

846. Thermodynamic Properties of Organic Oxygen Compounds.
*Part XIV.*¹ *Purification and Vapour Pressures of Some Alkylphenols.*

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Samples of the following phenols have been prepared with purities greater than 99.9%: 3-ethyl-5-methyl-, 2,3,5-trimethyl-, *o*-s-butyl-, *p*-t-butyl-, and 3-methyl-6-t-butyl-. The purities of all the compounds have been measured by cryoscopic methods and the freezing points recorded. Vapour pressures of the first four compounds have been measured and Antoine equations have been fitted to the observations.

THE five phenols whose physical properties are reported in this Paper are industrial products; 3-ethyl-5-methyl- and 2,3,5-trimethyl-phenol have both been separated from low-temperature coal tars² and *o*-s-butyl-, *p*-t-butyl-, and 3-methyl-6-t-butyl-phenol are synthesized on a commercial scale for use as antioxidants and as intermediates for surface-coating resins.

The methods of purification of the phenols, and their purities, freezing points, and vapour pressures over the range 200—1000 mm. Hg are given in the Experimental section. Antoine equations, $\log_{10} P = A - B/(t + C)$, were fitted to the measured vapour-pressure values. The standard deviation of the differences between observed pressures and those calculated from the equations was ± 0.03 mm. Hg or less, for 3-ethyl-5-methyl-, 2,3,5-trimethyl-, and *o*-s-butyl-phenol. The accuracy of the measurements on *p*-t-butylphenol was lower (standard deviation of $P_{\text{obs}} - P_{\text{calc}}$ equalled ± 0.1 mm. Hg) and it was shown by gas-chromatographic analysis that some decomposition of this phenol had occurred during the ebulliometric measurements. The rate of decomposition of 3-methyl-6-t-butyl-phenol on boiling was so fast that it was not possible to measure the vapour pressure of this compound accurately.

¹ Part XIII, Biddiscombe, Handley, Harrop, Head, Lewis, Martin, and Sprake, *J.*, 1963, 5764.

² Kruber and Schmitt, *Ber.*, 1931, **64**, 2270.

Values for the freezing point and boiling points² of 3-ethyl-5-methyl- and 2,3,5-trimethyl-phenol and for the vapour pressures³ of 3-ethyl-5-methylphenol have been published, but differ appreciably from those now presented, which were obtained by modern methods of measurement on compounds of known high purity.

EXPERIMENTAL

Purification.—The starting materials for the preparation of the pure specimens were commercial products. 3-Ethyl-5-methylphenol was fractionally distilled without any preliminary chemical treatment but the other four phenols contained non-acidic material, which was removed by steam-distillation of alkaline solutions. Steam was passed through a boiling solution of the phenol (1 mole) and sodium hydroxide (1.5 moles) in water (4–5 l.) until non-acidic material no longer distilled. Small amounts of the phenols, particularly the weakly acidic 3-methyl-6-t-butylphenol, distilled in steam from the alkaline solution. The cooled alkaline solutions after steam distillation were acidified with 30% w/v sulphuric acid and the liberated phenols were separated and dried (CaSO₄). Small quantities of phenols, recovered from the acidified liquors by extraction with ether, were returned for further steam distillation. The dried phenols were distilled under reduced pressure (5 mm.) to remove any traces of water.

All the phenols except 3-methyl-6-t-butylphenol were fractionally distilled at a pressure of 50 mm. through columns of 45 theoretical plates and a reflux ratio of 50 : 1.^{4,5} Fractions with a boiling range of 0.5° were taken and the best, as shown by infrared spectroscopy, were combined. Final purification of the five phenols was carried out by fractional crystallization from the melt,⁵ by zone refining,⁶ or by both methods. In all operations on 3-methyl-6-t-butylphenol, it was essential to exclude all traces of moisture because this phenol readily forms a hydrate, C₁₁H₁₆O. $\frac{1}{4}$ H₂O, which has a higher melting point (37°) than that of the pure phenol (23.4°).

Four of the compounds yielded large, colourless crystals; 2,3,5-trimethylphenol, persistently developed a yellow colour after each melting operation. It was purified further by three recrystallizations from benzene–petroleum (b. p. 60–80°) (1 : 3), during which operation the boiling solution was treated with activated charcoal, followed by zone melting and fractional crystallization from the melt. Large, water-white transparent crystals were finally obtained. The pure samples were stored in the dark, either under vacuum or in a nitrogen atmosphere. The purities of the samples were measured by melting or freezing point techniques.^{7,8} The results are given in Table 1.

TABLE 1.
Purities and freezing points of the alkylphenols.

