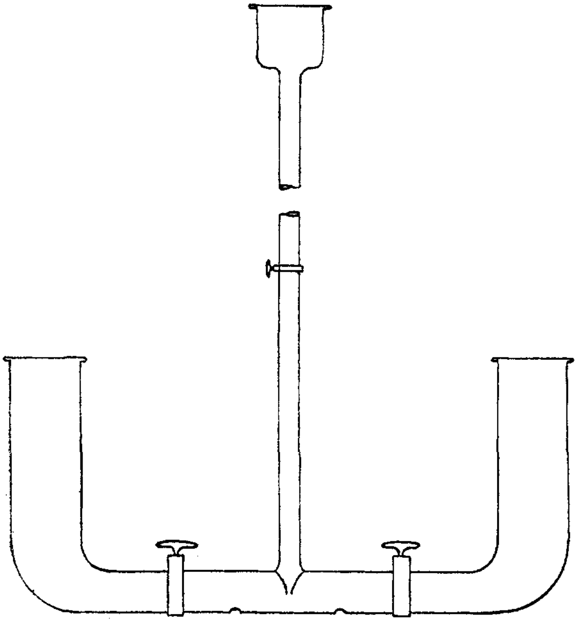

In use the apparatus is kept in a bath of continually flowing cold water, the container for which is preferably of glass so that the electrolysis may be more readily watched. The tube is filled with an electrolyte of suitable concentration (0.25 *N* for 110 v. current) and of such a nature that it will not interfere with the results and the electrolysis started. Two cc. or more of the substance to be tested are introduced through the thistle tube and the action allowed to run about one-half an hour when the side arms are closed and the contents tested.

For instance, with nitric acid as an electrolyte it can easily be shown after adding copper sulfate that the copper ion migrates to the cathode compartment and the sulfate ion to the anode, or, with calcium chloride that the calcium ion goes toward the cathode and the chloride ion toward the anode. With sodium hydrate as an electrolyte the complex ion of Fehling's solution, containing copper, or, the complex ion containing mercury of a solution of mercuric sulfide in sodium hydrate, probably HgS^{--}, migrates toward the anode. It was also used in the determination of the charge on inorganic colloids. RALPH W. G. WYCKOFF.

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[CONTRIBUTIONS FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 270.]

STUDIES ON CATALYSIS. I. THE ADDITION COMPOUNDS OF ESTERS WITH ORGANIC ACIDS.[1]

BY JAMES KENDALL AND JAMES ELIOT BOOGE.

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CONTENTS.—1. Introduction. Purpose and Scope of Investigation. 2. Review of Previous Work: (*a*) The Mechanism of Acid Catalysis of Ester Hydrolysis; (*b*)

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[1] For previous papers on addition compound formation see THIS JOURNAL, **36**, 1222, 1722, 2498 (1914); **37**, 149 (1915); **38**, 1309 (1916).

Addition Compound Formation in Systems Ester–Acid. 3. Experimental Procedure. 4. Experimental Data. 5. Relative Stability of Addition Compounds. 6. Compound Formation a General Phenomenon. 7. Structure of Addition Compounds Isolated. 8. Summary.

1. Introduction. Purpose and Scope of Investigation.

Few reactions have been more carefully studied than the catalysis of ester hydrolysis by acids. We have at our disposal, from among the multitude of experimental facts recorded, data for all the possible range of conditions—variation of the ester, variation of the acid, variation of temperature, variation of the concentration of ester, of acid, and of water. This being so, it is only natural that there should also exist an accumulation of hypotheses regarding the nature and the mechanism of the reaction. The strange thing is that, in spite of all, few reactions are still so little understood.

The main reason for this unfortunate state of affairs is that theories have always been thrust far in advance of facts, so far indeed that they have often lost touch of them altogether. The experimental data have been systematically overworked in their task of supporting unwieldy masses of premature speculation.

As one possible explanation of the catalysis of ester hydrolysis by acids, the theory of intermediate addition compounds has been advanced, and appears to hold the field at present. The great majority of chemists who have, in recent years, attempted to elucidate the mechanism of the reaction have regarded as the *first step* in the hydrolysis the addition of the acid to the ester to form an oxonium salt.[1] Although a number of papers do not give this first step definitely, the formulation most favored is

$$R.COO.R' + H^+ + X^- \rightleftarrows [R.COOR',H]^+ + X^-.$$

The formation of this complex ester-hydrogen-ion $[R.COO.R',H]^+$ necessitates the further assumption that the undissociated compound as given by the equilibrium

$$[R.COO.R',H]^+ + X^- \rightleftarrows R.COO.R',HX$$

must also be present. Until now only a single compound of the suggested type has definitely been isolated. We have therefore no direct proof that such compound formation is a *general phenomenon* in systems of the type ester–acid, and upon this assumption the whole theory rests. Consequently it seemed to the authors especially desirable to investigate *systematically* the general behavior of ester–acid mixtures with respect to compound formation.

The results of this investigation were very gratifying, as thirteen compounds of the type $(\text{ester})_m$, $(\text{acid})_n$ were isolated. Moreover it may be

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[1] In this paper the terms "addition compound" and "oxonium salt" are synonymous.

deduced that any ester, R.COO.R′, will combine directly with any acid, HX, to a greater or less amount, and the main factors governing the extent of addition compound formation are also made clear. By direct isolation of these compounds, which have heretofore merely been *assumed* to exist, strong support is thus given to the theory of intermediate oxonium salt formation in the catalytic hydrolysis of esters by acids.

2. Review of Previous Work.

A brief outline of some of the previous work in this field will aid in the consideration of our results.

(*a*) **The Mechanism of Acid Catalysis of Ester Hydrolysis.**—Various theories have been formulated to explain this phenomenon. The more prominent may be grouped into three classes.

Class I. Assumption: The Catalyst Acts by its Mere Presence.—The old view of catalysis was that the acid (hydrogen ion) acted in some mysterious manner, the reaction obediently proceeding with increased velocity.

A rational modification of this view has recently been advanced by Lewis[1] and coworkers. It is assumed that the (hydrated) methyl acetate molecule absorbs quanta of radiation in the infra-red region, sent out by the (hydrated) hydrogen ion, the consequent addition of energy to the ester molecule inducing great instability or chemical activity. This view is appealing in its simplicity but has not been sufficiently developed experimentally to judge whether it can explain the complicated relations holding between velocity of hydrolysis and concentration of the reacting substances. Moreover, it simply postulates the *driving force* which increases the velocity of the reaction without accounting for the mechanism or stages in which the reaction takes place.[2]

Class II. Assumption: Direct Ionization of Organic Compounds.—This was the natural outgrowth of the too enthusiastic application of the ionic theory. Direct ionization of the ester to $R.COO^-$ and R'^+ was postulated by Zengelis[3] and to RCO^+ and OR'^- by Euler.[4] Increased concentration of hydrogen ion would tend to remove one of the ions in each case, accelerating the hydrolysis of the ester. The decreased concentration of hydroxide ion would, however, simultaneously have the opposite effect. Due to the lack of verification of such ionizations and to the incorrect quantitative results[5] to which they lead, these views have been discarded.

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[1] *J. Chem. Soc.*, **105**, 2330 (1914); **107**, 233 (1915); **109**, 55, 67 (1916).

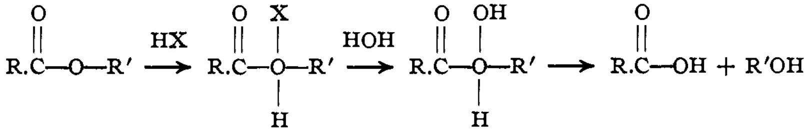
[2] In any metathesis there are necessarily but two possible mechanisms—either decomposition of AB and CD followed by combination of the parts, or intermediate combination to AB.CD followed by decomposition in another way. Both of these views have been advanced in ester hydrolysis (See II and III).

[3] "On Chemical Affinity," Athens, 1896, *Ber.*, **34**, 198 (1901).

[4] *Z. physik. Chem.*, **36**, 640 (1901).

[5] Stieglitz, *Am. Chem. J.*, **39**, 404, 423 (1908).

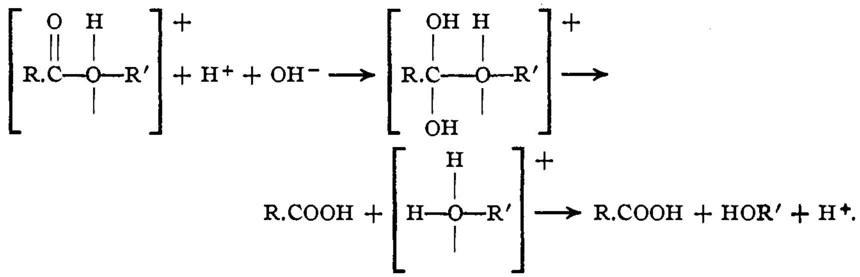
Class III. Assumption: Intermediate Addition Compounds are Formed.—Kastle,[1] in a paper read before the A. A. A. S. in 1896, first suggested the possibility that an "addition product" of the ester and catalyzing acid might be formed. His formulation of the reaction



$$R.\overset{\overset{O}{\|}}{C}-O-R' \xrightarrow{HX} R.\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{X}{|}}{O}}-R' \xrightarrow{HOH} R.\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{O}}-R' \longrightarrow R.\overset{\overset{O}{\|}}{C}-OH + R'OH$$

is undoubtedly incorrect, assuming as it does greater concentration of oxonium base in a more strongly acid solution. Bredig[2] suggested, in 1903, and again in 1904, that the complex ion $[R.COO.R',H]^+$ may be active in the hydrolysis of esters. Lapworth, in 1904 (Mellor's "Statics and Dynamics," p. 289), gave a more complete formulation of the hydrolysis in the presence of an acid. This view has likewise been severely criticized and has no experimental evidence in its support.[3] Acree,[4] Rosanoff,[5] Falk and Nelson,[6] and numerous other chemists have assumed the formation of intermediate addition compounds, the last named authors applying the electron conception of valence, without however considering the subject quantitatively.

