CLXXIII.—*The Hydrolysis of Sodium Phenoxides in Aqueous Solution.*

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SURPRISINGLY little is known with regard to the relative acidities of the various alkyl-substituted phenols. The dissociation constant for phenol has been determined by Walker (*Zeitsch. physikal. Chem.*, 1900, **32**, 137) and by Lundén (*ibid.*, 1910, **70**, 249). Hantzsch and Farmer (*Ber.*, 1899, **32**, 3066) have determined the dissociation constants for certain negatively-substituted phenols (chloro-, cyano-, and nitro-phenols), and measured the degrees of hydrolysis of the sodium salts of these phenols in aqueous solution. The only data, however, bearing upon the question of the comparative acidities of different alkyl-substituted phenols appear to be those due to Bader (*Zeitsch. physikal. Chem.*, 1890, **6**, 290), and some facts of a qualitative character ascertained by Raikow (*Chem.*

Zeit., 1903, **27**, 781). Bader measured the conductivities of aqueous solutions of a variety of phenols at 25°, and obtained some very remarkable results. According to Bader's data, all the cresols are stronger acids than phenol; *o*-cresol is more acidic than *o*- or *p*-chlorophenol; *o*-isobutylphenol is much more strongly acidic than *o*-cresol. Hantzsch (*loc. cit.*) has already questioned the accuracy of Bader's figures, which on general grounds appear improbable; they are, however, still quoted.

Raikow, on the other hand, finds that whilst *o*- and *m*-cresols are less acidic than phenol, *p*-cresol is a stronger acid. Raikow's method, however, is open to criticism, at least in its application to *p*-cresol. The supposed greater acidity of *p*-cresol was deduced from the fact that when a small quantity of solid potassium carbonate was added to an emulsion of *p*-cresol in a saturated solution of this salt, the liquid on shaking became clear, with separation at the same time of crystals of potassium *p*-tolylloxide. A similar emulsion of phenol is not affected on shaking with solid potassium carbonate. This difference of behaviour is, however, in all probability due merely to the comparative insolubility of potassium *p*-tolylloxide in a saturated potassium carbonate solution, and not, as supposed by Raikow, to greater acidity on the part of *p*-cresol.

From the results of some experiments recently carried out on the combination of sodium phenoxides with olefine oxides (Boyd and Marle, T., 1914, **105**, 2117), it appeared probable that all alkyl-substituted phenols are less acidic than phenol itself, and the experiments described in the present communication were instituted with the object of determining the correctness, or otherwise, of this view, and at the same time of ascertaining to what extent the position and character of the alkyl group affect the acidity of the phenol.

The method adopted for estimating the degree of hydrolysis of the sodium phenoxides was that of Shields (*Zeitsch. physikal. Chem.*, 1893, **12**, 167). In order that the results might be the more closely comparable with those obtained by Hantzsch and Farmer for negatively substituted phenols, the hydrolysis was measured, where possible, in *N*/32-solution. In some cases, however, the sparing solubility of the phenol made it necessary to employ solutions of much lower concentration. From the results obtained with these more dilute solutions, the degree of hydrolysis at V_{32} can be calculated approximately by means of the formula

$$\frac{x^2}{(1-x)V} = K_h,$$

where x represents the fraction hydrolysed at dilution V , and K_h

is the hydrolysis constant. When this formula, however, was tested by experiments made with phenol and certain of the xylenols, it was found that the values calculated for the hydrolysis at V_{100} or V_{200} from observations made at V_{32} were always greater than those actually observed; in other words, the hydrolysis constant was found to diminish somewhat with increasing dilution. A more satisfactory agreement between observed and calculated values was obtained by using the formula

$$\frac{x^2}{(1-x)V^{\frac{1}{2}}} = \text{constant},$$

and accordingly this formula has been employed in cases where direct observation of the hydrolysis at V_{32} was not possible.

The following table contains a summary of the results which have been obtained.

