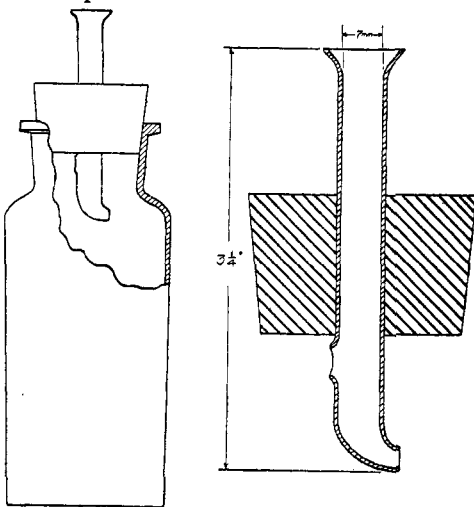


stopper between additions of iodate: on the other hand, the use of a simple open Erlenmeyer, as used in the Southwest copper district, limits more than desirable the freedom in shaking: both difficulties may be overcome by replacing the glass stopper by a two-hole rubber stopper, through which pass two glass tubes, 5-6 mm. in diameter and about 8 cm. long, one of the tubes being widened at the top to serve as an inlet for the iodate solution, the other serving as an outlet for vapor, their length preventing loss by ejection during shaking.

With a little additional trouble, a somewhat more efficient modification may be constructed: this is illustrated in the accompanying sketch. The tube is 7-8 mm. in diameter, flared above, narrowed and curved below, and provided with a blowhole just below the cork. This side hole acts not only as the pressure vent but also serves the purpose of washing the last drop of iodate down during the shaking without the use of a wash bottle.



This bottle has been in constant use by students for copper ore analyses in this laboratory for over a year and found quite satisfactory: besides its convenience, it saves the time required in removing the stopper or in shaking so very cautiously. The only objectionable feature is the action of chloroform or carbon tetrachloride on the rubber stopper if allowed to stand overnight: during titration the stopper is protected by an aqueous film and shows no deterioration even after long use.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,  
No. 265.]

## THE ADDITION COMPOUNDS OF PHENOLS WITH ORGANIC ACIDS.

BY JAMES KENDALL.

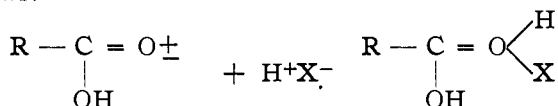
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It has been shown by the author in a recent communication<sup>1</sup> that *strong* organic acids (such as trichloroacetic acid) will combine directly with

<sup>1</sup> Kendall, *THIS JOURNAL*, 36, 1722 (1914).

*weak* organic acids (such as benzoic acid) to form equimolecular addition products. Compounds of this type are relatively unstable, in so far as they dissociate into their components to a considerable extent on fusion, but they can be readily isolated and identified by means of the freezing-point method described in a previous paper.<sup>1</sup> The stability of the addition products, as indicated by the curves obtained, increases with the difference between the acidic strengths of the two components.

The formation of compounds of this nature has been assumed to be due to the presence of the basic (or unsaturated) group  $\text{>C} = \text{O}^\pm$  in the weak acid. The oxygen atom in this group is potentially quadri-valent, and in the presence of a sufficiently strong acid the acidic properties of the weak organic acid are suppressed to such a degree that the basic nature of the group comes into prominence and an oxonium salt formation is obtained. The reaction is considered to be ionic and to take place as follows:



A great deal of evidence in favor of these views has been collected in a series of researches on organic substances of various types.<sup>2</sup>

The extension of this method of investigation to systems of the general type phenol-acid has seemed of importance to the author for several reasons. In the first place, most phenols belong to the class of weak organic acids and might therefore be expected to resemble them in exhibiting basic properties in the presence of a strong acid, with the consequent formation of oxonium salts analogous to those already described. Since, further, phenols in general are much more weakly acidic than the weak acids previously investigated (*e. g.*, benzoic acid), any addition products obtained should prove to be more stable in character, and less dissociated into their components in the liquid state.<sup>3</sup>

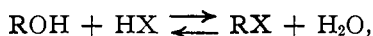
In the second place, the isolation and examination of addition compounds of the type phenol-acid are of interest because of the probability that the formation of such compounds constitutes an intermediate stage in the series of reactions involved in the direct production of phenolic esters of organic acids.<sup>4</sup> The general equation

<sup>1</sup> Kendall, *THIS JOURNAL*, **36**, 1222 (1914).

<sup>2</sup> Kendall and Carpenter, *Ibid.*, **36**, 2498 (1914); Kendall and Gibbons, *Ibid.*, **37**, 149 (1915).

<sup>3</sup> The validity of this assumption is discussed fully later (page 1320).

<sup>4</sup> Menshutkin, *Ann.*, **197**, 220 (1879). The extent of the esterification, when equilibrium is reached, is only small (as in the case of the tertiary alcohols); hence the method is not available for the *preparation* of phenolic esters unless some dehydrating agent is added.



(where R is the aryl radical) merely shows the initial and end products, and gives no indication as to the mechanism of the reaction. The present investigation is thus immediately connected with the previous work of Kendall and Carpenter,<sup>1</sup> in which it was shown that phenols form with sulfuric acid stable addition compounds which may be regarded as intermediate products in the process of sulfonation.