Phenol	Method	Purity (moles %)	Substance added as impurity	Depression produced by 1 mole % of impurity	F. p. of sample (<i>t</i>)	F. p. for 100% purity, (<i>t</i> , <i>s</i>)
3-Ethyl-5-methyl-	M. p.	99.921 ± 0.002°	1-Methyl-naphthalene	0.792 ± 0.033°	51.59 ± 0.01°	51.63 ± 0.01°
2,3,5-Tri-methyl-	M. p.	99.946 ± 0.005	Naphthalene	0.466 ± 0.042	93.71 ± 0.01	93.73 ± 0.02
<i>o</i> -s-Butyl-	M. p.	99.921 ± 0.002	1-Methyl-naphthalene	0.592 ± 0.012	16.02 ± 0.01	16.07 ± 0.01
<i>p</i> -t-Butyl-	F. p.	99.975 ± 0.001	1-Methyl-naphthalene	0.654 ± 0.008	99.54 ± 0.01	99.55 ± 0.01
3-Methyl-6-t-butyl-	M. p.	99.967 ± 0.012	2,2,4-Tri-methyl-pentane	0.645 ± 0.005	23.41 ± 0.01	23.43 ± 0.01

² Terres, Gebert, Hülsemann, Petereit, Toepsch, and Ruppert, *Brennstoff-Chem.*, 1955, **36**, 272.

⁴ Coulson and Herington, "Laboratory Distillation Practice," Newnes, London, 1958.

⁵ Andon, Biddiscombe, Cox, Handley, Harrop, Herington, and Martin, *J.*, 1960, 5246.

⁶ Herington, Handley, and Cook, *Chem. and Ind.*, 1956, 292; Herington, "Zone Melting of Organic Compounds," Blackwell, Oxford, 1963.

⁷ Herington and Handley, *J.*, 1950, 199.

⁸ Herington, *Analyt. Chim. Acta*, 1957, **17**, 15; Handley, *ibid.*, p. 115.

4406 *Properties of Organic Oxygen Compounds. Part XIV.*

Vapour Pressure-Temperature Relations, Normal Boiling Points, Value of (dP/dt) (at 760 mm.), and Enthalpies of Vaporization.—The measurement of vapour pressures by the ebulliometric method has been described.⁹ The experimental values of vapour pressure are given in Table 2

TABLE 2.

Vapour pressure of the alkylphenols (*t* in °C; *P* in mm. Hg at 0°C and standard gravity).

<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>
3-Ethyl-5-methylphenol							
195.082	248.05	215.581	450.03	229.550	651.04	240.440	852.57
201.372	299.99	219.456	499.96	232.279	697.57	242.656	899.02
206.593	349.47	222.985	549.16	235.080	748.03	244.794	945.71
211.388	400.55	226.374	600.03	237.858	800.86	247.169	999.77
2,3,5-Trimethylphenol							
186.482	199.12	214.675	449.83	229.041	651.63	240.130	851.97
193.614	247.68	218.644	499.72	231.852	698.43	242.511	900.75
200.127	300.05	222.382	550.67	234.759	749.61	244.811	949.92
205.448	349.23	225.707	599.37	237.500	800.58	247.062	1000.16
210.422	400.93						
o-s-Butylphenol							
178.735	199.09	206.860	448.86	221.317	650.92	232.465	851.05
185.796	247.21	210.886	499.28	224.159	698.02	234.936	901.32
192.314	299.57	214.558	549.07	227.163	750.59	237.136	948.05
197.770	349.95	218.023	599.58	229.890	801.03	239.512	1000.60
202.698	401.15						
p-t-Butylphenyl							
198.121	247.96	219.142	449.92	233.457	650.48	244.560	850.34
204.527	299.69	223.088	499.38	236.342	698.48	247.015	900.44
209.901	349.47	226.818	550.17	239.305	750.45	249.336	949.83
214.892	401.20	230.203	599.77	242.018	800.75	251.608	1000.24

TABLE 3.

Constants of Antoine equation, $\log_{10}P = A - B/(t + C)$; (*dP/dt* at 760 mm.); and molar enthalpies of vaporization.

Phenol	Temp. range	<i>A</i>	<i>B</i>	<i>C</i>	B. p./760 mm.	(<i>dP/dt</i> at 760 mm. (mm.Hg/°C))	Enthalpy of vaporization at 760 mm. Hg (cal./mole)
3-Ethyl-5-methyl-	195—247°	7.04025	1615.000	152.550	235.723°	18.748	12,250
2,3,5-Trimethyl-	186—247	7.08022	1685.973	166.150	235.329	18.305	11,940
o-s-Butyl-	178—239	6.95340	1594.781	163.099	227.680	18.198	11,480
p-t-Butyl-	198—251	6.99455	1623.046	154.716	239.83	18.245	12,080

and the calculated constants of the Antoine equations, the normal boiling points, the values of (*dP/dt*) at 760 mm., and the enthalpies of vaporization are listed in Table 3. The enthalpies of vaporization were calculated from the equation, $\Delta H = T(RT/P + B - V)dP/dT$. The values of *B*, the second virial coefficients of the vapours, were calculated from the Berthelot equation of state with estimated values of critical temperatures and critical pressures.¹⁰ The values assumed for the molar volumes of the liquids at their normal boiling points were: C₉H₁₂O, 171; C₁₀H₁₄O, 193 cm.³.

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⁹ Biddiscombe and Martin, *Trans. Faraday Soc.*, 1958, **54**, 1316.

¹⁰ Lydersen, "Estimation of Critical Properties of Organic Compounds by the Method of Group Contributions." University of Wisconsin, Engineering Experiment Station, Report No. 3, 1955; Ambrose, *Trans. Faraday Soc.*, 1963, **59**, 1988.