very rapidly, and becomes 50 or 100 times as large as the possible experimental error.

In the second part of this paper, these data will be used to calculate the degree of dissociation and the heat of formation of hydrogen molecules. The experiments at low pressures lead to a somewhat detailed knowledge of the mechanism of the reaction taking place on the surface of the wire.

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THE ADDITION COMPOUNDS OF ORGANIC ACIDS IN PAIRS.

BY JAMES KENDALL.

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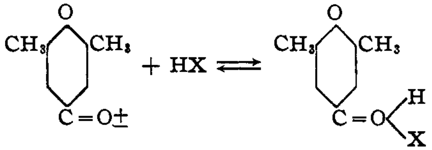
In a recent communication[1] the author has shown, by the application of the freezing-point method, that a large number of organic acids form addition compounds with dimethylpyrone, and that these compounds are to be regarded as true oxonium salts. The reaction is best expressed by the equation:



The formation of an equimolecular addition compound is thus considered to be due to the basic (or unsaturated) properties of the group $>C = O\pm$, in which oxygen functions as a quadrivalent atom.

This same group, $>C = O\pm$, is present in all organic acids themselves. Consequently it appeared probable that, if the acidic properties of an organic acid could be sufficiently suppressed, the basic nature of the group $>C = O\pm$ would become evident and formation of addition compounds with other substances could be obtained. Now the acidic properties of a weak acid can obviously be reduced to a minimum by the presence of a second, much stronger acid. In the present investigation, therefore, the validity of the general conclusions drawn in the previous paper is tested by this method—the examination of systems containing two organic acids of widely divergent strengths.

The experimental details and the main principles of the method followed have already been described in full. The formation of an addition compound can be immediately deduced from the freezing-point curve of a two-component system by the appearance of a maximum on the curve; the position of the maximum indicates the composition of the compound.

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[1] Kendall, THIS JOURNAL, 36, 1222 (1914).

Since these addition reactions are reversible, any compound formed is partially dissociated into its components on fusion; the extent of dissociation is indicated by the form of the curve near the maximum. In the previous investigation it was shown that the degree of dissociation (in other words, the relative stability of the salt) is a function of the strength of the acid used.

For the present work, the following acids were selected from among those previously employed:

SERIES A.—WEAK ACIDS.

Acid.	100 K.
Benzoic	0.0060
o-Toluic	0.0120
m-Toluic	0.00514
p-Toluic	0.00515
α-Toluic	0.00556
Cinnamic	0.00355
Acetic	0.00180
Crotonic	0.00204

SERIES B.—STRONG ACIDS.

Acid.	100 K.
Trichloroacetic	121.0
Dichloroacetic	5.14
Chloroacetic	0.155

The terms "weak" and "strong" are here applied to the acids in a relative sense only. The dissociation constants are those given by Ostwald;[1] for the stronger acids the values must be regarded as merely approximate.[2]

It will be seen that the acids under A are all of approximately the same strength, while the acids under B form a series covering a very wide range. By such a choice of material it was made possible to subject the views of the author on oxonium salt formation, as expressed above, to a very rigorous test. The tendency to form addition products should increase with the difference in acidic strength of the two components of the system. Acids of widely divergent strengths should readily give addition compounds, acids of similar strengths should show little tendency towards compound formation. In the above series, consequently, we should expect addition compounds (if produced at all) to be most stable in systems containing trichloroacetic acid, less stable when dichloroacetic acid is present, still less stable when chloroacetic acid is employed.

This was, indeed, found to be the case throughout. With trichloroacetic acid, equimolecular addition compounds were isolated in five out of eight cases. In the remaining three systems, the form of the freezing-point curve showed that such compounds were undoubtedly present in solution, but, owing either to persistent supercooling or to extremely low fusion points, could not be isolated. The form of the curves indicated also that the compounds were fairly considerably dissociated into their components on fusion, and were uniformly much less stable than those

