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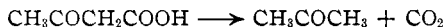
THE KETONIC DECOMPOSITION OF BETA-KETO CARBOXYLIC ACIDS

BY KAI JULIUS PEDERSEN

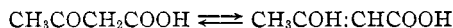
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It is well known that β -keto carboxylic acids, *e.g.*, acetoacetic acid, split off carbon dioxide according to the scheme

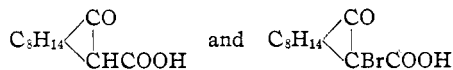


and that the cleavage is catalyzed by certain amines. This so-called ketonic decomposition is characteristic of β -keto acids, neither α - nor γ -acids showing any appreciable decomposition. Thus pyruvic and levulinic acids are stable. Unless both the α -hydrogen atoms are substituted, the β -keto acids consist of a mixture of two tautomers, a keto form and an enol form; for instance, in the case of acetoacetic acid



Opinions differ as to whether the keto or the enol form is the unstable form. The present work is an attempt to solve this problem. On the suggestion of Professor N. Bjerrum the α,α -dimethylacetoacetic acid, which exists only in the keto form, was investigated. If only the enol form of β -keto acids is unstable, the α,α -disubstituted acid must be stable in aqueous solution.

The kinetics of the ketonic decomposition of β -keto acids and the catalysis by amines have been investigated several times. G. Bredig and his school^{1,2,3} studied camphorcarboxylic acid and α -bromocamphorcarboxylic acid



While the former has a keto and an enol form, the latter is purely ketonic. It was first shown by Fajans³ that the latter splits off carbon dioxide and that its decomposition is catalyzed by amines. For camphorcarboxylic acid it has thus been established that the keto form can decompose.

The decomposition of acetoacetic acid has been studied by L. Pollak,⁴ N. O. Engfeldt,⁵ E. M. P. Widmark,⁶ H. v. Euler⁷ and G. Ljunggren.⁸

¹ G. Bredig, *Z. Elektrochem.*, **24**, 285 (1918).

² Pastanogoff, *Z. physik. Chem.*, **112**, 448 (1924).

³ K. Fajans, *ibid.*, **73**, 25 (1910).

⁴ Pollak, *Hofmeisters Beiträge*, **10**, 234 (1907).

⁵ Engfeldt, "Beiträge zur Kenntnis der Biochemie der Acetonkörper," Dissertation, Lund, 1920.

⁶ Widmark, *Acta Med. Scand.*, **53**, 393 (1920); *Skand. Arch. Physiol.*, **42**, 43 (1922).

⁷ H. v. Euler, *Z. anorg. Chem.*, **147**, 295 (1925).

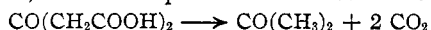
⁸ Ljunggren, "Katalytisk Kolsyreavspjälkning ur Ketokarbonsyror," Dissertation, Lund, 1925.

It has been shown that the rate of decomposition follows the law

$$-\frac{dc}{dt} = k'_m c(1 - \alpha) + k'_i c\alpha \quad (1)$$

where c is the concentration of acetoacetic acid, α its degree of dissociation and k'_m and k'_i are velocity constants for the decomposition of the undissociated acid and the ion. From experiments in buffer solutions it is possible to calculate the dissociation constant of acetoacetic acid (Widmark). Ljunggren's results are given in Table VI at the end of this paper. Widmark and Ljunggren have found that amines only catalyze when the PH of the solution is kept within a limited interval, while the amines are inactive in strong acid and alkaline solutions. This they explain by assuming that either the neutral amine reacts with the undissociated acetoacetic acid or the positive ammonium ion with the acetoacetate ion. It is impossible to distinguish between these possibilities on the basis of kinetic experiments. Ljunggren has found that only primary amines are good catalysts. Secondary and tertiary amines give only small effects.