Stieglitz[7] has treated the whole problem from a quantitative standpoint, starting from the fact that a *possible* mechanism for the catalysis is



$$\left[R.\overset{\overset{O}{\|}}{C}-\underset{|}{\overset{\overset{H}{|}}{O}}-R'\right]^+ + H^+ + OH^- \longrightarrow \left[R.\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{|}{\overset{\overset{H}{|}}{O}}-R'\right]^+ \longrightarrow$$

$$R.COOH + \left[H-\underset{|}{\overset{\overset{H}{|}}{O}}-R'\right]^+ \longrightarrow R.COOH + HOR' + H^+.$$

From this there is deduced the expression for the velocity of hydrolysis

$$\frac{dx}{dt} = K_s.C_{ester}.C_{H^+}.C_{H_2O}.$$

This was at the time supposed to represent the experimental facts, but in the light of more recent work becomes a rough approximation only. Thus

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[1] Stieglitz, *Am. Chem. J.*, **39**, 421 (1908).

[2] *Z. Electrochem.*, **9**, 118 (1903); **10**, 586 (1904).

[3] Stieglitz, "International Congress of Arts and Sciences" at St. Louis, **4**, 278 (1904); *Am. Chem. J.*, **39**, 424 (1908).

[4] *Am. Chem. J.*, **48**, 352 (1912).

[5] THIS JOURNAL, **35**, 173 (1913).

[6] *Ibid.*, **37**, 1732 (1915).

[7] *Am. Chem. J.*, **39**, 29, 60 (1908).

it has been demonstrated within the last few years that the velocity, $-dx/dt$, increases *more rapidly* than C_{ester} or C_{H^+}, *i. e.*, increase in the concentration of water (dilution of the solution) causes more of a retardation than that calculated by the law of mass action.[1]

To explain the abnormal acceleration of hydrolysis with increase of C_{H^+} several theories have been advanced, notably the theory of the negative catalytic effect of water and the theory that the undissociated acid molecules, HX, are also catalytically active. These theories, together with the bearing of the results of the present paper upon them, will be examined in a subsequent communication.

From the foregoing discussion it will be apparent that the catalytic activity of acids has not been satisfactorily explained in a quantitative way—and that this can scarcely be expected until the complete mechanism of the reaction is rigorously established.

(*b*) **Addition Compound Formation in Systems Ester–Acid.**—The *experimental* evidence of the existence of such compounds is very unsatisfactory.

Lewis has recently[2] advanced the hypothesis that an *ester-water* compound R.COO.R′,HOH is active in hydrolysis. Absorption in the infrared region is the only evidence brought forward that such compounds exist. A compound of this type has never been isolated and moreover the work of Rivett[3] indicates that such a compound does not exist, to any appreciable extent, in an aqueous solution of ethyl acetate. From his results for the freezing-point depression of water by this ester, *recalculated to weight concentrations*,[4] it is seen that the depression is exactly linear; hence no combination, or at most only a minute trace, occurs.

On the other hand, the results of the present paper definitely establish the existence of binary compounds, *ester-acid.* Previous evidence on this question is almost entirely indirect. Thus the increasing molecular conductivity with increase of concentration of esters dissolved in liquid hydrogen halides is taken as being due to combination followed by ionization.[5] Many classes of organic oxygen compounds, as alcohols, acids, phenols, ketones, etc., form oxonium salts with various inorganic and organic acids; esters would be expected to form analogous compounds. The validity of such indirect evidence is, however, always open to suspicion and cannot have the same weight as the actual isolation of the compounds in question.

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[1] Taylor, *Meddel. K. Vetensk. Nobelinst.*, **2**, Nos. 34, 35, 37 (1913); Dawson and Powis, *J. Chem. Soc.*, **103**, 2139 (1913); Lewis, *Ibid.*, **109**, 67 (1916).

[2] *Ibid.*, **109**, 80 (1916).

[3] *Z. physik. Chem.*, **80**, 547 (1912).

[4] Noyes and Falk, THIS JOURNAL, **32**, 1013 (1910).

[5] Walker, McIntosh and Archibald, *J. Chem. Soc.*. **85**, 1100 (1904).

Direct Evidence.—Baeyer and Villiger[1] obtained "compounds" of $H_3Fe(CN)_6$ with ethyl acetate, ethyl benzoate and diethyl oxalate and of $H_4Fe(CN)_6$ with diethyl oxalate. Some uncertainty is introduced into the assumption that these are actually compounds by the work of McIntosh,[2] who conclusively proved that Baeyer and Villiger's "compounds" of ether and of acetone with $H_4Fe(CN)_6$ are in reality solid solutions. The only definite isolation of oxonium compounds of an ester with an acid is given by Maass and McIntosh,[3] who completely investigated the system, ethyl acetate–hydrogen chloride. The compounds formed were $CH_3.COO.C_2H_5,HCl$; $CH_3.COO.C_2H_5,4HCl$; and $2CH_3.COO.C_2H_5,5HCl$.

3. Experimental Procedure.

The complete examination of 22 ester–acid systems has been accomplished by the freezing-point method previously described. A number of mixtures of known composition are successively prepared for a binary system and the freezing point, *i. e.*, the temperature at which a minimum (negligible) amount of solid is in *equilibrium* with the liquid phase, is taken for each mixture. A series of such points determines the temperature-composition curve. In the diagram so obtained a break in the curve indicates a change in the solid phase crystallizing out. A maximum point indicates a compound, the position of the maximum with reference to the molecular composition axis gives the formula of the compound and the slope of the curve around the maximum indicates the extent of dissociation of the compound into its components, here ester and acid. For further details previous papers of this series should be consulted.[4]

The behavior of systems of the type R.COO.R′–HX will be dependent upon the character of the three radicals R, R′ and X.[5] In order to make our conclusions as general as possible, all three radicals have been widely varied in the different systems examined.

The acids, HX, employed were trichloroacetic (the strongest of the simple organic acids), chloroacetic (a typical transition acid), and acetic (a typical weak acid). Esters of both monobasic and dibasic aliphatic and aromatic acids were chosen, the acids varying in strength from acetic to oxalic. The third radical, R,′ was varied by working with ethyl, methyl, benzyl, phenyl, and α- and β-naphthyl esters. The following table gives the dissociation constants of the acids used and of the acids from which the esters were derived:

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[1] *Ber.*, 34, 2692 (1901).

[2] THIS JOURNAL, 30, 1097 (1908).

[3] *Ibid.*, 34, 1288 (1912).

[4] Kendall, *Ibid.*, 36, 1225 (1914).

[5] Kendall and Gibbons, THIS JOURNAL, 37, 159 (1915).

TABLE I.—DISSOCIATION CONSTANTS OF ACIDS.[1]

	100 K.		100 K.
Trichloroacetic	121.0	Salicylic	0.102
Monochloroacetic	0.155	Benzoic	0.0060
Acetic	0.0018	α-Toluic	0.00556
		p-Toluic	0.00515
Oxalic	10.0	Cinnamic	0.00355
Malonic	0.158	Anisic	0.0032
Succinic	0.00665	Terephthalic	0.015 (approx.)

From previous work on binary mixtures[2] the following relations are to be expected:

(1) **Varying X.**—Strong acids should give marked compound formation, with the possibility of isolating the compounds; weak acids, on the other hand, should exhibit less combination.

(2) **Varying R.**—Compound formation should be less for derivatives of strong than for those of weak acids. Making R more "negative" (as in passing from ethyl acetate to ethyl benzoate) should decrease the amount of combination.

(3) **Varying R′.**—As R′ becomes more "negative" (for example, as we pass from phenyl benzoate to ethyl benzoate) the ester should exhibit less compound formation with acids. Thus the "basic properties" (tendency to form onium compounds) of the ester oxygen atoms should be repressed by the proximity of "negative" groups.

These expectations were indeed realized, as will be shown in Section 5. The views in regard to the relative stability of oxonium compounds put forward in previous papers of this series have thus received further confirmation.