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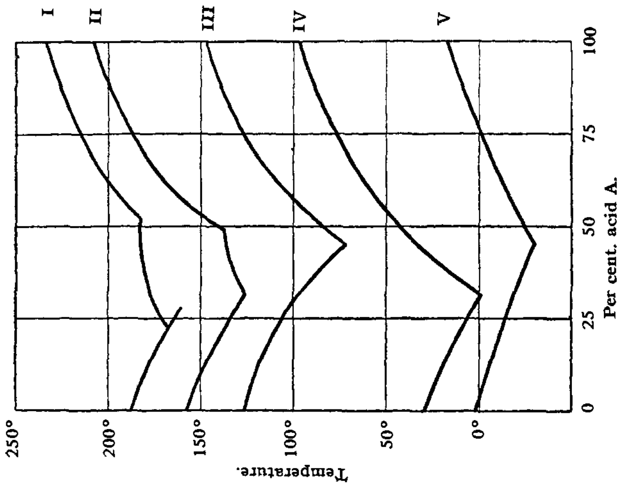
[1] Ostwald, *Z. physik. Chem.*, 3, 418 (1889).

[2] Kendall, *J. Chem. Soc.*, 101, 1275 (1912); *Meddel. från K. Vet.-Akads. Nobelinstitut*, Band 2, No. 38 (1913).

obtained in the previous investigation with dimethylpyrone. This was to be expected, since there the components were one acidic and one basic, while here both are primarily acidic.

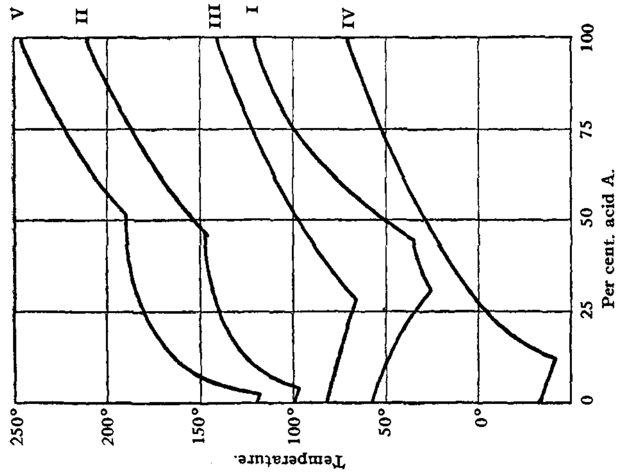
With systems containing dichloroacetic acid, addition products were obtained in two out of eight cases. In the remaining six, compounds were present in solution, but could not be isolated. (All solutions containing dichloroacetic acid were extremely difficult to investigate, owing to persistent supercooling.) The compounds obtained were much less stable than those with trichloroacetic acid.

From systems containing chloroacetic acid no addition compounds were obtained, and the curves indicate that the tendency towards com-



I. *o*-Toluic acid—Trichloroacetic acid. Subtract 130° from temperature scale.
II. *m*-Toluic acid—Trichloroacetic acid. Subtract 100° from temperature scale.
III. α-Toluic acid—Trichloroacetic acid. Subtract 70° from temperature scale.
IV. α-Toluic acid—Dichloroacetic acid. Subtract 20° from temperature scale.
V. α-Toluic acid—Chloroacetic acid. Add 60° to temperature scale.

Fig. 1.



I. Benzoic acid—Trichloroacetic acid. Temperature scale correct.
II. Benzoic acid—Dichloroacetic acid. Subtract 90° from temperature scale.
III. Benzoic acid—Chloroacetic acid. Subtract 20° from temperature scale.
IV. Benzoic acid—Acetic acid. Add 50° to temperature scale.
V. Cinnamic acid—Dichloroacetic acid. Subtract 110° from temperature scale.

Fig. 2.

pound formation is extremely slight. This is in keeping with the relatively weak acidic nature of chloroacetic acid. The examination of several similar systems (in which both acids taken were either from Series A or Series B) confirmed the conclusion that, with acids of only slightly divergent strengths, no addition compounds are formed.

The experimental results are given in the tables below; these are arranged as in the previous paper. A few typical curves are shown in the accompanying diagrams.

Experimental.

