

the oven. A metal loop on the front engages the handle C with which they are lifted while hot.

This equipment has been in use for several years in the writer's laboratory and has proved its worth. In laboratories used by students its value is especially high because the rule, one tray to a student, can be followed and one student in inserting or removing his material need not interfere with the work of the others.

Since the trays rest on the original shelves of the oven, it takes but a minute to remove them all and again convert the oven interior into one large compartment.

Although this equipment increases the amount of metal subject to corrosion it cannot be said to increase the danger of contamination beyond what any increased use of the oven would involve. C. W. FOULK.

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**Correction.**—The figures for the ordinates of Fig. 5, in our article on "The Transference Numbers of Lithium Chloride, etc." in the June 1920 JOURNAL, have been printed one division too high in each case; for instance, the figure 0.270 should be 0.280.

D. A. MACINNES,  
JAMES A. BEATTIE.

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, SCIENCE COLLEGE, TOHOKU IMPERIAL UNIVERSITY.]

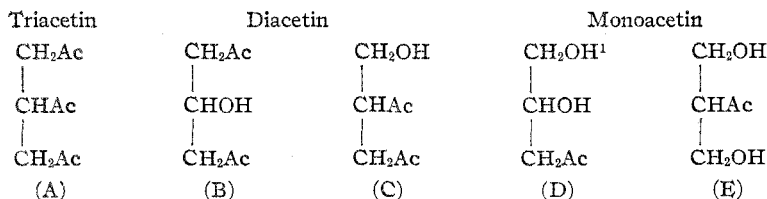
### THE SUCCESSIVE STAGES OF THE HYDROLYSIS OF TRIACETIN.

By EIICHI YAMASAKI.

Received March 22, 1920.

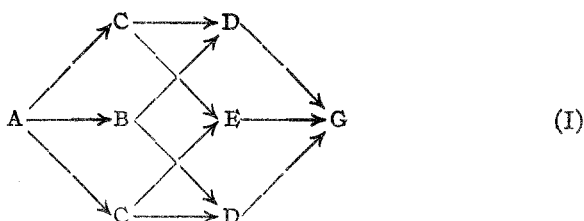
#### Introduction.

The various acetins, or glycerin esters of acetic acid, some of them, however, being still unknown, are as follows:



If the ester A is hydrolyzed, the reaction will proceed successively by the following steps to glycerine, C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub> (G)

<sup>1</sup> Esters (C) and (D) have one asymmetric carbon atom, respectively. Hence both of them must have 3 modifications, *i. e.*, the racemic and the optically active antipodes.



Evidently such a reaction is very complex and its chemical kinetics almost hopelessly involved. However, according to the investigation of A. de Hemptine<sup>1</sup> and R. Löwenherz,<sup>2</sup> the esters of the same acid have one property in common, namely, the rate of hydrolysis is independent of the nature of the alcoholic radicals: that is, esters of primary, secondary and tertiary alcohols have the same velocity constant  $k$  of hydrolysis when the acid is the same. If this holds true in the case of the esters of polyvalent alcohol such as glycerin, the kinetics of the triacetin hydrolysis is simplified and can be ascertained by a suitable method.

#### Previous Investigations.

Geitel<sup>3</sup> prepared triacetin (A), diacetin (B) and monoacetin (D),<sup>4</sup> and studied their rates of decomposition with various reagents. He found that the hydrolysis of acetins with dil. hydrochloric acid takes place as follows.

1. Monoacetin (D) decomposes normally as a mono-molecular reaction.
2. The constants for diacetin, calculated as a reaction of the first order, do not show a sufficient concordance.
3. The velocity constants for triacetin increase steadily (results obtained at 40°).

He expressed these results by the following differential equations

$$\frac{dz}{dt} = k_1(e - z); \quad \frac{dy}{dt} = k_2(z - y); \quad \frac{dx}{dt} = k_3(y - x), \quad (1)$$

where  $e$  is the initial concentration of triacetin;  $z$ ,  $y$  and  $x$  are, respectively, the amounts of tri-, di- and monoacetin decomposed at the moment under consideration.

He transformed these Equations 1 into

$$\frac{dz}{dy} = n \frac{e - z}{z - y}; \quad \frac{dz}{dx} = n_1 \frac{e - z}{y - x}; \quad \frac{dy}{dx} = n_2 \frac{z - y}{y - x}, \quad (2)$$

<sup>1</sup> de Hemptine, *Z. physik. Chem.*, **13**, 561 (1894).

<sup>2</sup> Löwenherz, *ibid.*, **15**, 389 (1894).

<sup>3</sup> Geitel, *J. prakt. Chem.*, **55**, 417 (1897); **57**, 113 (1898).