Relative Acidities of Phenols at 25°.

Phenol.	K_h at V_{32} .	Percentage hydrolysis at V_{32} .	K_a .
Guaiacol	0.000103	5.58	1.17×10^{-10}
Phenol	0.000104	5.60	1.15×10^{-10}
<i>m</i> -Cresol	0.000123	6.08	0.98×10^{-11}
<i>p</i> -Cresol	0.000178	7.27	0.67×10^{-10}
<i>o</i> -Cresol	0.000192	7.54	0.63×10^{-10}
<i>o</i> -4-Xylenol ...	0.000233	8.28	0.52×10^{-10}
<i>p</i> -Xylenol	0.000251	8.57	0.48×10^{-10}
Carvacrol	0.000267	8.83	0.45×10^{-10}
<i>m</i> -6-Xylenol ...	0.000352	10.07	0.34×10^{-10}
Thymol	0.000373	10.34	0.32×10^{-10}
ψ -Cumenol	0.000422	10.96	0.28×10^{-10}
Mesitol	0.000694	13.83	0.17×10^{-10}

In column 1 are given the hydrolysis constants, K_h , for the sodium phenoxides at 25° and V_{32} dilution. In the case of carvacrol, thymol, ψ -cumenol, and mesitol, the value for K_h was not obtained directly, but is calculated from the degree of hydrolysis of the sodium phenoxide by means of the formula

$$\frac{x^2}{(1-x)V} = K_h.$$

In column 2 are given the degrees of hydrolysis of the sodium phenoxides at V_{32} , the values for carvacrol, thymol, ψ -cumenol, and mesitol being calculated, as explained above, from data obtained with solutions of greater dilution by means of the formula

$$\frac{x^2}{(1-x)V^{\frac{1}{2}}} = \text{constant}.$$

Column 3 contains the dissociation constants, K_a , for the free phenols in aqueous solution at 25°, calculated from the hydrolysis

constants, according to the equation $K_a = \frac{K_w}{K_h}$; K_w , the dissociation constant of water, being taken equal to 1.2×10^{-14} .

The value for the dissociation constant of phenol obtained in this way from the hydrolysis constant measured at V_{32} is 1.15×10^{-10} . Walker (*loc. cit.*) found 1.3×10^{-10} , and Lundén (*loc. cit.*) found 0.97×10^{-10} . It may be remarked, however, that if one calculates the dissociation constant of phenol from the hydrolysis constant measured at V_{101} , namely, 0.0000875, one obtains the value 1.37×10^{-10} . The mean of the values 1.15×10^{-10} and 1.37×10^{-10} (1.26×10^{-10}) agrees well with Walker's value.

A consideration of the data summarised in the table leads to the following conclusions:

- (1) The acidity of phenol is diminished by the introduction of alkyl groups.
- (2) The alkyl group is most effective when in the ortho-position with respect to the hydroxyl group, slightly less effective in the para-position, and much less effective in the meta-position. This rule applies to dialkyl and trialkyl derivatives of phenol as well as to the cresols.
- (3) An isopropyl group in the ortho-position acts much more strongly than a methyl group in the same position, but there is very little difference between the effectiveness of the two groups when they occupy meta-positions with respect to the hydroxyl group.
- (4) The introduction of a methoxy-group in the ortho-position scarcely alters the acidity of phenol.

From the figures obtained for ortho-, meta-, and para-placed methyl groups in the case of the cresols, it is possible to calculate rough values for the degrees of hydrolysis of the dimethyl- and trimethyl-substituted phenols. The values so obtained are always less than those actually observed, but the difference is particularly noticeable in the case of mesitol.

Such an exaltation of the effect of the individual methyl groups, owing to the peculiar grouping which occurs in mesitol, is perhaps not surprising. It is, however, desirable to notice in this connexion a peculiar observation which was made in the course of the experiments with mesitol.