1. **Benzoic Acid—Trichloroacetic Acid.**—The equimolecular compound, C_6H_5.COOH, CCl_3.COOH, was obtained, m. p. 36.4° (by extrapolation). The compound is not stable at its maximum, and crystallizes only from solutions containing excess of trichloroacetic acid. The freezing-point curve is shown in Fig. 2.

(*a*) Solid phase, C_6H_5.COOH.

% C_6H_5.COOH	100.0	80.1	68.3	63.6	60.1	55.5	52.0	47.1
T	121.0	105.6	89.7	79.9	72.8	64.0	54.4	43.1

(*b*) Solid phase, C_6H_5.COOH, CCl_3.COOH.

% C_6H_5.COOH	42.9	39.2	33.3	31.5
T	34.6	32.6	28.1	26.6

(*c*) Solid phase, CCl_3.COOH.

% C_6H_5.COOH	26.7	22.5	21.9	16.7	9.4	0
T	32.3	36.9	38.0	45.0	50.5	57.3

2. ***o*-Toluic Acid—Trichloroacetic Acid.**—The compound C_7H_7.COOH, CCl_3.COOH was obtained, m. p. 52.9°; stable at its maximum. (See Fig. 1.)

(*a*) Solid phase, C_7H_7.COOH.

% C_7H_7.COOH	100.0	90.0	81.2	73.9	67.2	58.3	53.8
T	103.4	97.6	90.5	83.9	76.8	64.7	55.7

(*b*) Solid phase, C_7H_7.COOH, CCl_3.COOH.

% C_7H_7.COOH	49.8	45.5	40.8	37.6	33.1	28.8	23.5
T	52.9	52.6	51.8	50.4	48.1	45.1	39.4

(*c*) Solid phase, CCl_3.COOH.

% C_7H_7.COOH	27.9	21.5	15.0	8.7	0
T	30.7	38.9	45.5	51.3	57.3

3. ***m*-Toluic Acid—Trichloroacetic Acid.**—The compound C_7H_7.COOH, CCl_3.COOH was obtained, unstable at its maximum; m. p. 37.4° (by extrapolation). (See Fig. 1.)

(*a*) Solid phase, C_7H_7.COOH.

% C_7H_7.COOH	100.0	89.3	78.1	65.7	60.2	55.7	51.4
T	107.6	100.2	89.8	75.3	66.6	56.9	45.4

(*b*) Solid phase, C_7H_7.COOH, CCl_3.COOH.

% C_7H_7.COOH	49.6	45.8	41.9	36.7
T	37.3	36.3	34.6	31.3

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

% $C_7H_7.COOH$	31.4	26.5	21.0	15.9	7.7	0
T	26.2	32.4	38.6	44.1	51.5	57.3

4. ***p*-Toluic Acid—Trichloroacetic Acid.**—An equimolecular compound was obtained, unstable at its maximum; m. p. 69.0° (by extrapolation).

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	87.2	76.2	65.5	57.6	50.1	44.8	40.0	36.9
T	178.6	170.4	160.1	145.9	131.9	115.5	100.2	84.1	69.1

(*b*) Solid phase, $C_7H_7.COOH$, $CCl_3.COOH$.

% $C_7H_7.COOH$	34.5	30.5	25.7	22.3	18.1
T	63.5	60.3	55.7	51.8	45.0

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

% $C_7H_7.COOH$	12.9	6.9	0
T	46.6	52.2	57.3

5. **α-Toluic Acid—Trichloroacetic Acid.**—No compound was here isolated. The curve is shown in Fig. 1.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	90.5	81.4	70.8	63.1	55.4	47.9
T	76.7	70.8	63.3	51.7	40.1	25.9	9.2

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

% $C_7H_7.COOH$	41.2	34.9	28.4	20.8	11.7	0
T	10.2	21.2	31.3	41.2	49.3	57.3

6. **Cinnamic Acid—Trichloroacetic Acid.**—The compound $C_8H_7.COOH$, $CCl_3.COOH$ was obtained, unstable at its maximum; m. p. 63.0° (by extrapolation).

(*a*) Solid phase, $C_8H_7.COOH$.

% $C_8H_7.COOH$	100.0	87.0	76.1	65.8	56.6	50.3
T	136.8	122.2	108.5	94.8	79.9	68.5

(*b*) Solid phase, $C_8H_7.COOH$, $CCl_3.COOH$.