A similar reaction, the decomposition of acetone-dicarboxylic acid



has recently been studied by E. O. Wiig.⁹ He determined the velocity of the decomposition in water, aniline and various alcohols and also the effect of catalysts. Wiig does not take into account the dissociation equilibrium of acetone-dicarboxylic acid. This acid is fairly strong. According to Angeli¹⁰ its dissociation constant in aqueous solution is 0.79×10^{-3} . Consequently its aqueous solution contains both undissociated acid and univalent ion, and these will probably decompose with different velocities. It seems to the author that this is the simplest explanation of Wiig's experiments in aqueous hydrochloric acid, where he finds that the velocity constant at first decreases and then remains constant with increasing concentration of hydrochloric acid. He explains the retardation by assuming that hydrogen chloride adds to the keto group, forming a stable compound, but it is simpler to assume that the undissociated acetone-dicarboxylic acid decomposes somewhat more slowly than its univalent ion. Addition of hydrochloric acid to the solution causes a depression of the dissociation until the acid is completely undissociated. On p. 970 Wiig takes into account the hydrogen-ion concentration due to the dissociation of the carbonic acid formed by the reaction in an aqueous solution of acetone-dicarboxylic acid, while he disregards the much greater hydrogen-ion concentration from the acetone-dicarboxylic acid itself.

Experimental Part

The velocity of the ketonic decomposition of α, α -dimethylacetoacetic acid was determined at the temperature 18.00° by means of an apparatus

⁹ Wiig, *J. Phys. Chem.*, **32**, 961 (1928).

¹⁰ Angeli, *Gazz. chim. ital.*, II, **22**, 31 (1892).

described by J. N. Brönsted.^{11,12} The pressure of carbon dioxide above the solution in the closed apparatus is measured during the reaction. Experiments were made in solutions of hydrochloric acid sufficiently concentrated to make the dimethylacetoacetic acid practically completely undissociated, and in glycolate and acetate buffer solutions, where the dimethylacetoacetic acid is partially dissociated.

Impurities of acetoacetate and monomethylacetoacetate were removed from the ethyl ester of α,α -dimethylacetoacetic acid (Kahlbaum) by shaking for an hour with an equal volume of 25% potassium hydroxide solution.¹³ After separation from the aqueous layer and two distillations it boiled at 184–185° (boiling point found by Perkin¹⁴ 184.8–185.0°).

The amount of the ethyl ester used for an experiment (0.001–0.002 mole) was weighed out, an excess of sodium hydroxide added and the mixture was left at room temperature until the next day. Rough determinations of the rate of hydrolysis of the ester had shown that this was sufficient for practically complete hydrolysis. Acid was added, the solution diluted to 100 cc. and poured into the reaction flask in the apparatus.

Experiments in Solutions of Hydrochloric Acid.—The reaction follows the unimolecular law

$$-k_m t = \log c + \text{constant} \quad (2)$$

where k_m is the velocity constant expressed by means of decadic logarithms, t is the time in minutes and c the concentration of dimethylacetoacetic acid at the time t . P denotes the difference, $p_\infty - p$, between the pressure p_∞ above the solution after the reaction is complete and the pressure p at the time t . As P and c are proportional during the reaction, $c = fP$ and Equation 2 may be written

$$-k_m t = \log P + \text{constant}$$

k_m was computed according to this equation by plotting $\log P$ against t ; f does not enter into the calculations when the reaction follows the unimolecular law. Only when this law does not hold, as in experiments in buffer solutions, is a knowledge of the value of f necessary. f can be calculated from the known concentration of the reacting substance before the experiment (c_0) and the total increase in pressure during the experiment (P_0); $f = c_0/P_0$.

The results of the experiments in hydrochloric acid are given in Table I. Owing to the method of preparation of the solutions they all contain a little ethyl alcohol ($<0.02 M$) originating from the ester. By comparison of Expts. 1 and 2 with 4, where extra alcohol has been added, it is seen that 0.02 M alcohol can have no detectable effect. Hydrochloric acid,

¹¹ Brönsted and King, *THIS JOURNAL*, **47**, 2523 (1925).