Mesitol dissolves in an equivalent quantity of a cold, dilute solution of sodium hydroxide to give a colourless solution, but it was found that after the dilute ($N/100$) sodium mesityloxyde solution had been kept in the thermostat at 25° for about an hour it showed a distinct pink colour. If such a dilute solution is heated to boiling, the colour gradually becomes an intense rose-red, so

that the appearance of the liquid resembles that of an alkaline solution to which a little phenolphthalein has been added. On cooling, the red colour persists for some time, but it gradually diminishes in intensity. The coloration again becomes strong if the liquid is once more boiled.

It was at first supposed that this phenomenon must be due to the presence of some impurity in the specimen of mesitol employed, since it seemed unlikely that such a striking property, if possessed by mesitol, could have escaped the notice of previous workers with this substance. The mesitol in question had been prepared from a specimen of mesidine (Schuchardt), boiling at $232-233^{\circ}$, from which a benzoyl derivative, melting at $202-203^{\circ}$ (uncorr.), had been prepared. (Bamberger and Rising [*Ber.*, 1900, **33**, 3637] give 200.5° as the melting point of the benzoyl derivative of mesidine.)

It melted at $72-72.5^{\circ}$, boiled at $221-222^{\circ}$, and showed, in general, the characteristics of a pure substance. It was, however, redistilled after the observation above referred to had been made. It was then found to boil constantly at 221° . On testing a portion of this redistilled sample with dilute sodium hydroxide solution, the same intense red coloration was obtained on boiling.

In order to leave no doubt as to the identity of the mesitol, its phenylurethane was prepared by heating for some hours with phenylcarbimide. In agreement with the description of Auwers (*Ber.*, 1899, **32**, 19), the product formed fine needles, melting at $140-142^{\circ}$. It would appear, therefore, that the property of giving a red coloration on heating with dilute sodium hydroxide solution is one possessed by pure mesitol. The reason why this property has not hitherto been observed is probably to be found in the fact that the colour is not developed strongly except in dilute solutions, and is destroyed on addition of a considerable excess of sodium hydroxide. Further investigation showed that some chemical transformation accompanies the production of the red colour, for if the dilute solution is boiled until no more mesitol escapes, the red colour is not destroyed, and if the solution is now concentrated, acidified, and extracted with ether, an oily product is obtained, which is not mesitol.

The nature of the chemical change involved is now under investigation. At present it is not possible to express any definite opinion on this point, or as to whether the process proceeds with sufficient rapidity at 25° to produce any appreciable effect on the value obtained for the degree of hydrolysis of sodium mesityloxide at that temperature by the application of the methyl acetate method.

EXPERIMENTAL.

Shields (*loc. cit.*) deduced the equation

$$K_h = \frac{C_0}{C - C_0} \log \text{nat.} \frac{C_2 - x_0}{C_0 - x_1} - \frac{C}{C - C_0} \log \text{nat.} \frac{C - x_0}{C - x_1},$$

$$k(t_1 - t_0)$$

where K_h is the hydrolysis constant, C_2 is the concentration of the sodium phenoxide, C the concentration of the methyl acetate, x the concentration of the sodium acetate which has been formed at time t , and k is the velocity constant for the saponification of methyl acetate by sodium hydroxide. This equation does not hold until the reaction has proceeded so far that the magnitude of A , the amount of free sodium hydroxide present at time t on account of the hydrolysis of the sodium phenoxide, is negligible in comparison with the value of x . Hence, in the case of dilute solutions of the salts of very feebly acidic phenols, where the hydrolysis amounts to between 20 and 30 per cent., the value of the expression does not become constant until about four-fifths of the sodium phenoxide has reacted with the ester.

The value of k for methyl acetate and sodium hydroxide at 25° was found by Hantzsch and Farmer to be 10·2, and this figure has been used in calculating the hydrolysis constants. In the following tables, the concentrations of the sodium phenoxide and of the methyl acetate are given in 0·001 gram-molecule per litre, unless otherwise stated. The time is given in minutes.

Phenol.