<sup>4</sup> He gave only the chemical formulas  $C_3H_5(OH)(Ac)_2$  and  $C_3H_5(OH)_2Ac$ . The above constitutional formulas are given according to the Beilstein. But the point is not important for this investigation.

when  $n = k_1/k_2$ ,  $n_1 = k_1/k_3$ , and  $n_2 = k_2/k_3$ ; and he integrated Equations 2 as follows:<sup>1</sup>

$$\begin{aligned}
 x &= e - \frac{u}{(n-1)(n_1-1)} + \frac{n^2 e^{(n-1)/n}}{(n-1)(n_1-n)} u^{1/n} - \frac{n_1 u^{1/n_1}}{(n_1-1)(n_1-n) e^{1/n_1}} \\
 y &= e - \frac{u}{n-1} - \frac{n}{n-1} e^{(n-1)/n} u^{1/n} \\
 z &= e - u
 \end{aligned}
 \tag{3}$$

where  $u$  is the concentration of the triacetin at any moment.

Then, assuming that the regularity observed by Hemptine and Löwenherz, that the decomposition constants of the esters of a single acid are independent of the nature of the alcoholic radicals, also holds good in the case of the esters of polyvalent alcohols, he put

$$k_1 : k_2 : k_3 = 3 : 2 : 1. \tag{4}$$

Introducing Relation 4 into Equations 3 and simplifying them by putting  $e = 1$ ,

$$\begin{aligned}
 z &= 1 - u \\
 y &= 1 + 2u - 3(\sqrt[3]{u})^2 \\
 x &= 1 - u - 3\sqrt[3]{u} + 3(\sqrt[3]{u})^2 \\
 x + y + z &= 3 - 3\sqrt[3]{u}.
 \end{aligned}
 \tag{5}$$

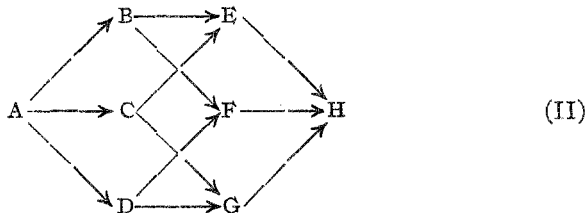
Consequently, if the function  $u = f(t)$  were solved,  $x$ ,  $y$  and  $z$  would be also obtained as known functions of  $t$ . So he gave the arbitrary value 0.05 to the constant  $k_1$ , and calculated  $u$  from Equations 3 and 4 between the limits

$$u = 1 (= e) \text{ and } u = 0;$$

that is, from the initial concentration (= 1) to the complete hydrolysis. From the value of  $u$ , he deduced the corresponding values of  $x$ ,  $y$  and  $z$  by means of Equation 5 and expressed  $u$ ,  $x$ ,  $y$  and  $z$  graphically to explain the course of the reaction.

Unfortunately, he could not find the real value of the velocity constant  $k_1$ . Consequently, he could not make use of his experimental results to explain quantitatively the actual course of the reaction.

Recently Treub<sup>2</sup> made an interesting investigation of the successive hydrolysis of trilaurin with sulfuric acid. He gave the following reaction scheme



<sup>1</sup> *Loc. cit.*

<sup>2</sup> Treub, *J. chim. phys.*, 16, 107 (1918); *Proc. Akad. Sci. Amsterdam*, 20, 343 (1917).

where A is trilaurin and H glycerin; B, C, and D are, respectively, dilaurin, and E, F and G monolaurin. When  $r$ ,  $x$  and  $y$  are, respectively, the concentrations of tri-, di- and monolaurin, and  $s$  and  $z$  are the concentrations of glycerin and acetic acid, their relative concentrations,  $R$ ,  $X$ ,  $Y$ ,  $S$  and  $Z$  are, respectively,

$$R = \frac{r}{a}, \quad X = \frac{x}{a}, \quad Y = \frac{y}{a}, \quad S = \frac{s}{a}, \quad Z = \frac{z}{3a}, \quad (6)$$

where  $a$  is the initial concentration of trilaurin. He also assumed that each radical of the ester is decomposed at the same rate, and gave the following differential equations,

$$\begin{aligned} -\frac{dr}{dt} &= 3kr; & \frac{dx}{dt} &= kr - 2kx; & \frac{dy}{dt} &= 2kx - ky; & \frac{ds}{dt} &= 3ky; \\ \frac{dz}{dt} &= 3\left(\frac{dx}{dt} + 2\frac{dy}{dt} + \frac{ds}{dt}\right) & &= 3k(r + 2x + y)^1 \end{aligned} \quad (7)$$

where  $k$  is the uniform value that the decomposition constants of the various esteric radicals are assumed to have, according to de Hemptine and Löwenherz. Equations 7 he transformed to

$$-\frac{dr}{3r} = \frac{dx}{r - 2x} = \frac{dy}{2x - y} = \frac{ds}{3y} = \frac{dz}{3(r + 2x + y)}. \quad (8)$$

After an ingenious mathematical treatment of the above equation, he found the relation

$$S = Z^3;$$

that is, the relative concentration of glycerin is always equal to the cube of the relative concentration of lauric acid throughout the course of the reactions, and this relation is quite independent of the progress of the reactions. He sought to confirm the above relation by the direct determination of the concentration of the lauric acid and glycerin produced by the hydrolysis of trilaurin.

Contrary to expectations, he could not obtain sufficient confirmation.<sup>2</sup> This can probably be attributed to the difficulty of a quantitative determination of glycerin.