% $C_8H_7.COOH$	45.3	41.4	35.3	29.2	25.9
T	62.1	59.7	55.7	49.3	44.9

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

% $C_8H_7.COOH$	24.8	19.7	17.4	9.3	0
T	36.1	42.5	45.0	51.1	57.3

7. **Acetic Acid—Trichloroacetic Acid.**—No compound was here isolated.

(*a*) Solid phase, $CH_3.COOH$.

% $CH_3.COOH$	100.0	91.3	84.6	75.7	69.0
T	16.4	9.9	3.1	—10.1	—25.3

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

% $CCl_3.COOH$	51.0	46.1	38.5	30.2	22.5	12.8	0
T	— 13.3	— 0.1	15.4	28.4	37.6	47.3	57.3

8. **Crotonic Acid—Trichloroacetic Acid.**—Here also no compound was isolated.

(*a*) Solid phase, $C_3H_5.COOH$.

% $C_3H_5.COOH$........	100.0	91.0	82.7	75.7	65.7	60.0	54.2	49.9
T....................	71.0	63.7	53.9	44.2	27.5	16.1	2.1	—9.9

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

% $C_3H_5.COOH$........	45.1	40.7	34.4	26.6	19.1	10.2	0
T....................	—12.7	1.2	16.4	30.4	40.3	49.6	57.3

9. **Benzoic Acid—Dichloroacetic Acid.**—The compound $C_6H_5.COOH$, $CHCl_2.COOH$ was obtained; unstable at its maximum; m. p. 58.2° (by extrapolation). The freezing-point curve is shown in Fig. 2.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$.	100.0	81.5	70.7	61.1	50.8	48.4	45.7
T.............	121.0	104.0	91.6	79.1	64.6	61.2	56.7

(*b*) Solid phase, $C_6H_5.COOH$, $CHCl_2.COOH$.

% $C_6H_5.COOH$.	44.3	40.2	37.4	34.9	29.4	25.3	16.9	11.6	8.3	5.4
T.............	57.8	57.2	56.4	55.6	52.8	50.1	42.6	33.6	25.5	15.3

(*c*) Solid phase, $CHCl_2.COOH$.

% $C_6H_5.COOH$.	1.8	0
T.............	8.6	9.7

10. ***o*-Toluic Acid—Dichloroacetic Acid.**—No addition compound was here isolated.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$......	100.0	89.5	78.6	69.1	60.7	51.2	43.0	37.9	28.2	20.4	14.4
T..................	103.4	97.1	89.5	81.6	74.1	63.0	52.1	44.9	28.4	13.0	—1.9

(*b*) Solid phase, $CHCl_2.COOH$.

% $C_7H_7.COOH$......	12.5	7.1	0
T..................	—1.0	3.9	9.7

11. ***m*-Toluic Acid—Dichloroacetic Acid.**—Here also no addition compound was isolated.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$...	100.0	87.4	74.6	66.1	56.4	46.4	35.9	28.2	23.0
T...............	107.6	98.5	87.5	79.4	68.2	53.8	35.8	19.9	6.1

(*b*) Solid phase, $CHCl_2.COOH$.

% $C_7H_7.COOH$...	17.1	11.0	6.1	0
T...............	—6.1	—0.2	4.2	9.7

12. ***p*-Toluic Acid—Dichloroacetic Acid.**—No compound was isolated.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$.	100.0	85.1	71.6	59.5	50.0	40.9	33.1	26.1	20.4	15.5	10.8
T..............	178.6	168.1	154.9	139.6	125.2	109.0	91.3	75.2	59.7	42.3	23.1

(*b*) Solid phase, $CHCl_2.COOH$.

% $C_7H_7.COOH$.	5.2	0
T..............	5.1	9.7

13. α-Toluic Acid—Dichloroacetic Acid.—No compound was isolated. (See Fig. 1.)

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$...	100.0	93.3	81.4	71.8	63.9	59.2	50.0	42.9	36.9
T..............	76.7	72.4	63.4	53.6	43.9	37.6	22.3	9.0	−5.5

(*b*) Solid phase, $CHCl_2.COOH$.

