

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

Compound Formation between the Isomeric Phenylphenols and Pyridine

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In the course of some synthetic work which was reported earlier,¹ heat changes were noted when the phenylphenols were dissolved in pyridine, and the effects for the isomeric phenols were different: (a) with *o*-phenylphenol, there was evidence of a definitely exothermic reaction; (b) practically no temperature change was noted when the meta isomer was dissolved in the base; (c) the temperature was lowered slightly upon dissolving *p*-phenylphenol in pyridine.

In an attempt to gain some insight into the types of changes involved in these situations, especially to determine the character of compound formation if any, thermal analyses of the three binary systems were made—freezing point-concentration curves were obtained—in much the same manner as in Kendall's studies.²

Experimental Part³

A. Purification of Materials

Pyridine.—Pyridine was allowed to stand over sodium hydroxide pellets for from six to eight weeks and then distilled through a 30-cm. Vigreux column. The middle fraction with a boiling range of not over 0.5° was collected. Different lots had *n*_D²⁰ varying between 1.5089 and 1.5087.⁴ It was stored in a brown glass-stoppered bottle, and over a period of two months the change in *n*_D²⁰ was never more than 0.0002. The freezing point (from cooling curve) was -41.7°.⁵

***o*-Phenylphenol.**—Eastman Kodak Company best grade product was recrystallized from ligroin, which had been dried over sodium hydroxide pellets and distilled from 70 to 80°. After standing in a vacuum desiccator containing paraffin shavings, the product had a freezing point (from cooling curve) of 57.1°.⁶

***m*-Phenylphenol.**⁷—The *m*-phenylphenol was recrystallized from carbon tetrachloride ("analytical reagent") and allowed to stand in a vacuum desiccator in the same manner as described for the ortho isomer. The freezing point (from cooling curve) of the product was 75.3°.⁸

***p*-Phenylphenol.**—Eastman Kodak Co. *p*-phenylphenol was recrystallized from carefully dried and redistilled benzene and placed in a desiccator as indicated for the other phenols. The freezing point (from cooling curve) of this material was 165.1°.⁹

B. Apparatus

The apparatus used in this work was essentially the same as that conventionally employed in such experiments. It consisted of a 2 cm. × 15 cm. "Pyrex" test-tube fitted with

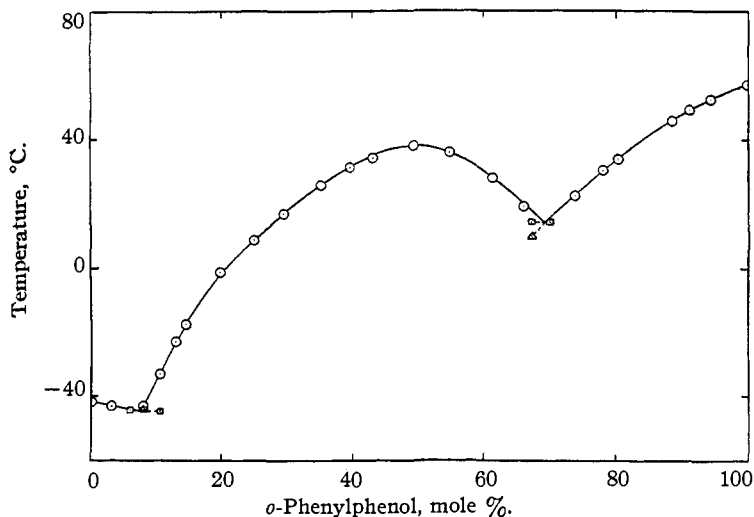


Fig. 1.—*o*-Phenylphenol + pyridine: ○, freezing point; ◻, eutectic temperature; △, freezing point, metastable state.

a two-hole cork covered with tin foil. Through one hole there was the appropriate thermometer and through the other there was a short glass sleeve through which the stirrer passed. This inner vessel was surrounded by another test-tube with a diameter about 7 mm. greater than the smaller one; this provided an air jacket to smooth out and to retard the rate of cooling or heating. The whole apparatus was securely clamped in a larger beaker or unsilvered Dewar flask which served as a control bath. The materials in this bath were varied to suit the range of temperatures involved; in order of decreasing temperature they were: cottonseed oil, water, ice-water, ice-salt-water, and ethyl acetate-methanol-solid carbon dioxide. For temperatures above -10°, a set of 15-cm. Anschütz pre-

(1) Hazlet, *THIS JOURNAL*, **59**, 287 (1937).