Besides, he did not determine numerically the value of the velocity constant  $k$  and evaluate  $r$ ,  $x$ ,  $y$ ,  $z$  and  $s$  as known functions of the time

<sup>1</sup>  $dz/dt$ , the rate of the formation of the lauric acid is not directly given, as is the velocity of formation of the other components, in the original paper. But the above equation will be easily understood if we count the number of esteric radicals decomposed by the formation of  $x$ ,  $y$  and  $s$ .

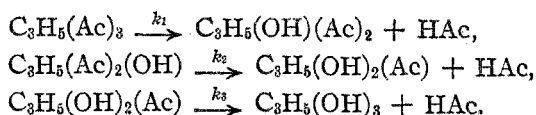
<sup>2</sup> He found actually that the relative concentration of glycerin is smaller than the cube of the concentration of its acid. Consequently, he assumed further that the velocity constants of the hydrolysis of the esters of primary and of secondary alcohols have *different* values and gave the following differential equation according to Scheme III (below),  $-dr/dt = (p + 2)kr$ ;  $dx_1/dt = kr - (p + 1)kx_1$ ;  $dx_2/dt = pkx_2 - 2kx_1$ ;  $dy_1/dt = pkx_1 + kx_2 - ky_1$ ;  $dy_2/dt = 2kx_1 - pk_2y_2$ ;  $dS/dt = 2ky_1 + pk_2y_2$ , where  $k'$  is the

and of the initial concentration of trilaurin. Consequently, the present problem, the hydrolysis of the polyvalent ester is not yet in a way of settlement from the point of view of chemical kinetics.

The present writer has, however, evaluated the constant  $k$  of the reaction for triacetin numerically and has given the concentration of the components of the system under consideration as known functions of the time and of the initial concentration of triacetin. The results will be given in order.

**Theoretical Part.**

The successive hydrolysis of triacetin takes place according to the following equations.



Consequently, each reaction must be separately carried out as one of the first order, having, respectively, the velocity constants  $k_1$ ,  $k_2$  and  $k_3$ .

In the initial stage of the reaction ( $t = 0$ ) acetic acid is formed only by

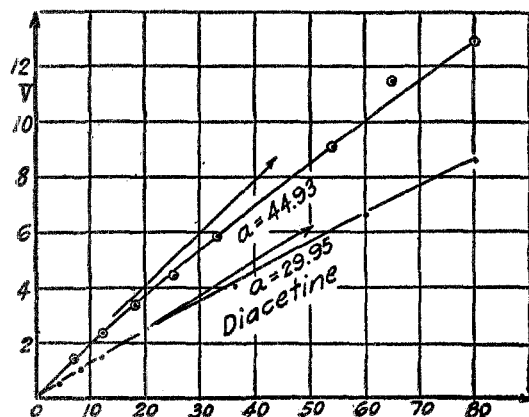


Fig. 1.

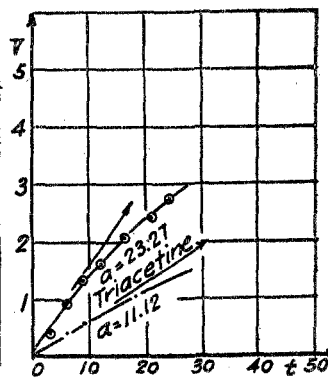
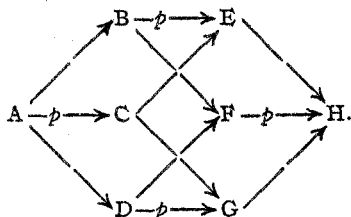


Fig. 2.

velocity constant of the ester of the secondary alcohol which is equal to  $k_p$ , i. e.,  $k'/k = p$ .



(III)

By a skilful computation, he obtained the relation,  $S < Z^3$ , to explain his experimental results. But he did not definitely determine whether the constants  $k$  and  $k'$  actually differ or not in the polyvalent esters. Consequently the treatment must be said to be mere assumption.

the hydrolytic decomposition of triacetin. Hence, the velocity constant  $k_1$  can be accurately determined, if the exact value of the initial velocity of the formation of acetic acid ( $C_A$ ) is obtained. Then the relative initial velocity or the velocity constant  $k$  can be determined graphically, because, if  $C_A$  and  $C$  are the relative concentrations of acetic acid and triacetin, respectively,

$$\left(\frac{dC_A}{dt}\right)_{t=0} = \left(-\frac{dC}{dt}\right)_{t=0}$$

and

$$\left(-\frac{d \ln C}{dt}\right)_{t=0} = k_1.$$

Such a graphical method is not adapted for obtaining a very exact value of the velocity constant  $k_1$ , but the value of  $k_1$  obtained by it is sufficiently accurate to verify the theory. Again returning to the data of Geitel's experiments, I drew the diagram ( $V, r, t$ ) instead of ( $c, V, t$ ), where  $V$  is the volume of barium hydroxide used to neutralize the acetic acid. From the initial tangents, the following are obtained,

$$\frac{1}{a} \left(\frac{dV}{dt}\right)_{t=0} = \frac{1}{V_{\infty}/3} \left(\frac{dV}{dt}\right)_{t=0} = k_1$$

for triacetin, and

$$\frac{1}{a'} \left(\frac{dV}{dt}\right)_{t=0} = \frac{1}{V_{\infty}/2} \left(\frac{dV}{dt}\right)_{t=0} = k_2,$$