% $C_7H_7.COOH$...	25.9	15.3	7.5	0
T..............	−14.6	−3.3	3.5	9.7

14. Cinnamic Acid—Dichloroacetic Acid.—The equimolecular compound $C_8H_7.COOH$, $CHCl_2.COOH$ was obtained; unstable at its maximum; m. p. 80.1°. (See Fig. 2.)

(*a*) Solid phase, $C_8H_7.COOH$.

% $C_8H_7.COOH$.....	100.0	86.1	74.1	62.8	55.0	51.5
T................	136.8	124.3	111.0	97.6	86.1	80.0

(*b*) Solid phase, $C_8H_7.COOH$, $CHCl_2.COOH$.

% $C_8H_7.COOH$.....	51.5	50.0	44.8	37.3	29.8	24.6	17.1	12.8	7.8	6.0	4.1
T................	80.0	80.1	79.7	77.8	74.2	69.6	61.4	54.0	42.8	35.7	24.7

(*c*) Solid phase, $CHCl_2.COOH$.

% $C_8H_7.COOH$.....	1.6	0
T................	8.6	9.7

15. Acetic Acid—Dichloroacetic Acid.—No addition compound was isolated. The central portion of the curve could not be completed, since at the very low temperature required for solidification the mixture sets to a hard, glassy mass.

(*a*) Solid phase, $CH_3.COOH$.

% $CH_3.COOH$...........	100.0	91.4	79.2	70.5	63.6	55.0
T......................	16.4	10.3	−0.7	−10.8	−21.5	−37.0

(*b*) Solid phase, $CHCl_2.COOH$.

% $CH_3.COOH$...........	43.4	29.7	17.9	8.6	0
T......................	−40.8	−18.2	−4.2	3.9	9.7

16. Crotonic Acid—Dichloroacetic Acid.—No addition compound could be isolated.

(*a*) Solid phase, $C_3H_5.COOH$.

% $C_3H_5.COOH$.	100.0	93.6	86.8	80.6	71.1	65.3	55.8	47.4	40.4
T............	71.0	65.5	59.1	52.6	41.4	34.0	20.5	5.1	−9.7

(*b*) Solid phase, $CHCl_2.COOH$.

% $C_3H_5.COOH$.	31.0	17.1	8.9	0
T............	−18.5	−4.2	2.7	9.7

17. Benzoic Acid—Chloroacetic Acid.—No compound was obtained in any system containing chloroacetic acid. The freezing-point curve is given in Fig. 2.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100.0	81.0	69.8	58.5	52.9	44.2	38.6	32.0
T	121.0	107.2	96.8	86.1	80.4	69.9	62.4	52.6

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

% $C_6H_5.COOH$	25.1	21.1	14.4	5.9	0
T	48.7	50.7	54.5	58.6	61.4

18. *o*-Toluic Acid—Chloroacetic Acid.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	89.1	77.0	66.4	57.4	50.5	44.4	38.2	32.4
T	103.4	97.0	89.6	82.3	75.5	70.2	64.9	58.8	52.3

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

% $C_7H_7.COOH$	27.5	22.1	16.5	11.5	5.8	0
T	47.9	50.7	53.3	55.7	58.5	61.4

19. *m*-Toluic Acid—Chloroacetic Acid.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	90.1	79.6	68.4	56.9	45.2	35.7
T	107.6	101.0	93.6	84.7	75.3	64.1	53.9

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

% $C_7H_7.COOH$	28.4	21.2	14.4	7.7	0
T	46.7	50.5	54.2	57.7	61.4

20. *p*-Toluic Acid—Chloroacetic Acid.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	83.1	70.4	56.9	45.4	34.0	22.7	17.1	12.9
T	178.6	167.2	155.8	141.8	128.5	114.0	95.5	83.1	71.1

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

% $C_7H_7.COOH$	9.3	4.7	0
T	56.8	59.1	61.4

21. α-Toluic Acid—Chloroacetic Acid.—The freezing-point curve is shown in Fig. 1.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100	89.5	80.9	72.5	64.8	56.6	49.9
T	76.7	70.1	63.8	56.9	49.9	42.3	35.2

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

% $C_7H_7.COOH$	41.6	32.9	23.9	14.9	6.7	0
T	33.6	40.0	46.7	52.7	57.9	61.4

22. Cinnamic Acid—Chloroacetic Acid.

(*a*) Solid phase, $C_8H_7.COOH$.