¹² Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

¹³ A. Michael, *Ber.*, **38**, 2096 (1905).

¹⁴ Perkin, *J. Chem. Soc.*, **83**, 1231 (1903).

sodium chloride and glycolic acid all have a small accelerating effect. If we assume that the effects vary linearly with the concentrations of the substances, and that they are independent of one another, we get the following values for the increase in k_m per mole/liter of added substance: hydrochloric acid, 50×10^{-6} ; sodium chloride, 37×10^{-6} ; undissociated glycolic acid, 25×10^{-6} . By means of these data we find by extrapolation the velocity constant for the decomposition of undissociated dimethylacetoacetic acid in pure water, $k_{m0} = 723 \times 10^{-6}$.

TABLE I
THE VELOCITY OF DECOMPOSITION OF DIMETHYLACETOACETIC ACID IN HYDROCHLORIC ACID

No.	Concn. of dimethylacetoacetic acid, α	Concn. of HCl	Concn. of NaCl	Other substances	$k_m \times 10^{-6}$
1	0.01801	0.175	0.040	729
2	.01562	.108	.040	730
3	.01604	.551	.040	752
4	.01747	.175	.040	0.20 M C_2H_5OH	724
5	.01465	.108	.640	752
6	.01576	.108	.040	1.18 M $CH_2OHCOOH$	759

Experiments in Buffer Solutions.—These measurements were made in order (1) to determine the dissociation constant of dimethylacetoacetic acid, (2) to obtain an idea of the velocity of decomposition of the dimethylacetoacetate ion and (3) to examine whether the reaction like the decomposition of the acetoacetic acid itself is catalyzed by amines.

The velocity of decomposition in a buffer solution depends on the degree of dissociation (α) of the dimethylacetoacetic acid at the P_H of the solution. Equation 1 holds as for acetoacetic acid.

Glycolate buffer solutions were chosen for the determination of the dissociation constant of dimethylacetoacetic acid because this constant and that of glycolic acid are of the same order of magnitude. The ratio $L = K_D/K_G$, where K_D and K_G are the concentration dissociation constant of dimethylacetoacetic acid and glycolic acid, is presumably almost independent of the salt concentration even in fairly concentrated solutions, although the dissociation constants themselves are very sensitive to salt. In order to minimize the change in hydrogen-ion concentration due to the disappearance of the dimethylacetoacetic acid, rather concentrated buffer solutions were used. A correction formula was also applied.

It will be shown later that for experiments in glycolate buffer solutions the decomposition of the dimethylacetoacetate ion is negligible compared with that of the undissociated acid, at least when no catalyst is present. Equation 1 reduces to

$$\frac{dP}{Pdt} = -k'_m(1 - \alpha) \quad (3)$$

α increases during the decomposition. α_0 denotes its value at the time ∞ when the concentration of dimethylacetoacetic acid is 0. We want to calculate the velocity constant

$$k' = k'_m (1 - \alpha_0) \quad (4)$$

corresponding to this concentration.

From the mass action law we get

$$\frac{a + \alpha c}{b - \alpha c} \frac{\alpha}{1 - \alpha} = L$$

where a and b are the stoichiometric or final concentrations of glycolic acid and sodium glycolate, respectively. Hence

$$\alpha = \frac{L(b - \alpha c)}{a + Lb - (L - 1)\alpha c} \quad \text{and} \quad \alpha_0 = \frac{Lb}{a + Lb} \quad (5)$$

$$\alpha_0 - \alpha = \frac{L(a + b)\alpha c}{(a + Lb - (L - 1)\alpha c)(a + Lb)}$$