for diacetin, where  $a$  denotes the initial concentration of triacetin and  $a'$  that of diacetin. Taking the mean value of the constants  $k_1$  and  $k_2$ , respectively, from these two diagrams, we obtain

$$k_1 = 0.00638 \quad \text{and} \quad k_2 = 0.00423.$$

Now  $k_3$  is the velocity constant of the hydrolysis of monoacetin, which is, of course, a monomolecular reaction. Hence, the constant  $k_3$  can be easily determined from the equation,

$$k_3 = \frac{1}{t} \ln \frac{V}{V_{\infty}},$$

I take the mean value of two series of experiments given by Geitel and obtain

$$k_3 = 0.002213.$$

If each alcoholic radical of acetin has an equal rate of hydrolysis as supposed, the following relation exists among them

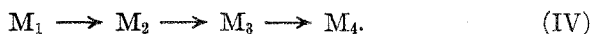
$$1/3 k_1 = 1/2 k_2 = 1/1 k_3 = k.$$

In agreement with this, the experimental values are found to be closely equal

$$\left. \begin{array}{l} k_1/3 = 0.002127 \\ k_2/2 = 0.002115 \\ k_3/1 = 0.002213 \end{array} \right\} \text{mean } k = 0.002152.$$

This confirms the assumption made by Geitel and Treub that each alcoholic radical of the polyvalent esters has an equal rate of hydrolysis irrespective of whether the radical be primary or secondary.

Then the successive hydrolysis of triacetin given by Scheme I is simplified to



And the differential equations which express the progress of the reaction are given as follows:

$$\begin{aligned} \frac{dx_1}{dt} &= k_1(a - x_1) = 3k(a - x_1) \\ \frac{dx_2}{dt} &= k_2(x_1 - x_2) = 2k(x_1 - x_2) \\ \frac{dx_3}{dt} &= k_3(x_2 - x_3) = k(x_2 - x_3) \end{aligned} \quad (10)$$

where  $a$  is the initial concentration of triacetin, and  $x_1$ ,  $x_2$  and  $x_3$  are, respectively, the concentration of  $M_1$ ,  $M_2$  and  $M_3$  decomposed at any time  $t$ . The above equations are integrated according to Rakowski<sup>1</sup> and  $C_0$  is substituted for  $a$  as usual:

$$\begin{aligned} C_{M_1} &= C_0 e^{-kt} \\ C_{M_2} &= 3C_0 (1 - e^{-kt}) e^{-2kt} \\ C_{M_3} &= 3C_0 (1 - e^{-kt})^2 e^{-kt} \\ C_{M_4} &= C_0 (1 - e^{-kt})^3 \end{aligned} \quad (11)$$

As the concentration of acetic acid  $C_A$ , formed by the reaction is expressed as follows,

$$C_A = C_{M_2} + 2C_{M_3} + 3C_{M_4}$$

it becomes

$$C_A = 3C_0 (1 - e^{-kt}) \quad (12)$$

from Equation 11.

When  $C_{M_4}$  and  $C_A$  are compared the following relation is easily found,

$$\left( \frac{C_A}{3C_0} \right)^3 = \left( \frac{C_{M_4}}{C_0} \right) \quad (13)$$

Now both terms of Equation 13 express the relative concentrations of acetic acid and glycerin which were denoted as  $Z$  and  $S$ , respectively, by Treub. That is,  $S = Z^3$ , which is the relation deduced by him.

#### Experimental Part.

Unfortunately, the number of experimental results given by Geitel are few. In addition to this, the degree of hydrolysis of triacetin at 25° only amounts to 10%. Therefore, I prepared triacetin according to his method and undertook the hydrolysis with  $N$  hydrochloric acid at 35°. As a result, I obtained sufficient confirmation of the theory above enunciated.

<sup>1</sup> Rakowski, *Z. physik. Chem.*, 57, 321 (1907).

**Mode of Experiment.**—Triacetin was dissolved to make a 0.25 *N* solution. 5, 10, 15 and 20 cc. of the solution were made up to 20 cc. in a thermostat at 35° and mixed with 10 cc. of 3 *N* hydrochloric acid of the same temperature. Two cc. of the solution was drawn off with a pipet from time to time and titrated with a 0.05 *N* solution of barium hydroxide.

The concentration of hydrochloric acid was determined by the volume of barium hydroxide solution used for the titration immediately after the reacting mixture had been prepared as above.

The initial concentration of the ester was determined from the concentration of the acetic acid obtained at  $t = \infty$ , *i. e.*,  $(C_A/3)_{t=\infty} = C_0$ . In order to determine the concentration of acetic acid,  $(C_A)_{t=\infty}$  at the end of the reaction, 5 cc. of the same hydrochloric acid was mixed with the same volume of ester solution in a sealed tube. The solution in the tube was heated in a water bath for a long while until the titrations of the solution became constant, independent of the time of heating. The concentration of acetic acid  $(C_A)_{t=\infty}$ , corresponding to the former series of experiments, was determined by calculation from that of the latter experiment.

