[CONTRIBUTION FROM THE HYGIENIC LABORATORY OF THE UNITED STATES PUBLIC HEALTH SERVICE]

PARA-CRESOL. A NEW METHOD OF SEPARATING PARA-CRESOL FROM ITS ISOMERS AND A STUDY OF THE BOILING POINT

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RECEIVED NOVEMBER 15, 1926 PUBLISHED MARCH 9, 1927

Introduction

During some work upon phenol[2] it became desirable to prepare *p*-cresol of known purity. All available samples gave a strong, characteristic indophenol reaction with quinone chloroimides, especially the 2,6-dichloro- (and dibromo-) quinone chloro-imide. This was attributed to the presence of the *ortho* or *meta* isomers or both, since it is generally supposed that the *para* derivative does not react under the conditions of indophenol formation. Definite proof on this point also was desired and obtained.

After a purified *p*-cresol was obtained, it was found to boil considerably above the generally accepted value and therefore the careful study of the boiling point was made. Since my value is at least 1° above that given in the latest standard compilation,[3] it seems desirable to present the data which will have to be considered before the final accepted value is reached.

The average value I have found is 202.3°, which is believed to be fairly accurate, under the experimental conditions and apparatus employed, for the sample of *p*-cresol investigated.

Purification of *p*-Cresol

It is generally presumed that indophenol formation, through the reaction of phenols and quinone chloro-imides in alkaline solutions, requires that the position *para* to the hydroxyl group be open. This reaction

$$\underset{\text{Phenol}}{HO.C_6H_5} + \underset{\text{Quinone chloro-imide}}{ClN{:}C_6H_4{:}O} + 2NaOH = \underset{\text{Indophenol}}{NaO.C_6H_4.N{:}C_6H_4{:}O} + NaCl + 2H_2O$$

discovered by Hirsch,[4] was employed since the *ortho* and *meta* derivatives react readily. It has been found that the 2,6-dichloro- and the 2,6-dibromoquinone chloro-imide react most completely and therefore these compounds were employed in the purification, rather than simpler quinone chloro-imides.

One kg. of technical *p*-cresol was purified by treatment with 100 g. of 2,6-dichloroquinone chloro-imide according to the procedure required to produce the type of indophenols made with *o*- and *m*-cresols as described

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[1] Senior Chemist, Hygienic Laboratory, United States Public Health Service.

[2] Gibbs, *J. Biol. Chem.*, **71**, 445 (1927).

[3] International Critical Tables, McGraw-Hill Book Co., New York, **1926**, vol. 1.

[4] Hirsch, *Ber.*, **13**, 1903 (1880).

by Gibbs, Cohen and Cannan.[5] The quinone chloro-imide dissolves readily in the liquid cresol; the reaction being highly exothermic, care must be taken to prevent overheating. A further study of this phenomenon will be reported in a later paper. This solution is chilled and a 10% solution of sodium hydroxide slowly dropped into it, during rapid stirring, until an apparent degree of alkalinity of about *P*H 10 is reached. The indophenol formation is very rapid at this range and should be complete in less than one hour. The blue color of the indophenol has been found to be due to impurities in the *p*-cresol, for the latter can be recovered unchanged.

After the reaction had proceeded for more than one hour at a temperature between 5° and 10°, the solution was filtered; no precipitated indophenol was obtained.

By the addition of salt some indophenol may be precipitated on standing in the cold for a number of hours. The blue solution was acidified with sulfuric acid and distilled with steam. The *p*-cresol distilled, leaving a mass, of undistillable, tarry material. The liquid *p*-cresol was separated from the aqueous layer and the latter extracted with ether to obtain the dissolved *p*-cresol. After evaporation of the ether, the two portions of *p*-cresol were united and purified by distillation. Almost all of the substance distilled between 202° and 203°, uncorrected, and the distillate crystallized beautifully in colorless crystals on chilling.