(2) Kendall, *ibid.*, **36**, 1222 (1914).

(3) All temperatures, unless otherwise indicated, are corrected.

(4) (a) Brühl, *Z. physik. Chem.*, **16**, 215 (1895), reported *n*_D²⁰ 1.50919. (b) The values reported here were determined in the same manner and with the same apparatus as other data reported by Schutz, *THIS JOURNAL*, **61**, 2691 (1939).

(5) The reported freezing point is -42°; Zawadzki, *Chem. Zeit.*, **30**, 299 (1906), and Weger, *Z. anorg. Chem.*, **22**, 394 (1900); "Beilstein's Handbuch der organischen Chemie," 4th ed., Julius Springer, Berlin, 1935, Vol. 20, p. 183.

(6) Jacobson, Franz and Hönigsberger, *Ber.*, **36**, 4080 (1903), reported m. p. 56°.

(7) The *m*-phenylphenol used in this work was generously furnished by the Dow Chemical Company, Midland, Michigan.

(8) Briner and Bron, *Helv. Chim. Acta*, **15**, 1239 (1932), reported m. p. 76°.

(9) Latschinoff and Engelhardt, *Ber.*, **6**, 194 (1873), reported m. p. 164-165°.

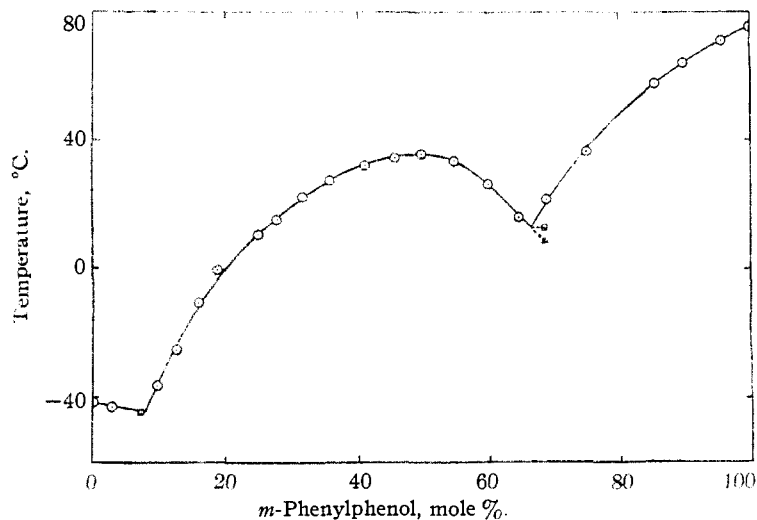


Fig. 2.—*m*-Phenylphenol + pyridine: \odot , freezing point; \square , eutectic temperature; \triangle , freezing point, metastable state.

precision thermometers graduated in one-fifth degrees was used for determining freezing points. These were calibrated against a thermometer certified by the United States Bureau of Standards. For temperatures below -10° , a -50 to 50° alcohol thermometer graduated in one-fifth degrees was used. This thermometer was calibrated against the freezing points of mercury and water. The temperature of the outer bath was determined by an ordinary laboratory thermometer when above 0° and by a copper-constantan thermocouple when below that temperature. As an aid in observing temperatures, which were

