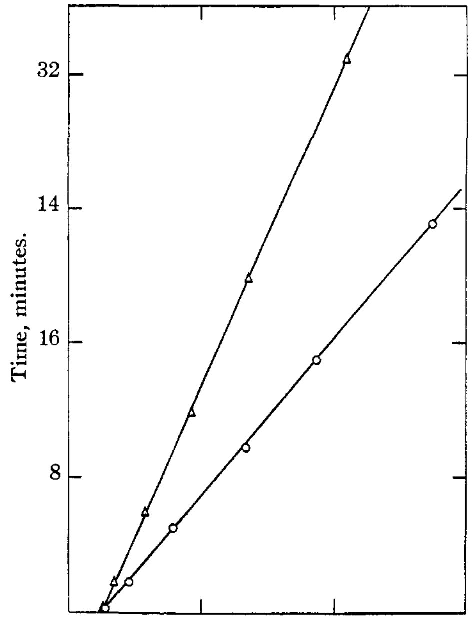
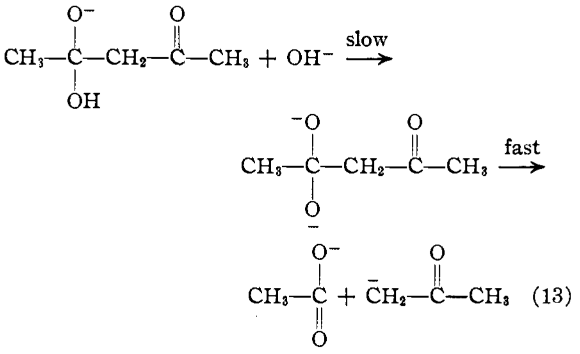
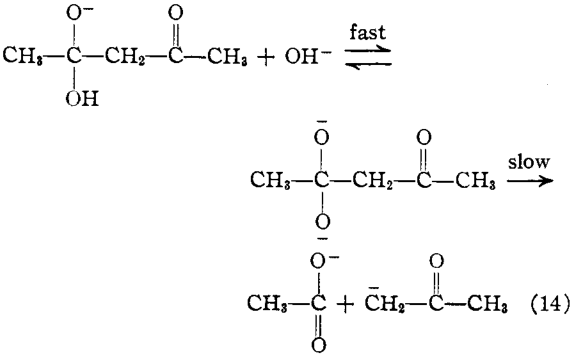


Fig. 5.—Dimethylacetylacetone + $Ba(OH)_2$: ○, 0.0104 *M* base and ketone at 13°; △, 0.0104 *M* base and ketone at 0°.



$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 + OH^- \xrightarrow{\text{slow}} CH_3-\underset{\underset{O^-}{|}}{\overset{\overset{^-O}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{\text{fast}} CH_3-\underset{\underset{O}{\|}}{\overset{\overset{O^-}{|}}{C}} + \bar{C}H_2-\overset{\overset{O}{\|}}{C}-CH_3 \qquad (13)$$

or, there may be a fast, reversible formation of the double negative ion which then slowly cleaves



$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 + OH^- \overset{\text{fast}}{\rightleftharpoons} CH_3-\underset{\underset{O^-}{|}}{\overset{\overset{O^-}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{\text{slow}} CH_3-\underset{\underset{O}{\|}}{\overset{\overset{O^-}{|}}{C}} + \bar{C}H_2-\overset{\overset{O}{\|}}{C}-CH_3 \qquad (14)$$

The first of these possibilities is identical with the mechanism proposed by Gustafsson and Johanson[6] for the hydrolysis of chloral hydrate. It has the

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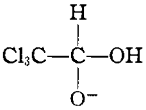
(11) Mills, Ph.D. thesis, Northwestern University, 1949.

(12) Pearson and Sandy, THIS JOURNAL, **73**, 93 (1951).

feature of being general base catalyzed since any base could perform the function of removing the proton in the rate determining step. Actually since the kinetics for chloral hydrate satisfy equation (7) it was claimed by the above authors that general base catalysis does occur. The first term in (7) is due to a water molecule acting as a base, the second term to hydroxide ion and the third term to the anion of chloral hydrate acting as a base. The relative magnitudes of k_1', k_2' and k' are consistent with this. The anion of chloral hydrate  $Cl_3C—\overset{H}{\underset{O^-}{C}}—OH$ is identical with the addition complex postulated in (13) and is the substrate on which the three bases work.

The second mechanism is kinetically distinguishable from the first in that specific hydroxide ion catalysis would be found and other bases would not be effective as such. In the work presented here no evidence of catalysis by the carbanion of the diketone was noted, though the first term of equation (8) could be interpreted as due to the catalysis by water. It must be pointed out that it is difficult to detect catalysis by other bases in the presence of large terms due to water and to hydroxide ion so that general base catalysis is not ruled out.

The cleavage of dimethylacetylacetone evidently involves the reaction of the neutral diketone with only one hydroxide ion. The disappearance of the term in the observed rate constant dependent on the hydroxide concentration might be argued as evidence that such a term involves the carbanion which is impossible for the dialkyl compound. However the fact that this term has diminished in importance on substituting one methyl group (k_2'/k_1' is 38 for acetylacetone and 9 for methylacetylacetone) indicates a gradual disappearance rather than an abrupt one. This may be due to a weakening of the carbon–carbon bond which renders less necessary the helping effect of the double charged anion in cleaving.

