1099. *Thermodynamic Properties of Organic Oxygen Compounds. Part XIII.*[1] *Preparation and Physical Properties of Pure Ethylphenols.*

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Specimens of *o*-, *m*-, and *p*-ethylphenol have been purified to obtain samples of 99·9 moles % purity. Freezing points, vapour pressures up to 1000 mm., normal boiling points, densities, and heats of combustion have been measured. Latent heats of vaporisation and heats of formation have been calculated.

Previous publications [2,3] from this laboratory have described the purification of phenol, the cresols, and the xylenols, and the measurement of their physical properties. The work now reported is concerned with the three ethylphenols, which occur as constituents of coal tar.[4] Pure *o*- and *p*-ethylphenol were obtained from commercial samples, and the *m*-compound was synthesised and purified in this laboratory.[5] The purities of the samples were measured by freezing-point methods, vapour pressures by an ebulliometric method and by gas transpiration, and heats of combustion by static-bomb calorimetry.

Experimental

Purification.—The synthesis and purification of *m*-ethylphenol for this work have been reported.[5] Commercial samples were the starting materials for preparation of the pure *o*- and *p*-isomers by the following treatment. Steam was passed through a boiling solution containing 1 mole of the phenol and 1·75 moles of sodium hydroxide (10% aqueous solution) until no further non-acidic material distilled. The cooled residue was acidified with 30% v/v sulphuric acid. The liberated phenol was extracted with ether and washed with water, and the solution dried ($CaSO_4$). After removal of solvent, the phenol was distilled at a pressure of 100 mm. through a Stedman gauze-packed column equivalent to 45 theoretical plates,[3] and a series of fractions, with an overall boiling range of 0·5°, was collected at a reflux ratio of 50 : 1. On the evidence obtained by infrared spectroscopy the best fractions were combined, and further purified by fractional crystallisation from the melt,[3] by zone refining,[6] or by a combination of both freezing techniques. In the later stages of purification all samples were manipulated under dry nitrogen.

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[1] Part XII, Green, *Trans. Faraday Soc.*, 1963, **59**, 1559.
[2] Biddiscombe and Martin, *Trans. Faraday Soc.*, 1958, **54**, 1316.
[3] Andon, Biddiscombe, Cox, Handley, Harrop, Herington, and Martin, *J.*, 1960, 5246.
[4] Moehrle and Franck, *Brennstoff-Chem.*, 1949, **30**, 392; Kruber and Schmitt, *Ber.*, 1931, **64**, 2270.
[5] Connett and Ditcham, *J.*, 1962, 5301.
[6] Herington, Handley, and Cook, *Chem. and Ind.*, 1956, 292.

During fractional crystallisation from its melt, *o*-ethylphenol formed a " glass " readily on rapid undercooling, but, occasionally, cooling of the liquid to −30° gave a metastable crystalline form, m. p. ∼−28°; when kept for 24—48 hr., this changed into the stable crystalline form, m. p. −3·4°.

Physicochemical Measurements.—The values for the fundamental constants used in this work were: 0°c = 273·15°K; ***R*** = 1·98718 cal. deg.$^{-1}$ mole^{-1} = 8·31435 J deg.$^{-1}$ mole^{-1} = 0·082054 l. atm. deg.$^{-1}$ mole^{-1}; 1 cal. = 4·1840 J. The molecular weight of the ethylphenols (122·1683) was calculated from the 1961 Table of International Atomic Weights.

Freezing points, and the quantitative determination of purity. The results of measurements are given in Table 1. The purities of the compounds were established by a melting-point procedure.[7] Initial freezing points (t_f) and the freezing-point depressions produced by addition of measured amounts of 1-methylnaphthalene were found by means of a U-tube apparatus.[8] No freezing-point values could be obtained for *m*-ethylphenol because it became viscous on cooling and could not be induced to solidify without much undercooling.

TABLE 1.

Freezing constants for the ethylphenols.

Compound	Purity (moles %)	F. p. of sample (t_f)	F. p. for 100% purity ($t_{f,0}$)
o-Ethylphenol	99·94 ± 0·01	−3·36° ± 0·01°	−3·31° ± 0·01°
m-Ethylphenol	99·94 ± 0·02	—	—
p-Ethylphenol	99·97 ± 0·01	45·06 ± 0·01	45·08 ± 0·01

Vapour pressures, normal boiling points, values of (d*P*/d*t*), *and latent heats of vaporisation.* Vapour pressures from 200 to 1000 mm. were measured by an ebulliometric method,[2,9] and below 50° by a gas-saturation procedure.[2] The experimental values are given in Table 2. The experimental results for the higher pressure range were fitted to the Antoine equation,[10] $\log_{10}P = A - B/(t + C)$, by the method of least squares.[11] The equation, $\log_{10}P = A - B/(t + 273)$, was used to correlate data for the lower pressure range. In the least-squares

TABLE 2.