In the complete examination of the field covered by systems of the general type phenol-acid, another point which deserves investigation is encountered. Phenols exhibit among themselves just as considerable a variation in acidic strength as do organic acids, consequently it is possible to construct systems which may be expected to behave quite differently from those already described. A convenient method of increasing the acidity of a phenol is to introduce nitro groups into the benzene nucleus. The effect of this will be to diminish the stability of the oxonium compounds obtained with strong acids, or even to prevent the formation of addition products altogether. By continued introduction of nitro groups into the nucleus we can obtain phenols (for example, picric acid) which are, indeed, quite as strongly acidic as the strongest organic acids. Such phenols may be expected to function similarly to *strong* acids, and to give oxonium compound formation both with *weak* acids and also with *weak* phenols. We can, therefore, by suitable variation of the acidic strengths of our two components, obtain most diverse examples of the general type, and these may be predicted to exhibit very different behavior when examined by the freezing-point curve method.

In the experiments tabulated below, this method has been employed in order to study the whole field, the acidic strengths of both phenols and acids being varied as widely as possible. As a typical strong acid, trichloroacetic acid has been chosen; it is easily obtained pure, has a convenient point of fusion, and has already been extensively used in previous work on addition compounds.<sup>2</sup> As a typical strong phenol, picric acid was selected; it is the simplest of its class and the most readily obtainable. Its disadvantages are a high melting point (which is unfavorable for the isolation of addition products, since their stability decreases with rise of temperature), the formation of dark-colored solutions with weak phenols (in which it is extremely difficult to detect the appearance or disappearance of crystals), and its highly explosive nature. The friction involved in the stirring of a molten mass largely consisting of picric acid constituted a source of constant danger, nevertheless it was found possible to complete the systems required with only a few minor accidents.

<sup>1</sup> Kendall and Carpenter, *Loc. cit.*

<sup>2</sup> Hence the results obtained here are directly comparable with those of previous papers. (See page 1317.)

The weak acids and phenols included in the investigation, with their ionization constants in aqueous solution at 25°, are given below.

Acids.	K.	Phenols.	K.
Acetic <sup>1</sup>	$1.85 \times 10^{-5}$	Phenol <sup>3</sup>	$1.15 \times 10^{-10}$
<i>o</i> -Toluic <sup>2</sup>	$12.0 \times 10^{-5}$	<i>o</i> -Cresol <sup>3</sup>	$0.63 \times 10^{-10}$
<i>m</i> -Toluic <sup>2</sup>	$5.14 \times 10^{-5}$	<i>m</i> -Cresol <sup>3</sup>	$0.98 \times 10^{-10}$
$\alpha$ -Toluic <sup>2</sup>	$5.56 \times 10^{-5}$	<i>p</i> -Cresol <sup>3</sup>	$0.67 \times 10^{-10}$
Chloroacetic <sup>2</sup>	$1.55 \times 10^{-3}$	Thymol <sup>3</sup>	$0.32 \times 10^{-10}$
Trichloroacetic <sup>2</sup>	$2.57 \times 10^{-1}$	<i>o</i> -Nitrophenol <sup>4</sup>	$6.8 \times 10^{-8}$
		<i>m</i> -Nitrophenol <sup>4</sup>	$1.0 \times 10^{-8}$
		<i>p</i> -Nitrophenol <sup>4</sup>	$6.5 \times 10^{-8}$
		$\alpha$ -Naphthol <sup>6</sup>	$1.0 \times 10^{-8}$
		$\beta$ -Naphthol	not determined
		Picric acid <sup>6</sup>	$2.52 \times 10^{-1}$

The ionization constants for the two strong acids employed, which are appended for comparison, are calculated for the concentration  $v = 32$ . The values given would, of course, change considerably with dilution, but the relative strengths of the two acids remain nearly constant. In alcohol, picric is the stronger acid<sup>7</sup> of the two.

The acids and phenols employed were either Kahlbaum specimens of a satisfactory degree of purity (as evidenced by the melting point) or were specially purified by recrystallization from a suitable solvent.

The experimental method followed was exactly as described in the previous papers of this series, the freezing-point curve of the two-component system being determined and all the desired information regarding the existence and stability of the addition products obtained being derived directly therefrom. In the tables below, T denotes the temperature of *incipient* solidification<sup>8</sup> of the mixtures, the compositions of which are expressed in molecular percentages. Examples of the curves obtained are reproduced in the accompanying diagram.

For convenience, the various types of systems examined from which oxonium salt formation may be expected are given under three divisions:

I. Systems: weak phenol-strong acid (Tables 1-10).

II. Systems: weak phenol-strong phenol (Tables 11-15).

III. Systems: weak acid-strong phenol (Tables 16-19).

The fourth possible compound-forming type, systems: weak acid-strong acid, has already been fully investigated in a previous communication.<sup>9</sup>

<sup>1</sup> Kendall, *Medd. K. Vetenskapsakad. Nobelinst.*, Band. 2, No. 38 (1913).