We now use as an approximation in the numerator $\alpha = \alpha_0$ and in the denominator $c = 0$. Using $c = f \times P$ and (5), we get

$$\alpha_0 - \alpha = \frac{L^2 b(a + b)fP}{(a + Lb)^3}$$

From (3), (4) and (5) we get

$$-\frac{dP}{Pdt} - k' = k'_m (\alpha_0 - \alpha) = \frac{L^2 b(a + b)f \times k'_m}{(a + Lb)^3} \times P$$

$$= \frac{L^2 b(a + b)f \times k'_m}{(a + Lb)^2 a} P = A \times k' \times P$$

where A denotes

$$\frac{L^2(a + b)b \times f}{(a + Lb)^2 \times a}$$

Hence by integration

$$\log_e \left(\frac{1}{P} + A \right) = k't + \text{constant, or}$$

$$\log_{10} \left(\frac{1}{P} + A \right) = kt + \text{constant} \quad (6)$$

In order to use this formula we require an approximate value of L . We find this by plotting $\log P$ against t . We get in this way a curve which deviates only slightly from a straight line. The slope gives an approximate value of $k = k'_m(1 - \alpha_0)$. We now calculate L from Equation 5. Knowing L we can calculate A . We finally plot $\log (1/P + A)$ against t and find k . The calculation of an experiment has been given in Table II.

In Table III are given the values of k computed in this way for glycolate buffer solutions.

It has been found in the experiments in hydrochloric acid that sodium chloride and undissociated glycolic acid have a small accelerating effect on the decomposition of the undissociated dimethylacetoacetic acid and the magnitude of these effects has been found. From a comparison of Expts. 7 to 10 or 11 and 12 (Table III) we see that sodium glycolate has a

TABLE II
EXPERIMENT No. 11

$c_0 = 0.01361$; $a = 0.2924$; $b = 0.2009$; $f = 0.01361/9.11 = 0.00149$; $L = 2$; $A = 0.0042$.

t , min.	P (cm. Hg)	$\log \left(\frac{1}{P} + A \right)$	t , min.	P (cm. Hg)	$\log \left(\frac{1}{P} + A \right)$
0	9.11 ^a	...	350	7.01	0.167
23	9.02	0.061	380	6.87	.176
120	8.33	.094	395	6.78	.181
153	8.12	.105	453	6.50	.199
178	7.98	.112	1505	3.00	.528
212	7.78	.123	1562	2.88	.546
240	7.60	.133	1606	2.77	.562
276	7.40	.144	1750	2.50	.607
315	7.20	.156	1795	2.40	.624

$$k = 315 \cdot 10^{-6}$$

^a Extrapolated

TABLE III
THE VELOCITY OF DECOMPOSITION OF DIMETHYLACETOACETIC ACID IN GLYCOLATE BUFFER SOLUTIONS

No.	Concn. of glycolic acid, a	Concn. of glycolate, b	$k \times 10^6$, exp.	L^*	$k_m \times 10^6$	$1 - \alpha_0$	L	$k \times 10^6$, calcd.
7	0.1937	0.2009	243	1.925	759	0.320	2.05	244
8	.1937	.2009 ^a	250	1.900	774	.323	2.02	248
9	.3858	.4034	253	1.815	795	.318	2.05	254
10	.581	.603	265	1.720	831	.319	2.06	267
11	.2924	.2009	315	1.920	761	.414	2.06	317
12	.5847	.4018	331	1.790	800	.414	2.06	333
13	.7804	.4034	396	1.695	805	.492	2.00	392
14	.782	.402	396	1.705	805	.492	2.00	392
15	.572	.020	680	...	740	.920	..	692
16	1.164	.020	725	...	755	.960	..	730

^a Added 0.40 M NaCl. Mean value $L = 2.04$.

similar effect. Although $1 - \alpha_0$ is almost constant within these experiments, k varies much more than can be accounted for by the small effect of the undissociated glycolic acid and the sodium chloride. We first calculate L without taking into account the effect of the sodium glycolate. We denote by * the data in the calculation of which this effect has been neglected.

$$1 - \alpha_0^* = \frac{k}{k_m^*} \quad L = \frac{a}{b} \times \frac{\alpha_0^*}{1 - \alpha_0^*} \quad (7)$$

where $k_m^* = (723 + 37 c_{\text{NaCl}} + 25 a) \times 10^{-6}$.