% $C_8H_7.COOH$	100	89.3	77.5	68.0	54.4	44.7	36.4	31.4
T	136.8	128.2	118.6	109.0	95.9	83.8	70.2	60.5

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

% $C_8H_7.COOH$	25.0	19.0	13.9	8.2	0
T	48.3	51.2	54.0	57.1	61.4

23. Acetic Acid—Chloroacetic Acid.

(*a*) Solid phase, $CH_3.COOH$.

% $CH_3.COOH$	100	91.8	79.6	71.0
T	16.4	10.7	1.7	—4.5

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

% $CH_3.COOH$	71.0	62.0	50.3	40.3	29.4	15.5	0
T	5.0	12.8	22.2	29.7	38.0	49.4	61.4

24. Crotonic Acid—Chloroacetic Acid.

(*a*) Solid phase, $C_3H_5.COOH$.

% $C_3H_5.COOH$	100	91.2	83.4	75.4	65.9	56.5
T	71.0	64.4	57.7	50.7	41.1	30.9

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

% $C_3H_5.COOH$	46.8	38.6	30.0	19.9	10.4	0
T	29.9	36.5	42.6	50.0	55.8	61.4

25. Benzoic Acid—*α*-Toluic Acid.—In this and the two following systems the acids are both from Series A; no compound formation was indicated.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100	91.0	82.1	70.0	57.9	48.7	38.3
T	121.0	115.2	108.5	97.8	85.3	74.0	57.4

(*b*) Solid phase, $C_7H_7.COOH$.

% $C_6H_5.COOH$	28.9	18.9	10.1	0
T	56.9	63.7	69.5	76.7

26. Benzoic Acid—Cinnamic Acid.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100	86.8	76.9	69.9	61.7
T	121.0	111.0	102.0	95.4	87.2

(*b*) Solid phase, $C_8H_7.COOH$.

% $C_6H_5.COOH$	52.5	42.3	33.1	19.9	9.6	0
T	87.3	100.5	109.5	121.5	130.1	136.8

27. Benzoic Acid—Acetic Acid.—The freezing-point curve is shown in Fig. 2.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100	87.6	72.6	61.0	50.6	43.4	35.3	28.3	20.8	14.5
T	121.0	111.5	100.3	90.1	79.1	71.5	60.9	50.9	38.2	19.2

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

% $C_6H_5.COOH$	9.7	5.2	0
T	10.4	13.0	16.4

28. Chloroacetic Acid—Dichloroacetic Acid.—In this and the following systems the acids are both from Series B; no addition compounds were isolated.

(*a*) Solid phase, $CH_2Cl.COOH$.

% $CH_2Cl.COOH$	100	90.1	82.5	75.8	66.4	54.0	40.4	32.7
T	61.4	56.8	52.5	47.5	40.5	29.6	10.8	—5.5

(*b*) Solid phase, $CHCl_2.COOH$.

% $CH_2Cl.COOH$	24.7	12.2	0
T	—5.8	2.8	9.7

29. Chloroacetic Acid—Trichloroacetic Acid.

(*a*) Solid phase, $CH_2Cl.COOH$.

% $CH_2Cl.COOH$	100	84.8	74.5	65.5	58.2	51.4
T	61.4	53.5	46.5	38.9	31.0	22.4

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

% $CH_2Cl.COOH$	41.7	31.9	24.1	15.5	0
T	24.3	33.2	39.9	46.1	57.3

30. Dichloroacetic Acid—Trichloroacetic Acid.

(*a*) Solid phase, $CHCl_2.COOH$.

% $CHCl_2.COOH$	100	93.7	82.2	68.7
T	9.7	7.0	1.0	—7.9

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

% $CHCl_2.COOH$	56.9	46.5	31.8	21.2	12.2	0
T	—0.6	14.5	32.9	42.5	49.6	57.3

Consideration of Results.