Measurement of Temperatures.—Above —35° several mercury thermometers with convenient ranges of scale, graduated in tenths, were used. These were calibrated as usual at 0° and 100° and also compared with certified thermometers. The toluene thermometer employed for temperatures below —35° was accurate down to —35° by calibration with a certified mercury thermometer. At —78.2° (CO_2–alcohol paste) and —82.8° (m. p. of pure ethyl acetate)[3] it was still accurate to within ±1°.[4]

The melting points given are corrected as usual for exposed stem. The stem correction for the toluene thermometer was so large (7–8°) that it was deemed safer to determine it directly than to use the coefficient of expansion of toluene, which varies with the temperature. The stem

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[1] Ostwald, *Z. physik. Chem.*, 3, 377, 418 (1889).

[2] Kendall, *Loc. cit.*

[3] Guttmann, THIS JOURNAL, 29, 345 (1907).

[4] A greater accuracy at these temperatures is very difficult to obtain. See Guttmann, *Loc. cit.*, and Beckmann and Waentig, *Z. anorg. Chem.*, 69, 17 (1910).

corrections found experimentally at a number of temperatures were plotted and used in correcting observed melting points between —35° and —100°.

The temperatures given later in the tables may be taken as having the following degree of accuracy:

Temperatures from 150° to 100°	Possible error 0.2–0.5°
Temperatures from 100° to —10°	Possible error 0.1–0.2°
Temperatures from —10° to —35°	Possible error 0.2–0.5°
Temperatures from —35° to —100°	Possible error 1.0–2.0° (usually ±1°)

A somewhat greater comparative accuracy for points on the same curve was attained, as is evidenced also by the smoothness of the curves.

For cooling below —20° carbon dioxide snow and acetone were used, and for temperatures below —80°, liquid air. Supercooling of the mixtures was quite general. To induce a compound to crystallize when no solid was available for seeding, it was often necessary to cool the mixture some 50° below the freezing point (to a glass), and allow it to warm slowly, vigorously scratching the walls of the tube. After several hours' repetition of this procedure the compound could usually be persuaded to crystallize out.

In all cases the melting point was determined by warming the partially frozen mixture very slowly and observing the temperature at which the last traces of crystals were *just in equilibrium* with the liquid, *i. e.*, the true temperature of incipient freezing. Points on a curve could be duplicated with a separate mixture of the same composition to within the limits of experimental error. Likewise even after it had stood for several days with the exclusion of moisture a given mixture exhibited the same melting point as immediately after mixing. This proves that the formation of the addition compound is not a time reaction, but is practically instantaneous even at temperatures below —50°.

In the following tables, as elsewhere in the paper, the composition of every mixture is expressed in *molecular* percentages.

4. Experimental Data.

A. Systems with Trichloroacetic Acid.—Trichloroacetic acid, after prolonged desiccation over sulfuric acid, *in vacuo*, gave a melting point of above 58° (55° in literature).

1. Ethyl Acetate.—The ethyl acetate used was a pure commercial sample, washed with water and carefully fractionated after standing over calcium chloride. It froze at a constant temperature of —83° ± 1°. The compound, $CH_3.COO.C_2H_5,CCl_3.COOH$, was obtained, crystallizing in large glistening plates, melting at —27.5°.

(*a*) Solid Phase, $CH_3.COO.C_2H_5$.

Per cent. ester	100	95.5
Temp.	—83.0	—88.0

(*b*) Solid Phase, $CH_3.COO.C_2H_5,CCl_3.COOH$.

Per cent. ester.....	87.1	78.9	70.5	59.9	50.0	47.8	45.3
Temp.............	—70.5	—53.0	—42.0	—32.5	—27.5	—28.1	—28.9

(*c*) Solid Phase, $CCl_3.COOH$.

Per cent. ester.....	40.1	32.7	24.6	17.6	8.5	0
Temp.............	—18.3	10.7	30.4	42.8	52.3	58.8

2. **α-Naphthyl Acetate.**—This ester was prepared from acetyl chloride and α-naphthol, the product being decolorized with animal charcoal, recrystallized three times from alcohol and finally from CCl_4. The compound $CH_3.COO.C_{10}H_7,CCl_3.COOH$, crystallizing in prismatic needles and melting at 10.7°, was isolated.

(*a*) Solid Phase, $CH_3.COO.C_{10}H_7$.

Per cent. ester.....	100	90.4	82.3	76.0	69.6	64.0	58.6
Temp.............	44.8	40.0	34.8	29.7	23.6	16.5	7.5

(*b*) Solid Phase, $CH_3.COO.C_{10}H_7,CCl_3.COOH$.

Per cent. ester.....	54.3	50.1	46.2	40.7	35.4
Temp.............	10.0	10.7	10.2	8.0	6.0

(*c*) Solid Phase, $CCl_3.COOH$.

Per cent. ester.....	30.0	23.3	15.5	8.1	0
Temp.............	21.0	33.5	44.5	51.9	58.0

3. **β-Naphthyl Acetate.**—This ester, after preparation from β-naphthol and acetic anhydride, was, with difficulty, purified by repeated rapid recrystallization from alcohol. The work was carried out below 0° to retard hydrolysis. An equimolecular compound with a rather high melting point (66.3°) was obtained, crystallizing in thin, oblong plates. (See Curve V, Fig. 1.)

(*a*) Solid Phase, $CH_3.COO.C_{10}H_7$.

Per cent. ester........................	100	89.9	82.4
Temp.....	68.5	63.9	59.4

(*b*) Solid Phase, $CH_3.COO.C_{10}H_7,CCl_3.COOH$.

Per cent. ester......................	71.1	65.2	60.1	55.1	50.0
Temp............................	55.5	60.9	63.6	65.4	66.3
Per cent. ester......................	45.6	43.0	38.1	32.4	24.5
Temp............................	65.7	64.8	62.3	57.7	48.7

(*c*) Solid Phase, $CCl_3.COOH$.

Per cent. ester......................	16.1.	8.6	0
Temp............................	43.8	51.5	58.2

4. **Ethyl Benzoate.**—A pure sample was fractionated and the portion boiling between 208.3° and 208.6° used. This gave a melting point of —32.7° (not previously determined). A second crystalline form (m. p. —40°) was also found to exist. (Compare methyl benzoate.) A compound, $C_6H_5.COO.C_2H_5,CCl_3.COOH$, crystallizing in sheaves of needles, was isolated; m. p. —23.4°.

(*a*) Solid Phase, $C_6H_5.COO.C_2H_5$.

Per cent. ester.....	100	87.7	78.8
Temp.............	—32.7	—38.4	—45.0

(*b*) Solid Phase, $C_6H_5.COO.C_2H_5,CCl_3.COOH$.

Per cent. ester.....	71.0	64.4	61.1	54.4	50.0	47.3	45.2
Temp.............	—38.5	—31.6	—28.5	—24.7	—23.4	—23.5	—24.0

(*c*) Solid Phase, $CCl_3.COOH$.

Per cent. ester.....	40.7	35.3	29.8	24.4	19.7	14.0	7.2	0
Temp.............	—10.1	6.0	20.0	30.5	38.5	46.2	53.2	58.7

5. **Methyl Benzoate.**—The methyl benzoate was prepared as usual from benzoic acid and absolute methyl alcohol by saturation with hydrogen chloride. The fraction boiling constantly at 197.8° gave a melting point of —12.3° (not previously determined). A metastable crystalline form also exists with m. p. —13.7°. This gives rise to a second melting-point curve paralleling that of the stable form. An equimolecular compound (also existing in two crystalline modifications, m. p. —10.6° and —8.8°, both crystallizing in needles) was isolated. (See Curve II, Fig. 1.)

(*a*) Solid Phase, $C_6H_5.COO.CH_3$.

Metastable Form.

Per cent. ester..	100	95.7	94.0	92.9
Temp..........	—13.7	—15.0	—16.3	—17.0

Stable Form.

Per cent. ester..	100	94.0	92.3	90.5	87.2	83.4	78.0	75.0
Temp..........	—12.3	—14.7	—15.4	—16.5	—18.6	—21.5	—25.5	—28.5

(*b*) Solid Phase, $C_6H_5.COO.CH_3,CCl_3.COOH$.

Per cent. ester..	72.7	70.7	66.3	65.4	62.5	
Temp..........	—25.5	—23.3	—18.6	—17.9	—15.3	
Per cent. ester..	60.0	55.8	52.5	50.0	47.7	44.3
Temp..........	—13.1	—10.5	—9.3	—8.8	—9.2	—10.1

(*c*) Solid Phase, $CCl_3.COOH$.

Per cent. ester..	43.2	39.7	36.2	31.4	26.2	20.2	14.3	8.2	0
Temp..........	—15.6	—4.8	4.2	15.9	26.4	36.5	44.2	50.9	57.5

6. **Benzyl Benzoate.**—By fractionation under reduced pressure benzyl benzoate of m. p. 18.3° was obtained. The compound $C_6H_5.COO.CH_2C_6H_5,CCl_3.COOH$, crystallizing in clusters of needles (m. p. 11.9°), was isolated.

(*a*) Solid Phase, $C_6H_5.COO.CH_2C_6H_5$.

