water were added. From a buret, 10% hydrochloric acid was added in 4 cc. portions with constant shaking, the temperature being maintained at 20–25°. When all oily drops had disappeared, further 20 cc. of dilute acid was added and the mixture was left over night in a cool place. The solution was then decanted and the zinc was precipitated as carbonate with soda. The filtrate from the zinc carbonate was evaporated on the water bath after acidulating with dilute hydrochloric acid. The residue obtained was powdered on a mortar and extracted with absolute alcohol. The alcoholic extract was evaporated on the water bath and the residue was again extracted with a mixture of equal volumes of absolute alcohol and ether, and the extract evaporated. The substance thus obtained was free from ammonium and sodium chlorides. It was a white crystalline deliquescent substance. The fact that guanidine hydrochloride, like most other amine hydrochlorides, is soluble in alcohol or in a mixture of alcohol and ether, and the insolubility of sodium and ammonium chlorides, rendered its separation simple.

0.3161 g. gave 0.4690 g. AgCl; calc. for $NHC(NH_2)_2HCl$: Cl = 36.84; found: 36.69.

0.1050 g. chloroplatinate gave 0.0392 g. Pt; calc. for $[NHC(NH_2)_2HCl]_2PtCl_4$: Pt = 37.00; found: 37.38.

The residue from the first extract was dissolved in a small quantity of water and distilled with caustic soda. The distillate was found to be ammonia pure and simple.

This reduction was also carried through with tin and hydrochloric acid, with subsequent removal of the tin as sulfide. In this case the product obtained was a mixture of ammonium chloride and guanidine hydrochloride.

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[CONTRIBUTIONS OF THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 234.]

THE ADDITION COMPOUNDS OF DIMETHYLPYRONE WITH ORGANIC ACIDS.[1]

BY JAMES KENDALL.

Received April 20, 1914.

The addition products of dimethylpyrone with acids are of special interest in view of their connection with the oxonium theory of Collie and Tickle.[2] The hypothesis that oxygen may function as a quadrivalent atom was first brought into prominence by a study of these compounds, the action being regarded as proceeding according to the equation:

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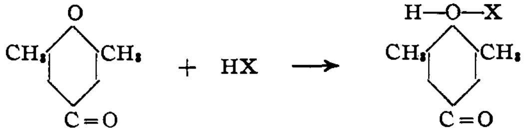
[1] Presented at the Cincinnati meeting of the American Chemical Society, April 9, 1914.

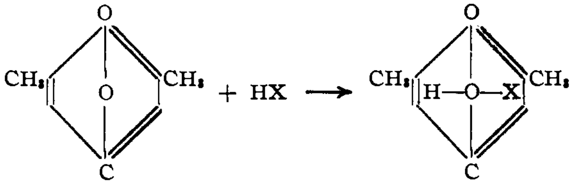
[2] *J. Chem. Soc.*, **75**, 710 (1899).



(I)

It is assumed in this equation (no reason being given) that addition takes place by means of the oxygen in the ring. Subsequent investigators have regarded the "carbonyl" oxygen in the side-chain as active, the addition products formed being considered as analogous with those given by aldehydes and ketones with acids. Since, however, ethers also react with acids to form addition compounds, it is evident that either assumption may be correct.

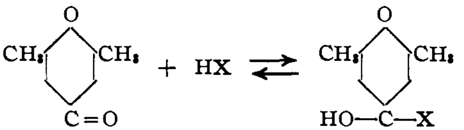
Collie's later views regarding the structural formulae of dimethylpyrone and its salts[1] lead to the following equation:



(II)

Here dimethylpyrone itself is considered as containing a quadrivalent oxygen atom, and, in the addition compound, both oxygen atoms are regarded as quadrivalent. These assumptions are supported by the work of Homfray on molecular refraction,[2] and also by the spectroscopic measurements of Baly.[3] On the other hand, Willstätter and Pummerer[4] have advanced reasons against the assumption of quadrivalent oxygen in dimethylpyrone itself.

It does not seem to be regarded as definitely established, indeed, that oxygen functions as a quadrivalent atom at all in the above reaction. Werner[5] has explained the constitution of the addition products with the help of his theory of subsidiary bonds. Gomberg and Cone[6] have denied the formation of an oxonium salt entirely, and consider the action as taking place according to the scheme:



(III)

A great deal of evidence in favor of this view is adduced.

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[1] *J. Chem. Soc.*, **85**, 973 (1904).

[2] *Ibid.*, **87**, 1443 (1905).

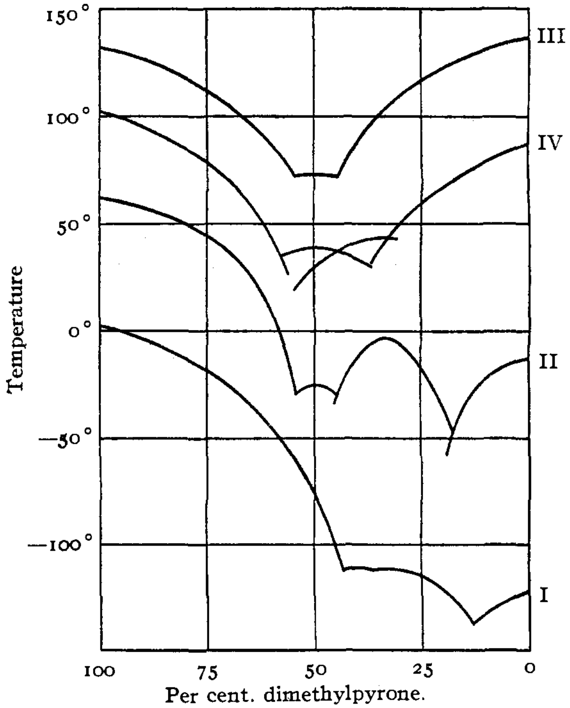
[3] *Ibid.*, **96**, 144 (1909).

[4] *Ber.*, **37**, 3740 (1904); 38, 1461 (1905).

[5] *Ann.*, **322**, 296 (1902).

[6] *Ibid.*, **376**, 217 (1910).

The most cogent arguments against the above conception of the reaction are to be obtained from the work of McIntosh,[1] who has investigated these addition compounds by physico-chemical methods. Dimethylpyrone, dissolved in liquid hydrogen bromide or hydrogen chloride, gives a conducting solution. Dimethylpyrone itself is not an electrolyte, consequently, combination with the solvent must have taken place. The compound cannot be represented according to (III) above, since an addition product of such nature (with a halogen and hydroxyl attached to the carbon) should not be ionized. Furthermore, the addition products isolated were not necessarily equimolecular; for example, with HBr the three compounds $C_7H_8O_2$, HBr; $C_7H_8O_2$, 2HBr; $C_7H_8O_2$, 4HBr were obtained. These latter compounds can be represented satisfactorily only on the assumption that both oxygen atoms in dimethylpyrone are unsaturated, and may function as quadrivalent. In the most complex salt, indeed, oxygen is regarded by McIntosh as hexavalent.



I. Formic acid. Add 130° to temperature scale.
II. Trichloracetic acid. Add 70° to temperature scale.
III. Cinnamic acid. Temperature scale correct.
IV. Mandelic acid. Add 30° to temperature scale.

Fig. 1.

The work of Maass and McIntosh on the addition compounds of ethers and alcohols with the halogen acids[2] is also of importance, since in these substances there is no carbonyl oxygen present, and the action cannot be represented according to (III) above. In these investigations the existence of compounds is shown by an examination of the freezing point curve of the two-component system, ether (or alcohol)–acid. The experimental difficulties connected with the work (due to the very low temperatures of fusion of the substances studied) have caused the

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[1] This Journal, 32, 542 (1910).