(1) $V=32$.

Time.	$C_2 - x$.	$C - x$.	K_h .
0	31·25	110·9	—
10	24·15	103·8	(0·0000902)
21	20·84	100·5	0·000104
33	18·90	98·55	0·0000983
53	16·15	95·80	0·000104
74	14·36	94·01	0·0000999
96	12·53	92·18	0·000104
120	10·90	90·55	0·000107
144	9·76	89·41	0·000107
168	8·85	88·50	0·000106
195	7·91	87·56	0·000106

Mean = 0·000104

Therefore A (concentration of sodium hydroxide at commencement of experiment) = 0·001751 gram-molecule per litre, and hydrolysis = 5·60 per cent.

A second experiment, with $C_2=31·34$ and $C=103·4$, gave $K_h=0·000107$, or hydrolysis = 5·68 per cent.

(2) $V=101$.

Time	C_2-x .	$C-x$.	K_h .
0.0	9.90	20.89	—
32.0	7.16	18.15	(0.0000745)
50.1	6.40	17.39	0.0000851
67.1	5.98	16.97	0.0000858
99.0	5.25	16.24	0.0000913
129.0	4.87	15.86	0.0000877

Mean = 0.0000875

Therefore $A=0.000888$ and hydrolysis = 8.97 per cent.

Hantzsch and Farmer (*loc. cit.*) found 8.80 per cent. as the degree of hydrolysis of sodium phenoxide in $N/100$ -solution at 25° .

Guaiacol. $V=32$.Time, 0—66.3 min. C_2-x 31.22—12.48. $C-x$ 149.1—130.4. $K_h=0.0000980$ — 0.000108 ; mean, 0.000103 .Therefore $A=0.001743$ and hydrolysis = 5.58 per cent.

A second experiment with $C_2=31.39$ and $C=158.9$ gave $K_h=0.0000998$, or hydrolysis = 5.48 per cent.

o-Cresol. $V=32$.Time, 0—120 min. C_2-x 31.25—6.25. $C-x$ 123.4—98.4. $K_h=0.000182$ — 0.000200 ; mean, 0.0001915 .Therefore $A=0.002356$ and hydrolysis = 7.54 per cent.

A second experiment with $C_2=31.29$ and $C=289.2$ gave $K_h=0.000190$, or hydrolysis = 7.50 per cent.

m-Cresol. $V=32$.Time, 0—180 min. C_2-x 31.22—6.04. $C-x$ 131.5—106.3. $K_h=0.000118$ — 0.000128 ; mean = 0.000123 .Therefore $A=0.001898$ and hydrolysis = 6.08 per cent.

A second experiment with $C_2=31.34$ and $C=129.7$ gave $K_h=0.0001254$, or hydrolysis = 6.13 per cent.

p-Cresol. $V=32$.Time, 0—150 min. C_2-x 31.20—5.30. $C-x$ 125.8—99.9. $K_h=0.000168$ — 0.000185 ; mean = 0.000178 .Therefore $A=0.00227$ and hydrolysis = 7.27 per cent.

A second experiment with $C_2=31.20$ and $C=128.3$ gave $K_h=0.0001833$, or hydrolysis = 7.37 per cent.

