207. *The Relative Strengths of Certain Monohydric Phenols in Aqueous-alcoholic Solution.*

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All previous work on the relative acidities of the phenols has been carried out in aqueous solution (Hantzsch and Farmer, *Ber.*, 1899, **32**, 3066; Bader, *Z. physikal. Chem.*, 1890, **6**, 290; Raikow, *Chem. Ztg.*, 1903, **27**, 781). Boyd (J., 1915, **107**, 173, 1538) drew up a comparative list of acidities by using the sodium phenoxide–methyl acetate reaction and applying Shields's equation (*Z. physikal. Chem.*, 1893, **12**, 167), but his results were at variance with those obtained by some of the previous workers. No attempt has hitherto been made to study the relative acidities in aqueous-alcoholic solution, yet Robertson and Acree (*J. Physical Chem.*, 1915, **19**, 381) found very marked deviations in the behaviour of the phenoxides of sodium and potassium in ethyl alcohol as compared with results obtained in aqueous solution.

The method adopted in this work was to compare the relative reactivities of the potassium salts of the various monohydric phenols towards ethyl acetate, propionate, and butyrate under exactly analogous conditions. Three esters were used in order to have a countercheck of the results obtained with one ester with those obtained when using another, for since the reactivity of the potassium salt is dependent upon the extent of hydrolysis of the phenoxide employed, the latter may be assumed to be the same no matter which ester is used, provided that there is no material change in the solvent medium.

By application of the formulæ shown in the preceding paper, composite velocity constants [*Kk*] were calculated. The reaction were carried out at 60° with *N*/4-potassium phenoxide and *N*/2-ester in ethyl alcohol with addition of 5% of water. The potassium salts of α- and β-naphthol were also examined and are included in Table I.

Table I.

Potassium salt of	Value of $Kk \times 10^6$ for ethyl ester.			Potassium salt of	Value of $Kk \times 10^6$ for ethyl ester.		
	Acetate.	Propionate.	Butyrate.		Acetate.	Propionate.	Butyrate.
*iso*Eugenol	0·289	0·157	0·084	*p*-Xylenol	2·22	1·09	—
Guaiacol	0·352	0·201	0·124	*o*-3-Xylenol	—	1·54	0·842
Eugenol	0·480	0·273	0·147	*m*-4-Xylenol	3·05	1·65	0·887
Phenol	0·488	0·273	0·153	Carvacrol	3·32	1·82	1·05
o-Ethylphenol	0·752	0·423	0·227	*ψ*-Cumenol	4·09	2·24	1·22
m-Cresol	0·788	0·403	0·257	Thymol	5·06	2·77	1·45
p-Cresol	1·02	0·590	0·376	α-Naphthol	0·237	0·140	0·0789
o-4-Xylenol	1·42	0·772	0·435	*β*-Naphthol	0·295	0·161	0·0914
o-Cresol	1·66	0·940	0·507				

Since the equilibrium constant *K* has the same value irrespective of the ester used, provided the same phenoxide is employed, $R{\cdot}OK + H_2O \rightleftharpoons KOH + R{\cdot}OH$, it is possible to obtain the reactivity factors of the esters concerned. These are shown in Table II.

The values of *Kk* did not, in general, vary beyond the limits of experimental error, and it may be assumed, therefore, that all the monohydric phenols examined follow precisely the same course as *o*-cresol (see preceding paper) in their reactions with the aliphatic esters.

Relative Acidities of the Phenols.—The composite velocity constants obtained by application of the formulæ are the product of the equilibrium constant *K* and the velocity constant of saponification of the ester *k*. Now, in any series of reactions carried out under analogous conditions, with different phenoxides but with the same ester throughout, *k* will have a

TABLE II.