Per cent. ester.....	100	90.8	80.9	76.1	74.8	72.1	71.3	69.9	67.5
Temp.............	18.3	15.4	13.3	6.8	6.4	4.5	4.0	2.0	—1.0

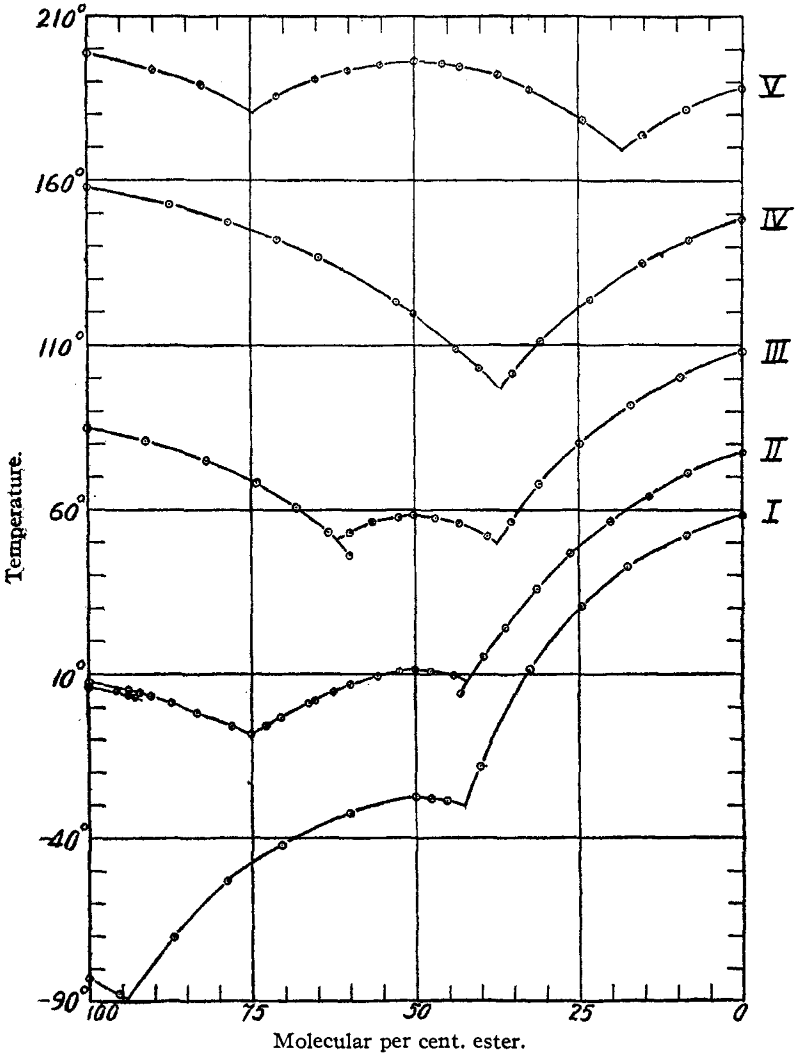
(*b*) Solid Phase, $C_6H_5.COO.CH_2C_6H_5,CCl_3.COOH$.

Per cent. ester.....	69.8	67.5	63.1	57.9	54.1	50.2	48.8	44.6	39.8
Temp.............	—1.5	1.5	6.5	9.5	10.9	11.9	11.8	11.5	10.2

(*c*) Solid Phase, $CCl_3.COOH$.

Per cent. ester.....	35.6	30.0	25.2	19.7	13.8	6.3	0
Temp.............	10.0	21.6	30.3	38.7	45.5	53.1	57.9

Fig. 1.—Freezing-point curves of esters of monobasic acids with trichloroacetic acid.



I. Ethyl acetate (scale correct).
II. Methyl benzoate (subtract 20°).
III. Methyl cinnamate (subtract 50°).
IV. Phenyl benzoate (subtract 90°).
V. β-Naphthyl acetate (subtract 130°).

7. **Methyl Anisate.**—Methyl anisate was prepared from anisic acid, absolute methyl alcohol and sulfuric acid by refluxing. The product, recrystallized from methyl alcohol by cooling to 0°, gave a m. p. of 48.3° (45–46° in literature). A compound, $CH_3O.C_6H_4.COO.CH_3,CCl_3COOH$, crystallizing in small, glittering plates, m. p. —6.3°, was isolated. This compound also crystallized in a metastable form of lower melting point.

(*a*) Solid Phase, $CH_3O.C_6H_4.COO.CH_3$.

Per cent. ester	100	91.4	84.7	78.8	73.1	67.2	61.6	58.2	56.2
Temp.	48.3	43.7	39.2	34.0	27.9	19.5	9.5	0.0	—5.5

(*b*) Solid Phase, $CH_3O.C_6H_4.COO.CH_3,CCl_3.COOH$.

Per cent. ester	54.7	50.0	44.9	40.6
Temp.	—7.4	—6.3	—7.0	—9.5

(*c*) Solid Phase, $CCl_3.COOH$.

Per cent. ester	37.6	34.6	29.5	22.7	16.5	9.2	0
Temp.	—6.5	5.0	17.0	31.5	41.1	50.6	58.1

8. **Methyl Cinnamate.**—Methyl cinnamate (prepared by passing hydrogen chloride into a solution of cinnamic acid in absolute methyl alcohol) was recrystallized from alcohol with the addition of water until turbid, followed by cooling on ice. The ester showed no test for chlorine and melted at 34.7° (33° in literature). With trichloroacetic acid an equimolecular compound, crystallizing in slender needles, was obtained. That the double bond has nothing to do with the formation of this compound is evidenced by the fact that HCl does *not* add on *permanently* during the preparation of the ester.[1] (See Curve III, Fig. 1.)

(*a*) Solid Phase, $C_6H_5.CH:CH.COO.CH_3$.

Per cent. ester	100	91.2	81.8	74.3	68.0	63.2	59.9
Temp.	34.7	30.8	25.0	18.4	10.9	3.3	—3.7

(*b*) Solid Phase, $C_6H_5.CH:CH.COO.CH_3,CCl_3.COOH$.

Per cent. ester	59.9	56.5	52.4	50.2	46.9	43.2	38.0
Temp.	3.2	6.4	7.9	8.5	7.7	6.0	1.9

(*c*) Solid Phase, $CCl_3.COOH$.

Per cent. ester	35.2	31.0	24.9	17.1	9.4	0
Temp.	6.5	17.8	30.0	41.9	50.4	58.3

9. **Methyl *p*-Toluate.**—The ester was prepared from *p*-toluic acid dissolved in absolute methyl alcohol and saturated with hydrogen chloride. After several recrystallizations from diluted methyl alcohol the ester melted at 33.2° (32° in literature). A compound crystallizing in rectangular plates, m. p. 9°, was obtained.

(*a*) Solid Phase, $CH_3C_6H_4.COO.CH_3$.

Per cent. ester	100	86.7	81.0	75.5	68.4	62.1
Temp.	33.2	28.8	25.4	21.1	13.6	4.7

(*b*) Solid Phase, $CH_3C_6H_4.COO.CH_3,CCl_3.COOH$.

Per cent. ester	57.5	53.0	50.0	46.4	42.2	37.7
Temp.	6.0	8.2	9.0	8.6	7.1	3.4

(*c*) Solid Phase, $CCl_3.COOH$.

Per cent. ester	33.8	26.4	16.8	8.9	0
Temp.	11.0	28.6	43.1	52.0	59.2

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[1] The addition of HCl at the double bond would give a stable saturated compound not again decomposed by addition of water as are the oxonium compounds. Also here, as in previous work, the cinnamic acid behaves normally with respect to stability of the compound, etc.—the double bond having no apparent effect. No compound could be isolated with chloroacetic acid. (See System 20, below.)

10. Phenyl Benzoate.—The phenyl benzoate was prepared by the Schotten-Baumann reaction and purified by several recrystallizations from alcohol. No compound could be isolated, but the slope of the curve shows much compound formation in the liquid phase. (See Curve IV, Fig. 1.)

(*a*) Solid Phase, $C_6H_5.COO.C_6H_5$.

Per cent. ester......	100	87.4	78.4	70.9	64.5	52.7	50.2	43.8	40.3
Temp.............	67.8	62.8	57.3	52.1	46.7	33.0	29.6	19.0	13.2

(*b*) Solid Phase, $CCl_3.COOH$.

Per cent. ester......	35.0	30.7	23.3	15.2	8.0	0
Temp.............	11.5	21.0	33.7	44.7	52.1	58.5

11. Phenyl Salicylate.—A commercial specimen of satisfactory m. p. was employed. Although no compound could be isolated, yet the form of the curve (see later) again indicated much combination in the liquid phase.

(*a*) Solid Phase, $HO.C_6H_4.COO.C_6H_5$.

Per cent. ester..............	100	95.1	87.9	84.3	80.4	76.3
Temp......................	41.9	39.9	36.4	34.4	32.1	29.5
Per cent. ester..............	72.4	67.7	64.7	58.6	50.3	
Temp......................	27.5	23.8	21.6	15.8	8.0	

(*b*) Solid Phase, $CCl_3.COOH$.

Per cent. ester..............	19.8	14.2	8.2	0
Temp......................	39.5	45.4	51.7	57.9

12. Diethyl Succinate.—A specimen from a well-known manufacturer, after fractionation, gave a m. p. of —20.8°, identical with that given in the literature. The central portion of the curve could not be completed, as mixtures in this region refused to crystallize even after standing for some time in liquid air. However, the form of the curve (as far as it could be traced) leaves little reason for doubt that the compound $C_2H_4(COO.C_2H_5)_2,2CCl_3.COOH$ is present in the liquid mixture (compare dimethyl succinate below). (See Curve III, Fig. 2.)