<sup>2</sup> Ostwald, *Z. physik. Chem.*, 3, 418 (1889).

<sup>3</sup> Boyd, *J. Chem. Soc.*, 107, 1540 (1915).

<sup>4</sup> Holleman, *Rec. trav. chim. Pays-Bas*, 21, 432 (1902).

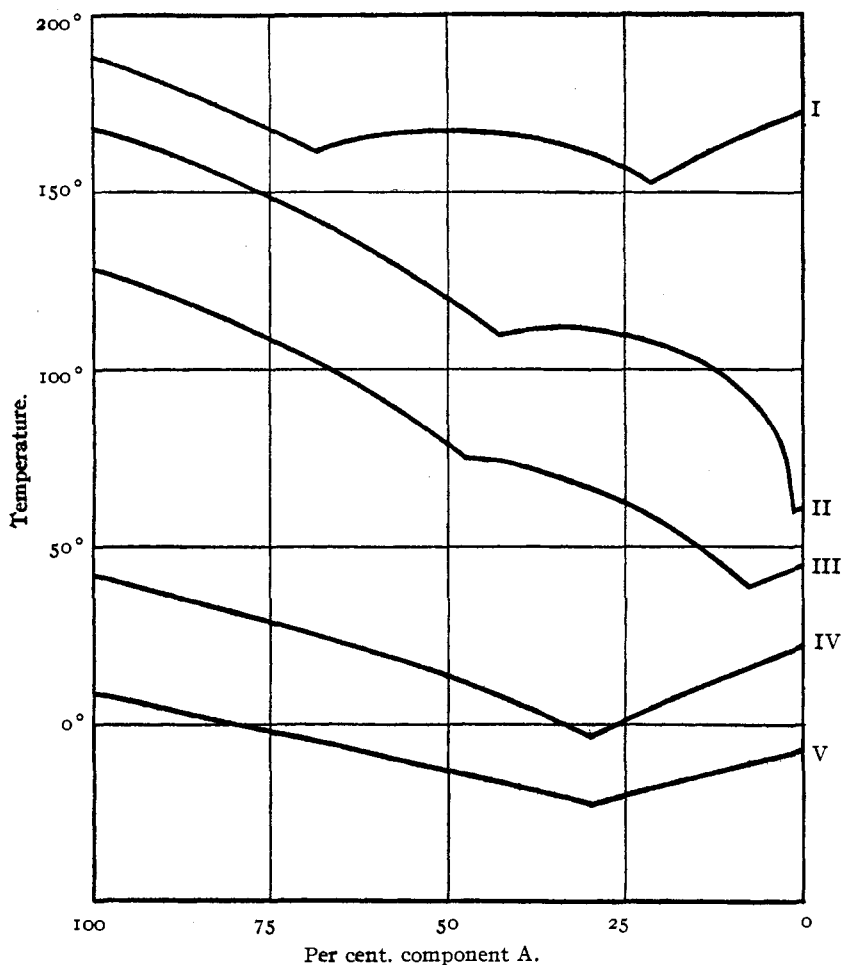
<sup>5</sup> Walden, *Ber.*, 24, 2025 (1891).

<sup>6</sup> Kendall, *Proc. Roy. Soc.*, (A) 85, 200 (1911).

<sup>7</sup> Sneath, *Z. Elektrochem.*, 18, 543 (1912).

<sup>8</sup> All temperatures are corrected for exposed stem.

<sup>9</sup> Kendall, *THIS JOURNAL*, 36, 1722 (1914).



- I. Trichloroacetic acid-phenol. Subtract  $130^{\circ}$  from temperature scale.
- II. Picric acid-*m*-cresol. Subtract  $50^{\circ}$  from temperature scale.
- III. Picric acid-*p*-cresol. Subtract  $10^{\circ}$  from temperature scale.
- IV. Chloroacetic acid-phenol. Add  $20^{\circ}$  to temperature scale.
- V. Picric acid-*o*-toluic acid. Add  $110^{\circ}$  to temperature scale.

A system containing two components of not widely different acidic strength may be predicted not to give oxonium compounds. Thus, in the investigation quoted above, all examples of the two types: weak acid—weak acid and strong acid—strong acid gave on examination uniformly negative results. In the present work, a few examples of the types: weak phenol—weak acid and weak phenol—weak phenol are appended in order to cover the field completely and to illustrate that this rule holds for phenols also.

### I. Systems: Weak Phenol-Strong Acid.

Several investigations have been made on systems of this type by previous workers, but the results have been mainly negative, few addition compounds having been obtained. Maass and McIntosh<sup>1</sup> examined a great number of phenols with hydrobromic and hydrochloric acids, but isolated no compounds except in the case of resorcinol. Gomberg and Cone,<sup>2</sup> on the other hand, obtained addition products of orcinol, phloroglucinol and hydroquinone with HBr, but found no indication of compound formation with resorcinol and other phenols. Kendall and Carpenter<sup>3</sup> isolated a number of oxonium salts of phenols with sulfuric acid.

In the following table the positive results recorded in these researches are summarized: the compositions of the compounds obtained are indicated by condensed formula (A = phenol, B = acid) to economize space.