We assume that the effect of the sodium glycolate on k_m is proportional to its concentration, $k_m = k_m^* + \beta b$. By introduction in (7)

$$L^* = \frac{a}{b} \times \frac{k_m - \beta b - k}{k} = \frac{a}{b} \frac{k_m - k}{k} - \beta \frac{a}{k}$$

$$L^* = L - \beta \times \frac{a}{k} \quad (8)$$

From this equation we see that we can find β by plotting L^* against a/k . See the diagram. The value of the slope is $-\beta = -155 \times 10^{-6}$. We can now calculate k_m , $1 - \alpha_0$ and L . The values are given in Table III. The mean value of L is 2.04. Using this value for L and

$$10^6 \times k_m = 723 + 37 c_{\text{NaCl}} + 25 a + 155 b$$

we calculate the k values given in the last column of Table III. They are in good agreement with the experimental values.

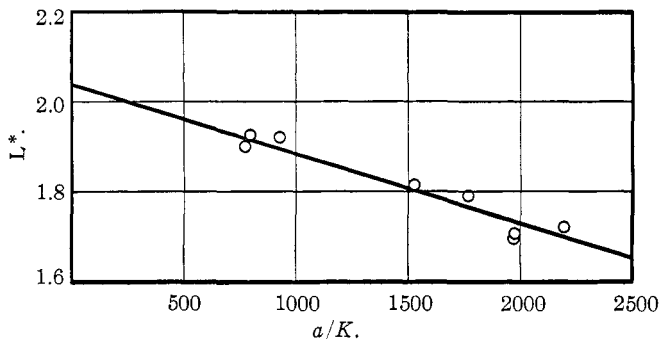


Fig. 1.—Graphical determination of the effect of sodium glycolate on the rate of decomposition of undissociated dimethylacetoacetic acid, Equation 8. The slope is $-\beta = -155 \times 10^{-6}$.

We have now determined the ratio between the dissociation constants of dimethylacetoacetic acid and glycolic acid, $L = 2.04$ at 18° . The dissociation constant of glycolic acid has been determined by J. Böeseken and H. Kalshoven.¹⁵ They found at 25° the value 1.54×10^{-4} for dilutions from 4 to 512 liter/mole. It is permissible to use the same value at 18° , because the dissociation constants of weak acids in general do not vary much with the temperature. We thus find for dimethylacetoacetic acid the dissociation constant 3.14×10^{-4} .

In order to get an idea of k_i , the velocity of the decomposition of the dimethylacetoacetate ion, some measurements were made in acetate buffer solutions, where the dimethylacetoacetic acid is almost completely dissociated (Table IV). In the calculation of the velocity constant k Equation 6 has been applied. By means of the dissociation constant ratio for dimethylacetoacetic and acetic acid, $L = K_D/K_A = (3.14 \times 10^{-4})/(1.80 \times 10^{-5}) = 17.5$, $1 - \alpha_0$ is calculated. If we neglect the effect of the medium (acetic acid and sodium acetate) on the decomposition of the undissociated dimethylacetoacetic acid, we can calculate $k_{m0}(1 - \alpha_0)$, the part of k which is due to the decomposition of undissociated dimethylacetoacetic acid. The part of k which is due to the decomposition of the ion is probably smaller than the difference given in the last column of Table IV, because

¹⁵ Böeseken and Kalshoven, *Rec. trav. chim.*, **37**, 130 (1918).

we have used k_{m0} instead of k_m . Thus the velocity constant for the decomposition of the dimethylacetoacetate ion k_i is smaller than 4×10^{-6} , while that for the undissociated acid is $k_{m0} = 723 \times 10^{-6}$. In the experiments in glycolate buffers, k_i has been neglected. The results will only be slightly different if we use $k_i = 4 \times 10^{-6}$.