Vapour pressures of the ethylphenols.

t in °c; *P* in mm. Hg at 0° and standard gravity.

t	*P*	*t*	*P*	*t*	*P*	*t*	*P*	*t*	*P*
o-*Ethylphenol* (*liquid*)									
4·98°	0·0251	15·01°	0·0657	24·93°	0·153	34·84°	0·344	45·00°	0·772
10·00	0·0388	20·01	0·103	29·53	0·231	39·99	0·555		
150·425	153·45	176·174	349·73	192·115	549·31	204·350	756·71	212·651	929·64
158·137	199·08	180·808	400·46	195·266	597·82	206·632	801·55	215·149	987·39
164·876	247·49	184·869	449·63	198·382	649·01	208·429	838·22	218·047	1057·81
171·143	300·67	188·565	498·49	200·845	691·87	209·854	868·29		
m-*Ethylphenol* (*liquid*)									
4·96	0·0071	15·06	0·0197	25·05	0·0503	35·06	0·123	44·98	0·282
10·06	0·0116	20·05	0·0326	30·00	0·0811	40·02	0·194	49·98	0·424
172·071	199·14	194·711	400·23	209·302	599·72	220·520	801·37	229·592	1000·69
178·846	247·81	198·819	449·98	212·412	651·09	222·970	851·82		
184·980	299·82	202·582	499·82	215·101	698·21	225·213	900·11		
190·094	349·68	206·047	549·53	217·955	751·15	227·399	949·31		
p-*Ethylphenol* (*solid*)									
5·00	0·0036	15·00	0·0121	25·03	0·0372	35·00	0·107	43·97	0·256
10·00	0·0068	19·99	0·0211	30·02	0·0632	39·99	0·175		
(*liquid*)									
171·757	199·30	194·356	400·65	208·892	599·89	220·026	800·19	229·147	1000·72
178·525	248·04	198·419	450·03	211·911	649·75	222·543	852·06		
184·585	299·59	202·227	500·56	214·673	698·23	224·769	900·04		
189·724	349·80	205·607	549·13	217·535	751·37	226·933	948·71		

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[7] Herington, *Analyt. Chim. Acta*, 1957, **17**, 15; Handley, *Analyt. Chim. Acta*, 1957, **17**, 115.

[8] Herington and Handley, *J.*, 1950, 199.

[9] Herington and Martin, *Trans. Faraday Soc.*, 1953, **49**, 154.

[10] Thomson, *Chem. Rev.*, 1946, **38**, 1.

[11] Willingham, Taylor, Pignocco, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **35**, 219.

TABLE 3.

Constants of vapour-pressure equations, $\log_{10}P = A - B(t + C)$; (dP/dt); and molar latent heats of vaporisation at the normal boiling point and at 25°.

Compound	Temp. range	A	B	C
1. *o*-Ethylphenol	5—45°	10·3131	3313·50	273
	150—218	7·00742	1548·923	170·833
2. *m*-Ethylphenol	5—50	10·6342	3554·69	273
	172—230	7·04124	1571·995	159·427
3. *p*-Ethylphenol	5—44	12·6090	4183·81	273
	171—229	7·01297	1548·754	156·820

	B. p. at 760 mm.	(dP/dt) at 760 mm. (mm. Hg/°c)	Ht. of vaporisn. at 760 mm. (cal./mole)	(dP/dt) at 25° (mm. Hg/°c)	Ht. of vaporisn. at 25° (cal./mole)
1.	204·517°	19·238	11,500	0·01437	15,200
2.	218·417	19·268	12,150	0·005010	16,300
3.	217·985	19·294	12,150	0·004308	19,200

calculations, all observations were given equal weight. The constants for the vapour-pressure equations are given in Table 3. The differences between the observed and calculated pressure values satisfy tests for randomness.[12] The standard deviation of any one value of pressure is ±0·03 mm. The corresponding standard deviation for the low-pressure data is ±0·003 mm. Values for the normal boiling points, dP/dt at the normal boiling point and at 25°, and heats of vaporisation, uncorrected for deviations of the vapours from the ideal-gas laws, are also given in Table 3.

The vapour-pressure results listed in Table 2 differ considerably (by 4—59 mm. at the normal boiling point) from values, published previously, obtained on samples of undefined purity.[13]

Densities. The densities of liquid *o*- and *m*-ethylphenol were measured at 20° and 30° in a modified Sprengel–Ostwald pycnometer [14] and that of solid *p*-ethylphenol at 25° in a flask-type pycnometer with mercury as the confining liquid.[3] The results and the coefficients of cubical expansion are shown in Table 4.