Systems.	Compounds.	Systems.	Compounds.
Resorcinol-HBr.....	AB <sub>4</sub>	Phenol-H <sub>2</sub> SO <sub>4</sub>	A <sub>2</sub> B
Resorcinol-HCl.....	AB <sub>3</sub> or AB <sub>4</sub>	<i>p</i> -Cresol-H <sub>2</sub> SO <sub>4</sub>	A <sub>2</sub> B; AB <sub>2</sub>
Orcinol-HBr.....	A <sub>2</sub> B	<i>o</i> -Xylenol-H <sub>2</sub> SO <sub>4</sub>	A <sub>2</sub> B; AB
Phloroglucinol-HBr.....	A <sub>2</sub> B	<i>p</i> -Xylenol-H <sub>2</sub> SO <sub>4</sub>	AB; AB <sub>2</sub>
Hydroquinone-HBr.....	?	<i>m</i> -Nitrophenol-H <sub>2</sub> SO <sub>4</sub>	A <sub>2</sub> B
		<i>p</i> -Nitrophenol-H <sub>2</sub> SO <sub>4</sub>	A <sub>2</sub> B

It will be noticed that no single case of compound formation has been previously recorded from a system of the simplest type—monobasic acid and monobasic phenol. The results obtained from such systems in the present investigation are given in the tables below.

1. Phenol-Trichloroacetic Acid.—The freezing-point curve of this system is shown in the diagram on page 1313. An equimolecular addition product, C<sub>6</sub>H<sub>5</sub>OH, CCl<sub>3</sub>.COOH, is indicated by the curve; this crystallizes out from a mixture of the two components in the form of beautiful white needles, m. p. 37.6°. The extraordinary flatness of the maximum for this compound on the freezing-point curve shows that it is very considerably dissociated into its constituents on fusion.

(a) Solid phase, CCl<sub>3</sub>.COOH.

% CCl <sub>3</sub> .COOH.....	100	90.2	82.6	75.7	68.8
T.....	57.3	50.7	45.2	38.9	31.9

(b) Solid phase, C<sub>6</sub>H<sub>5</sub>OH, CCl<sub>3</sub>.COOH.

% CCl <sub>3</sub> .COOH.....	65.1	63.1	60.0	57.0	53.7	50.2	44.8	41.1	35.4
T.....	34.0	34.9	36.0	36.8	37.4	37.6	37.2	36.3	34.2

(c) Solid phase, C<sub>6</sub>H<sub>5</sub>.OH.

% CCl <sub>3</sub> .COOH.....	18.3	13.2	7.2	0
T.....	25.9	31.8	37.0	42.4

<sup>1</sup> THIS JOURNAL, 33, 70 (1911).

<sup>2</sup> Ann., 376, 236 (1911).

<sup>3</sup> THIS JOURNAL, 36, 2498 (1914).

**2. *o*-Cresol-Trichloroacetic Acid.**—An exactly similar curve to that described above was obtained. The addition product,  $C_7H_7.OH, CCl_3.COOH$ , is stable at its maximum and highly dissociated on fusion; m. p.  $27.0^\circ$ .

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

% $CCl_3.COOH$ .....	100	90.3	82.7	76.0	64.6	56.0	
T.....		57.3	50.3	44.4	38.3	25.6	15.3

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

% $CCl_3.COOH$ .....	60.5	56.0	50.8	45.5	40.1	35.0	30.2	
T.....		25.3	26.6	27.0	26.7	25.3	23.4	20.8

(c) Solid phase,  $C_7H_7.OH$ .

% $CCl_3.COOH$ .....	30.2	23.0	14.9	6.4	0	
T.....		9.5	15.6	21.3	26.5	30.4

**3. *m*-Cresol-Trichloroacetic Acid.**—From this system the addition compound  $C_7H_7.OH, CCl_3.COOH$  was obtained, m. p.  $14.5^\circ$ . The curve resembles those of the preceding systems.

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

% $CCl_3.COOH$ .....	100	92.9	85.9	77.2	71.0	62.7	56.4	
T.....		57.3	52.5	47.4	39.5	33.9	24.3	16.1

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

% $CCl_3.COOH$ .....	51.1	46.6	40.4	35.6	30.1	25.3	
T.....		14.4	14.1	12.9	11.1	7.8	3.9

(c) Solid phase,  $C_7H_7.OH$ .

% $CCl_3.COOH$ .....		15.5	8.8	0
T.....		—0.4	4.5	10.9

**4. *p*-Cresol-Trichloroacetic Acid.**—An equimolecular addition compound,  $C_7H_7.OH, CCl_3.COOH$ , was obtained, similar in its character to those already described; m. p.  $37.6^\circ$ .

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

% $CCl_3.COOH$ .....	100	91.6	85.1	76.9	70.0	
T.....		57.4	51.6	46.9	39.9	32.3

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

% $CCl_3.COOH$ .....	63.5	58.3	53.1	49.2	44.8	37.0	29.9	22.2	
T.....		34.7	36.4	37.4	37.6	47.0	34.5	30.2	23.5

(c) Solid phase,  $C_7H_7.OH$ .