The general conclusions of the investigation have already been stated in the introduction. In the following pages, by closer examination of the freezing-point curves obtained, some quantitative results are deduced and discussed.

From the diagrams given, it will be seen that the freezing-point curves are different in type, even where no addition compound is isolated, according to which acid of Series B is present in the system. In systems containing chloroacetic acid, the curves obtained are approximately linear, the change in slope as the eutectic point is approached being very slight. In systems where dichloroacetic acid is present, the curves deviate more from the straight line, and the "dip" before the eutectic is more pronounced. Finally, in systems containing trichloroacetic acid, the curves fall away rapidly in the neighborhood of the eutectic point.

It remains to show how this difference in character is connected with the relative extent of compound formation in the mixture. The freezing point of a pure substance, A, will, under normal conditions,[1] be equally

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[1] That is, provided the substance added is not *associated* or *dissociated* in the solution.—It is not intended to imply, in the following discussion, that association or dissociation of the substances present in the systems considered can be entirely disregarded. Organic acids, as a class, are certainly associated to some extent in the liquid state, also the conception that the addition reaction taking place in the solution is *ionic* (Kendall, THIS JOURNAL, 36, 1242 (1914)) assumes dissociation. Nevertheless, the regularity of the results obtained indicates clearly that the figures given in Table I are legitimately comparable, and that the above disturbing influences are only of secondary importance.

depressed on addition of equimolecular amounts of different foreign substances, provided no chemical reaction has occurred. If, however, the addition of a second 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 will have been replaced by a foreign substance, the compound AB. The more stable the addition product is, the greater will be the abnormal depression of the freezing point. Hence, the form of the curves obtained, when different substances are added to A, indicates the relative extent of compound formation in each case.

In the systems examined above, chloroacetic acid shows no tendency to compound formation throughout, and the freezing point curves approximate to straight lines.[1] Where dichloroacetic acid is present, on the other hand, addition products are formed and can in some cases be isolated, although they are evidently, from the flatness of their curves near the maximum point, largely dissociated into their components in the liquid state. On first addition of dichloroacetic acid to an acid in Series A, the extent of compound formation will be very small.[2] Further addition of dichloroacetic acid will increase the amount of the compound present,[3] and that this corresponds with an abnormal depression of the freezing point is indicated by the "falling away" of the curves as the eutectic is approached. Systems in which trichloroacetic acid is a component are similar in type, but the addition products formed are more stable. In accordance with this, the freezing point depression in the central part of the curve becomes still more abnormal, as is evidenced by the systems shown in Diagram I.

We are, therefore, able to discover by comparison to what extent compound formation has occurred in any particular system, from the form of the freezing-point curve alone, even if it is not possible actually to isolate the compound. This is illustrated by the figures given in Table I, where the freezing-point depressions of the acids in Series A, due to addition of equimolecular amounts of the various acids in Series B, are col-

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[1] Where the point of fusion of the second acid of the system is very high (*e. g.*, *p*-toluic acid) a sharp final bend in the curve is necessary to enable it to reach the eutectic point at all. The main portion of the curve, however, still remains linear. Compare Fig. 2, Curve IV.

[2] The reversible reaction $A + B \rightleftharpoons AB$ gives the equation for equilibrium:

$$c_{AB}/c_A c_B = k$$

(c = molecular concentration, k = constant.) If the compound AB is largely dissociated on fusion, the constant k of the reaction will be small. Hence, when c_B is small, c_{AB} is also very small. The extent of compound formation will obviously be greatest in the central portion of the curve.

[3] Not only for the reason given in the previous note, but also since the addition products formed are more stable, the lower the temperature.

lected. The values given are obtained directly by interpolation from the freezing-point curves.[1] (T_{50} = freezing point of 50% mixture: Δ = depression.)

TABLE I.