**Explanation of the Experimental Results.**—The concentrations of acetic acid  $C_A$  obtained from the reacting mixtures—namely, 4 different initial concentrations of esters—were divided by the corresponding concentrations of the acetic acid at infinite time. The series of relative concen-

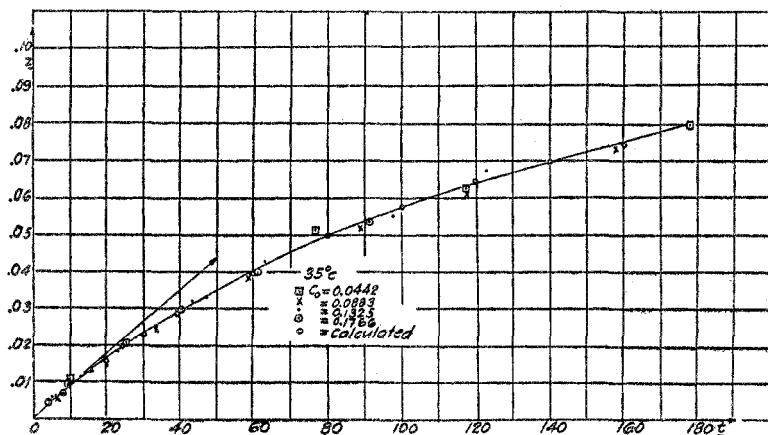


Fig. 3.

trations of acetic acid ( $Z$ ), are expressed by the ordinates of Fig. 3 and the corresponding times (in minutes) by the abscissas. As the concentration of the hydrochloric acid is constant and equal to 0.961, the respective curves must coincide with one another in spite of the fact that the initial concentrations of the ester  $C_0$  differ, because



$$Z = \frac{C_A}{3C_0} = (1 - e^{-kt}) \quad (14)$$

from Equation 12, and the right side of the above equation is quite independent of the value of  $C_0$ .

The results obtained in the 4 different series of experiments do indeed coincide sufficiently well to verify our expectations. The tangent line drawn at the starting point of the axes of the coordinates gives

$$\left(\frac{dZ}{dt}\right)_{t=0} = \frac{1}{3} \left(-\frac{d \ln C}{dt}\right)_{t=0} = k. \quad (15)$$

Consequently,  $k$  or  $0.4343 k = k' = 0.00373$  is determined graphically.  $Z$ , given in Fig. 3, is calculated back with this  $k'$  by Equation 14, and compared with the observed results to show their sufficient agreement.

**Tables of Experimental Data.**—The experimental data are summed up in the following tables, in which  $t$  is the interval of time in minutes;  $Z$ , the relative concentration of acetic acid;  $C_A(\text{obs.})$ , the concentration of acetic acid;  $C_A(\text{calc.})$ , that calculated from Equation 12; and  $C_{M_1}$ ,  $C_{M_2}$ , and  $C_{M_3}$  are the concentrations of tri-, di-, and monoacetins at any time and  $C_{M_4}$  the concentration of glycerin. The experimental conditions, with the exception of those for the initial concentration of triacetin, were exactly the same for all 4 series of results. That is,  $C_{\text{HCl}}$ , the concentration of hydrochloric acid, was  $0.961 N$  and the temperature of the observation,  $35^\circ$ .

TABLE I.

$C_0 = 0.0442.$							
$t$ .	$Z$ .	$C_A(\text{obs.})$ .	$C_A(\text{calc.})$ .	$C_{M_1}$ .	$C_{M_2}$ .	$C_{M_3}$ .	$C_{M_4}$ .
10.00	0.104	0.0138	0.0108	0.0342	0.0092	0.0008	0.0000
25.18	0.202	0.0268	0.0256	0.0231	0.0167	0.0040	0.0003
47.00	0.332	0.0440	0.0424	0.0132	0.0196	0.0098	0.0016
76.37	0.513	0.0680	0.0637	0.0062	0.0172	0.0159	0.0049
116.94	0.629	0.0833	0.0842	0.0022	0.0113	0.0195	0.0113
177.17	0.800	0.1061	0.1036	0.0005	0.0049	0.0177	0.0211

TABLE II.

$C = 0.0883.$							
$t$ .	$Z$ .	$C_A(\text{obs.})$ .	$C_A(\text{calc.})$ .	$C_{M_1}$ .	$C_{M_2}$ .	$C_{M_3}$ .	$C_{M_4}$ .
6.67	0.058	0.0154	0.0152	0.0744	0.0132	0.0009	0.0000
15.50	0.135	0.0357	0.0332	0.0593	0.0254	0.0036	0.0002
33.00	0.246	0.0652	0.0654	0.0377	0.0371	0.0122	0.0013
58.67	0.386	0.1024	0.1050	0.0195	0.0383	0.0251	0.0055
88.22	0.513	0.1359	0.1405	0.0091	0.0309	0.0350	0.0132
117.52	0.620	0.1642	0.1680	0.0043	0.0224	0.0389	0.0226
157.45	0.730	0.1934	0.1960	0.0015	0.0131	0.0376	0.0359
213.37	0.809	0.2143	0.2227	0.0004	0.0057	0.0299	0.0524
283.62	0.867	0.2300	0.2415	0.0001	0.0019	0.0193	0.0670

TABLE III.