TABLE IV

THE VELOCITY OF DECOMPOSITION OF DIMETHYLACETOACETIC ACID IN ACETATE BUFFER SOLUTIONS

No.	Concn. of acetic acid	Concn. of sodium acetate	$k \times 10^6$	$1 - \alpha_0$, calcd.	$k_{m0} (1 - \alpha_0) 10^6$	Diff.
17	0.300	0.300	44	0.059	42	2
18	.300	.600	25	.029	21	4
19	.500	.500	46	.059	42	4

The Catalysis by Amines.—In Table V are given two experiments in which the catalysis of an amine, aniline, was examined. The results are only approximate because no correction has been made for the change in α during the reaction. Nevertheless, it is clear from a comparison of the last two columns of Table V that aniline has a very great accelerating effect. In the calculation of α the value found by Brönsted and Duus¹² for the acid strength¹⁶ of the anilinium ion

$$K_{C_6H_5NH_3^+} = \frac{(C_6H_5NH_2)(H^+)}{(C_6H_5NH_3^+)} = 2.06 \times 10^{-5}$$

has been used. The ratio $L = K_D/K_{C_6H_5NH_3^+}$, unlike L for glycolic acid, is highly salt sensitive. The α -values calculated in this way are therefore only rough approximations.

TABLE V

THE CATALYTIC EFFECT OF ANILINE ON THE DECOMPOSITION OF DIMETHYLACETOACETIC ACID

No.	Concn. of acetic acid	Concn. of sodium acetate	Concn. of aniline hydrochloride	Concn. of aniline	$k \times 10^6$	$k \times 10^6$ calcd. without catalysis
20	0.500	0.500	0.0986	0.122	1310	40
21	.000	.000	.0585	.0426	680	61

Discussion

In Table VI the velocity constants found by Ljunggren for acetoacetic acid are given together with the constants found in the present work for dimethylacetoacetic acid. Ljunggren worked at 37 and 25°. His values have been extrapolated to 18° by means of the formula $d \log k/d(1/T) = \text{constant}$, where T is the absolute temperature. As seen from the table, the undissociated dimethylacetoacetic acid, that is, a pure ketone, at 18° decomposed 4.5 times as quickly as the undissociated acetoacetic acid. At 18° dimethylacetoacetic acid decomposes with the same velocity as

¹⁶ J. N. Brönsted, *Rec. trav. chim.*, **42**, 718 (1923); *J. Phys. Chem.*, **30**, 777 (1926).

acetoacetic acid at about 29°. It has thus been shown that the keto form is unstable. Probably only the keto form decomposes.

TABLE VI

ACETOACETIC AND DIMETHYLACETOACETIC ACID. VELOCITY CONSTANTS FOR THE KETONIC DECOMPOSITION (DECAD. LOG., MIN.⁻¹) AND DISSOCIATION CONSTANTS

	37°	Acetoacetic acid 25° (Ljunggren)	18° (extrap.)	Dimethylaceto- acetic acid, (K. J. P.) 18°
Undissociated acid $k_m^0 10^6$	2080	430	161	723
Ion $k_i \times 10^6$	38.5	8.95	3.6	<4
Dissociation constant	2.04×10^{-4}	2.21×10^{-4}	2.29×10^{-4}	3.14×10^{-4}

Engfeldt⁵ has by means of the bromination method of K. H. Meyer¹⁷ determined the amount of ketone and enol in acetoacetic acid dissolved in water. Bromine reacts instantaneously with the enol form while it has no effect on the keto form. The accuracy of the analysis is not great owing to the formation of enol from the ketone during the analysis. Engfeldt therefore considers his results as being only rough approximations. He finds that undissociated acetoacetic acid (free acid + an excess of hydrochloric acid) consists of 18% keto form and 82% enol form. This result is not confirmed by a work which the author is doing on the applicability of the bromination method for the enol determination in aqueous solutions of acetoacetic acid and ester and similar substances. This together with a study of the velocity of the reaction ketone \rightarrow enol will be the subject of a later publication. It was found that an aqueous solution of acetoacetic acid contains only very little enol, less than 1%.