[2] *Ibid.*, 34, 1273 (1912).

important point that the above is a *general method* for the examination of organic addition reactions, to escape observation.

In the following pages this freezing point method is applied to the study of the addition compounds formed by dimethylpyrone with organic acids. The addition products of dimethylpyrone itself have been little investigated, in spite of the large amount of speculation on the nature of oxonium compounds. It was consequently hoped that the results obtained by a systematic examination would throw some light on the problems involved in the above discussion.

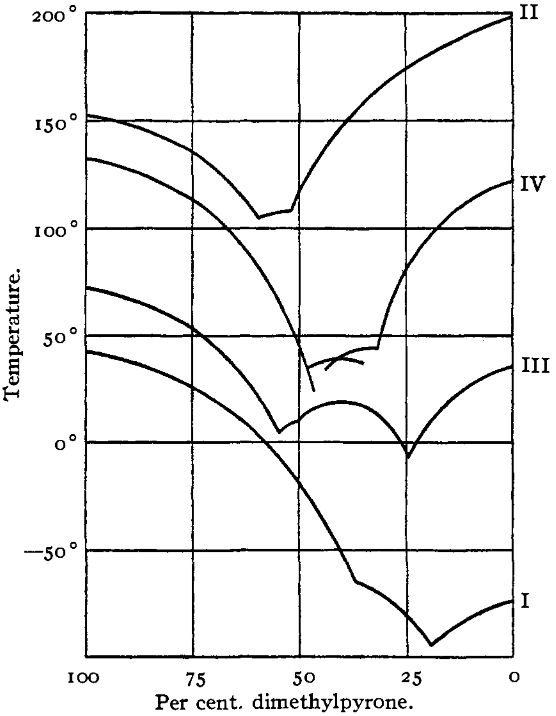
The following compounds of dimethylpyrone with organic acids have already been described:

(*a*) Collie and Tickle,[1] oxalate, tartrate, salicylate, chloroacetate, picrate. (All attempts to isolate the acetate were unsuccessful.)

(*b*) Plotnikow:[2] trichloroacetate, tribromoacetate.

The present investigation comprises more than thirty organic substances of acidic nature (monobasic, aliphatic and aromatic acids, and phenols).

The theoretical basis of the method may be briefly outlined. If, to a pure substance, A, we add a second, B, the freezing point of A is lowered; similarly, addition of A lowers the freezing point of B. Plotting temperature against molecular concentration, we obtain two curves, which intersect at the eutectic point.



I. Acetic acid. Add 90° to temperature scale.
II. p-Toluic acid. Subtract 20° from temperature scale.
III. α-Naphthol. Add 60° to temperature scale.
IV. β-Naphthol. Temperature scale correct.

Fig. 2.

If, however, a compound A_xB_y is formed, this also acts as a pure substance, and its freezing point is lowered by addition of either A or B.

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[1] *Loc. cit.*

[2] *J. Russ. phys. chem. Ges.*, 36, 1088 (1904); 40, 64 (1908).

Hence the freezing point curve exhibits, in this case, a maximum, the position of the maximum on the axis of molecular concentration indicating the composition of the compound. A series of compounds is indicated by a series of maxima on the curve.

Now the action $xA + yB \longrightarrow A_xB_y$ is a reversible reaction, and the addition compound is always more or less dissociated into its two components. The maximum of the curve, therefore, is not sharp, but more or less "rounded-off." The flatness of the curve in the neighborhood of the maximum serves, indeed, as a measure of the degree of the dissociation.[1] This is important in the consideration of the relative dissociation of the various compounds described below.

In certain cases a compound is not stable at its maximum. Its composition must then be determined either from the curve, by extrapolation, or experimentally by analysis of the solid phase separating from the solution.

Experimental.

The ordinary Beckmann freezing point apparatus was employed. The outer bath (paraffin, water, ice—salt, or ether—carbon dioxide snow, according to the temperature required) was maintained at a temperature slightly below the freezing point of the mixture contained in the inner tube, and the latter slowly cooled, with constant stirring. In favorable cases the solid phase separated out after very slight supercooling, and the temperature rose rapidly to the true freezing point.[2] More frequently, however, considerable supercooling took place before crystallization began; it was then necessary to melt up again, preserving a small portion of the solid phase in the upper part of the tube, and repeat the experiment, seeding the liquid at intervals with crystals by means of the stirrer. In cases where crystallization was so sluggish that no rise of temperature on freezing could be obtained, the first sign of crystallization *in* the liquid under the above conditions was taken as indicating the freezing point. The temperature thus obtained could be confirmed by raising the temperature of the outer bath very slowly, and observing the disappearance of the solid phase.

The thermometers employed in the investigation were:

(*a*) a mercury thermometer, —10° to 110°, graduated in 1/10°.

(*b*) a mercury thermometer, 90° to 200°, graduated in 1/5°.

(*c*) an alcohol thermometer, 50° to —50°, which could be read to 1/5°.

The thermometers were standardized at the freezing point and boiling point of water by the usual methods, and at other temperatures by com-

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[1] Kremann, *Monats.*, **25**, 1222 (1904).

[2] This method is obviously inapplicable on steep portions of the curve, where the freezing point of the mixture changes rapidly with change of composition. Here also it was necessary to employ the more tedious method of observing appearance or disappearance of solid phase.

parison with a standard thermometer. A temperature-correction curve for exposed stem was also obtained, and the necessary correction applied to every reading taken.[1] The constancy of the thermometers during the course of the investigation was examined by careful repetition of the above tests at intervals. The temperatures given in the tables below may be taken as having the following degree of accuracy:

(*a*) between 200° and 100°: 0.2–0.5°.
(*b*) between 100° and 0°: 0.1–0.2°.
(*c*) between 0° and —50°: 0.2–0.5°.

The difficulty of measurement varied very considerably with the system under examination. In some systems, especially at low temperatures, a glassy mass was obtained in which it was extremely difficult to observe appearance or disappearance of crystals.

The composition of the mixtures examined is expressed throughout, in the tables below, in molecular percentages of the components. A known weight of one component was taken, and successive quantities of the second introduced into the apparatus through the side tube in the form of compressed tablets. Liquids were added by means of the Lunge pipet. Deliquescent substances were introduced from a weighing bottle after careful drying in a desiccator, and contact with the outer air was made as short as possible.

Dimethylpyrone melts at 132.1°, but begins to sublime below 80°, and above 100° the amount of sublimation in a short time is appreciable.[2] Hence the freezing points of mixtures containing, in general, more than 70% dimethylpyrone could not be determined by the ordinary Beckmann method. The following method was adopted, and, by it, results of approximate but sufficient accuracy were obtained. A weighed amount of dimethylpyrone (about 0.1 g.) and a smaller amount (unweighed) of acid were introduced into a narrow glass tube, the tube sealed, and attached to the thermometer. Thermometer and tube were now immersed together in sulfuric acid, contained in the inner freezing point tube, and the outer bath (paraffin) heated until the contents of the tube melted. It was usually necessary to repeat fusion several times before a homogeneous mixture was obtained. The freezing point could be determined, within 0.5° to 1.0°, by observing disappearance of crystals with a slowly rising temperature. Finally, the composition of the mixture was determined by cooling the tube, dissolving the contents in water, and titrating the acid against a standardized solution of barium hydroxide.[3]

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[1] This correction varied from 0.1° at 50° to 1.6° at 180°.

[2] This does not apply to mixtures containing only a small percentage of dimethylpyrone. Such mixtures could be investigated up to 150° without appreciable sublimation.

[3] Where the acid was insoluble in water, or could not be titrated accurately against barium hydroxide, larger amounts were taken, and the acid used directly weighed.

The above procedure was necessary, in a few systems, throughout a more extended range of concentration, owing to the volatility of the acid employed (*e. g.*, formic acid, acetic acid) at high temperatures.