TABLE 4.

Densities of the ethylphenols.

Compound	d_{20} (g./ml.)	d_{30} (g./ml.)	d_{25} (g./ml.) *	α_{25} †
o-Ethylphenol	1·01885 ± 0·00001	1·01033 ± 0·00001	1·01459	0·000840
m-Ethylphenol	1·01143 ± 0·00000	1·00374 ± 0·00001	1·00758	0·000764
p-Ethylphenol	—	—	1·054 ± 0·001	—

* $d_{25} = 0·5(d_{20} + d_{30})$. † $\alpha_{25} = 0·2(d_{20} - d_{30})/(d_{20} + d_{30})$.

Heats of combustion. The heats of combustion were measured using the static-bomb calorimeter previously described.[15] The energy equivalent (17134·3 J deg.$^{-1}$; standard deviation of the mean, ±1·1 J deg.$^{-1}$ on eight observations) was determined in terms of electrical standards.[16] Temperature measurements were made with a platinum resistance thermometer in conjunction with a Smith No. 3 resistance bridge.

The ethylphenols are hygroscopic and the samples for a combustion experiment were therefore sealed in polyethylene bags by the technique already described.[3] The energy of combustion of the polyethylene film was determined in a separate series of experiments. The value obtained ($-\Delta U_c{}^\circ = 46394·4 \pm 14·8$ J g.$^{-1}$) differs slightly from that for the sample used in earlier work.[3]

Before each combustion experiment, 1 ml. of water was added to the bomb (volume 0·297 l.) which was filled with purified oxygen to a pressure of 30·95 atm. (25°). After each experiment, in which the final temperature of the calorimeter was within the range 24·7—25·0°, the liquid

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[12] Bennett, *Ind. Eng. Chem.*, 1951, **43**, 2063.

[13] Pardee and Weinrich, *Ind. Eng. Chem.*, 1944, **36**, 595; Terres, Gebert, Hülsemann, Petereit, Toepsch, and Ruppert, *Brennstoff-Chem.*, 1955, **36**, 272.

[14] Biddiscombe, Coulson, Handley, and Herington, *J.*, 1954, 1957.

[15] Cox, Challoner, and Meetham, *J.*, 1954, 265.

[16] Challoner, Gundry, and Meetham, *Phil. Trans.*, 1955, **247**, 553; Gundry and Meetham, *Trans. Faraday Soc.*, 1958, **54**, 664.

in the bomb was analysed for nitric acid. No evidence for the formation of nitrophenols was found (cf. ref. 3). The combustions were normally clean and the amounts of soot negligibly small: only one experiment out of eighteen was rejected because the quantity of soot was significant.

In the majority of combustion experiments the carbon dioxide in the bomb gases was determined. When allowance was made for the combustion of polyethylene, which was shown to yield 99·97% of the carbon dioxide calculated from the formula $(CH_2)_n$, good agreement with the theoretical value was obtained for the solid *p*-isomer (99·98%), but the values for liquid *o*- and *m*-ethylphenol differed from 100% by more than the experimental uncertainty of $\pm$0·02%. The values for the percentage recovery of carbon dioxide were reproducible for both compounds (*o*- 99·904%, standard deviation of the mean $\pm$0·010%, 5 determinations; *m*- 99·950%, standard deviation of the mean $\pm$0·008%, 4 determinations). Therefore the low values are probably due not to incomplete combustion but rather to absorption of moisture during sealing into bags or weighing, even though operations involving exposure of the phenols to air were conducted in a dry-box with normal precautions. In calculation of the energy evolved per unit mass burnt, the mass of sample taken for each combustion was corrected to the actual mass of ethylphenol burnt, by use of the mean value of the yield of carbon dioxide from each compound, referred to above.

Values of the standard energy of combustion, $-\Delta U_c^\circ$, are reported in absolute joules per gram. For the correction of weights in air to weights *in vacuo* the densities shown in Table 4 for the phenols, and the value 0·92 g. ml.$^{-1}$ for polyethylene, were used. The results of the combustion experiments are presented in Table 5, where the symbols have the following meanings: Δt = corrected temperature rise, q_p = energy evolved in the combustion of polyethylene, q_{HNO_3} = energy evolved in formation of nitric acid, q_s = energy correction to standard states.[17] The electrical energy supplied to the calorimeter during firing had been shown previously to be 0·6 J.[18]

TABLE 5.

Energies of combustion of the ethylphenols.