(*a*) Solid Phase, $C_2H_4(COO.C_2H_5)_2$.

Per cent. ester.....	100	90.8	82.7	75.1	67.3	59.8
Temp............	—20.8	—23.3	—26.5	—30.2	—35.6	—44.0

(*b*) Solid Phase, $CCl_3.COOH$.

Per cent. ester.....	30.9	28.1	23.9	19.5	14.5	9.9	0
Temp............	—26.0	—9.1	9.5	25.5	38.2	47.1	58.3

13. Dimethyl Succinate.—This ester was prepared by the usual method. The compound isolated, $C_2H_4(COO.CH_3)_2,2CCl_3.COOH$, crystallized in slender prisms, m. p. 8.0°. (See Curve IV, Fig. 2.)

(*a*) Solid Phase, $C_2H_4(COO.CH_3)_2$.

Per cent. ester.....	100	91.5	82.0	76.2	69.9	64.5	60.3
Temp............	18.2	15.4	10.7	6.8	1.4	—4.2	—9.8

(b) Solid Phase, $C_2H_4(COO.CH_3)_2,2CCl_3.COOH$.

Per cent. ester.....	56.9	52.5	50.2	47.5	44.9	43.4	40.3
Temp.............	—13.4	—6.9	—3.3	—1.0	1.9	2.7	5.5
Per cent. ester.....	37.1	33.2	30.2	26.7			
Temp.............	7.1	8.0	7.0	5.5			

(c) Solid Phase, $CCl_3.COOH$.

Per cent. ester.....	23.2	15.8	8.6	0
Temp.............	17.7	37.2	49.7	58.1

14. Dimethyl Malonate.—The ester was prepared in the usual manner, the product being finally fractionated *in vacuo*. The ester has not previously been frozen (m. p. —62°). Owing to supercooling with formation of glasses, mixtures containing between 60% and 100% of ester could not be examined. (The probable form of the curve is indicated by a broken line in Curve I, Fig. 2.)

A compound crystallizing in plates was isolated. It is unstable at its maximum but obviously, from the form of the curve near the break, is the compound $CH_2(COO.CH_3)_2,2CCl_3.COOH$ (compare Systems 12 and 13); m. p. —28.5 (by extrapolation).

(a) Solid Phase, $CH_2(COO.CH_3)_2$.

Per cent. ester.....	100
Temp.............	—62.0

(b) Solid Phase, $CH_2(COO.CH_3)_2,CCl_3.COOH$.

Per cent. ester.....	60.9	54.4	50.0	45.8	41.7	37.8
Temp.............	—60.0	—46.1	—39.0	—34.0	—31.0	—29.2

(c) Solid Phase, $CCl_3.COOH$.

Per cent. ester.....	37.7	35.0	28.7	24.2	19.3	10.6	0
Temp.............	—28.7	—15.1	8.7	21.7	32.3	47.7	58.9

15. Diethyl Oxalate.—The m. p. of a Kahlbaum specimen was raised from —45° to that given in the literature (—41°) by fractionation under diminished pressure. A compound just stable at its maximum was isolated, crystallizing in thin, seemingly triclinic plates (m. p. 3.4°). (See Curve II, Fig. 2.)

(a) Solid Phase, $(COO.C_2H_5)_2$.

Per cent. ester	100	89.6	82.5
Temp........	—41.0	—43.5	—46.5

(b) Solid Phase, $(COO.C_2H_5)_2,2CCl_3.COOH$.

Per cent. ester	74.6	69.3	63.1	56.7	50.0	48.3	42.7	38.9	33.3	32.8
Temp........	—46.5	—35.0	—23.6	—13.9	—5.9	—4.1	0.1	1.9	3.4	3.4

(c) Solid Phase, $CCl_3.COOH$

Per cent. ester	35.9	30.8	23.9	17.0	8.7	0
Temp........	—10.6	8.5	25.5	38.8	50.5	58.6

16. Dimethyl Oxalate.—A Kahlbaum specimen of satisfactory melting point was used. No compound could be isolated; on repeated trials mixtures around 50 mol per cent. always froze spontaneously to give characteristic plates of the ester. The form of the curve indicates, however, that much combination occurs in the liquid mixture.

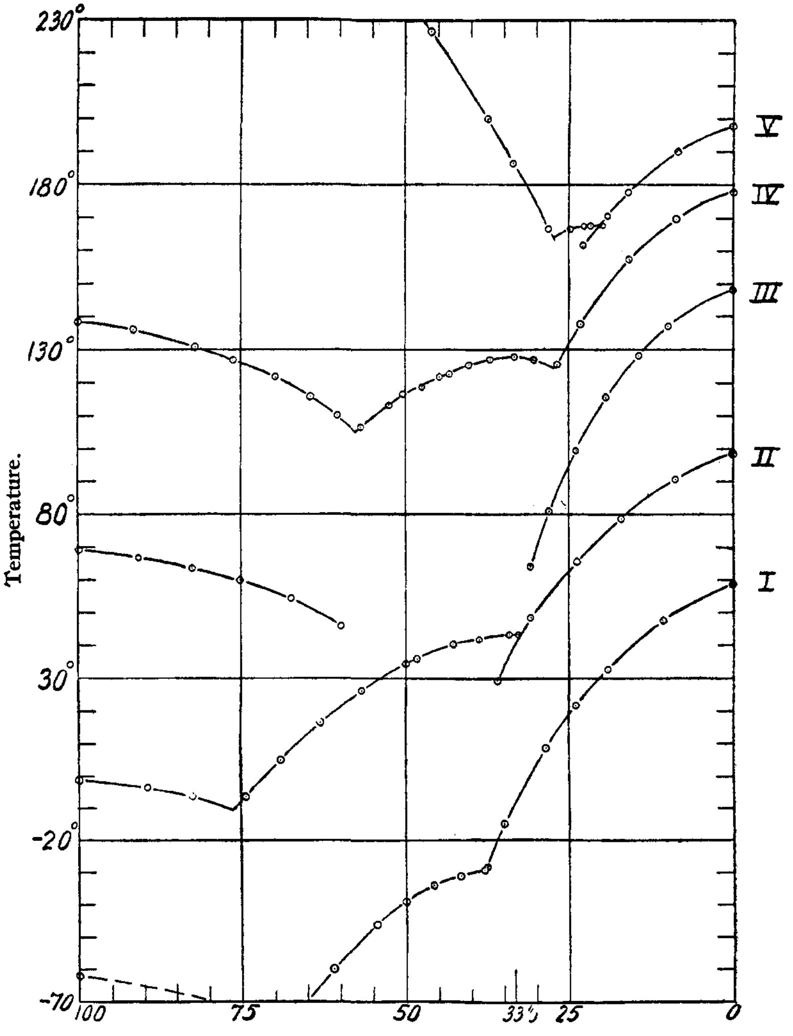
(*a*) Solid Phase, $(COO.CH_3)_2$.

Per cent. ester	100	91.3	80.6	72.9	63.6	56.7	50.0	45.3
Temp.	53.3	49.4	42.9	36.4	28.4	20.0	10.3	2.3

(*b*) Solid Phase, $CCl_3.COOH$.

Per cent. ester	40.0	33.8	26.9	17.2	8.3	0
Temp.	2.5	15.5	27.5	41.6	50.9	57.9

Fig. 2.—Freezing-point curves of esters of dibasic acids with trichloroacetic acid.



I. Dimethyl malonate (scale correct).
II. Diethyl oxalate (subtract 40°).
III. Diethyl succinate (subtract 90°).
IV. Dimethyl succinate (subtract 120°).
V. Dimethyl terephthalate (subtract 140°).

17. Dimethyl Terephthalate.—A pure specimen of the ester (m. p. 140.3) was furnished by Mr. C. P. Harris. This system is especially interesting, due to the fact that a compound, $C_6H_4(COO.CH_3)_2,4CCl_3.COOH$, was isolated. It would be expected by analogy to dimethyl malonate and succinate that only a compound AB_2 should be formed. It is probable that a compound AB_2 exists but its curve never enters the stable region.

As will be seen from Curve V, Fig. 2, the compound AB_4 is only just stable at its maximum (m. p. 27.9°); it was consequently deemed advisable to analyze it. This was done by filtering and drying the large needles of the compound at a temperature of between 25° and 26°. The extremely hygroscopic crystals were weighed and added to water, whereby the compound was decomposed into its components. The acid was then titrated.

0.4563 g. crystals required 12.80 cc. 0.1683 normal NaOH. Found: 0.3520 g. trichloroacetic acid. Calc. for 1 : 4 compound: 0.3519 g.

(*a*) Solid Phase, $C_6H_4(COO.CH_3)_2$.

Per cent. ester	100	89.2	80.2	70.8	61.5	52.9	46.1	37.3	33.4	28.1
Temp	140.3	135.4	129.5	121.7	111.0	98.2	85.6	59.7	46.3	36.4

(*b*) Solid Phase, $C_6H_4(COO.CH_3)_2,4CCl_3.COOH$.