Acid A.	Trichloroacetic.		Dichloroacetic.		Chloroacetic.	
	T_{50}.	Δ.	T_{50}.	Δ.	T_{50}.	Δ.
Benzoic	50.6	70.4	63.7	57.3	77.2	43.8
o-Toluic	47.2	56.2	61.6	41.8	69.8	33.6
m-Toluic	40.4	67.2	59.4	48.2	68.8	38.8
p-Toluic	115.2	63.4	125.2	53.4	134.1	44.5
α-Toluic	14.4	62.3	22.3	54.4	35.3	41.4
Cinnamic	68.0	68.8	77.5	59.3	90.9	45.9
Crotonic	—9.6	80.6	9.8	61.2	23.2	47.8

The above results show that, throughout the entire series, the freezing-point depression caused by trichloroacetic acid is greater than that caused by dichloroacetic acid, which is in turn greater than that caused by chloroacetic acid.

This dependence of compound formation upon difference in acidic strength is evidently in complete accordance with the views on oxonium salt formation developed in the introduction. The regularity of the values obtained indicates that the results are not greatly influenced by any disturbing factors (association or dissociation in the solution).[2] Further evidence on the point is to be obtained from systems containing acids of similar strengths (25–27, above). From these we have:

TABLE II.

Original acid.	Acid added.	T_{50}.	Δ.
Benzoic	α-Toluic	75.5	45.5
Benzoic	Cinnamic	75.6	45.4
Benzoic	Acetic	78.5	42.5
Benzoic	Chloroacetic	77.2	43.8)
Cinnamic	Benzoic	90.4	46.4
Cinnamic	Chloroacetic	90.9	45.9)

Here T_{50} and Δ have the same significance as in Table I; the figures for chloroacetic acid are included for comparison. The constancy of Δ for benzoic acid with different acids exhibiting no tendency to compound formation shows that conditions in the above systems are, if not normal, at least comparable.[3] The freezing-point depression caused by chloro-

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[1] In a few cases a short extrapolation is necessary. The figures for acetic acid are not given, since here a longer extrapolation is required and accurate values cannot be obtained. The curves indicate, however, that the results are qualitatively similar to those given above.

[2] See note on page 1731.

[3] For small additions of B to A (up to 20%), the freezing-point curves are practically identical, whatever acid in Series B is added. In this region the extent of compound formation is small in all cases (see Note 2, page 1732).

acetic acid is approximately normal; it is evident that its acidic strength is insufficient to suppress the acidic properties of the weaker acid of the system so far as to induce combination.

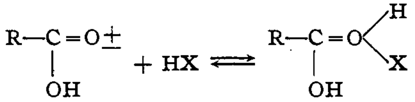
Addition reactions of the nature dealt with in this paper have been little investigated; a few compounds of the type acid—acid have been previously described[1] but not systematically examined. The similarity of the components accounts for the small number of compounds isolated in the present research, but further experiments indicate that formation of addition products is of very general occurrence in organic reactions, *e. g.*, as an intermediate stage in condensations.[2] That this is not generally recognized is due to the neglect of the freezing-point method in the study of organic reactions.

It seems to be still the rule in experimental work to torture substances into combination by the drastic method (inherited from the alchemists) of applying *heat*. This certainly gives us the final products of a reaction (or series of reactions), but affords no clue to its mechanism. If, on the other hand, we mix the components at as low a temperature as possible and then, by *freezing* the mixture, isolate addition products, we have obtained definite knowledge of an intermediate stage of the reaction. This will be exemplified in a forthcoming paper on sulfonation.

Summary.

The freezing-point curves of a series of weak organic acids with the chloro-substituted acetic acids have been investigated. The tendency towards formation of addition compounds is found to be dependent upon the difference in acidic strengths of the two components. Acids widely divergent in strength give addition compounds which may readily be isolated.

The reaction is regarded as an oxonium salt formation, and may be expressed as follows:



The quantitative results obtained are in complete agreement with this view.

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[1] Hoogewerff and van Dorp, *Rec. trav. chim. Pays-Bas*, **21**, 353 (1902); Pfeiffer, *Ber.*, **47**, 1593 (1914).

[2] Compare Guye, *J. chim. physique*, **8**, 119 (1910). The view has also been advanced by Michael that an addition process represents an intermediate stage in substitution reactions (This Journal, **32**, 1001 (1910)).