The purity of the substances used was tested by their point of fusion. For dimethylpyrone, Poma[1] has obtained the m. p. 132°, the value obtained with the Kahlbaum specimens employed[2] was 132.1°. Most of the acids were also pure Kahlbaum samples, and gave satisfactory points of fusion without preliminary purification. Only in a few cases was it necessary to obtain a purer product by crystallization from a suitable solvent (*e. g.*, trichlorobutyric acid from ligroin) or by freezing partially an impure liquid (*e. g.*, formic acid) and rejecting the liquid portion.

The following substances were investigated:

Aliphatic acids.

1. Formic
2. Acetic
3. Chloroacetic
4. Dichloroacetic
5. Trichloroacetic
6. Trichlorobutyric
7. Trichlorolactic
8. β-Iodopropionic
9. Crotonic
10. Chlorocrotonic

Aromatic acids.

11. Benzoic
12. *o*-Toluic
13. *m*-Toluic
14. *p*-Toluic
15. α-Toluic
16. Salicylic
17. *o*-Nitrobenzoic
18. Cinnamic
19. Hydrocinnamic
20. Mandelic

Phenols, etc.

21. Phenol
22. *o*-Cresol
23. *m*-Cresol
24. *p*-Cresol
25. *o*-Nitrophenol
26. *m*-Nitrophenol
27. *p*-Nitrophenol
28. (2,4)-Dinitrophenol
29. Picric acid
30. Trinitrotoluene
31. α-Naphthol
32. β-Naphthol

Dibasic acids and phenols are not considered in the present paper. The results obtained are given in tabular and graphical form below. The freezing point temperature is indicated by T.

1. Formic Acid.—A Kahlbaum sample froze at 7.3°. By means of repeated partial solidification, with rejection of the liquid remainder, the pure acid was obtained, melting at 8.5°.[3] With dimethylpyrone two compounds were obtained: $2C_7H_8O_2.3H.COOH$ and $C_7H_8O_2.2H.COOH$, melting at 19.6° and 19.0°, respectively; both were confirmed by analyses of the solid phases separating from the solutions. From the freezing point curve (page 1224, Fig. 1) it is evident that both compounds are considerably dissociated in the liquid state, the maxima on the curve being very flat. The following results are collected from several series of experiments:

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$...	100	85.6	76.0	65.9	60.1	54.6	50.8	47.8	45.9	44.1	43.5	43.3
T	132.1	122.5	112.5	98.0	84.5	70.9	58.1	45.0	35.1	24.9	20.4	19.0

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[1] *Gazz. chim. ital.*, 41, II, 518 (1911).

[2] For one sample the author desires to express his thanks to Professor Gomberg.

[3] Compare Ewins, *J. Chem. Soc.*, **105**, 350 (1914).

(*b*) Solid phase, $2C_7H_8O_2.3H.COOH$.

% $C_7H_8O_2$...	42.6	41.9	41.7	40.7	40.5	40.0	39.6	39.0	38.5	37.3	36.5	..
T...........	18.9	19.1	19.3	19.6	19.5	19.6	19.5	19.6	19.4	19.2	18.8	..

(*c*) Solid phase, $C_7H_8O_2.2H.COOH$.

% $C_7H_8O_2$...	36.1	34.9	34.6	33.3	33.0	31.5	30.9	29.5	28.2	26.0	25.0	..
T...........	18.7	18.9	18.9	19.0	19.0	18.9	18.7	18.3	17.6	16.3	15.5	..
% $C_7H_8O_2$...	23.9	21.5	18.9	15.3	13.6	..	..	..	..	..	..	..
T...........	14.3	11.1	7.0	—0.3	—4.3	..	..	..	..	..	..	..

(*d*) Solid phase, $H.COOH$.

% $C_7H_8O_2$...	12.0	8.3	5.7	0	..	..	..	..	..	..	..	..
T...........	—5.5	0.0	3.1	8.5	..	..	..	..	..	..	..	..

2. *Acetic Acid.*—From Kahlbaum's glacial acetic acid a pure product, freezing at 16.4°, was obtained by the method of partial solidification described above. With dimethylpyrone the compound $C_7H_8O_2.CH_3.COOH$ was obtained; m. p., 30° (by extrapolation). The compound is not stable at its maximum. This explains the failure of Collie and Tickle to isolate dimethylpyrone acetate, since the salt can be crystallized only from solutions containing excess of acetic acid. The composition was determined by analysis of the solid phase. The freezing point diagram is given on page 1225, Fig. 2.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$..........	100	87.1	75.0	64.8	57.2	50.9	46.6	43.2	39.6	37.5
T..................	132.1	125.5	115.0	102.5	88.6	73.3	61.1	50.3	37.3	28.3

(*b*) Solid phase, $C_7H_8O_2.CH_3.COOH$.

% $C_7H_8O_2$..........	34.9	33.4	28.5	23.9	20.4	..	..	..	..	..
T..................	23.8	22.4	15.6	7.5	—0.4	..	..	..	..	..

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

% $C_7H_8O_2$..........	17.7	15.3	9.0	0	..	..	..	..	..	..
T..................	—2.0	2.1	9.6	16.4	..	..	..	..	..	..

3. *Chloroacetic Acid.*—This acid has been shown to exist in three[1] (perhaps four)[2] crystalline modifications, melting at 61.3°, 56.2°, 50.2° (and 43.75°), respectively. The first three of these points were experimentally confirmed with the acid employed; all other values tabulated below are on the freezing point curve of the stable modification. An equimolecular compound was obtained, melting point 39.9°, just stable at its maximum, and comparatively little dissociated.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$..........	100	90.5	79.9	67.2	62.8	58.4	55.2	51.8	50.8
T..................	132.1	126.0	116.5	97.2	87.9	75.0	63.4	46.8	41.0

(*b*) Solid phase, $C_7H_8O_2.CH_2Cl.COOH$.

% $C_7H_8O_2$..........	48.8	47.4	45.0	41.4	38.7	33.8	30.0	..	..
T..................	39.7	39.1	37.7	34.1	29.7	19.1	5.1	..	..

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[1] Muller, *Z. physik. Chem.*, **86**, 196 (1914).

[2] Pickering, *J. Chem. Soc.*, **67**, 664 (1895).

(c) Solid phase, $CH_2Cl.COOH$.

% $C_7H_8O_2$	27.4	23.0	17.5	9.5	0	0	0	..	..
T	14.4	27.5	41.6	53.9	61.3	56.2	50.2	..	..

4. Dichloroacetic Acid.—The point of fusion of this acid is still given in all books of reference as —4°, although the value +10.8° was found by Pickering.[1] The Kahlbaum sample employed gave considerable difficulty owing to persistent supercooling, but finally two freezing points were obtained:

(*a*) +9.7° (by rapid cooling with ether—carbon dioxide). Attempts at further purification of the acid did not raise this point of fusion at all.

(*b*) —4.1° (by supercooling to —10° and long stirring). Hence it appears that the acid exists in two crystalline modifications. With dimethylpyrone the compound $C_7H_8O_2.CHCl_2.COOH$ was obtained, m. p., 22.9°, just stable at its maximum. It is possible that a second compound exists but was not isolated (the curve could not be completed between 31.4–20.0% $C_7H_8O_2$, owing to the mixture supercooling to a stiff glass without crystallization).

(a) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.9	75.5	69.0	63.6	59.8	56.4	54.1	51.5
T	132.1	124.0	111.0	99.1	85.3	72.5	56.6	43.2	26.0

(b) Solid phase, $C_7H_8O_2.CHCl_2.COOH$.

% $C_7H_8O_2$	50.1	47.2	43.3	40.2	35.1	31.4	..	..	..
T	22.9	21.7	17.1	11.1	—4.1	—21.2	..	..	..