$C = 0.1325.$

$t$	$Z$	$C_A(\text{obs.})$	$C_A(\text{calc.})$	$C_{M_1}$	$C_{M_2}$	$C_{M_3}$	$C_{M_4}$
5.00	0.059	0.0234	0.0167	0.1165	0.0153	0.0007	0.0000
12.20	0.117	0.0464	0.0397	0.0968	0.0322	0.0036	0.0001
23.00	0.181	0.0720	0.0713	0.0733	0.0479	0.0105	0.0008
43.00	0.320	0.1273	0.1225	0.0438	0.0587	0.0262	0.0038
63.00	0.431	0.1699	0.1662	0.0271	0.0563	0.0404	0.0097
90.75	0.550	0.2189	0.2151	0.0128	0.0453	0.0534	0.0210
121.17	0.674	0.2681	0.2574	0.0058	0.0321	0.0588	0.0359
162.33	0.761	0.3026	0.2992	0.0020	0.0184	0.0558	0.0564

TABLE IV.

$C = 0.1766.$

$t$	$Z$	$C_A(\text{obs.})$	$C_A(\text{calc.})$	$C_{M_1}$	$C_{M_2}$	$C_{M_3}$	$C_{M_4}$
4.00	0.045	0.0240	0.0180	0.1593	0.0168	0.0006	0.0000
9.33	0.090	0.0480	0.0406	0.1389	0.0348	0.0029	0.0000
25.00	0.197	0.1046	0.1022	0.0927	0.0665	0.0159	0.0013
40.00	0.295	0.1565	0.1544	0.0630	0.0776	0.0318	0.0044
60.50	0.400	0.2119	0.2144	0.0371	0.0759	0.0517	0.0117
91.00	0.535	0.2838	0.2871	0.0169	0.0602	0.0713	0.0281

From these results, it is clearly seen that the concentration of acetic acid as observed agrees very well with that calculated. Or, in other words, the theory given above is sufficiently verified by experiment.

**Graphical Representation of the Results and Explanation of the Diagrams.**—The results given in the above tables are reproduced in the two figures, 4 and 5, in which the concentration of the components of the reacting system and the corresponding times are taken as the 2 axes. Then the courses of the successive hydrolysis of polyvalent esters having

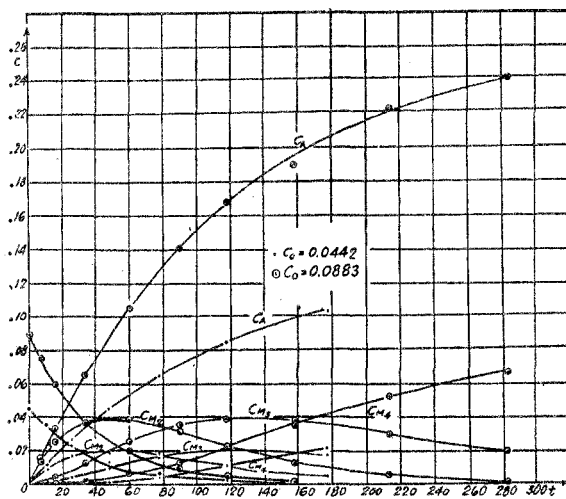


Fig. 4.

4 different components, *i. e.*,  $M_1 \longrightarrow M_2 \longrightarrow M_3 \longrightarrow M_4$ , are fully explained graphically.

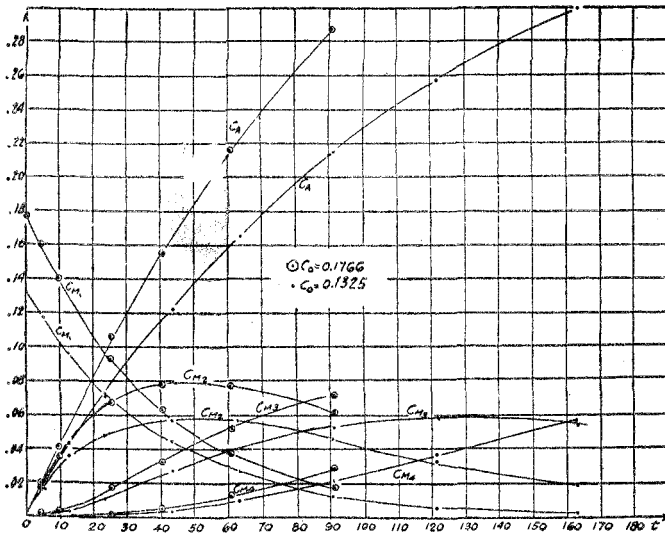


Fig. 5.

