[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

p-Cymene Studies. VI. Vapor Pressure of *p*-Cymene, Some of its Derivatives and Related Compounds

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During the course of work on the nitration and halogenation of *p*-cymene the vapor pressures of the isomeric 2- and 3-compounds were desired to show the best pressures for separation by fractional distillation. The vapor pressure curve for *p*-cymene had been determined by Woringer,[1] but doubt has been cast on his work by Kassel[2] and Linder.[3] The data for *p*-cymene derivatives are over very short ranges or are boiling points at various reduced pressures. It was the purpose of this work to determine the complete vapor pressure curves for *p*-cymene, its important derivatives and some of the closely related compounds.

Method.—The isoteniscope method was employed for some of the compounds. The isoteniscope was modified (Fig. 1) by the addition of a tube A with stopcock B leading from the vapor trap D to the source of vacuum C. A vacuum pump was used which would give a pressure down to 2 mm. in the system. A 5-gallon bottle was used as a surge reservoir. The absolute manometer used was calibrated against the barometer of the U. S. Weather Bureau and was read to 0.1 mm. Readings were reduced to mm. mercury at 0°. The heating-baths for the isoteniscope were either oil or phosphoric acid which would give temperatures to 250°. The temperatures were measured with total immersion Anschütz type thermometers graduated in 0.2° and calibrated against a U. S. Bureau of Standards calibrated set. The bulb of the thermometer was adjacent to the vapor bulb D of the isoteniscope. Vapor pressure and temperature were measured on both descending and ascending pressures. For other compounds the method of Pickett[4] was used, which was modified by the use of a calibrated thermocouple instead of a resistance thermometer. The data were plotted on large scale log P *vs.* $1/T$ scales and the best straight line drawn through the points. The temperatures calculated from the equations given represent the best values within 0.1°. The deviation of the experimental points from the line rises to a maximum of 2% in the low pressure range.

Preparation of the Substances.—The substances, except where special mention is made, were the best available commercial compounds and in general were distilled three times in a vacuum, retaining the middle portion which had a boiling range from 0.1 to 0.5° depending upon the compound. *p*-Cymene was purified by the method of LeFèvre and co-workers.[5]

The methods of Doumani and Kobe were used for the preparation of 2-nitro,[6] 3-nitro,[7] 2-amino[8] and 3-amino-*p*-cymene.[7]

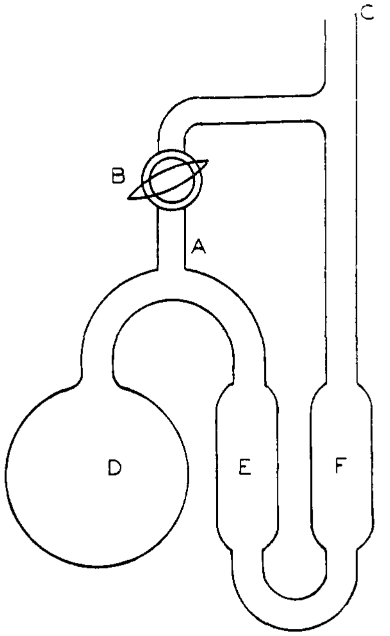

Fig. 1.

2-(and 3-)-hydroxy-*p*-cymene was the synthetic compound, obtained from Givauden-Delawanna, Inc. The carvacrol was steam distilled in alkaline solution to remove non-phenolic impurities, acidified and steam distilled from the solution. The oily liquid was diluted with ether, dried over calcium chloride and fractionated several times *in vacuo*. The product was water white and discolored very little during the determination. Satisfactory results could not be obtained with the isoteniscope because of the high viscosity of the carvacrol and the difficulty in degassing the liquid. Vapor pressures were determined by distilling the sample from a Claisen flask at a regulated pressure. Pressures and temperatures were measured with the same equipment. The temperature recorded was the mean of the fraction which distilled over a 0.2° range. The thymol was fractionated twice *in vacuo* and the middle portion taken.

2-(and 3-)Chloro-(and bromo)-*p*-cymene.—These were prepared by the action of phosphorus pentachloride or pentabromide on synthetic carvacrol (or thymol). The mixture was steam distilled, the oily layer washed with sodium carbonate solution followed by sulfuric acid, then washed with water. The washed product was diluted with

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[1] Woringer, *Z. physik. Chem.*, **34**, 257 (1900).

[2] Kassel, THIS JOURNAL, **58**, 670 (1936).

[3] Linder, *J. Phys. Chem.*, **35**, 531 (1931).

[4] Pickett, *Ind. Eng. Chem., Anal. Ed.*, **1**, 36 (1929).

[5] LeFèvre, LeFèvre and Robertson, *J. Chem. Soc.*, 480 (1935).

[6] Kobe and Doumani, *Ind. Eng. Chem.*, **31**, 257–263 (1939).

[7] Doumani and Kobe, THIS JOURNAL, **62**, 562–565 (1940).

[8] Doumani and Kobe, *Ind. Eng. Chem.*, **31**, 264–265 (1939).

ether, dried over calcium chloride and then fractionated *in vacuo*.

The data given in the literature for *p*-toluidine are reported here for the sake of completeness. These data were plotted and the line treated as an experimental line.