% $CCl_3.COOH$ .....		17.6	12.7	6.6	0
T.....		19.9	24.7	29.8	34.5

**5. Thymol-Trichloroacetic Acid.**—It was not found possible to isolate any compound from this system, probably owing to persistent supercooling.

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

% $CCl_3.COOH$ .....	100	92.2	84.6	76.4	69.1	62.0	55.2	
T.....		57.3	52.8	46.8	39.6	32.1	23.5	15.0

(b) Solid phase,  $C_{10}H_{13}OH$ .

% $CCl_3.COOH$ .....	49.4	43.0	35.4	28.6	21.7	13.6	7.0	0	
T.....		10.1	18.0	25.8	32.0	37.5	42.4	46.1	49.6

6. *o*-Nitrophenol-Trichloroacetic Acid.—No addition compound formation was indicated by this system.

(a) Solid phase,  $\text{CCl}_3\text{COOH}$ .

% $\text{CCl}_3\text{COOH}$ .....	100	92.0	84.8	77.7	68.9	59.8	51.0
T.....	57.3	52.8	47.8	41.9	34.1	26.2	18.1

(b) Solid phase,  $\text{C}_6\text{H}_4\text{NO}_2\text{OH}$ .

% $\text{CCl}_3\text{COOH}$ .....	48.6	40.5	33.3	25.1	21.1	11.9	6.0	0
T.....	17.6	23.1	27.9	32.4	34.6	39.6	42.1	44.7

7. *m*-Nitrophenol-Trichloroacetic Acid.—Here also no compound formation was obtained.

(a) Solid phase,  $\text{CCl}_3\text{COOH}$ .

% $\text{CCl}_3\text{COOH}$ .....	100	92.6	85.5	78.4	71.4
T.....	57.3	53.3	49.2	44.9	40.5

(b) Solid phase,  $\text{C}_6\text{H}_4\text{NO}_2\text{OH}$ .

% $\text{CCl}_3\text{COOH}$ .....	71.4	64.3	53.8	39.9	30.2	19.9	10.1	0
T.....	43.2	50.9	60.4	71.4	78.1	84.7	90.1	95.3

8. *p*-Nitrophenol-Trichloroacetic Acid.—The curve resembles that of the two preceding systems in indicating no compound formation.

(a) Solid phase,  $\text{CCl}_3\text{COOH}$ .

% $\text{CCl}_3\text{COOH}$ .....	100	94.1	87.7	81.8	75.8
T.....	57.3	54.4	51.2	47.8	44.0

(b) Solid phase,  $\text{C}_6\text{H}_4\text{NO}_2\text{OH}$ .

% $\text{CCl}_3\text{COOH}$ .....	70.6	59.4	45.5	30.3	16.0	0
T.....	51.0	65.1	79.7	92.6	103.7	113.8

9.  $\alpha$ -Naphthol-Trichloroacetic Acid.—No compound formation was indicated in this or the following system.

(a) Solid phase,  $\text{CCl}_3\text{COOH}$ .

% $\text{CCl}_3\text{COOH}$ .....	100	91.2	83.1	75.2
T.....	57.3	52.6	47.7	42.1

(b) Solid phase,  $\text{C}_{10}\text{H}_7\text{OH}$ .

% $\text{CCl}_3\text{COOH}$ ...	66.8	59.0	50.6	43.0	35.7	28.6	21.3	14.9	7.6	0
T.....	48.7	55.1	61.5	67.3	72.5	76.9	81.6	85.3	89.9	94.2

10.  $\beta$ -Naphthol-Trichloroacetic Acid.—

(a) Solid phase,  $\text{CCl}_3\text{COOH}$ .

% $\text{CCl}_3\text{COOH}$ .....	100	93.4	88.2	80.4
T.....	57.3	53.1	49.3	43.5

(b) Solid phase,  $\text{C}_{10}\text{H}_7\text{OH}$ .

% $\text{CCl}_3\text{COOH}$ .....	74.0	67.4	62.2	55.0	46.4	36.2	25.0	13.4	0
T.....	49.2	58.8	67.6	77.0	86.2	95.9	105.2	113.9	121.6

### Consideration of Results.

Of the ten phenols examined with trichloroacetic acid, four (phenol and the three cresols) gave equimolecular addition products. The flatness of the maxima on the freezing-point curves indicates that these compounds are very highly dissociated into their components on fusion. In the case of thymol no compound could be isolated, but the form of





(under which assumption addition takes place on the carbonyl group, as in the case of acids) but this is neither a necessary<sup>1</sup> nor, indeed, a satisfactory explanation of the compound formation. Alcohols and ethers, substances with which such a rearrangement is not possible, give well-defined oxonium salts with acids.<sup>2</sup> Here the carbonium structure suggested by Gomberg and Gone for the addition products is altogether excluded, since no double-bonded oxygen is present in the original molecule. The isolation by Maass and McIntosh<sup>3</sup> of addition compounds of resorcinol with acids also conflicts with the conclusions expressed by Gomberg and Cone.<sup>4</sup>

Our present data with regard to oxonium compounds of substances lacking the carbonyl group are, however, insufficient to enable any definite opinion to be expressed as to the mechanism of the reaction. If, as is probable, it forms the first stage in the formation of the phenolic esters or organic acids, then it would seem reasonable to infer that the reaction takes place in successive steps corresponding with those involved in the general process of esterification. The discussion of this subject will be taken up again in a subsequent communication.