Per cent. ester	24.9	22.7	21.9	20.0
Temp	26.7	27.6	27.7	27.9

(*c*) Solid Phase, $CCl_3.COOH$.

Per cent. ester	22.7	20.0	19.2	15.9	8.3	0
Temp	21.5	28.2	30.4	37.9	50.1	57.8

B. Systems with Chloroacetic and Acetic Acids.—For curves see Fig. 4.

18. Dimethyl Oxalate–Chloroacetic Acid.—Both components, dried *in vacuo* over H_2SO_4, exhibited satisfactory melting points.

(*a*) Solid Phase, $(COO.CH_3)_2$.

Per cent. ester	100	89.3	76.5	71.0	64.3	57.2	50.1	49.3
Temp	53.2	49.3	44.7	41.0	37.3	32.6	27.6	27.0

(*b*) Solid Phase, $CH_2Cl.COOH$.

Per cent. ester	43.4	34.7	30.9	24.2	16.6	8.9	0.0
Temp	29.4	37.6	40.8	46.3	51.8	56.9	61.7

19. Dimethyl Succinate–Chloroacetic Acid.—

(*a*) Solid Phase, $C_2H_4(COO.CH_3)_2$.

Per cent. ester	100	90.3	81.0	71.4	62.4
Temp	18.2	14.8	10.8	5.9	0.1

(*b*) Solid Phase, $CH_2Cl.COOH$.

Per cent. ester	57.0	49.8	42.3	41.9	34.7	26.7	18.1	8.5	0.0
Temp	—3.5	7.4	18.0	18.5	28.1	38.0	47.4	56.2	61.9

20. Methyl Cinnamate–Chloroacetic Acid.—

(*a*) Solid Phase, $C_6H_5.CH:CH.COO.CH_3$.

Per cent. ester	100	84.8	77.2	73.4	63.9
Temp	34.4	27.4	23.4	20.0	14.5

(*b*) Solid Phase, $CH_2Cl.COOH$.

Per cent. ester	56.8	49.1	40.5	25.2	14.8	10.2	4.0	0.0
Temp.	14.0	22.0	30.0	43.5	51.9	55.3	59.2	61.4

21. Dimethyl Oxalate-Acetic Acid.—A fractionation of 500 cc. of "glacial" acetic acid gave 65 cc. boiling between 118–119°, showing a m. p. of 16.4° and therefore 99.9% pure. Distillation from conc. H_2SO_4 failed to give a good product.

(*a*) Solid Phase, $(COO.CH_3)_2$.

Per cent. ester	100	90.4	80.5	70.7	60.8	
Temp.	53.2	50.3	47.5	44.5	41.3	
Per cent. ester	51.4	41.8	38.1	34.7	28.5	18.8
Temp.	37.3	32.5	30.5	28.2	23.8	14.1

(*b*) Solid Phase, $CH_3.COOH$.

Per cent. ester	9.9	0.0
Temp.	10.6	16.4

22. Dimethyl Succinate-Acetic Acid.—

(*a*) Solid Phase, $C_2H_4(COO.CH_3)_2$.

Per cent. ester	100	90.1	79.3	69.3	60.5	52.3	42.6
Temp.	18.2	15.5	12.4	9.3	6.2	2.5	−2.2

(*b*) Solid Phase, $CH_3.COOH$.

Per cent. ester	32.7	22.9	17.7	6.1	0.0
Temp.	−5.3	1.4	5.2	12.7	16.4

From the preceding data it will be seen that, in each of the thirteen compounds isolated, trichloroacetic acid was the acid component. In no case did the weaker chloroacetic and acetic acids combine with the ester to a sufficient extent to allow a compound to be isolated. Likewise, the esters *not* yielding compounds with trichloroacetic acid are those of strong acids (dimethyl oxalate) or phenyl esters of moderately strong acids (phenyl benzoate and salicylate).

5. Relative Stability of Addition Compounds.

With regard to the relative stability of the oxonium salts obtained (*i. e.*, the extent of the combination of ester and acid in the liquid phase, as discussed on p. 1718), two lines of evidence may be brought forward.

(*a*) **Sharpness of Maxima.**—The addition compounds isolated are all more or less dissociated into their components in the liquid state. Their stability may be approximately determined from the sharpness of the maximum,[1] *i. e.*, the decrease in the temperature of fusion of the compound on addition of either component. The less the depression, or the flatter the curve in the neighborhood of the maximum, the greater is the dissociation at the melting point as expressed by the equation

$$A_xB_y \rightleftarrows xA + yB.$$

In the following table some freezing-point lowerings for the compounds of trichloroacetic acid with esters are compared.

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[1] Kendall, *Loc. cit.* See also Kremann, *Monatshefte*, **25**, 1215 (1904).

TABLE II.—FREEZING-POINT DEPRESSIONS OF COMPOUNDS OF TRICHLOROACETIC ACID WITH ESTERS ON ADDITION OF EITHER COMPONENT.

System and type of compound. (A = ester. B = acid.)			M. p.[1]	Depression of freezing point (ΔT).	
				(a) 5 mol % from maximum	(b) 10 mol % from maximum.
1.	Ethyl acetate	AB	—27.5°	1.5°	5.2°[3]
2.	α-Naphthyl acetate	AB	10.7	0.9	2.8[2]
3.	β-Naphthyl acetate	AB	66.3	0.8	2.7
4.	Ethyl benzoate	AB	—23.4	1.2	4.4[2]
5.	Methyl benzoate	AB	—8.8	1.1	4.2[2]
6.	Benzyl benzoate	AB	11.9	0.9	2.7
7.	Methyl anisate	AB	—6.3	0.9	3.5[2]
8.	Methyl cinnamate	AB	8.5	1.5	5.3
9.	Methyl *p*-toluate	AB	9.0	1.1	4.1
13.	Dimethyl succinate	AB_2	8.0	1.6[2]	4.8[2]
14.	Dimethyl malonate	AB_2	—28.2[3]	1.0[2,3]	4.0[2,3]
15.	Diethyl oxalate	AB_2	3.4	1.2[2]	3.8[2]

For esters of monobasic acids (1 to 9), Column 4 gives the mean depression resulting from the addition of sufficient ester or acid to give a mixture containing, respectively, 55 or 45 molar per cent. of ester. Similarly, Column 5 gives the mean depression for mixtures containing 60 and 40 molar per cent. ester. For esters of dibasic acids (13–15) $61^2/_3$ and $56^2/_3$ molar per cent. of ester are chosen.

This method gives only an *approximate* indication of the relative stability of compounds of different esters with trichloroacetic acid. First of all the comparisons are not made at the same temperature, and secondly, the heat of fusion of the complex, related as it is to the freezing-point lowering, ought to be taken into consideration. Nevertheless, that the method is of value in affording qualitative relationships is evident from the following examples.

A sharper maximum, indicating greater stability, is obtained with the ethyl acetate compound than with the α- or β-naphthyl acetates. So also is the depression somewhat greater for ethyl than for methyl benzoate and for these in turn markedly greater than in the case of benzyl benzoate. When we compare the methyl esters, the order of stability of the compounds becomes methyl cinnamate > methyl benzoate (or *p*-tolu-

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[1] There is but little regularity in the melting points of the compounds isolated. They fall below or between those of the components. McIntosh's rule that the melting point of an oxonium compound is above that of either component is not general, but holds only for compounds with the low-melting hydrogen halides. In some cases the rule fails even here, as with $C_3H_7OH, 2\ HBr$ and $C_3H_7OH,5HCl$, which melt lower than the respective hydrogen halides. (Archibald and McIntosh, *J. Chem. Soc.*, **85**, 928 (1904).)

[2] Depression caused by one component only.

[3] Obtained by a short extrapolation. Results are not included where extrapolation would be too great for accuracy.

ate) > methyl anisate.[1] Likewise ethyl acetate exhibits a sharper maximum than ethyl benzoate. These relations are all to be expected from the comparative dissociation constants of the acids (see p. 1718). It is apparent from the above examples that the stability of the complex is greater for esters of weaker acids and where R′ is more "positive" (*i. e.*, $C_2H_5 > CH_3 > C_6H_5.CH_2$, etc.). For esters of the dibasic acids the same rule holds, as will also be more clearly indicated by Method B below.

The quantitative investigation of the degree of dissociation of these compounds into the components, acid + ester, will be given in a later contribution.

(*b*) **Relative Slope of Curves.**—Addition compounds may be formed in the liquid phase and yet not be induced to crystallize out, especially if the degree of dissociation into the components at the melting point is large. In such cases, however, the extent of compound formation can be deduced from the change in slope of the freezing-point curve of either component. This gives, indeed, a more *general* method of detecting compound formation[2] than the actual isolation of the products.

On addition of any second substance, B, to a pure substance, A, the resultant lowering of the freezing point of A depends upon the molar fraction of the solute, B, present. If no combination of B with A occurs, the depression of the freezing point is expressed by the equation[3]

$$-\log x = \frac{Q}{RT_0}\left(\frac{T_0}{T} - 1\right)$$

(where x = mol. fraction of A in mixture; Q = mol. heat of fusion of A; T_0 = temperature of fusion of A; T = temperature of fusion of mixture; $R = 1.988$). The form of this curve varies greatly with the relative values of Q and T_0. For organic compounds, in general, the values of Q and T_0 are such that the ideal curve is, for the greater part of its length, approximately a straight line.