Mass of sample (g.)	Mass of polyethylene (g.)	Δt(°C)	Total energy evolved (J)	q_p (J)	q_{HNO_3} (J)	q_s (J)	$-\Delta U_c^\circ$ (J/g.)
			o-*Ethylphenol* (*liquid*)				
0·79095	0·07847	1·86042	31880·5	3640·5	6·5	17·3	35707·4
0·75086	0·07439	1·76571	30258·1	3451·2	3·4	16·3	35708·9
0·77502	0·07738	1·82536	31278·6	3590·0	3·5	16·9	35733·5
0·78962	0·08964	1·88883	32367·2	4158·7	18·1	17·3	35712·8
0·79001	0·07709	1·85520	31790·5	3576·5	17·2	17·3	35703·3
0·77773	0·07545	1·82624	31294·1	3500·6	12·5	16·8	35732·6
						Mean =	35716·4
			m-*Ethylphenol* (*liquid*)				
0·76841	0·07618	1·80717	30967·7	3534·1	7·4	16·5	35687·7
0·77240	0·07458	1·80957	31007·7	3460·2	3·5	16·7	35655·7
0·72011	0·07666	1·70684	29247·7	3556·6	3·6	15·6	35667·0
0·78570	0·07736	1·84551	31623·6	3589·3	3·8	17·3	35670·9
0·78500	0·07619	1·84063	31541·0	3535·0	3·7	17·0	35667·1
0·73934	0·07579	1·74515	29905·6	3516·3	3·8	16·3	35682·9
						Mean =	35671·9
			p-*Ethylphenol* (*solid*)				
0·80973	0·07933	1·89917	32544·7	3680·3	34·7	17·9	35588·4
0·81991	0·08056	1·92254	32946·0	3737·6	17·0	17·9	35587·7
0·82532	0·08103	1·93448	33159·1	3759·4	15·1	16·3	35590·5
0·76766	0·08240	1·81866	31162·4	3822·9	8·6	16·9	35587·2
0·77349	0·08012	1·82470	31267·0	3717·3	7·9	17·1	35591·4
						Mean =	35589·0

From the energies of combustion have been calculated the corresponding standard molar energies of combustion, standard molar heats of combustion, and heats of formation of the phenols in the standard state and in the gaseous state at 25°. The values are presented in

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[17] Hubbard, Scott, and Waddington, " Experimental Thermochemistry," Interscience, New York, 1956, Vol. I, Ch. 5.

[18] Gundry, Head, and Lewis, *Trans. Faraday Soc.*, 1962, **58**, 1309.

Table 6; the known heats of formation [19] of carbon dioxide and of water, and the latent heats of vaporisation shown in Table 3, were used in the calculations. An uncertainty interval equal to twice the overall standard deviation of the mean has been ascribed to the values of energy and heat of combustion. This includes the standard deviations of the means from the combustion experiments (*o*- ±0·015%, *m*- ±0·013%, *p*- ±0·0023%), the electrical calibration experiments (±0·0063%), and the carbon dioxide determinations (see above), and the errors associated with certain correction factors in determinations of the electrical equivalent.[16] The uncertainties in the heats of formation include uncertainties in the heats of formation of carbon dioxide and of water,[19] and in the latent heats of vaporisation.

TABLE 6.

Energies and heats of combustion and formation of the ethylphenols.

Compound	$-\Delta U_c^\circ$ (kcal. mole^{-1})	$-\Delta H_c^\circ$ (kcal. mole^{-1})	$-\Delta H_f^\circ$ (kcal. mole^{-1})	$-\Delta H_f^\circ$ (g.) (kcal. mole^{-1})
o-Ethylphenol...	1042·88 ± 0·42	1044·07 ± 0·42	49·92 ± 0·43	34·75 ± 0·48
m-Ethylphenol..	1041·58 ± 0·37	1042·77 ± 0·37	51·22 ± 0·38	34·94 ± 0·40
p-Ethylphenol...	1039·16 ± 0·22	1040·35 ± 0·22	53·64 ± 0·24	34·48 ± 0·27

The uncertainties associated with the calibration experiments are common to the values obtained for all three compounds. When allowance is made for this, the difference between the heats of formation in the gaseous state of *m*- and *p*-ethylphenol is just significant. It may be noted that the order of stability, $m > o > p$, is the same as that reported for the isomeric cresols, where the differences between heats of formation are greater.[3] The mean value of ΔH_f°(gas) for ethylphenol (−34·7 kcal. mole^{-1}) is in fair agreement with that (−35·9 kcal. mole^{-1}) predicted by a recently postulated bond-energy scheme.[20] No values for the heats of combustion of the ethylphenols have been previously published.

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[19] Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

[20] Cox, *Tetrahedron*, 1962, **18**, 1337.