## II. Systems: Weak Phenol-Strong Phenol.

The results of previous investigations upon systems of this type are summarized in the following table. It will be seen that a number of simple phenols have already been examined with picric acid, and in some cases addition compounds have been isolated:

Systems.	Compounds.	Observer.
Phenol-picric acid.....	AB	Philip <sup>5</sup>
<i>o</i> -Nitrophenol-picric acid.....	None	Kreemann and Rodinis <sup>6</sup>
<i>m</i> -Nitrophenol-picric acid.....	None	Kreemann and Rodinis
<i>p</i> -Nitrophenol-picric acid.....	None	Kreemann and Rodinis
$\beta$ -Naphthol-picric acid.....	AB	Kuriloff <sup>7</sup>
Catechol-picric acid.....	AB	Philip and Smith <sup>8</sup>
Guaiacol-picric acid.....	AB	Philip and Smith
Resorcinol-picric acid.....	AB	Philip and Smith

The methods employed in the above researches were substantially the same as those of the present paper, the existence and stability of the addition compounds being determined from the freezing-point curve. Consequently the results recorded above are directly available for comparison with those of this investigation, and only those phenols listed on

<sup>1</sup> Kendall and Carpenter, *THIS JOURNAL*, 36, 2511 (1914).

<sup>2</sup> Maass and McIntosh, *Ibid.*, 34, 1273 (1912).

<sup>3</sup> *Ibid.*, 33, 70 (1911).

<sup>4</sup> *Loc. cit.*, pages 236-7.

<sup>5</sup> *J. Chem. Soc.*, 83, 814 (1903).

<sup>6</sup> *Monatsh.*, 27, 152 (1906).

<sup>7</sup> *Z. physik. Chem.*, 23, 673 (1897).

<sup>8</sup> *J. Chem. Soc.*, 87, 1735 (1905).

page 1312 not hitherto examined with picric acid are therefore included here.

**11. *o*-Cresol-Picric Acid.**—An equimolecular addition compound,  $C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$ , was obtained, highly dissociated on fusion (as evidenced by the flatness of the maximum on the freezing-point curve), m. p.  $89.8^\circ$ . The compound crystallizes as beautiful yellow prisms from a very dark red solution.

(a) Solid phase,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	100	89.1	80.9	72.7	65.5
T.....	118.5	110.5	104.1	96.5	89.1

(b) Solid phase,  $C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	62.0	57.7	49.7	42.0	34.1	27.5	19.9	13.5	9.2
T.....	87.4	89.0	89.8	89.1	86.7	83.3	76.9	68.9	60.8

(c) Solid phase,  $C_7H_7OH$ .

% $C_6H_2(NO_2)_3OH$ .....	1.6	0
T.....	29.4	30.4

**12. *m*-Cresol-Picric Acid.**—From this system the compound  $2C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$  was isolated, fine, yellow needles melting at  $61.6^\circ$ . The freezing-point curve is shown in the diagram on page 1313.

(a) Solid phase,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	100	90.1	81.5	73.8	66.6	59.8	53.1	45.3
T.....	118.5	111.4	104.8	97.5	90.6	82.2	74.7	63.3

(b) Solid phase,  $2C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	41.7	37.4	32.4	28.6	23.6	19.6	14.6	9.9	5.7	3.4
T.....	60.0	61.2	61.5	60.8	58.7	56.5	52.6	46.7	38.5	30.3

(c) Solid phase,  $C_7H_7OH$ .

% $C_6H_2(NO_2)_3OH$ .....	1.1	0
T.....	10.2	10.9

**13. *p*-Cresol-Picric Acid.**—This system gives the compound  $C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$ , unstable at its maximum, m. p.  $65.6^\circ$  (by extrapolation). The freezing-point curve is given in the diagram on page 1313.

(a) Solid phase,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	100	91.1	80.2	69.9	62.8	56.4	51.0
T.....	118.5	112.0	103.4	93.7	86.2	78.0	70.3

(b) Solid phase,  $C_7H_7OH$ ,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	46.5	43.9	38.8	32.8	27.6	22.3	16.9	11.4
T.....	65.2	64.4	62.3	58.5	54.7	49.6	43.1	35.5

(c) Solid phase,  $C_7H_7OH$ .

% $C_6H_2(NO_2)_3OH$ .....	5.9	0
T.....	30.1	34.5

**14. Thymol-Picric Acid.**—The equimolecular addition compound  $C_{10}H_{13}OH$ ,  $C_6H_2(NO_2)_3OH$  was obtained, stable at its maximum; m. p.  $96.8^\circ$ .

(a) Solid phase,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	100	89.8	81.1	75.4	69.3	62.5
T.....	118.5	113.0	108.0	105.0	102.0	99.8

(b) Solid phase,  $C_{10}H_{18}OH$ ,  $C_6H_2(NO_2)_3OH$ .