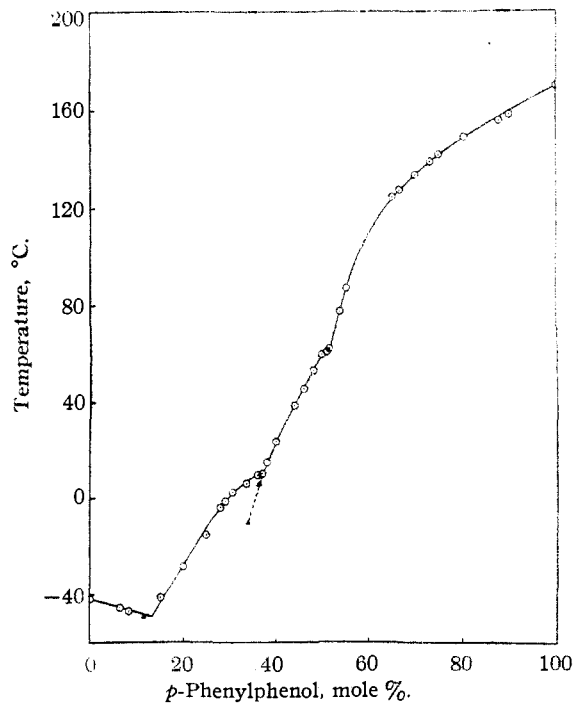


Fig. 3.—*p*-Phenylphenol + pyridine: \odot , freezing point; \square , eutectic temperature; \triangle , freezing point, metastable state.

read to the nearest 0.1° through a magnifying glass, and the condition of the material in the reaction tube, a source of light was placed in the rear of the apparatus. In the study of the *p*-phenylphenol-pyridine system where temperatures near or above the boiling point of pyridine were involved, the stirrer was dispensed with and only a thermometer in a tight-fitting cork was used; mixing was accomplished by shaking the melted material; no loss of pyridine was detected.

C. Procedure

The phenols were weighed by difference and placed in the freezing point apparatus. The approximate quantity of pyridine was delivered to the apparatus from a weight buret, and the exact weight of the sample was determined by difference. In general, the weight of each mixture was 6 to 8 g., but for those samples with compositions within 10 mole % on either side of eutectics the amount was doubled or trebled.

A mixture was warmed slightly if necessary to effect solution, thoroughly stirred, and, while stirring was continued, cooled slowly to obtain an approximate freezing point. From the information thus obtained, the bath was regulated to an appropriate temperature, and the freezing point of the mixture was determined from the cooling curve.

For compositions representing a nearly pure compound there was very little tendency to supercool, but for other compositions considerable supercooling was encountered. To induce crystallization, seeding with a crystal of the solid phase was done at approximately the expected freezing point.

D. Results

Below in tabular and graphical form the experimental data are shown. Compositions, as indicated, are shown in mole %.

Discussion

From the graphical representations of the three systems studied the following conclusions can be drawn.

A. Pyridine and *o*-phenylphenol form a compound, $C_8H_8N \cdot C_{12}H_{10}O$, f. p. 38.2° , which appears to be quite stable. The two eutectics are: (1) 7.5 mole % *o*-phenylphenol, f. p. -44.7° , and (2) 69.3 mole % *o*-phenylphenol, f. p. 14.3° . The determination of freezing points near the eutectic at 69.3 mole % was difficult; supercooling often caused the phenol to crystallize in the metastable state.

B. Pyridine and *m*-phenylphenol form one compound, $C_8H_8N \cdot C_{12}H_{10}O$, f. p. 35.5° , much the same as the ortho isomer. In this case the two

TABLE I

THE SYSTEM: PYRIDINE AND <i>o</i> -PHENYLPHENOL			
<i>o</i> -Phenyl-phenol, mole %	F. p., °C. ^a	<i>o</i> -Phenyl-phenol, mole %	F. p., °C. ^a
0.00	-41.7	49.39	38.2
3.21	-43.3	54.88	36.0
(5.17)	(-44.7)(E ₁)	61.39	28.2
8.10	-43.1	66.26	19.1
(8.10)	(-44.4)(E ₁)	(67.22)	(9.8)(M)
10.52	-33.1	(67.22)	(14.4)(E ₂)
(10.52)	(-44.8)(E ₁)	(70.13)	(14.3)(E ₂)
13.05	-23.0	73.88	22.4
14.54	-17.8	78.11	30.4
19.81	-1.4	80.34	33.9
24.86	8.8	88.53	45.9
29.52	17.0	91.24	49.4
35.10	25.8	94.41	52.5
39.65	31.5	100.00	57.1
43.11	34.5		

^a In this table (E₁) refers to the first eutectic temperature obtained from the mixture with composition as shown, (E₂) to the second, and (M) to the temperature for the crystallization of the component in the metastable state.