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

% $C_7H_8O_2$	20.0	14.1	8.1	0	0	..	..	..	..
T	—23.8	—9.0	0.8	9.7	—4.1	..	..	..	..

5. Trichloroacetic Acid.—The freezing point diagram is given on page 1224 (Fig. 1). Two compounds are obtained, $C_7H_8O_2.CCl_3.COOH$ (m. p. 44.8°) and $C_7H_8O_2.2CCl_3.COOH$ (m. p. 66.8°), both evidently quite stable and very little dissociated. Mixtures containing more than 60% $C_7H_8O_2$ decompose very rapidly at their melting points, with evolution of carbon dioxide, hence this part of the curve must be regarded as only approximate.

(a) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.0	71.4	66.1	61.1	57.6	55.5	..	..	..	..
T	132.1	124.5	110.0	99.2	83.8	67.1	52.9	..	..	..	..

(b) Solid phase, $C_7H_8O_2.CCl_3.COOH$.

% $C_7H_8O_2$	52.7	49.9	47.6	45.4	..	..	..	..	..	..	..
T	43.0	44.8	44.0	41.4	..	..	..	..	..	..	..

(c) Solid phase, $C_7H_8O_2.2CCl_3.COOH$.

% $C_7H_8O_2$	45.4	43.2	41.0	36.9	35.5	33.8	32.0	29.5	27.1	23.6	19.7
T	36.4	46.9	54.6	63.8	65.6	66.7	66.1	63.0	58.1	49.3	33.6

(d) Solid phase, $CCl_3.COOH$.

% $C_7H_8O_2$	19.0	16.5	12.9	7.5	0	..	..	..	..	..	..
T	12.5	28.1	41.0	51.5	57.2	..	..	..	..	..	..

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[1] *Loc. cit.*

6. *Trichlorobutyric Acid.*—The curve obtained is very similar to that given by trichloroacetic acid above. Two compounds, $C_7H_8O_2.CH_3.$-$CHCl.CCl_2.COOH$ and $C_7H_8O_2.2CH_3.CHCl.CCl_2.COOH$ were obtained, melting at 56.2° and 33.8°, respectively. Mixtures containing excess of $C_7H_8O_2$ decompose slowly at their temperature of fusion, with evolution of carbon dioxide. The pure acid was obtained from a Kahlbaum sample by recrystallizations from ligroin.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.8	81.6	73.2	67.1	64.8	61.5	58.2
T	132.1	127.0	121.0	110.2	98.0	91.8	82.1	66.5

(*b*) Solid phase, $C_7H_8O_2.C_3H_4Cl_3.COOH$.

% $C_7H_8O_2$	54.4	50.4	46.1	41.2	38.8	36.8	36.6	..
T	53.4	56.1	53.8	47.8	42.5	35.2	35.1	..

(*c*) Solid phase, $C_7H_8O_2.2C_3H_4.Cl_3.COOH$.

% $C_7H_8O_2$	34.3	32.7	30.5	27.6	23.4	..	..	..
T	33.5	33.7	33.0	30.2	25.0	..	..	..

(*d*) Solid phase, $C_3H_4Cl_3.COOH$.

% $C_7H_8O_2$	28.1	24.9	20.4	17.3	13.1	7.5	0	..
T	—7.2	9.7	27.1	37.1	45.9	53.0	57.9	..

7. *Trichlorolactic Acid.*—An equimolecular compound $C_7H_8O_2.CCl_3.$-$CHOH.COOH$ (m. p. 54.5°) was obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.0	77.7	69.2	65.0	62.2	...	...
T	132.1	126.5	113.0	92.9	77.1	65.1	...	...

(*b*) Solid phase, $C_7H_8O_2.CCl_3.CHOH.COOH$.

% $C_7H_8O_2$	58.5	55.3	50.5	44.9	41.8	39.3	36.8	33.9
T	49.5	52.7	54.4	52.6	49.8	46.9	43.6	38.5

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

% $C_7H_8O_2$	33.9	30.0	26.8	22.0	17.0	10.1	0	...
T	21.2	43.2	59.3	83.0	95.4	106.6	113.8	...

8. *β-Iodopropionic Acid.*—Here no compound was isolated, but, from the form of the curves, it is evident that combination in the mixture has occurred. (The freezing point of each component is abnormally lowered by addition of the other; contrast with *o*-nitrophenol, page 1237.) It is possible that the melting point of the compound is so low that its curve never enters the stable region (compare *o*-toluic acid, page 1232; it is more likely, however, that supercooling persisted, preventing the isolation of the compound as the solid phase.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.0	75.7	65.0	57.2	50.3	44.4	..
T	132.1	123.5	108.0	87.4	67.2	44.0	18.4	..

(*b*) Solid phase, $CH_2I.CH_2.COOH$.

% $C_7H_8O_2$	41.2	37.8	31.6	27.3	23.8	20.5	11.7	0
T	8.9	18.8	35.4	45.1	52.2	58.4	70.9	81.2

9. Crotonic Acid.—An equimolecular compound, $C_7H_8O_2.CH_3.CH$:- CH.COOH is obtained; m. p. 52.2° (by extrapolation). The compound is unstable at its maximum, and crystallizes only from solutions containing excess of acid.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	87.6	76.1	62.8	54.6	49.9	45.4
T	132.1	125.5	116.5	100.7	86.0	75.2	62.3

(*b*) Solid phase, $C_7H_8O_2.C_3H_5.COOH$.

% $C_7H_8O_2$	41.0	36.8	32.8	28.7	..	..	..
T	50.0	47.5	44.1	39.2	..	..	..

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

% $C_7H_8O_2$	21.3	15.8	9.0	0	..	..	..
T	49.4	56.7	63.6	71.0	..	..	..

10. α-Chlorocrotonic Acid.—The compound $C_7H_8O_2.CH_3.CH$: CCl.COOH was obtained; m. p. 45.8°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.5	78.6	68.2	62.8	59.0	54.1	51.2	..	..
T	132.1	125.5	115.0	100.1	89.6	78.5	60.8	46.5	..	..

(*b*) Solid phase, $C_7H_8O_2.C_3H_4Cl.COOH$.

% $C_7H_8O_2$	49.5	46.7	43.3	40.7	38.0	37.6	..	..	..	..
T	45.7	45.1	43.9	41.7	38.5	38.0	..	..	..	..

(*c*) Solid phase, $C_3H_4Cl.COOH$.

% $C_7H_8O_2$	38.0	35.6	35.3	34.5	31.8	28.3	25.9	19.0	10.4	0
T	39.0	46.3	47.4	49.9	57.3	65.4	71.1	82.8	92.9	99.0

11. Benzoic Acid.—The compound $C_7H_8O_2.C_6H_5.COOH$ was obtained, melting at 50.5°, and only just stable at its maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.5	81.1	74.2	68.5	63.5	58.9	55.9	53.0	50.5	50.0
T	132.1	127.0	120.0	111.5	102.4	93.1	82.6	74.2	63.8	53.5	50.5

(*b*) Solid phase, $C_7H_8O_2.C_6H_5.COOH$.

% $C_7H_8O_2$	50.0	49.4	47.4	45.9	43.8	...	...	...	..	..	..
T	50.5	50.5	50.2	49.6	48.5	...	...	...	..	..	..

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

% $C_7H_8O_2$	41.3	37.9	34.7	30.9	25.3	18.1	9.5	0	..	..	..
T	54.8	66.8	76.7	85.6	95.2	105.2	113.6	120.8	..	..	..