The intermediate component,  $M_2$ , has its maximum value at the time when

$$\frac{dC_{M_2}}{dt} = 3kC_0e^{-2kt}(3e^{-kt} - 2) = 0, \text{ i. e., } t_1 = \frac{1}{k} \ln \frac{3}{2} \quad (16a)$$

and the substance  $M_3$  has its maximum concentration at the time when

$$\frac{dC_{M_3}}{dt} = 3kC_0(1 - e^{-kt})(3e^{-kt} - 1)e^{-kt} = 0, \text{ i. e., } t_2 = \frac{1}{k} \ln 3. \quad (16b)$$

The numerical values ( $C_{M_2}$ ) and ( $C_{M_3}$ ) of their maximum concentrations are calculated by introducing the times  $t_1$  and  $t_2$  into Equation 13.

$$(C_{M_2}) = 3C_0(1 - e^{-\ln 3/2})e^{-2 \ln 3/2} = 4/9 C_0$$

and

$$(C_{M_3}) = 3C_0(1 - e^{-\ln 3})^2e^{-\ln 3} = 4/9 C_0$$

*i. e.*,

$$(C_{M_2}) = (C_{M_3}) = 4/9 C_0. \quad (17)$$

That is, the maximum concentrations of  $M_2$  and  $M_3$  are equal in numerical value, but the corresponding times, of course, differ.<sup>2</sup> The relations above enunciated are satisfied in the diagrams.

Further, the curve if  $C_{M_2}$  has one inflection point at

$$t'_1 = 1/k \ln 9/4 \quad (18)$$

<sup>1</sup>  $e^{-2kt} = 0$  when  $t = \infty$ , the same for  $e^{-kt} = 0$ ; and  $1 - e^{-kt} = 0$  when  $t = 0$ . The times have no relation to the maximum values of  $C_{M_2}$  and  $C_{M_3}$ .

<sup>2</sup> Such a simple relation does not hold, of course, generally. Such results are due to the fact that the 3 constants have a simple ratio,  $k_1 : k_2 : k_3 = 3 : 2 : 1$ .

where

$$\frac{d^2C_{M_2}}{dt^2} = 3k^2C_0(4 - 9e^{-kt}) = 0.$$

And the curve of  $C_{M_2}$  has two inflexion points at  $t'_2$  and  $t'_3$ , respectively,

$$t'_2 = 1/k \ln \alpha, \quad \text{and} \quad t'_3 = 1/k \ln \beta,$$

where

$$\frac{1}{\alpha} = \frac{4 + \sqrt{7}}{9}, \quad \text{and} \quad \frac{1}{\beta} = \frac{-\sqrt{7}}{9}$$

in which times,

$$\frac{d^2C_{M_3}}{dt^2} = 3k^2C_0 e^{-kt} (9e^{-2kt} - 8e^{-kt} + 1) = 0.$$

Now,  $t'_1$  is greater than  $t'$ , and  $t'_3$  greater than  $t_2$ , but  $t'_2$  is less than  $t_2$ . The last time,  $t'_2$ , suggests that the nature of the increase of  $C_{M_2}$  and  $C_{M_3}$  is quite different up to their maximum concentrations. That is,  $dC_{M_2}/dt$  always decreases from  $t = 0$  to  $t = t'_1$ , and the curve  $C_{M_2}$  is always concave to the  $t$ -axis till  $t = t'_1$ . But  $dC_{M_3}/dt$  increases at first till it reaches  $t'_2$ , then it begins to decrease steadily to the second inflexion point  $t'_3$ . The curve  $C_{M_3}$  is convex to the axis  $t$  in the initial stage up to  $t'_2$ , then it becomes concave to the same axis till  $t$  increases up to  $t'_3$ .

Now, when we investigate the curve  $C_{M_4}$

$$dC_{M_4}/dt = 3kC_0(1 - e^{-kt})2e^{-kt} = kC_{M_3}.$$

The curve  $C_{M_4}$  has no maximum, but has one inflexion point at the time when the curve  $C_{M_3}$  has their maximum concentration, i. e.,  $t_2 = 1/k \ln 3$ . Lastly consider the curve  $C_A$ ,

$$dC_A/dt = 3C_0 e^{-kt} = k(3C_0 - C_A).$$

But the value  $3C_0$  is the concentration of acetic acid at  $t = \infty$ . Consequently

$$dC_A/dt = k(C_{A\infty} - C_A). \quad (19)$$

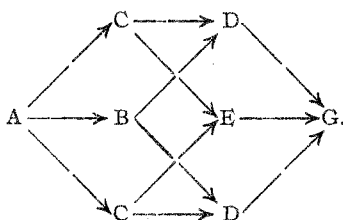
That is, the curve must be a logarithmic one which has neither a maximum nor an inflexion point. Furthermore, the rate  $dC_A/dt$  is the same as that of the chemical reaction,



where  $C_A$  corresponds to the concentration of  $A_2$ .

### Conclusion.

The hydrolysis of the ester formed by a polyvalent alcohol and a monobasic acid, such as triacetin, takes place according to the simple rule that each ester radical has an equal rate of hydrolysis. Consequently, their rates are simply expressed in the same way as those of the successive reactions  $M_1 \rightarrow M_2 \rightarrow M_3 \rightarrow M_4$ , which have, respectively, the velocity constants  $3k$ ,  $2k$  and  $k$ , though the actual reactions would be carried out according to the following scheme,



Consequently an explanation in detail of the results of experiment would give a clear idea of the course of the successive chemical reactions.

Appendix.

1. For the sake of comparison, the results obtained at 40° by Geitel for triacetin are calculated by the same method and are given in Table V.