TABLE II

THE SYSTEM: PYRIDINE AND <i>m</i> -PHENYLPHENOL			
<i>m</i> -Phenyl-phenol, mole %	F. p., °C. ^a	<i>m</i> -Phenyl-phenol, mole %	F. p., °C. ^a
0.00	-41.7	45.68	34.3
2.87	-43.0	49.75	35.5
(7.21)	(-44.3)(E ₁)	54.87	33.3
9.76	-36.3	59.86	26.0
12.54	-25.3	64.61	15.7
15.92	-10.9	(68.68)	(8.8)(M) ^b
18.71	-0.9	(68.68)	(12.6)(E ₂)
24.97	10.4	68.98	21.5
27.67	15.2	74.92	36.5
31.62	22.2	85.36	57.9
35.75	27.2	89.87	64.0
41.19	31.9	95.72	71.1
		100.00	75.3

^a See note, Table I. ^b Obtained by seeding the mixture with compound C₅H₅N·C₁₂H₁₀O.

eutectics are: (1) 8 mole % *m*-phenylphenol, f. p. -44.3° and (2) 66.5 mole % *m*-phenylphenol, f. p. 12.6°. Freezing points of mixtures with between 30 and 70 mole % *m*-phenylphenol were got only by seeding the liquid with a sample of material obtained by freezing a mixture of the latter composition in carbon dioxide-ethyl acetate.

C. Pyridine and *p*-phenylphenol appear, from the shape of the graph, to form two compounds. Both are unstable at their melting points and crystallize only from solutions containing an excess of pyridine. A sample (approximately 7 g.) of one of these, apparently C₅H₅N·C₁₂H₁₀O, was cooled to -5° (uncor.); at this temperature it

TABLE III

THE SYSTEM: PYRIDINE AND <i>p</i> -PHENYLPHENOL			
<i>p</i> -Phenyl-phenol, mole %	F. p., °C. ^a	<i>p</i> -Phenyl-phenol, mole %	F. p., °C. ^a
0.00	-41.7	44.00	38.7
6.34	-45.5	46.03	45.6
8.40	-46.8	48.12	53.0
(11.42)	(-49.3)(E ₁)	49.83	59.7
15.20	-41.3	51.13	61.0
19.98	-28.4	51.64	62.1
25.14	-15.2	53.80	77.4
28.13	-3.3	55.31	87.1
29.28	1.1	65.09	124.2
30.86	2.5	66.64	127.0
33.76	6.0	69.84	133.0
(33.97)	(-10.5)(M)	73.12	138.5
36.13	9.8	74.86	141.4
(36.57)	(6.0)(M)	80.46	148.4
37.15	10.4	87.77	155.5 ^b
38.15	15.2	90.06	157.6 ^b
40.05	23.6	100.00	165.1

^a See note, Table I. ^b Uncorrected.

was in the form of a crumbly, snow-white solid. It was allowed to warm slowly. At 8-9° (uncor.) it showed signs of softening—the snow-white solid became rather glassy; this corresponds approximately to the incongruent melting point. As the temperature was increased, the material became soft and sticky at 15-17° (uncor.); this may be the approximate melting point of the compound. Between 55 and 60° (uncor.), which corresponds approximately to a composition of 50 mole % *p*-phenylphenol as read from the freezing point curve of the system, the last crystals disappeared. A small sample of the other material, apparently C₅H₅N·2C₁₂H₁₀O, was isolated, excess pyridine was absorbed on porous plate, and its melting range was determined in a capillary tube. It softened at 62-64° (uncor.) which corresponds to its incongruent melting point. On raising the temperature, the material showed signs of further change over the range of 85-90° (uncor.); possibly this corresponds to the approximate melting point of the material. Above 90° the system behaved as an equilibrium mixture and the last crystals disappeared at 125-128° (uncor.), which corresponds to the freezing point of the system containing approximately 67 mole % of the phenol. The only eutectic is 13.3 mole % *p*-phenylphenol, f. p. -49.3°.

Summary

The freezing point-composition diagrams have been determined for the two component systems of pyridine and of the three isomeric phenyl-

phenols. With (1) pyridine and *o*-phenylphenol: one compound, $C_6H_5N \cdot C_{12}H_{10}O$, is formed; (2) pyridine and *m*-phenylphenol: one compound, $C_6H_5N \cdot C_{12}H_{10}O$, is formed; (3) pyridine and *p*-

phenylphenol: two compounds, (a) $C_6H_5N \cdot C_{12}H_{10}O$ and (b) $C_6H_5N \cdot 2C_{12}H_{10}O$, are formed; both are unstable at their melting points.