12. o-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ was obtained, m. p. 48.0° (by extrapolation). The compound is unstable at its maximum; its total range of stability, from the freezing point diagram, extends only through 2% of the concentration range.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.1	80.5	70.2	64.9	60.5	55.7	51.1	48.3	45.1	44.9
T	132.1	126.0	117.5	104.0	94.9	86.1	74.6	62.0	53.4	43.6	43.0

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$.......	45.2	44.3	43.8	...	..	..	..	..	..	...	..
T..............	47.2	46.6	46.2	...	..	..	..	..	..	...	..

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

% $C_7H_8O_2$.......	44.9	43.8	42.2	40.1	35.4	29.6	20.7	10.5	0	...	..
T..............	43.0	46.2	50.4	55.7	66.0	77.2	89.3	97.8	103.4	...	..

13. m-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ was obtained, melting at 64.1°. In common with the other compounds derived from the similar acids in 11, 12 and 14, this compound is considerably dissociated in the liquid state, as is shown by the flatness of the maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$.......	100	90.0	79.0	68.6	64.4	58.6	54.0
T..............	132.1	126.5	116.0	102.0	94.4	81.0	69.1

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$.......	51.9	49.1	45.3	42.5	40.1	...	..
T..............	63.8	64.0	62.9	61.7	60.5	...	..

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

% $C_7H_8O_2$.......	37.5	33.2	26.3	18.6	9.9	0	..
T..............	59.8	70.0	84.8	95.6	103.0	107.6	..

14. p-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ (m. p. 88.0°, by extrapolation) was obtained. This compound is unstable at its maximum, and crystallizes only from solutions containing excess of dimethylpyrone. In this respect it is unique among the unstable compounds here obtained, since all others are crystallized from solutions with excess of acid. The difference is due merely to the very high point of fusion of the *p*-toluic acid. The freezing point curve of the system is given on page 1225, Fig. 2.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$......	100	87.3	79.2	72.6	67.4	63.0	60.1
T.............	132.1	126.5	120.0	112.0	103.1	93.4	86.3

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$......	59.5	57.2	55.0	53.2	...	...	...
T.............	85.0	86.2	87.1	87.7	...	...	...

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

% $C_7H_8O_2$......	50.6	47.3	41.4	32.1	21.4	10.3	0
T.............	93.2	106.9	124.4	143.2	158.6	170.0	178.5

15. Phenylacetic Acid (α-toluic acid).—The compound $C_7H_8O_2.C_7H_7.COOH$ was obtained; m. p. 24.6° (by extrapolation). The compound is unstable at its maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$.......	100	88.0	76.3	70.1	64.4	60.0	54.1	48.9	47.0	43.4	40.2
T..............	132.1	125.0	113.0	105.5	94.9	85.1	69.0	51.6	44.2	25.4	5.5

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$	41.1	40.2	38.5	38.0	..	..	..	..	..	..	..
T	21.7	21.0	19.2	18.7	..	..	..	..	..	..	..

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

% $C_7H_8O_2$	36.0	34.3	30.1	23.6	16.4	8.0	0	..	..	..	..
T	19.2	25.9	37.8	51.6	62.4	70.8	76.7	..	..	..	..

16. Salicylic Acid.—The compound $C_7H_8O_2.C_6H_4.OH.COOH$ was obtained, m. p. 71.9°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.1	79.3	67.8	63.4	60.4	57.3
T	132.1	128.0	119.5	100.5	89.2	80.1	68.9

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.OH.COOH$.

% $C_7H_8O_2$	56.0	53.5	51.1	49.9	47.5	44.0	...
T	69.1	70.7	71.6	71.9	71.1	68.9	...

(*c*) Solid phase, $C_6H_4.OH.COOH$.

% $C_7H_8O_2$	43.2	39.3	32.7	27.7	17.4	10.1	0
T	70.3	92.1	115.8	127.6	144.2	152.2	158.9

17. o-Nitrobenzoic Acid.—The compound $C_7H_8O_2.C_6H_4.NO_2.COOH$, melting at 72.3°, was obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	86.5	75.4	68.6	64.3	60.1
T	132.1	123.0	111.0	98.9	90.1	76.3

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.NO_2.COOH$.

% $C_7H_8O_2$	57.0	52.1	49.9	46.9	43.9	40.8
T	68.9	71.6	72.3	71.6	69.6	66.1

(*c*) Solid phase, $C_6H_4.NO_2.COOH$.

% $C_7H_8O_2$	37.7	34.2	28.6	21.0	11.5	0
T	76.1	90.5	108.4	124.9	137.4	147.0

18. Cinnamic Acid.—The compound $C_7H_8O_2.C_6H_5.CH : CH.COOH$ (m. p. 73.2°) was obtained. The system is represented graphically on page 1224, Fig. 1. It is evident that the compound formed is considerably dissociated in the liquid state.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.2	81.0	71.9	64.3	60.6	56.9	54.3
T	132.1	126.5	119.5	107.8	95.7	88.4	79.9	72.7

(*b*) Solid phase, $C_7H_8O_2.C_8H_7.COOH$.

% $C_7H_8O_2$	52.0	50.0	48.2	44.6	...	...	...	...
T	73.1	73.2	73.1	72.4	...	...	...	...

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

% $C_7H_8O_2$	43.5	40.3	36.3	30.5	24.8	15.9	9.1	0
T	75.0	87.0	97.4	109.0	116.4	126.3	131.8	136.8

19. Hydrocinnamic Acid.—Here no compound was isolated. The freezing point diagram of the system, however, indicates the presence of a compound in the solution (compare β-iodopropionic acid, page 1231).

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.9	80.2	72.3	69.4	66.0	63.0	59.5	56.7	53.1	50.2
T	132.1	126.5	119.0	110.0	105.4	99.5	93.3	86.7	80.1	69.7	60.6
% $C_7H_8O_2$	47.0	43.3	39.9	36.6	...	..	..	..	..	..	..
T	49.7	35.3	22.0	4.8	...	..	..	..	..	..	..

(*b*) Solid phase, $C_8H_9.COOH$.

% $C_7H_8O_2$	33.7	26.7	21.1	15.3	8.6	5.0	0	..	..	..	..
T	5.9	21.1	29.4	35.8	41.0	43.2	45.2	..	..	..	..

20. Mandelic Acid.—Two compounds were obtained: $C_7H_8O_2.C_6H_5.CHOH.COOH$ (m. p. 69.3°) and $C_7H_8O_2.2C_6H_5.CHOH.COOH$ (m. p. 74.0°). The solutions of this system exhibit supercooling to a marked degree, consequently it was found possible to follow all the curves into their unstable regions, and to obtain several freezing points for the same mixture, according to the solid phase separating out. Results are shown in diagram form on page 1224, Fig. 1.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.5	81.0	76.0	72.4	67.5	62.4	58.4	55.9	..	..	..
T	132.1	123.5	116.0	109.7	104.7	94.8	82.0	68.1	66.4	..	..	..

(*b*) Solid phase, $C_7H_8O_2.C_6H_5.CHOH.COOH$.

% $C_7H_8O_2$	56.1	54.6	52.1	50.0	47.3	44.5	42.8	39.3	36.6	..	..	..
T	66.5	67.5	68.9	69.3	68.8	67.2	66.1	62.9	60.0	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2C_6H_5.CHOH.COOH$.

% $C_7H_8O_2$	54.6	50.0	44.5	43.5	41.3	39.3	36.6	34.3	33.3	32.8	32.5	30.5
T	49.0	59.3	67.2	67.9	70.0	71.7	72.7	73.8	74.0	73.7	73.6	73.0

(*d*) Solid phase, $C_6H_5.CHOH.COOH$.

% $C_7H_8O_2$	36.6	32.5	30.5	28.4	25.3	18.8	10.6	0	..	..	..	..
T	61.7	73.6	78.2	82.8	88.6	98.5	108.0	117.0	..	..	..	..