TABLE V.  
Temperature 40°.  $k' = 0.00253$ .  
 $C_0 = 0.2000$ .

<i>t</i> .	<i>Z</i> .	$C_A$ (obs.).	$C_A$ (calc.).	$C_{M_1}$ .	$C_{M_2}$ .	$C_{M_3}$ .	$C_{M_4}$ .
12	0.0720	0.0432	0.0407	0.1621	0.0355	0.0026	0.0000
24	0.1381	0.0829	0.0778	0.1315	0.0590	0.0088	0.0004
36	0.1937	0.1162	0.1136	0.1066	0.0746	0.0174	0.0014
60	0.3059	0.1835	0.1769	0.0701	0.0880	0.0368	0.0051
84	0.4060	0.2436	0.2323	0.0461	0.0873	0.0551	0.0116
120	0.5249	0.2149	0.3021	0.0246	0.0746	0.0755	0.0255

As can be seen from the above table, the concentration  $C_A$  as observed shows sufficient agreement with that calculated.

2. Now, diacetin (B) decomposes according to the scheme  $M_1 \rightarrow M_2 \rightarrow M$ , respectively, the velocity constants being  $2k$  and  $k$ . Then the concentrations of the components in the system are expressed as known functions of the initial concentration of diacetins and the time

$$\begin{aligned}
 C_{M_1} &= C_0 e^{-2kt} \\
 C_{M_2} &= 2C_0 e^{-kt} (1 - e^{-kt}) \\
 C_{M_3} &= C_0 (1 - e^{-kt})^2.
 \end{aligned}
 \tag{20}$$

The data at 25° obtained by Geitel are calculated according to the above equation and given in Table VI.

TABLE VI.  
Temp. 25°.  $CHCl = 0.05$ .  $C_0 = 0.05$ .  $k' = 0.000836$ .

<i>t</i> .	<i>Z</i> .	$C_A$ (obs.).	$C_A$ (calc.).	$C_{M_1}$ .	$C_{M_2}$ .	$C_{M_3}$ .
7	0.0164	0.00164	0.00150	0.0485	0.00148	0.00001
12	0.0264	0.00264	0.00250	0.0475	0.00244	0.00003
18	0.0375	0.00375	0.00380	0.0463	0.00366	0.00007
25	0.0515	0.00515	0.00519	0.0449	0.00493	0.00013
33	0.0653	0.00653	0.00691	0.0434	0.00643	0.00024
54	0.1015	0.01015	0.01101	0.0396	0.00979	0.00061
65	0.1282	0.01282	0.01311	0.0378	0.01139	0.00086
80	0.1448	0.01448	0.01580	0.0354	0.01330	0.00125

These also show that the calculated values agree tolerably well with the observed.

3. The effect of temperature on the constant  $k'$ , have been calculated from Geitel's experiment at 25° and 40°. According to this,

$$\begin{aligned} k' &= 0.00253 && \text{at } 40^{\circ} \\ &= 0.000936 && \text{at } 25^{\circ} \end{aligned}$$

Consequently, the temperature coefficient becomes 1.94; that is, the velocity of reaction is almost doubled for every successive 10° elevation of temperature.

SENDAI, JAPAN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

## THE PREPARATION OF TRIMETHYL ARSINE AND TRIMETHYL ARSINE SELENIDE.<sup>2</sup>

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### Trimethyl Arsine.

Trimethyl arsine,  $(\text{CH}_3)_3\text{As}$ , has not previously been isolated in a pure condition. Its preparation seems to have been mentioned first by Cahours and Hofmann,<sup>4</sup> who state that it can be obtained by the action of potassium hydroxide on the double salt resulting from the interaction of arsenic trichloride and zinc methyl. In 1859 Cahours<sup>5</sup> claims to have prepared the compound by the dry distillation of the double salt of tetramethyl arsonium iodide and zinc iodide with potassium hydroxide. He described this arsine as a colorless liquid boiling under 100°. In a later publication<sup>6</sup> the author again mentions this preparation and subsequently<sup>7</sup> states that the pure compound boils at about 70°.

Hibbert, in 1906,<sup>8</sup> seems to have produced the compound by the action of arsenic tribromide on magnesium methyl iodide. He did not isolate the free arsine.

The authors have tried variations of 2 methods for the preparation of this substance: (1) the action of arsenic trichloride or bromide on magnesium methyl iodide and (2) the action of arsenic trichloride on zinc methyl. The latter method seems to be preferable.

<sup>1</sup> The magnitude of the constant obtained from Geitel's results seems to be excessive, compared with that of my own results.

<sup>2</sup> Published by permission of the Director of the Chemical Warfare Service.

<sup>3</sup> The authors wish to express their appreciation for the generosity shown by Dr. E. Emmet Reid in whose laboratory the work was done.

<sup>4</sup> Cahours and Hofmann, *Compt. rend.*, 41, 831. *Abst. Jahr.*, 1855, 538.

<sup>5</sup> Cahours, *Ann.*, 112, 228 (1859).

<sup>6</sup> Cahours, *ibid.*, 122, 197 (1862).

<sup>7</sup> Cahours, *ibid.*, 337.

<sup>8</sup> Hibbert, *Ber.*, 39, 160 (1906).