% $C_6H_2(NO_2)_3OH$ .....	53.5	51.5	47.0	42.0	36.7	32.5	28.1	22.8	16.6
T.....	96.0	96.6	96.1	94.2	91.6	89.2	86.3	81.1	71.9

(c) Solid phase,  $C_{10}H_{18}OH$ .

% $C_6H_2(NO_2)_3OH$ .....	3.2	0
T.....	48.2	49.6

15.  $\alpha$ -Naphthol-Picric Acid.—This system gives an addition product—probably  $C_{10}H_7.OH$ ,  $C_6H_2(NO_2)_3OH$ —but the melting point of the compound is so high that mixtures containing more than a small amount of picric acid become very explosive, consequently the curve could not be determined.

### Consideration of Results.

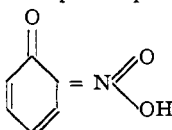
Of the thirteen phenols examined with picric acid in this and previous investigations, ten are found to give addition products, the three nitrophenols alone providing negative results.<sup>1</sup> This is again in accordance with the views advanced in the introductory section regarding the nature of the reaction, since the nitrophenols are the most highly acidic of all those investigated<sup>2</sup> and therefore exhibit the least tendency towards compound formation with a *strong* acid.

When the freezing-point curves of phenols with picric acid are compared with those given with trichloroacetic acid in an earlier section, it is seen that picric acid behaves as the stronger acid of the two. The maxima for the addition compounds with this acid are sharper throughout the whole series of curves in spite of the higher temperatures involved. Picric acid, also, gives addition products with the naphthols, which do not combine at all with trichloroacetic acid. The phenols thus resemble alcohol in being better dissociating media for picric acid than for trichloroacetic, although in aqueous solution the two acids are very nearly equally ionized. In the same way sulfuric acid, as will be evident from the table on page 1314, is a stronger acid than picric in phenol solutions, since it is capable of compound formation even with the nitrophenols. In aqueous solution the order is reversed.

Eight of the ten compounds obtained from systems of the type: weak phenol-picric acid are equimolecular.<sup>3</sup> The reaction for their formation may be expressed, in accordance with the arguments advanced previously,

<sup>1</sup> The system quinol-picric acid gives no compound owing to decomposition of the quinol (Philip and Smith, *J. Chem. Soc.*, 87, 1735 (1905)).

<sup>2</sup> *o*- and *p*-Nitrophenols (also picric acid) may well be stronger acids in the *nitronic*

forms,  , than in the phenol forms. It is instructive to note that

*m*-nitrophenol is a much weaker acid than its *o*- and *p*-isomers (see page 1312).

<sup>3</sup> The composition of the  $\alpha$ -naphthol-picric acid compound could not be determined.

by Equation II on page 1317. The compound of *m*-cresol with picric acid is peculiar in containing two molecules of *m*-cresol to one of acid.

### III. Systems: Weak Acid-Strong Phenol.

No previous work has been done upon systems of this class. The examples of this type investigated below gave only negative results, no compounds being isolated. The same is true of two systems of the type: weak acid-weak phenol, which are also recorded in the following tables:

#### 16. Acetic Acid-Picric Acid.—

(a) Solid phase,  $C_6H_2(NO_2)_3.OH$ .

% $C_6H_2(NO_2)_3.OH$ .....	100	76.0	63.6	53.5	45.0	35.9	25.3	17.0	12.5
T.....	118.5	106.5	100.1	94.9	90.0	84.7	76.7	65.1	55.1

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

% $C_6H_2(NO_2)_3.OH$ .....	3.6	0
T.....	14.1	16.4

17. *o*-Toluic Acid-Picric Acid.—This system is shown in the diagram on page 1313.

(a) Solid phase,  $C_6H_2(NO_2)_3.OH$ .

% $C_6H_2(NO_2)_3.OH$ .....	100	88.2	75.1	64.5	54.9	44.1	35.0
T.....	118.5	113.5	108.0	103.8	99.2	94.9	90.3

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

% $C_6H_2(NO_2)_3.OH$ .....	27.3	18.4	9.0	0
T.....	89.0	93.5	98.4	103.4

#### 18. *m*-Toluic Acid-Picric Acid.—

(a) Solid phase,  $C_6H_2(NO_2)_3.OH$ .

% $C_6H_2(NO_2)_3.OH$ .....	100	92.7	85.7	78.0	70.4	61.0	50.4	41.9	34.0
T.....	118.5	114.9	112.0	108.8	105.7	101.7	97.0	93.1	89.9

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

% $C_6H_2(NO_2)_3.OH$ .....	27.8	20.0	10.2	0
T.....	90.2	96.0	102.5	109.6

#### 19. $\alpha$ -Toluic Acid-Picric Acid.—

(a) Solid phase,  $C_6H_2(NO_2)_3.OH$ .

% $C_6H_2(NO_2)_3.OH$ .....	100	91.1	79.7	67.5	56.3	45.0	35.1	23.3	13.2
T.....	118.5	114.6	109.7	104.9	100.0	95.2	90.0	82.7	74.0

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

% $C_6H_2(NO_2)_3.OH$ .....	7.5	0
T.....	72.4	76.7

20. Phenol-Chloroacetic Acid.—No compound formation was observed between phenol and this moderately weak acid. (See diagram, page 1313.)