From measurements at only two temperatures the approximate activation energy for k_1' has been calculated for all three compounds. These are recorded in Table IV. On the assumption that equation (12) is correct and that the reaction involves only the neutral diketone, the "true" rate constants k_1 and k_2 have been calculated from the apparent rate constants, k_1' and k_2' by using the relation $k_1 = k_1'K_{eq}$, etc. In addition since K_{eq} is known as a function of temperature,[11] the "true" heats of activation have been calculated for acetylacetone and methylacetylacetone from

$$\Delta H^{\ddagger}_{\text{true}} = \Delta H^{\ddagger}_{\text{obs}} + \Delta H^0_{\text{a}} - \Delta H^0_{\text{w}} \qquad (15)$$

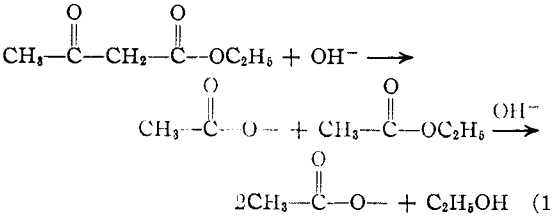
where the subscripts *a* and *w* refer to the ionization of the diketone and water, respectively. For dimethylacetylacetone the "true" rate constant and heat of activation are identical with the observed. These data have been collected in Table IV.

TABLE IV

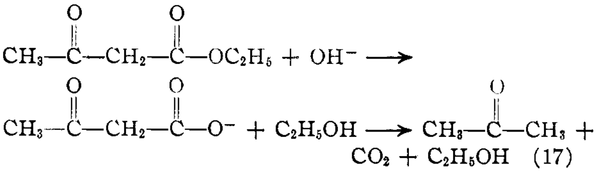
	Acetylacetone	Methylacetylacetone	Dimethylacetylacetone
k_1', min.$^{-1}$	4.40×10^{-4}	3.08×10^{-2}	9.1
k_2', l./mole-min.	1.69×10^{-2}	2.79×10^{-1}	...
K_{eq}.	6.40×10^4	1.24×10^3	...
k_1, l./mole-min.	28	39	9.1
k_2, l.^{2}/mole^2-min.	1080	346	...
$E_{act.}$, kcal.	15	15	7.4
$\Delta H^{\ddagger}_{\text{true}}$	6	9	6.8

The "true" rate constants, k_1, are all about the same for the three diketones. Hence the experimental fact that alkylation increases the ease of alkaline hydrolysis of such compounds[13] is to be attributed to the fact that it is the neutral molecule which is cleaved and the greater the acid strength, the less neutral molecule is left in solution at equilibrium in the presence of alkali. The strongest acid, acetylacetone, is protected from cleavage by being converted to the non-reactive carbanion. The same is true for methylacetylacetone but to a lesser degree since the alkyl group weakens the acidity. Dimethylacetylacetone not being capable of forming a carbanion is readily attacked by alkali.

It is also worthwhile pointing out that the existence of a term in the rate expression proportional to the hydroxide ion concentration helps to explain the phenomena of "acid" and "ketone" cleavage of acetoacetic ester.[14] The acid cleavage is similar to the reaction studied here, and its rate is accelerated by excess hydroxide ion. The ketone cleavage involves preliminary hydrolysis of the ester followed by decarboxylation.



$$CH_3—\overset{O}{\overset{\|}{C}}—CH_2—\overset{O}{\overset{\|}{C}}—OC_2H_5 + OH^- \longrightarrow CH_3—\overset{O}{\overset{\|}{C}}—O^- + CH_3—\overset{O}{\overset{\|}{C}}—OC_2H_5 \xrightarrow{OH^-} 2CH_3—\overset{O}{\overset{\|}{C}}—O^- + C_2H_5OH \qquad (16)$$



$$CH_3—\overset{O}{\overset{\|}{C}}—CH_2—\overset{O}{\overset{\|}{C}}—OC_2H_5 + OH^- \longrightarrow CH_3—\overset{O}{\overset{\|}{C}}—CH_2—\overset{O}{\overset{\|}{C}}—O^- + C_2H_5OH \longrightarrow CH_3—\overset{O}{\overset{\|}{C}}—CH_3 + CO_2 + C_2H_5OH \qquad (17)$$

The rate of hydrolysis of the ester is independent of the hydroxide ion concentration because of the acidity of the acetoacetic ester.[6] Hence the ketone cleavage which is fastest in dilute alkali (or in acid) loses ground to the acid cleavage as the concentration of alkali increases until finally the acid cleavage predominates.

EVANSTON, ILLINOIS RECEIVED JUNE 5, 1950

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[13] Adkins and Kutz, THIS JOURNAL, **52**, 4391 (1930); Dieckmann, *Ber.*, **33**, 2670 (1900); **41**, 1260 (1908).

[14] Wislicenus, *Ann.*, **190**, 257 (1878); **206**, 308 (1881).