21. Phenol.—No addition compounds of dimethylpyrone with phenols have been previously described. On examination, however, it was found that such compounds existed, and were little dissociated in the liquid state, the maxima obtained being usually quite sharp. With phenol itself the compound $C_7H_8O_2.2C_6H_5.OH$ was obtained, with m. p. 36.8°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.1	77.5	68.4	60.8	53.7	50.9	48.4	45.4
T	132.1	126.0	116.0	103.5	88.9	69.1	59.3	46.6	32.1

(*b*) Solid phase, $C_7H_8O_2.2C_6H_5OH$.

% $C_7H_8O_2$	43.1	40.4	38.5	35.4	32.6	29.3	24.8	21.2	18.5
T	28.0	32.0	34.1	36.1	36.7	35.6	29.7	22.3	15.6

(*c*) Solid phase, C_6H_5OH.

% $C_7H_8O_2$	13.8	8.4	0	...	..	..	..	..	..
T	16.6	31.3	42.4	...	..	..	..	..	..

22. o-Cresol.—Here two addition compounds were obtained: $C_7H_8O_2.C_7H_7.OH$, melting at 54.4°, and $C_7H_8O_2.2C_7H_7.OH$, melting at 50.4°, both compounds are stable at their maxima. (See diagram, page 1240, Fig. 3.)

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.5	80.0	69.5	61.4	55.2	52.4	..	..
T	132.1	126.5	119.5	105.5	91.1	74.3	64.0	..	..

(*b*) Solid phase, $C_7H_8O_2.C_7H_7OH$.

% $C_7H_8O_2$	49.2	46.6	43.1	39.6	..	..	..	..	..
T	54.3	53.5	51.5	47.2	..	..	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2C_7H_7OH$.

% $C_7H_8O_2$	39.6	36.6	33.4	29.5	24.0	20.6	17.2	15.2	13.9
T	47.2	49.4	50.4	49.2	43.2	37.0	27.5	21.8	16.6

(*d*) Solid phase, $C_7H_7.OH$.

% $C_7H_8O_2$	13.9	11.0	5.5	0	..	..	..	..	..
T	16.6	21.0	26.9	30.3	..	..	..	..	..

23. m-Cresol.—The compound $C_7H_8O_2.2C_7H_7.OH$ was obtained; m. p. 25.4°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.0	74.4	64.8	58.7	53.6	50.0	45.9	43.9	41.0
T	132.1	123.0	112.0	97.2	84.2	69.8	55.6	35.3	24.7	4.3

(*b*) Solid phase, $C_7H_8O_2.2C_7H_7OH$.

% $C_7H_8O_2$	41.6	38.2	34.7	32.0	28.4	23.0	19.0	14.3	..	..
T	21.3	23.9	25.0	25.3	23.7	17.4	9.5	—5.0	..	..

(*c*) Solid phase, C_7H_7OH.

% $C_7H_8O_2$	9.5	4.8	0	..	..	..	..	...	..	..
T	—1.2	6.1	10.9	..	..	..	..	...	..	..

24. p-Cresol.—Two compounds were obtained: $C_7H_8O_2.C_7H_7.OH$ (m. p. 29.5°, by extrapolation) and $C_7H_8O_2.2C_7H_7OH$ (m. p. 20.3°). The former compound is unstable at its maximum point. The form of the curve indicates strongly the presence of a third compound of the formula $C_7H_8O_2.4C_7H_7.OH$, but it was not found possible to isolate a compound of the composition, since the mixture of this composition supercools to a hard, glassy mass, and no freezing point can be obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.5	77.2	67.6	61.4	54.9	51.0	48.2	44.9
T	132.1	125.5	115.0	102.0	90.2	73.6	59.6	46.6	31.8

(*b*) Solid phase, $C_7H_8O_2.C_7H_7OH$.

% $C_7H_8O_2$	41.5	38.7	37.0	...	..	..	..	..	..
T	25.7	22.4	19.6	...	..	..	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2C_7H_7OH$.

% $C_7H_8O_2$	35.8	33.2	31.6	29.2	25.9	23.3	..	..	..
T	19.6	20.3	19.7	17.5	11.2	1.2	..	..	..

(*d*) Solid phase, C_7H_7OH.

% $C_7H_8O_2$	17.1	13.3	7.1	0	..	..	..	..	..
T	—0.5	14.6	26.6	34.1	..	..	..	..	..

25. *o-Nitrophenol.*—With this system the peculiar result was obtained that, not only could no compound be isolated, but the form of the curve shows conclusively that none exists in solution. The results are shown in graphic form, together with those of the other mononitrophenols, which exhibit quite different behavior, on page 1240, Fig. 3. It is evident that *o*-nitrophenol and dimethylpyrone have no tendency to form addition products; this is perhaps due to the influence of the nitro group in the *o*-position.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.4	79.7	68.0	61.5	56.1	51.3	46.8	42.2	37.3	32.3	27.5
T	132.1	126.5	119.0	110.4	104.9	98.6	92.9	85.9	77.9	68.3	57.1	45.8

(*b*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	22.7	18.7	13.2	7.6	0	..	..	..	..	..	..	..
T	32.7	35.1	38.2	41.0	44.7	..	..	..	..	..	..	..

26. *m-Nitrophenol.*—The compound $C_7H_8O_2.C_6H_4.NO_2.OH$, melting at 68.8°, was obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.6	80.7	70.3	65.3	61.0	57.4	..	..
T	132.1	127.0	118.5	104.2	93.8	81.5	67.0	..	..

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	53.8	50.8	48.3	45.4	42.1	39.2	36.2	33.0	31.5
T	68.1	68.7	68.4	66.9	63.0	58.8	52.9	45.9	42.6

(*c*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	29.0	25.1	20.4	14.5	8.4	0	..	..	..
T	52.4	63.4	72.9	82.9	89.7	95.3	..	..	..

27. *p-Nitrophenol.*—Two compounds were obtained: $C_7H_8O_2.C_6H_4.NO_2.OH$, melting at 72.3°, and $C_7H_8O_2.2C_6H_4.NO_2.OH$, melting at 58.2°. Both compounds are stable at their maxima.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.1	77.0	68.8	64.6	60.8	57.8
T	132.1	125.5	114.5	101.3	91.4	80.2	68.3

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	57.2	53.5	50.6	47.2	43.8	40.4	37.4
T	68.3	71.3	72.2	70.9	67.2	62.1	56.4

(*c*) Solid phase, $C_7H_8O_2.2C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	37.4	34.3	33.6	32.9	31.6	30.0	...
T	57.0	58.1	58.2	58.1	57.9	57.4	...

(*d*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	30.0	28.2	26.2	22.4	15.5	9.1	...
T	57.4	65.4	72.2	82.2	96.6	105.2	113.8

28. *2,4-Dinitrophenol.*—The compound $C_7H_8O_2.C_6H_3.(NO_2)_2.OH$ was obtained; m. p. 78.4°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.4	80.1	69.9	63.9	58.2	...
T	132.1	126.0	118.0	105.6	95.2	83.2	...

(*b*) Solid phase, $C_7H_8O_2.C_6H_3.(NO_2)_2.OH$.

% $C_7H_8O_2$	55.2	51.8	48.1	45.0	41.8	...	...
T	77.5	78.3	78.1	77.5	75.8	...	...

(*c*) Solid phase, $C_6H_3.(NO_2)_2.OH$.

% $C_7H_8O_2$	37.7	34.8	31.9	25.1	17.1	9.3	0
T	75.0	81.1	86.3	95.1	102.9	109.0	114.0

29. Picric Acid.—The compound $C_7H_8O_2.C_6H_2(NO_2)_3.OH$ was obtained; point of fusion, 100.8°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.0	78.7	74.4	70.6	67.5	...	...	...	..	..	..
T	132.1	124.0	111.2	101.1	90.0	83.5	...	...	...	..	..	..