Potassium salt of	$\frac{[Kk]_{\text{Acetate}}}{[Kk]_{\text{Butyrate}}}$.	$\frac{[Kk]_{\text{Propionate}}}{[Kk]_{\text{Butyrate}}}$.	Potassium salt of	$\frac{[Kk]_{\text{Acetate}}}{[Kk]_{\text{Butyrate}}}$.	$\frac{[Kk]_{\text{Propionate}}}{[Kk]_{\text{Butyrate}}}$.
α-Naphthol	3·0	1·8	*p*-Cresol	2·7	1·6
*iso*Eugenol	3·4	1·9	*o*-Cresol	3·2	1·8
β-Naphthol	3·2	1·8	*o*-4-Xylenol	3·2	1·8
Guaiacol	2·9	1·7	*o*-3-Xylenol	—	1·8
Eugenol	3·3	1·9	*p*-Xylenol	—	1·9
Phenol	3·2	1·8	Carvacrol	3·1	1·7
o-Ethylphenol	3·3	1·8	ψ-Cumenol	3·2	1·9
m-Cresol	3·1	1·6	Thymol	3·5	1·9
			Mean	3·2	1·8

common value; therefore under these conditions $[Kk]_A/[Kk]_B = [K]_A/[K]_B$, where $[K]_A$ and $[K]_B$ are the equilibrium constants for two different phenoxides.

The equilibrium constants are directly related to the extent of hydrolysis of the phenoxides, and hence to the degree of acidity of the phenols in question. Taking the equilibrium constant for potassium phenoxide as the standard for $[K]_B$ in each case, the relative acidic values $[K]_A/[K]_B$ of the phenols examined are as given in Table III.

TABLE III.

Phenol.	Values of $[K]_A/[K]_B$ in reaction with Acetate.	Propionate.	Butyrate.	Mean.
α-Naphthol	0·48	0·51	0·51	0·50
*iso*Eugenol	0·59	0·58	0·55	0·57
β-Naphthol	0·60	0·59	0·59	0·59
Guaiacol	0·72	0·75	0·81	0·75
Eugenol	0·98	1·00	0·97	0·98
Phenol	(1·00)	(1·00)	(1·00)	(1·00)
o-Ethylphenol	1·54	1·55	1·49	1·53
m-Cresol	1·61	1·50	1·67	1·59
p-Cresol	2·09	2·17	2·45	2·23
o-4-Xylenol	2·91	2·83	2·84	2·86
o-Cresol	3·40	3·46	3·31	3·39
p-Xylenol	4·40	4·30	—	4·35
o-3-Xylenol	—	5·64	5·51	5·58
m-4-Xylenol	6·25	6·05	5·80	6·03
Carvacrol	6·80	6·70	6·80	6·80
ψ-Cumenol	8·39	8·21	8·00	8·20
Thymol	10·36	10·20	9·50	10·02

Percentage Hydrolysis of the Phenoxides.—The equilibrium condition is given by $[K] = [\text{R·OH}][\text{KOH}]/[\text{R·OK}][\text{H}_2\text{O}]$. The phenoxide concentrations throughout were $N/4$, and the water was 5% by volume. If the extent of hydrolysis of any one phenoxide is expressed as z milliequivs. per l., then for any two phenoxides A and B we may write

$$\frac{[K]_A}{[K]_B} = \frac{[z_A]^2(250 - z_B)(2778 - z_B)}{[z_B]^2(250 - z_A)(2778 - z_A)} = \frac{[z_A]^2}{[z_B]^2}\text{ approx.}$$

Hence, $\sqrt{[K]_A/[K]_B} = z_A/z_B = r = p_A/p_B$, where r is the ratio value, and p_A and p_B represent the percentage hydrolysis of the respective phenoxides. By using the mean values from Table III and taking the percentage hydrolysis of potassium *o*-tolyloxide as 4·9 (p. 995), Table IV has been calculated to show the approximate percentage hydrolysis values (p) of the potassium salts of the given phenols.

TABLE IV.