This material may still give a slight test for impurities by treating with quinone chloro-imides as shown by the development of the blue indophenol color.

I have repeated the treatment described above four times upon the same sample, using both the 2,6-dichloro- and the 2,6-dibromoquinone chloro-imides, without entirely eliminating the blue color of this test. For the boiling-point determinations, a sample showing a blue color equivalent to one part of *o*- or *m*-cresol, or both, in 10,300 was employed. This sample had been distilled with a few small pieces of sodium.

I attribute the blue color of the indophenol to slight quantities of the isomers formed by the breaking down of the *o*- or *m*-cresol indophenol during the steam distillation.[6,7]

The quantitative determination of the amount of substances which produce indophenols was made by means of the spectrophotometer. The details of this method will be more fully treated in an article which is in preparation on the velocity of the indophenol formation.

The final product employed in the boiling-point determinations was

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[5] Gibbs, Cohen and Cannan, *U. S. Pub. Health Repts.*, **40**, 649 (1925). Reprint No. 1001.

[6] Bayrac, *Ann. chim. phys.*, [7] **10**, 18 (1897).

[7] Heller, *Ann.*, **418**, 259 (1919).

found to be very hygroscopic. Although no special apparatus was employed to prevent moisture being taken up from the atmosphere while the samples were being put into the boiling-point apparatus, I do not consider this to be a probable source of error, since traces of moisture are carried off in the first fraction of the distillate. Unless such precautions are taken in the determination of the boiling point by measurements of vapor pressure, the results will be subject to error.

No attempt has been made to check the boiling point with specimens of *p*-cresol prepared by other methods.

Literature on the Boiling Point of *p*-Cresol

Körner[8] found the melting point to be 35.5° and the boiling point 200°. He prepared the *p*-cresol by the action of water on diazotoluene sulfonate, a method also employed 20 years later by Pinette[9] who obtained a much higher value.

Barth[10] prepared *p*-cresol by sulfonating toluene, separating the *ortho* and *para* isomers by crystallization of the potassium salts, and fusing with potassium hydroxide. He states that it melts at 36°, solidifies at 34° and boils at 197°. Pinette prepared the *para* derivatives from *p*-toluidine and states the boiling point to be 201.8°.

Perkin[11] distilled the *p*-cresol with a small amount of sodium to prevent the distillate turning yellow, and corrected for barometer and errors in the thermometer by checking with a substance of known adjacent boiling point and found the boiling point to be 202° after the corrections were made.

Kahlbaum[12] measured the vapor pressures of a number of compounds obtained from C. A. F. Kahlbaum and found the boiling point of *p*-cresol to be 201.1°. It is presumed that he purified the compound by distillation.

Richards and Mathews[13] state the boiling point to be 200.5°.

Criticism of the Previous Work

The *p*-cresol employed by Körner[8] and by Pinette[9] was made from *p*-toluidine. This should produce a material free from isomers if the *p*-toluidine was properly purified. Körner obtained a boiling point of 200° and Pinette obtained 201.8°. The latter seems to be a preferable result.

Barth[10] evidently had an impure sample or measured the boiling point incorrectly, about 5° too low.

As I have previously mentioned,[14] the vapor-pressure method for de-

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[8] Körner, *Bull. acad. roy. med. Belg.*, [2] **24,** 154 (1898).

[9] Pinette, *Ann.*, **243,** 43 (1888).

[10] Barth, *Ann.*, **154,** 358 (1870).

[11] Perkin, *J. Chem. Soc.*, **69,** 1025, 1182 (1896).

[12] Kahlbaum, *Z. physik. Chem.*, **26,** 576 (1898).

[13] Richards and Mathews, *ibid.*, **61,** 449 (1908); THIS JOURNAL, **30,** 10 (1908).