o-4-Xylenol. $V=32$.Time, 0—167 min. C_2-x 31·23—5·30. $C-x$ 93·61—67·68. $K_h=0\cdot000231-0\cdot000236$; mean $=0\cdot000233$.Therefore $A=0\cdot002585$ and hydrolysis $=8\cdot28$ per cent. $V=100$.Time, 0—145 min. C_2-x 10·00—0·78. $C-x$ 62·59—53·37. $K_h=0\cdot000198-0\cdot000211$; mean, 0 000205.Therefore $A=0\cdot001334$ and hydrolysis $=13\cdot34$ per cent.*m*-6-Xylenol. $V=32$.Time, 0—179 min. C_2-x 31·28—3·17. $C-x$ 90·76—62·65. $K_h=0\cdot000344-0\cdot000359$; mean $=0\cdot000352$.Therefore $A=0\cdot00315$ and hydrolysis $=10\cdot07$ per cent. $V=100$.Time, 0—82 min. C_2-x 10·02—1·22. $C-x$ 57·37—48·57. $K_h=0\cdot000279-0\cdot000298$; mean $=0\cdot000291$.Therefore $A=0\cdot00157$ and hydrolysis $=15\cdot65$ per cent.*p*-Xylenol. $V=32$.Time, 0—180 min. C_2-x 31·24—4·46. $C-x$ 96·68—69·90. $K_h=0\cdot000240-0\cdot000256$; mean $=0\cdot000251$.Therefore $A=0\cdot00268$ and hydrolysis $=8\cdot57$ per cent.

A second experiment with $C_2=31\cdot07$ and $C=96\cdot83$ gave $K_h=0\cdot000255$, or hydrolysis $=8\cdot66$ per cent.

 $V=76\cdot1$.Time, 0—180 min. C_2-x 13·15—1·70. $C-x$ 47·03—35·58. $K_h=0\cdot000221-0\cdot000234$; mean $=0\cdot000230$.Therefore $A=0\cdot001627$ and hydrolysis $=12\cdot37$ per cent.

$V=187\cdot3$ (C_2-x and $C-x$ expressed in 0·0005 gram-molecule per litre).

Time, 0—120 mm. C_2-x 10·68—0·55. $C-x$ 90·34—80·21. $K_h=0\cdot000211-0\cdot000220$; mean $=0\cdot000216$.Therefore $A=0\cdot0009715$ and hydrolysis $=18\cdot20$ per cent.*Thymol*.

$V=158\cdot1$ (C_2-x and $C-x$ expressed in 0·0005 gram-molecule per litre).

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Time, 0—86 min. C_2-x 12.65—0.91. $C-x$ 90.90—79.16.

$K_h=0.000302-0.000308$; mean= 0.000305 .

Therefore $A=0.001244$ and hydrolysis= 19.67 per cent.

A second experiment with $C_2=13.10$ (0.0005 gram-molecule per litre) and $C=93.16$ gave $K_h=0.000296$, or hydrolysis= 19.10 per cent.

Carvacrol.

$V=181.1$ (C_2-x and $C-x$ expressed in 0.0005 gram-molecule per litre).

Time, 0—127 min. C_2-x 11.04—1.29. $C-x$ 58.40—48.65.

$K_h=0.000203-0.000224$; mean= 0.000215 .

Therefore $A=0.000988$ and hydrolysis= 17.89 per cent.

A second experiment with $C_2=10.73$ (0.0005 gram-molecule per litre) and $C=58.40$ gave $K_h=0.000214$, or hydrolysis= 18.09 per cent.

 ψ -Cumenol.

$V=193.6$ (C_2-x and $C-x$ expressed in 0.0005 gram-molecule per litre).

Time, 0—120 min. C_2-x 10.33—0.87. $C-x$ 46.48—37.02.

$K_h=0.000323-0.000346$; mean= 0.000336 .

Therefore $A=0.00116$ and hydrolysis= 22.46 per cent.

A second experiment with $C_2=9.16$ (0.0005 gram-molecule per litre) and $C=46.62$ gave $K_h=0.000316$, or hydrolysis= 23.05 per cent.

Mesitol.

$V=205.7$ (C_2-x and $C-x$ expressed in 0.0005 gram-molecule per litre).

Time, 0—103 min. C_2-x 9.72—0.38. $C-x$ 45.40—36.06.

$K_h=0.000533-0.000606$; mean= 0.000573 .

Therefore $A=0.001385$ and hydrolysis= 28.49 per cent.

A second experiment with $C_2=9.31$ (0.0005 gram-molecule per litre) and $C=45.32$ gave $K_h=0.000569$, or hydrolysis= 29.36 per cent.

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