If, however, the addition of a foreign substance, B, to A is accompanied by the formation of an addition compound, AB, then the freezing point of A will be abnormally lowered, since part of the original solvent has been replaced by the second foreign substance AB. The more stable the compound is, the greater will be the abnormal depression of the freezing point. Hence the deviations from the ideal curve when different substances are added to A indicate the relative extent of combination in each case.

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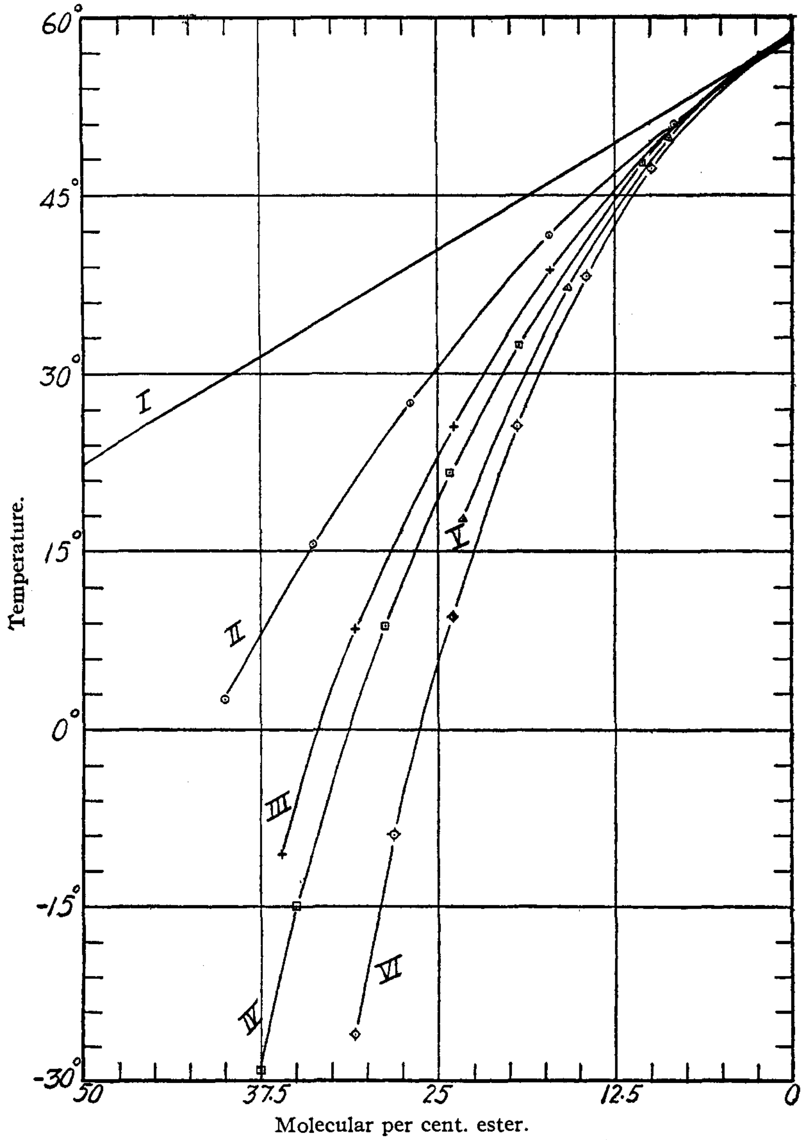
[1] Methyl anisate is an apparent exception to the general rule, as anisic acid being weaker than even cinnamic its ester should yield a compound *more* stable than that of the methyl cinnamate. That this is due to one of the factors making this but an approximate method is evidenced by the fact that methyl anisate shows a normal behavior by Method B, following.

[2] Kendall, THIS JOURNAL, **36**, 1731 (1914).

[3] Roozeboom, *Heterogene Gleichgewichte*, **2**, p. 273.

To establish the ideal curve for trichloroacetic acid it was examined with benzene, a substance with which it exhibits no compound formation. This is shown by the following table and more strikingly in Curve I, Fig. 3.

Fig. 3.—Freezing-point depressions of trichloroacetic acid with esters of dibasic acids (solid phase trichloroacetic acid throughout).



I. Benzene.
II. Dimethyl oxalate.
III. Diethyl oxalate.
IV. Dimethyl malonate.
V. Dimethyl succinate.
VI. Diethyl succinate.

23. Trichloroacetic Acid–Benzene.—

(*a*) Solid Phase, C_6H_6.

Per cent. C_6H_6	100	89.6	84.3
Temp.	5.4	1.5	—0.5

(*b*) Solid Phase, $CCl_3.COOH$.

Per cent. C_6H_6	76.4	68.6	62.7	55.6	
Temp.	—3.8	3.0	9.4	16.1	
Per cent. C_6H_6	47.2	35.2	25.5	16.4	0
Temp.	23.1	33.0	39.6	46.8	57.2

The comparison of this ideal freezing-point-depression curve for trichloroacetic acid with those caused by esters of various dibasic acids is shown in Fig. 3. Each of these esters lowers the temperature of fusion of trichloroacetic acid much more than does benzene, signifying extensive combination. If the reaction is represented as

$$2CCl_3.COOH + R(COO.R')_2 \rightleftarrows (CCl_3.COOH)_2,R(COO.R')_2$$

each mol of ester on combination removes two mols of solvent. Consequently the dip of the curve is more decided than when an equimolecular compound is formed.

The "falling away" of the curve is greatest with diethyl succinate. The divergences assume the following order: diethyl succinate > dimethyl succinate > dimethyl malonate > diethyl oxalate > dimethyl oxalate. The following conclusions may be drawn: (1) Esters of the stronger acids combine less than esters of the weaker acids. (2) The diethyl ester of succinic or oxalic acid exhibits more combination than the corresponding dimethyl ester (the ether radical being somewhat more "positive" than the methyl radical).

The monobasic acid esters follow the same rules, confirming the results of Method A. This is shown in the table below, where freezing-point depressions of trichloroacetic acid due to 30 or 40 mol % of ester are compared.

TABLE III.—FREEZING-POINT DEPRESSIONS OF TRICHLOROACETIC ACID CAUSED BY ADDITION OF (*a*) 30 MOL %; (*b*) 40 MOL % OF AN ESTER.

Ester added.	(*a*) $T_0 - T_{30}$.	(*b*) $T_0 - T_{40}$.
1. Ethyl acetate	39.8°	78.8°
2. α-Naphthyl acetate	37.0	....
4. Ethyl benzoate	39.7	67.0
5. Methyl benzoate	38.5	63.5
6. Benzyl benzoate	36.3	60 ± 1°[1]
10. Phenyl benzoate	31.0	....
11. Phenyl salicylate	30.2	43.8
9. Methyl *p*-toluate	39.0	....
7. Methyl anisate	41.9	75 ± 2°[1]
8. Methyl cinnamate	38.8	....

As an example of the application of these data, the extent of compound

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[1] Obtained by short extrapolation, the maximum uncertainty being indicated.

formation for the esters of benzoic acid is seen to be ethyl>methyl>benzyl>phenyl. Similarly methyl anisate manifests more combination than methyl cinnamate, benzoate, etc.[1] Other comparisons are readily made.

6. Compound Formation a General Phenomenon.

It has been established above that compound formation is general in systems containing trichloroacetic acid as acid component even in cases where no compound can actually be isolated. The same method may be employed to test the extent of compound formation in the similar systems (Nos. 18 to 22 above) containing weaker acids. We have here a means for determining the effect of variation of the third radical, X. At the same time we may compare the ideal curves for chloroacetic and acetic acids with those obtained on addition of different esters, and discover whether in these cases also general compound formation is indicated.

The normal curves for chloroacetic and acetic acids are established in the following tables:

24. Chloroacetic Acid–Benzene.—

(*a*) Solid Phase, C_6H_6.

Per cent. C_6H_6....	100	98.3
Temp............	5.4	4.8

(*b*) Solid Phase, $CH_2Cl.COOH$.

Per cent. C_6H_6....	95.0	91.4	89.0	80.6	75.7	70.0	64.4	57.4	47.0	39.4
Temp............	3.8	10.8	15.9	27.6	31.3	34.7	37.5	40.2	44.1	46.5
Per cent. C_6H_6....	30.9	24.9	18.3	8.7	0					
Temp............	49.7	52.0	54.2	57.8	61.4					

25. Acetic Acid–Benzene.[2]—

(*a*) Solid Phase, C_6H_6.

Per cent. C_6H_6...	100	84.6	75.5	64.9	58.6
Temp..........	5.5	0.6	—2.4	—6.0	—8.4

(*b*) Solid Phase, $CH_3.COOH$.

Per cent. C_6H_6...	54.0	49.7	39.6	29.9	21.4	11.0	3.1	0
Temp..........	—7.4	—6.0	—1.8	2.3	6.0	10.7	14.0	16.3

These ideal freezing-point curves are compared in Table IV with those given for the same acids by dimethyl oxalate and dimethyl succinate, representing esters of strong and weak acids, respectively. The corresponding data for trichloroacetic acid are added for comparison.