[14] Gibbs, *ibid.*, **27,** 851 (1905).

termining the boiling points of liquids, employed by Kahlbaum,[12] requires very carefully purified material if accurate results are to be obtained. The presence of very small quantities of water or other constituents more volatile than the liquid greatly increases the vapor pressure. The high vapor pressures, and consequently low boiling point as determined by Kahlbaum, are accounted for if one is permitted to assume the presence of moisture in the *p*-cresol. In view of the great hygroscopicity of this substance, as mentioned later in this paper, it seems a reasonable assumption. The value 201.1° is quoted in "International Critical Tables"[3] and "Chemists' Year Book,[15] and since this value is found in the literature only in Kahlbaum's work, it seems to be open to objection in accordance with the above criticism.

Apparatus

The Boiling-Point Apparatus.—The boiling point was determined in a Pyrex apparatus similar to that described by Landsberger.[16]

The Thermometers.—Three 12cm. mercury thermometers graduated 5 divisions to 1° were employed in this work. They were standardized by the United States Bureau of Standards and all required small corrections, none greater than 0.5°.

Results and Calculations

The observations and results of the calculations are recorded in Table I. The first three determinations were made with the Landsberger apparatus and the fourth with an ordinary distilling flask with the mercury thread entirely in the vapor.

TABLE I

THE BOILING POINT OF *p*-CRESOL

Detn. No.	Therm. No.	B. p. obs., °C.	B. p. obs., °C.[a]	Press., mm.	Temp. of air, °C.	Press., mm. (corr.)	B. p., °C. (corr.)[b]	B. p., °C. (corr.)[c]
1	23,770	202.4	202.75	766.7	22	764.0	202.53	202.55
2	23,771	202.8	202.58	766.7	22	764.0	202.36	202.38
3	23,770	202.0	202.34	765.7	23	762.8	202.18	202.20
4	35,864	202.8	202.37	766.5	24	763.6	202.17	202.20
						Av.	202.31	202.33

[a] After correction of the thermometers by the U. S. Bureau of Standards.

[b] Corrected by Equation 1.

[c] Corrected by Equation 2.

In Col. 8 are recorded the boiling points corrected to 760 mm. by Trouton's rule employing the equation

$$T = T_p\,(1 - 0.2 \log_{10} p) \tag{1}$$

in which T_p is the absolute boiling point at a pressure of p atmospheres.

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[15] "Chemists' Year Book," **1924**, The Chemical Catalog Co., Manchester, England, New York, U. S. A.

[16] Landsberger, *Ber.*, **31**, 458 (1898).

This approximate relation is a combination of Trouton's rule and the integrated van't Hoff equation.[17,18]

The observed boiling points at the observed barometric pressure (corr. to 0.0°) may be calculated to 760 mm. by means of the equation

$$dp/PdT = Q/2T^2 \tag{2}$$

in which P is the pressure in g.-cm. units, T the absolute temperature and Q the molecular heat of volatilization of the liquid expressed in small calories. Unfortunately I have not been able to find a determination of the molecular heat of vaporization of *p*-cresol. The value determined by Louguinine[19] for *m*-cresol is 10,860 cal.

This value has been employed for Q in Equation 2 and the results are recorded in Col. 9 of Table I.

Comparison of the Boiling Points of *p*-Cresol, Phenol and Naphthalene

By means of the Ramsay and Young relationship,[20] which holds for substances of closely related composition, the ratio of the absolute boiling

$$T'/T_I' = T/T_I \tag{3}$$

points of two substances is independent of the pressure. The same sample of *p*-cresol was compared with the homolog phenol and also with naphthalene. These two substances were selected for the reason that they were available in a high state of purity; one boils at 21° below, and the other at about 16° above *p*-cresol. The same Landsberger type of apparatus previously employed was used for these determinations.

The samples of phenols and naphthalene consisted of large constant-boiling fractions especially prepared. The data obtained are tabulated in Table II.