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.(NO_2)_3.OH$.

% $C_7H_8O_2$	66.7	65.2	63.8	61.9	59.5	55.7	52.6	50.0	47.7	43.6	38.4	34.1
T	81.9	86.7	89.5	92.9	96.1	98.9	100.2	100.8	100.4	98.8	94.9	87.6

(*c*) Solid phase, $C_6H_2.(NO_2)_3.OH$.

% $C_7H_8O_2$	30.0	26.1	22.4	15.5	9.6	0	...	...	...	..	..	..
T	87.5	92.4	97.4	104.8	110.6	118.4	...	...	...	..	..	..

30. Trinitrotoluene.—The pseudo-acid trinitrotoluene was examined with dimethylpyrone, but no indication of compound formation could be observed. The curve resembles that of *o*-nitrophenol.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	86.3	75.3	65.0	57.2	51.1	46.1	41.0	35.4
T	132.1	124.5	115.5	105.3	97.5	90.3	84.0	77.6	70.2

(*b*) Solid phase, $C_7H_5.(NO_2)_3$.

% $C_7H_8O_2$	29.1	24.1	15.6	7.8	0	..	..	..	..
T	64.2	67.4	72.4	76.7	80.7	..	..	..	..

31. α-Naphthol.—Interesting results were obtained with the naphthols; the freezing point diagrams are given on page 1225, Fig. 2. α-Naphthol gives two compounds with dimethylpyrone: $C_7H_8O_2.C_{10}H_7.OH$ (m. p. 69.8°, by extrapolation), and $2C_7H_8O_2.3C_{10}H_7.OH$ (m. p. 79.1°). The former is unstable at its maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.0	77.7	68.8	60.5	56.9	..	..
T	132.1	126.0	116.5	103.6	85.2	73.0	..	..

(*b*) Solid phase, $C_7H_8O_2.C_{10}H_7OH$.

% $C_7H_8O_2$	54.1	53.0	51.5	...	..	..	..	..
T	65.6	67.8	69.3	...	..	..	..	..

(*c*) Solid phase, $2C_7H_8O_2.3C_{10}H_7.OH$.

% $C_7H_8O_2$	50.0	48.8	47.3	45.3	42.7	40.6	38.8	37.3
T	70.5	73.2	75.6	77.4	78.3	79.0	78.8	78.4
% $C_7H_8O_2$	35.8	34.4	32.0	29.8	27.9	25.0	..	..
T	77.6	76.8	73.8	69.7	65.9	56.6	..	..

(*d*) Solid phase, $C_{10}H_7.OH$.

% $C_7H_8O_2$	23.4	20.7	17.7	12.0	6.2	0	..	..
T	56.0	65.7	73.8	84.2	90.7	96.1	..	..

32. β-Naphthol.—Two compounds were obtained: $2C_7H_8O_2.3C_{10}H_7.OH$ (m. p. 39.5°) and $C_7H_8O_2.2C_{10}H_7OH$ (m. p. 44.6°). The former compound is unstable at its maximum point, but, owing to the readiness with which solutions of this system exhibited persistent supercooling, it was found possible to carry the curve some distance into its unstable region. (See diagram, page 1225, Fig. 2.)

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$...	100	87.6	76.3	66.6	61.6	57.2	55.4	52.1	49.3	46.5
T..........	132.1	126.0	114.5	99.5	87.1	74.5	68.2	54.9	40.7	24.3

(*b*) Solid phase, $2C_7H_8O_2.3C_{10}H_7OH$.

% $C_7H_8O_2$...	46.5	44.7	43.8	42.2	40.6	37.3	35.0	..	..	..
T..........	36.6	38.0	38.4	39.0	39.4	38.8	37.4	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2C_{10}H_7OH$.

% $C_7H_8O_2$...	43.8	40.2	38.1	35.9	33.6	33.0	...	..	..	..
T..........	34.4	40.3	42.5	43.9	44.5	44.6	...	..	..	..

(*d*) Solid phase, $C_{10}H_7OH$.

% $C_7H_8O_2$...	30.2	27.3	25.1	21.4	14.1	9.6	0	..	..	..
T..........	54.5	70.6	79.9	92.0	107.9	113.8	121.6	..	..	..

Consideration of Results.

Thirty-two organic substances of acidic nature have been examined with dimethylpyrone, and the existence of thirty-seven addition compounds has been indicated by the freezing point curve. These compounds may be divided into three classes:

(*a*) 24 of the general type $C_7H_8O_2.HX$.
(*b*) 3 of the general type $2C_7H_8O_2.3HX$.
(*c*) 10 of the general type $C_7H_8O_2.2HX$.

No instances of the formation of compounds containing excess of dimethylpyrone, or of mixed crystals, were observed.

The addition compounds exhibited, in general, beautiful crystalline structure, either in the form of needles radiating from a common center, star-clusters, or lustrous plates. Consequently, in practically all of the systems examined, it was extremely easy to identify changes in the solid phase.

The melting points of the compounds are usually much below those of their components. The few exceptions are to be found in those cases where the melting point of one component is also very low.

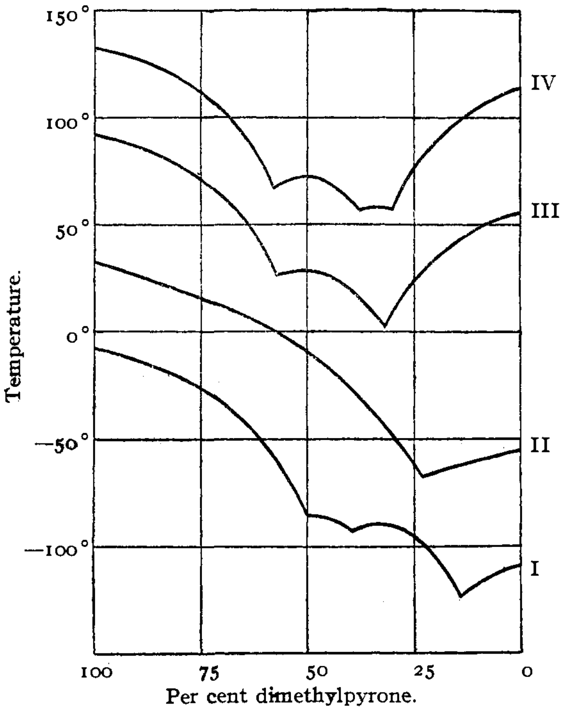
It is interesting to compare the difference in behavior of isomeric substances examined. As examples the following may be noted:

I. o-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ crystallizes only from solutions containing excess of acid. *m-Toluic acid.* The compound formed is stable at its maximum. *p-Toluic acid.* The compound crystallizes only from solutions containing an excess of dimethylpyrone.

II. o-Nitrophenol.—No compound is formed. *m-Nitrophenol.* The compound $C_7H_8O_2.C_6H_4.NO_2OH$ is formed. *p-Nitrophenol.* Two compounds: $C_7H_8O_2.C_6H_4NO_2.OH$ and $C_7H_8O_2.2C_6H_4NO_2.OH$ are formed.

III. α-Naphthol.—The compounds $C_7H_8O_2.C_{10}H_7OH$ and $2C_7H_8O_2.3C_{10}H_7OH$ are formed. *β-Naphthol.* The compounds $2C_7H_8O_2.3C_{10}H_7OH$ and $C_7H_8O_2.2C_{10}H_7OH$ are obtained.