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An Electrophoretic Study of the Proteins in Rubber Latex Serum

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The proteins in rubber latex serum (*Hevea brasiliensis*) have been the subject of several researches during the past fifteen years. Some of this work has been concerned with the chemical properties of the proteins¹ and some with their electrophoretic properties.² Recently, the improvements introduced by Tiselius³ in the electrophoretic technique have made it possible to increase the precision and significance of electrophoretic measurements very considerably. The work here reported is part of a program of electrophoretic research on latex proteins. This program was initiated in an attempt to obtain information which would be helpful in correlating protein behavior with the colloidal and other properties of latex.

Experimental

The Electrophoresis Apparatus.—The apparatus was supplied by the Klett Manufacturing Company of New York City and was built according to specifications furnished by Dr. L. G. Longworth of the Rockefeller Institute in New York. Details may be found in Longworth's publications.⁴ A few modifications of the apparatus are described in the following paragraphs.

Illumination System.—Many latex serum samples used in this work did not transmit the visible lines of the mercury spectrum very well. In some cases this was on account of slight turbidity, in others, on account of color. The transmission coefficient of such solutions was found to be much greater in the red. Consequently, the mercury arc supplied with the apparatus was replaced by a 500-watt Tungsten filament projection lamp in conjunction with a Corning no. 246 lighthouse red filter. The object of this arrangement was to produce the most uniform possible exposure of photographic plate over the entire length of the cell image when the cell contained either a turbid or colored protein solution separated from a colorless buffer solution by a boundary in the exposed

part of the cell. This expedient did not in all cases yield perfect results, but it was much more generally practicable than the use of the mercury arc, and well-defined Schlieren patterns were obtained.⁵ Wratten and Wainwright Contrast Thin Coated Panchromatic plates were used. They are insensitive at wave lengths greater than 6800 Å. and the red filter cuts out all light of wave length less than 5600 Å. These figures are extreme values. The range of practical intensities lies between 5800 and 6600 Å.

In using the mercury arc in cases where this was feasible, it was found advantageous to introduce a Corning yellow-yellow filter in order to filter out the violet part of the mercury spectrum. This resulted in the production of straighter base lines in the schlieren diagrams through the elimination of a small dispersion effect due to some undetermined cause in the optical system.

The Electrodes and Source of Potential.—The silver-silver chloride electrodes were replaced by copper electrodes dipping into a concentrated copper sulfate solution. These electrodes are perfectly reversible and are easier to prepare than the silver-silver chloride system. In addition, they require no special care or attention after they are made. The authors used no. 14 copper wire wound into a compact flat coil and soldered to a small copper tube which was cemented to a piece of glass tubing just as in the case of the silver electrodes. When an alkaline buffer solution was used, a layer of saturated sodium sulfate solution was introduced between the buffer and copper sulfate solutions in order to prevent the formation of insoluble basic copper compounds at the liquid junction.

The potential difference applied to the electrophoresis cell and electrodes was furnished by a bank of 45-volt heavy duty B batteries. Conditions were always adjusted so as to make the power consumption less than three watts in the cell and electrode system.

The field strength within the electrophoresis cell was calculated from measured values of the current passing, the specific conductance of the solution and the cross section of the cell.

The Compensating Device for Shifting Boundaries.—The motor-driven compensating device was replaced by a gravity feed through a one-meter U-shaped length of capillary glass tubing of 1-mm. inside diameter which was connected at one end to the closed electrode vessel and at the other end to a separatory funnel which served as a reservoir.

(1) Bishop, *Malayan Agr. J.*, **15**, 27 (1927); Bondy and Freundlich, *Rubber Age*, **44**, 377 (1938); Kemp and Straitiff, *J. Phys. Chem.*, **44**, 788 (1940).

(2) I. Kemp and Twiss, *Trans. Faraday Soc.*, **32**, 890 (1936).

(3) Tiselius, *ibid.*, **33**, 524 (1937).

(4) Longworth, *THIS JOURNAL*, **61**, 529 (1939); Longworth and MacInnes, *Chem. Rev.*, **24**, 271 (1939).

(5) Verbal communication from Prof. J. W. Williams has informed the writers that a similar expedient has also been used successfully in his laboratory.