TABLE IV.—COMPARATIVE FREEZING-POINT DEPRESSIONS OF ACIDS.

	ΔT with dimethyl succinate.		ΔT with dimethyl oxalate.		ΔT with benzene.	
Solvent.	25 mol %.	50 mol %.	25 mol %.	50 mol %.	25 mol %.	50 mol %.
$CCl_3.COOH$...	46.9°	...	27.4°	...	16.5°	36.2°
$CH_2Cl.COOH$..	21.9°	54.7°	15.5°	39.4°[3]	9.4°	18.4°
$CH_3.COOH$.....	16.3°	...	13 ± 1°[3]	...	11.8°	22.3°

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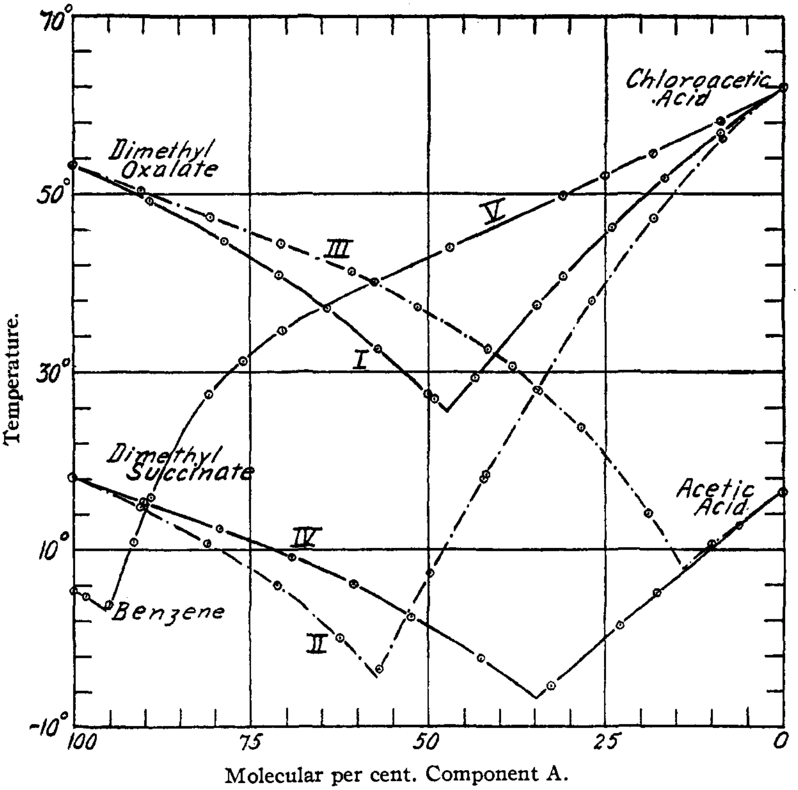
[1] See note 1, page 1730; methyl anisate here assumes its correct position.

[2] Data are those given by Roloff, *Z. physik. Chem.*, 17, 335 (1895); recalculated to molar concentrations.

[3] Values obtained by short extrapolation.

The observed freezing-point lowerings of chloroacetic and acetic acids by the three solutes selected are also shown graphically in Fig. 4. If we compare Curves I, II and V it is evident that benzene gives a normal curve throughout; both esters plainly cause abnormal depression. As before, combination is more extensive with the succinate than with the oxalate. The extent of compound formation with chloroacetic acid is, however, in both cases much less than with the strong acid, trichloroacetic.[1]

Fig. 4.—Freezing-point curves of chloroacetic and acetic acids with esters (solid phase for each curve is indicated at side of diagram).



I. Dimethyl oxalate—chloroacetic acid.
II. Dimethyl succinate—chloroacetic acid.
III. Dimethyl oxalate—acetic acid.
IV. Dimethyl succinate—acetic acid.
V. Benzene—chloroacetic acid.

The acetic acid curves are less satisfactorily compared, as the break (change in solid phase) is too near the acetic acid axis. However, Table IV shows that the freezing-point depressions due to 25 mol per cent. of solute assume the same order as with other acids: dimethyl succinate > dimethyl oxalate > benzene. Similarly, from the other (left hand) branch

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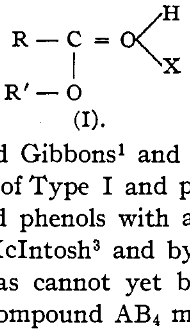
[1] See Figs. 2 and 3.

of the curves we see that the lowering of the temperature of fusion of dimethyl succinate by acetic acid deviates from the normal "straight line" curve throughout; with dimethyl oxalate a slight "dip" in the curve becomes perceptible only when excess of acetic acid has been added. It is evident, therefore, that even the weak acetic acid combines to some extent with esters. The deviations from the normal curve vary, as before, with the ester considered, but some compound formation is indicated even in such an unfavorable system as acetic acid–dimethyl oxalate.

All acids catalyze ester hydrolysis, the degree of acceleration (for ordinary concentrations) increasing with the strength of the acid. When this is correlated with the fact that all acids form addition compounds with esters, the extent of compound formation also increasing with the strength of the acid, we are led to conclude that the formation of these addition compounds constitutes in reality the first step in ester hydrolysis. Further evidence on this point will be adduced in a subsequent communication.

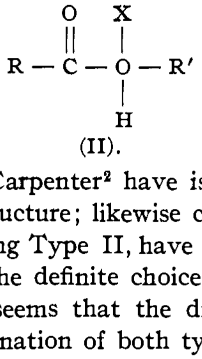
7. Structure of Addition Compounds Isolated.

In these oxonium compounds, either the carbonyl or the hydroxyl oxygen may be quadrivalent, as is shown in Formulas I and II, respectively:



$$R - \underset{\underset{\displaystyle R'-O}{|}}{C} = O\left\langle\begin{matrix}H\\X\end{matrix}\right.$$

(I).



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

(II).

Kendall and Gibbons[1] and Kendall and Carpenter[2] have isolated many compounds of Type I and proved their structure; likewise compounds of alcohols and phenols with acids, illustrating Type II, have been investigated by McIntosh[3] and by Kendall.[4] The definite choice between the two formulas cannot yet be made.[5] It seems that the dimethyl terephthalate compound AB_4 may be a combination of both types.

It is at present premature to attempt to discuss the whole mechanism of ester hydrolysis, *i. e.*, how the oxonium compound, or its positive ion, finally suffers hydrolysis. Several such formulations of the hydrolysis have been put forth, with little experimental support. The authors are now endeavoring to obtain direct experimental evidence on the course of the reaction after the first step, formation of the binary oxonium compound.

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[1] THIS JOURNAL, **37**, 149 (1915).

[2] *Ibid.*, **36**, 2498 (1914).

[3] *J. Chem. Soc.*, **85**, 928 (1904).

[4] THIS JOURNAL, **38**, 1309 (1916).

[5] Compare Falk and Nelson, *Loc. cit.* Formula II is the one more favored by organic chemists, Stieglitz, Nelson and others having used it, without apparent justification beyond convenience of formulation.

8. Summary.

1. The formation of binary compounds of the type ester–acid has been investigated by the freezing-point method. Such compounds have heretofore been assumed to exist, to explain the mechanism of ester hydrolysis as catalyzed by acids, but no conclusive evidence of their presence has been produced. In the present investigation thirteen oxonium compounds of widely differing esters with trichloroacetic acid have been isolated, esters of monobasic acids uniformly yielding equimolecular compounds.

2. Previous papers indicated that oxonium compound formation is in general more evident the more divergent the "acidic strength" of the components employed.[1] Applied to the present case this would demand that combination be most pronounced between *strong* acids and esters of *weak* acids (preferably the alkyl rather than the more "negative" aryl esters). All *three* radicals concerned were varied experimentally as widely as possible and the rule was found to hold throughout the whole range of systems examined.

3. The extent of compound formation varies within wide limits as the above factors are varied. Although decreasing rapidly with decrease in strength of the acid it is still perceptible even with the typical weak acid, acetic acid. We may, therefore, state definitely that *oxonium salt formation is a general phenomenon in systems ester–acid.* These experimental results are in significant agreement with the fact that acceleration of ester hydrolysis is a general property of acids and also decreases with decrease in strength of the acid.

4. The results obtained in this paper are in entire agreement with the "intermediate compound formation" theory as an explanation of acid catalysis of ester hydrolysis. The formation of addition compounds of the type ester–acid as the first step in the mechanism of the reaction may now be regarded as experimentally established.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE THERMAL DECOMPOSITION OF SYMMETRICAL DIARYLHYDRAZINES.[2]

BY JULIUS STIEGLITZ AND HELEN TREDWAY GRAHAM.[3]

Received June 28, 1916.

In the thermal decomposition of hydrazobenzene, azobenzene and aniline are formed according to the equation

$$2C_6H_5NH.NHC_6H_5 \longrightarrow C_6H_5N:NC_6H_5 + 2C_6H_5NH_2. \qquad (1)$$

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[1] Kendall and Gibbons, THIS JOURNAL, 37, 149 (1915).

[2] After the completion of the work reported in this paper and after the original