Potassium salt of	r.	p.	Potassium salt of	r.	p.
α-Naphthol	0·707	1·88	*o*-4-Xylenol	1·69	4·5
*iso*Eugenol	0·753	2·02	*o*-Cresol	1·84	(4·9)
β-Naphthol	0·768	2·04	*p*-Xylenol	2·08	5·5
Guaiacol	0·866	2·3	*o*-3-Xylenol	2·36	6·3
Eugenol	0·99	2·6	*m*-4-Xylenol	2·46	6·5
Phenol	(1·00)	2·7	Carvacrol	2·61	6·9
o-Ethylphenol	1·24	3·3	ψ-Cumenol	2·86	7·6
m-Cresol	1·26	3·3	Thymol	3·16	8·4
p-Cresol	1·49	4·0			

α- and β-Naphthoxides followed the same course in their reactions with the aliphatic esters as the potassium salts of the ordinary monohydric phenols. Both are feebly acidic but α-naphthol is the stronger. Catechol monomethyl ether, which gave a dull green, sparingly soluble potassium salt in ethyl-alcoholic solution, likewise reacted normally and behaved as an ordinary monohydric phenol, the methoxy-group apparently increasing the acidity of the phenolic nucleus.

The change from eugenol to *iso*eugenol causes increased acidity. Throughout the series the acidity of the phenolic nucleus is rapidly decreased by accumulation of alkyl groups. The effectiveness of the alkyl groups in decreasing the acidity is in the order ethyl, methyl, *iso*propyl, and the positional effectiveness of the methyl groups in decreasing the acidity diminishes in the order $o > p > m$.

In simple cases, substitution of methyl groups in the nucleus has an approximately additive effect on the extent of hydrolysis of the phenol; *e.g.*, from the values of r (Table IV), the extent to which the comparative hydrolysis is increased by the introduction of methyl ortho, para, and meta to hydroxyl is 0·84, 0·49, and 0·26, respectively. From these values the relative extent of hydrolysis of the xylenols may be built up additively, thus :

		Calc.	Found.
p-Xylenol	considered as phenol + o-CH_3 + m-CH_3 =	2·10	2·08
m-4-Xylenol	,, ,, ,, ,, ,, + p-CH_3 =	2·33	2·46
o-3-Xylenol	,, ,, ,, ,, ,, + m-CH_3 =	2·10	2·36
o-4-Xylenol	,, ,, ,, ,, m-CH_3 + p-CH_3 =	1·75	1·69

That the groups exercise a mutual influence on each other, however, is clearly shown in the case of *o*-3-xylenol, and in *ψ*-cumenol the mutual influences are so strong that it is not possible to obtain even an approximate additive value for the comparative hydrolysis, by a consideration of the group values obtained either from the xylenols or from the cresols.

EXPERIMENTAL.

The solutions of esters and phenoxides were prepared as described on p. 995. Some difficulty was experienced in choosing a suitable indicator. Litmus was satisfactory in the majority of cases, but not with guaiacol, eugenol, and *iso*eugenol solutions, which turned bluish-green on the addition of the indicator; potassium *o*-3-xylyloxide gave a green solution. For these cases phenol-red was satisfactory. The alcoholic solution of potassium β-naphthoxide (small plates, m. p. 39°), when fresh, was a faint golden brown, but on keeping turned through brown to dark green. With this salt the titrating acid must be kept at a suitable concentration, otherwise β-naphthol separates and interferes with the colour change of the end-point. Potassium *iso*eugenoxide is sparingly soluble in alcoholic solution but more soluble in water. On addition of potassium ethoxide to *iso*eugenol in alcohol, the mixture sometimes sets to a pink pasty mass which slowly redissolves on shaking and further addition of alcohol : the reaction is pronouncedly exothermic.

The potassium salt of eugenol (prismatic crystals, m. p. 127°) and that of guaiacol (needle-shaped crystals, m. p. 167°) are sparingly soluble in ethyl alcohol, but the latter is more soluble in water.

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