TABLE II

THE BOILING POINT OF *p*-CRESOL OBTAINED BY COMPARISON WITH PHENOL AND NAPHTHALENE

	p-Cresol		Phenol			Naphthalene			
Therm. No.	B. p. obs., °C.	B. p. obs., °C. (corr.)	B. p. obs., °C.	B. p. obs., °C. (corr.)	B. p., °C. (Ref. 3)	B. p. obs., °C.	B. p. obs., °C. (corr.)	B. p., °C. (Ref. 3)	B. p., °C., calcd. from Eq. 3
23,770	202.0	202.34	181.6	181.6	182	...	....	...	202.7
23,771	202.8	202.58	...	...	...	218.0	217.65	217.9	202.8

Summary

1. *p*-Cresol is separated from its isomers by means of the indophenol formation which takes place with quinone chloro-imides and phenolic compounds when the position *para* to the hydroxyl group is unsubstituted.

2. The boiling points of samples of *p*-cresol thus purified were deter-

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[17] van't Hoff, "Vorlesungen über Theoretische und physikalische Chemie," Vieweg, Braunschweig, **1901**, vol. 1, p. 13.

[18] Adams, THIS JOURNAL, **48**, 870 (1926).

[19] Louguinine, *Arch. sci. phys. Geneva*, [4] **9**, 5 (1900).

[20] Ramsay and Young, *Phil. Mag.*, [5] **20**, 515 (1885).

mined and corrected to 760 mm. by means of Trouton's rule, and by comparison with phenol and naphthalene according to the relationship discovered by Ramsay and Young. The molecular heat of vaporization of *p*-cresol not being available, that of *m*-cresol was substituted in the equation $dP/PdT = Q/2T^2$.

3. The values for the boiling point of *p*-cresol at 760 mm. by the three methods of correction were found to be 202.31° (corrected by Trouton's rule), 202.33° (corrected by the above equation) and 202.75° (corrected by comparison with phenol and naphthalene); av., 202.45°. The average of the first two values, 202.32°, is believed to be preferable even though the methods of correction involve the same principle.

The lowest of these values is 1.2° above the commonly accepted value of 201.1° given in the International Critical Tables.

4. A review and criticism of the literature is given.

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[CONTRIBUTION FROM THE UNITED STATES BUREAU OF CHEMISTRY, COLOR LABORATORY]

THE RATE OF CONVERSION OF NAPHTHALENE-2,7-DISULFONIC ACID TO THE ISOMERIC 2,6 ACID AT 160° IN THE PRESENCE OF SULFURIC ACID[1]

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RECEIVED NOVEMBER 15, 1926 PUBLISHED MARCH 9, 1927

In the commercial production of the 2,7-disulfonic acid of naphthalene, the pot method of sulfonation is used. The reaction proceeds in two steps. β-Monosulfonic acid is first produced; this is converted into disulfonic acids by further sulfonation.

As in all these sulfonations, a mixture of isomers is obtained; the product is principally β-monosulfonic acid which is converted to 2,7-disulfonic acid. Small amounts of the 1,6 acid also occur in the sulfonation mass. It is necessary to continue this heating for some time to complete the conversion of the monosulfonic acid, and as this heating is prolonged, the 1,6 and 2,7 acids which are formed gradually undergo a molecular rearrangement to form the symmetrical 2,6 acid, which is more stable under the existing conditions. The reaction has been studied by many investigators, whose reports vary greatly. Ebert and Merz[2] reported that heating for four hours at 160° produced equal quantities of 2,7 and 2,6 acids, and that heating for 24 hours at 180° gave complete conversion to the 2,6 acid. Armstrong[3] and Winne,[4] who also studied the reaction, re-

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[1] The work here described was completed in June, 1923, in the Bureau of Chemistry Color Laboratory.

[2] Ebert and Merz, *Ber.*, **9**, 592 (1876).

[3] Armstrong, *Ber.*, **15**, 204 (1882).

[4] Armstrong and Wynne, *Proc. Chem. Soc.*, 1885–1895.