As a result of the present work the following hypothesis is suggested.

Only the keto form of β -keto carboxylic acids undergoes the ketonic decomposition. The amines which catalyze the reaction form an intermediate compound of unknown constitution with the keto form (enol \rightleftharpoons ketone \rightleftharpoons ketone-catalyst), thus reducing the concentration of both enol and ketone. The intermediate compound splits off carbon dioxide much more quickly than the free keto form.

The α,α -disubstituted acetoacetic acid is especially suited for the study of the catalysis, the non-occurrence of enol making this case simpler than that of the ordinary acetoacetic acid. A theory of the decomposition and catalysis must take into account that only β -keto acids show the ketonic decomposition with appreciable velocity, and that only the primary amines are good catalysts, while the secondary and tertiary amines have a moderate or almost no effect.

The work is being continued and it is hoped to give a further test of the above hypothesis in a later publication.

In conclusion I wish to thank the Carlsberg Foundation for a grant which has defrayed the expenses of the apparatus. I also wish to express my in-

¹⁷ Meyer, *Ber.*, **44**, 2718 (1911); *ibid.*, **45**, 2843 (1912).

debtedness to Professor N. Bjerrum, whose many valuable suggestions have been of great importance to my work, and to Mr. E. A. Guggenheim for helpful criticism.

Summary

1. The kinetics of the ketonic decomposition of α, α -dimethylacetoacetic acid, $\text{CH}_3\text{COC}(\text{CH}_3)_2\text{COOH} \longrightarrow \text{CH}_3\text{COCH}(\text{CH}_3)_2 + \text{CO}_2$, have been studied. Experiments were made in hydrochloric acid, glycolate and acetate buffers.

2. The dissociation constant of α, α -dimethylacetoacetic acid has been calculated from the experimental results.

3. It has been shown that the decomposition is catalyzed by amines.

4. From the fact that α, α -dimethylacetoacetic acid is unstable it follows that the keto form of β -keto carboxylic acids is unstable.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF BRITISH COLUMBIA]

EXTRACTION OF COMMERCIAL RARE-EARTH RESIDUES WITH A VIEW TO THE CONCENTRATION OF ILLINIUM

BY ROBERT W. BALL¹ WITH J. ALLEN HARRIS²

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Historical

In 1926³ one of the writers, in conjunction with Professor B. S. Hopkins of the University of Illinois, was able to isolate, although in an impure state, sufficient of Element 61 to be able to identify it by means of x-ray analyses. Since, however, some 700 pounds of original material yielded a concentrate of but a few grams, it would seem to indicate that (a) the element is extremely rare and hence, in order to obtain quantities sufficiently great for purification, enormous amounts of the original material must be worked on, or (b) that while not rare, our method of concentration was inefficient and considerable of the element was lost at different stages of the treatment involved.

Assuming the latter possibility, one of the most likely sources of loss would be inefficiency in extraction of original residues; this possibility is discussed in this paper.

The element has not yet been obtained in a state of purity great enough to permit the mapping of its arc and absorption spectra, so it is impossible

¹ Part of this paper was presented as a thesis for the M.A. degree at the University of British Columbia.

² National Research Fellow. Paper completed at the Sorbonne, Paris, as part of work under National Research Council Award.

³ Harris with Hopkins, *THIS JOURNAL*, **48**, 1585 (1926).