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

% $CH_2Cl.COOH$ .....	100	88.5	78.1	67.9	58.3	46.7	37.9
T.....	61.4	56.0	50.4	44.9	39.1	30.9	23.6

(b) Solid phase,  $C_6H_5OH$ .

% $CH_2Cl.COOH$ .....	30.0	18.5	8.8	0
T.....	17.4	27.1	35.1	42.4

21. *o*-Cresol-Chloroacetic Acid.—Here also no compound is indicated.

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

% $CH_2Cl.COOH$ .....	100	86.3	75.2	63.0	51.1	39.4	30.6	
T.....		61.4	54.9	49.2	42.4	34.8	25.7	17.4

(b) Solid phase,  $C_7H_7OH$ .

% $CH_2Cl.COOH$ .....	27.6	17.9	8.6	0
T.....	16.7	21.8	26.6	30.4

## Consideration of Results.

None of the weak acids examined with picric acid in the above tables gave addition compound formation, and the freezing-point curves indicate that no compounds exist in solution. This is an unexpected result, since the same weak acids have been shown to form stable compounds with trichloroacetic acid<sup>1</sup> and with sulfuric acid.<sup>2</sup>

The conclusion must be drawn that the weak organic acids, unlike the phenols, are better dissociating media for trichloroacetic acid than for picric acid. Such differences of behavior, however, as have been noted here and in a preceding section do not deserve much emphasis, since the general results of work in this field indicate that, in cases of such weak combination, quite small variations in acidic strength are sufficient to induce or inhibit the isolation of compounds.

The two systems of the type: weak acid-weak phenol recorded above also gave no addition compounds, as was only to be expected from systems containing two components of not widely different acidic strengths. Similarly Paterno and Ampolla<sup>3</sup> found no compound formation in the systems thymol-acetic acid and thymol-phenol.

## Summary.

The examination of compound formation in two-component systems of the type: strong organic acid-weak organic acid has been completed by including phenols in the investigation. Systems of the general type: phenol-acid have been studied in which the acidic strengths of both components have been varied as widely as possible.

In accordance with the results of previous papers, it has been found that addition compounds are obtained only when the acidic strengths of the two components are very widely separated. Thus weak phenols give oxonium salts with a strong acid or a strongly acidic phenol (trichloroacetic acid or picric acid). A number of such compounds have been

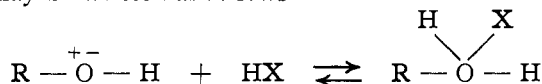
<sup>1</sup> Kendall, *THIS JOURNAL*, **36**, 1722 (1914).

<sup>2</sup> Kendall and Carpenter, *Ibid.*, **36**, 2498 (1914).

<sup>3</sup> Paterno and Ampolla, *Gazz.*, **27**, 481 (1897).

isolated and described. Systems containing components of not so widely divergent acidic strengths give no compound formation.

The reaction is assumed to be similar in its nature to those studied in previous papers, *i. e.*, the compounds are regarded as true oxonium salts. The equation may be written as follows:



This reaction probably represents the first stage in the formation of phenolic esters of organic acids. The further study of the mechanism of the esterification process will be the subject of a subsequent paper.

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## VI. FURTHER EVIDENCE FOR THE ELECTRONIC FORMULA OF BENZENE AND THE SUBSTITUTION RULE.<sup>1</sup>

By HARRY SHIPLEY FRY.

Received April 13, 1916.

In previous papers of this series<sup>2</sup> numerous facts have been presented and interpreted by means of the electronic formula of benzene (abbreviated formula, Fig. 1). A substitution rule was indicated maintaining that

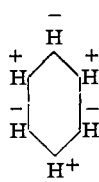


Fig. 1.

when substituents are of the same sign or polarity they will occupy positions which are meta to each other, but if two substituents are of opposite sign or polarity they will occupy either ortho or para positions to each other. This follows from the fact that the electronic formula of benzene is the only formula presenting conjointly a structural basis and an electronic interpretation of the relations between the ortho and para positions and substituents in contradistinction to the meta positions and substituents.

The purpose of the present paper is to present briefly additional experimental facts which further substantiate the electronic formula of benzene and the substitution rule. The facts here offered seem particularly significant since they involve polysubstituted derivatives of benzene.

Phenol, when directly nitrated, yields ortho- and para-nitrophenols. Further nitration yields the two isomeric 1,2,4- and 1,2,6-dinitrophenols.

<sup>1</sup> This and the two following papers constitute Parts VI, VII, and VIII of the series, "Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences." Parts VI and VIII were read before the Cincinnati Section of the American Chemical Society, May 12, 1915.

<sup>2</sup> Fry, *THIS JOURNAL*, 36, 248, 262, 1035 (1914); *Ibid.*, 37, 855, 863, 883, 2368 (1915); see also Fry, *Z. physik. Chem.*, 76, 385, 398, 591 (1911); *Ibid.*, 80, 29 (1912); *Ibid.*, 82, 665 (1913); *Ibid.*, 90, 458 (1915).