Results

The data obtained for *p*-cymene and cumene in this work give straight lines when plotted as log P *vs.* $1/T$. The data of Woringer[1] lie above these lines and give curves. This discrepancy has been reported for other compounds by Kassel[2] and by Linder.[3] The points obtained for these compounds by Linder at about 0° by the dynamic method lie slightly below the extrapolation of our straight line. The data of Kudryavtzev[9] give points considerably below the log P *vs.* $1/T$ line found in this work. For 2-nitro-*p*-cymene, the data of Mann, Montonna and Larian[10] fit exactly on the line from our data. For 2-amino-*p*-cymene their data lie below our line and a line through their points has a slope which differs considerably from ours and which leads to extraordinarily high values at higher pressures. The same thing is true of their values for methyl *p*-tolyl ketone, though their line differs less from ours than with the 2-amino-*p*-cymene. The *p*-nitrotoluene and *p*-toluidine are of importance as Kobe and Doumani[6,8] showed that in the nitration of *p*-cymene about 8% of the product was *p*-nitrotoluene accompanying the 2-nitro-*p*-cymene. This product could be reduced and the *p*-toluidine separated from the 2-cymidine. Our work on *p*-nitrotoluene substantiates the data of Berliner and May,[11] which are somewhat higher than those of Kahlbaum[12] and of Mann, Montonna and Larian[10] at low pressures. The data for *p*-toluidine were collated and those of Berliner and May[13] shown to agree well with Kahlbaum and be somewhat higher than the data of Mann, Montonna and Larian. The log P *vs.* $1/T$ plot for menthol shows a downward curvature at low pressures, necessitating a three constant equation. The boiling points, molal latent heats of vaporization, and vapor pressure equation constants are given in Table I.

TABLE I

Compound	B. p., °C., 760 mm.	L_v	Vapor pressure equation, log p =
p-Cymene	176.8	10,670	$-2{,}332/T + 8.063$
Cumene	152.6	9,950	$-2{,}175/T + 7.991$
2-Nitro-*p*-cymene	decomp.	14,100	$-3{,}075/T + 8.70$
3-Nitro-*p*-cymene	decomp.	12,900	$-2{,}820/T + 8.24$
2-Hydroxy-*p*-cymene	237.3	13,250	$-2{,}897/T + 8.556$
3-Hydroxy-*p*-cymene	232.5	12,750	$-2{,}787/T + 8.394$
2-Chloro-*p*-cymene	217.6	11,800	$-2{,}579/T + 8.138$
3-Chloro-*p*-cymene	217.1	11,270	$-2{,}463/T + 7.906$
2-Bromo-*p*-cymene	234.3	12,010	$-2{,}625/T + 8.053$
3-Bromo-*p*-cymene	234.1	11,500	$-2{,}525/T + 7.86$
p-Tolyl methyl ketone	224.4	12,440	$-2{,}719/T + 8.347$
p-Nitrotoluene	238.2	12,030	$-2{,}630/T + 8.025$
p-Toluidine	200.3	11,880	$-2{,}597/T + 8.366$
Carvone	229.0	12,320	$-2{,}694/T + 8.247$
Fenchone	193.2	10,820	$-2{,}366/T + 7.954$
Isopulegol	212.0	11,900	$-2{,}601/T + 8.243$
Menthol	216.5	12,050	$-4{,}695/T - 10.250 \log T + 40.033$

Summary

Vapor pressures have been determined for *p*-cymene, its important derivatives and some closely related compounds. Comparisons are made with the data in the literature.

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[9] Kudryavtzev, *J. Gen. Chem.* (U. S. S. R.), **4**, 563–566 (1934).

[10] Mann, Montonna and Larian, *Ind. Eng. Chem.*, **28**, 598–601 (1936).

[11] Berliner and May, THIS JOURNAL, **48**, 2630 (1926).

[12] Kahlbaum, *Z. physik. Chem.*, **26**, 624 (1898).

[13] Berliner and May, THIS JOURNAL, **49**, 1007 (1927).

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The Ultraviolet Absorption Spectra of the Monomethylchrysenes

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The effects of substitution and position isomerism on the ultraviolet absorption spectra of similarly constituted aromatic compounds have been studied by several investigators.[1,2,3,4] Brode[5] has shown that the substitution of a methyl radical in the ortho position of benzeneazophenol causes a decrease in the intensity of the absorption band, which can be correlated with the recent work of O'Shaughnessy and Rodebush[6] indicating a decrease in the intensity of the absorption band when steric hindrance is possible.

The recent interest in the carcinogenic activity of certain hydrocarbons has stimulated the development of methods for the synthesis of various types of these compounds, and made available

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[1] Baly, *J. Chem. Soc.*, **107**, 1058 (1915).

[2] Purvis, *ibid.*, **103**, 1088 (1913).

[3] Klingstedt, *Compt. rend.*, **175**, 365 (1922).

[4] De Laszlo, *Z. physik. Chem.*, **118**, 369 (1925).

[5] Brode, THIS JOURNAL, **51**, 1204 (1929).

[6] O'Shaughnessy and Rodebush, *ibid.*, **62**, 2906 (1940).