Particular attention is due to those compounds isolated, which are unstable at their maximum. These cannot be obtained at all by the simple method of mixing the components in the required proportions. The freezing point curve gives, however, all the necessary data for the preparation of such a compound. For example, dimethylpyrone acetate, which Collie and Tickle failed to isolate, may readily be obtained as follows (see diagram, page 1225, Fig. 2): A mixture of 35% dimethylpyrone and 65% acetic acid (molecular percentages) is taken. This melts at 24°, and, on cooling, the solid phase separating out is the equimolecular compound. The best yield may be obtained by cooling to 0°, filtering off the remaining liquid, and drying the crystals with filter paper. The compound thus obtained melts at 30°, at the same time decomposing into its components and depositing dimethylpyrone.



I. *o*-Cresol. Add 140° to temperature scale.
II. *o*-Nitrophenol. Add 100° to temperature scale.
III. *m*-Nitrophenol. Add 40° to temperature scale.
IV. *p*-Nitrophenol. Temperature scale correct.

Fig. 3.

The addition compounds obtained are always more or less dissociated into their components in the liquid state. For the acids examined, the rule holds, in general, that the extent of dissociation is greater, the weaker the acid is. The degree of dissociation may be approximately determined by the sharpness of the maximum, *i. e.*, the decrease in the temperature of fusion of the compound on addition of either component. If dissociation is slight the decrease is rapid, with more highly dissociated compounds the decrease is small and may even (in extreme cases) be converted into an increase.[1]

The following table shows the decrease in the temperature of fusion of the equimolecular compounds of dimethylpyrone and acid, due to the addition of 5% of acid, for all cases where data are available from the results given above. The dissociation constants of the acids[2] are included for comparison.

Acid.	T(50% $C_7H_8O_2$)—T(45% $C_6H_8O_2$).	100 K.
Chloroacetic	2.2°	0.155
Dichloroacetic	3.2	5.14
Trichloroacetic	4.3	121.0
Trichlorobutyric	3.5	10.0
Trichlorolactic	1.8	0.465
α-Chlorocrotonic	1.3	0.072
Benzoic	1.2	0.0060
m-Toluic	1.2	0.00514
Salicylic	2.1	0.102
o-Nitrobenzoic	1.8	0.616
Cinnamic	0.6	0.00355
Mandelic	1.6	0.0417

The connection between the degree of dissociation of the compound and the strength of the acid is made quite evident from the above figures; the two extreme cases (trichloroacetic and cinnamic acids) are illustrated in the diagram on page 1224, Fig. 1. The relation is important, but can, however, only be approximate, since for the acidic strengths we should compare values, not in aqueous solution, but in dimethylpyrone.[3] The dissociation of the compounds is also compared at their various points of fusion, whereas the temperature factor is important in regard to the degree of dissociation of addition compounds.[4]

The tendency to form addition products is greatest at low temperatures; this is well illustrated in the case of hydrates. The effect of temperature is best seen, in the results of the present investigation, in the compounds formed from phenol and its derivatives. These are little dissociated into their components in spite of the weak acidic nature of the substances employed, owing, in general, to their low temperatures of fusion. Temperature seems, indeed, to be more important here than acidic strength, thus (to compare the stable 50% compounds) the compound of *o*-cresol is less

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[1] Kremann, *Monats.*, **25**, 1222 (1904).

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

[3] The researches of Walden indicate that the general order of acidic strengths in two solvents will be the same, although exceptions are to be found. That dimethylpyrone is a good ionizing medium has been shown by Poma, *Gazz. chim. ital.*, **41**, II, 518 (1911).

[4] The heat of fusion of the compound, which will vary in different cases, is also to be considered.

dissociated than that of dinitrophenol, or even than that of picric acid, both of which have considerably higher melting points.

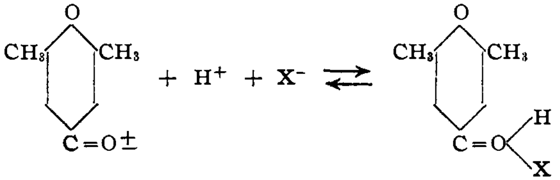
Constitution of Dimethylpyrone and its Addition Compounds.—It remains to discuss the bearing of the results obtained on the several hypotheses as to the constitution of dimethylpyrone and its addition products, considered in the introduction.

The difficulty of representing the structural formulae of compounds, more complex than equimolecular, except under the scheme (I), has already been mentioned. The thirteen compounds of the general types $2C_7H_8O_2.3HX$ and $C_7H_8O_2.2HX$, obtained in the research, cannot be accounted for by (II) or (III), but may readily be expressed structurally according to (I).

The mixture acid-dimethylpyrone was, in every system studied, colored. The color varied from pale yellow (with weak acids) to dark red (with strong acids). In this connection the view of Vorländer and Mumme,[1] that the change of color is due to a change in the degree of saturation of one or more elements composing the substances, is of importance.

A further point to be noticed is that the reaction between dimethylpyrone and acids is instantaneous. In no case could it be observed that the freezing point of a mixture changed at all with time; equimolecular mixtures gave the same point of fusion immediately after preparation as after several days. Similarly Baeyer and Villiger,[2] who first stated that time was necessary for the formation of dimethylpyrone hydrochloride, subsequently[3] withdrew this statement. Now, an organic reaction of the type (II), involving the breaking up of the simple acid molecule as well as of the carbonyl oxygen linkage, would probably be a time reaction. On the other hand, ionic reactions are *essentially* instantaneous.

We may consider the formation of the addition product $C_7H_8O_2.HX$ as proceeding as follows:



(IV)

Dimethylpyrone is here regarded as the ionizing medium,[4] and the carbonyl oxygen as primarily active. Formation of the more complex compounds involves the activity of the second oxygen atom.

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[1] *Ber.*, 36, 1470 (1903).

[2] *Ibid.*, 34, 2679 (1901).

[3] *Ibid.*, 35, 3612 (1902).

[4] The fact that dimethylpyrone is a good ionizing medium is also an indication of its unsaturated character. See Stieglitz, "Qualitative Chemical Analysis," Part I, 1912, p. 64, and Kendall, THIS JOURNAL, 36, 1069 (1914).

This view is supported by the fact that the equilibrium point of the above reversible reaction (*i. e.*, the extent of dissociation of the addition compound formed into its components) is a function of the acidic strength, as has been demonstrated above. The stronger the acid is, the more completely does the reaction from left to right proceed. In agreement with this, also, is the extent of color change on mixing the components; for example, cinnamic acid with dimethylpyrone gives the faintest tinge of yellow, while trichloroacetic acid gives a dark red solution.

The results of this investigation point, therefore, in favor of the assumption that the addition compounds of dimethylpyrone with acids are true oxonium salts, in which oxygen functions as a quadrivalent atom. The equilibrium of the reaction is best represented as in (IV) above.

In conclusion, the advantages of the method followed above, for the general study of addition reactions, may be pointed out. Its first advantage is its rapidity; after the technique has been mastered, a system presenting no special difficulties can easily be completed in two days. Secondly, it indicates *all* compounds formed between the components chosen, including such compounds as are not stable at their maxima and cannot be obtained by the ordinary methods. In few cases is a special analysis of the solid phase necessary, the composition of the compounds obtained is read directly from the freezing point curve.[1] It is possible that sometimes a compound cannot be isolated owing to supercooling; however, its existence may be recognized by the form of the curves. Finally the curves indicate also the degree of dissociation of the compounds into their simple components.

The method is being extended to other similar systems. It is hoped, also, that further evidence as to the nature of these reactions will be obtained from conductivity measurements.

Summary.

The freezing point curves of monobasic organic acids and phenols with dimethylpyrone have been examined. The existence of a large number of addition compounds has been demonstrated.

A consideration of the results obtained leads to the view that the reaction is ionic, and that the compounds formed are true oxonium salts.

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[1] Cases of "solid solutions" may be recognized by the fact that any maximum on the freezing point curve will not be (except by chance) at a point of simple molecular composition.