CXIV.—*The Velocities of Combination of Sodium Derivatives of Phenols with Olefine Oxides. Part II.*

By DAVID RUNCIMAN BOYD and MISS DORIS FELTHAM THOMAS.

A PREVIOUS communication (Boyd and Marle, T., 1914, 105, 2117) contained an account of experiments on the combination of ethylene and propylene oxides with the sodium derivatives of a variety of phenols. The nature of the reaction investigated is indicated by the equation

From the results of these experiments, the conclusion was drawn that combination probably, in the first instance, takes place between the phenoxy-ion and the olefine oxide molecule, thus.

the initial additive product afterwards reacting with the excess of phenol to give a glycol aryl ether and a new phenoxy-ion,

A comparison of the values for the velocity constant of the reaction with different phenols indicated that the speed of combination diminished with increase in the acidity of the phenol, and the suggestion was made that a certain analogy exists between the two reactions

In other words, where the tendency for a phenoxy-ion to change into undissociated phenol is great, the speed of combination of the phenoxy-ion with the ethylene oxide molecule should be relatively high, and vice versa. The data available at the time, however, with regard to the relative acidities of different phenols were comparatively few.

An investigation of the extent to which the sodium derivatives of alkyl substituted phenols are hydrolysed in aqueous solution was afterwards carried out by one of us (T., 1915, 107, 1538), and it then became possible to consider in more detail the relationship existing between the acidity of a phenol and the speed with which its sodium derivative combines with ethylene oxide. As a result, certain regularities with regard to the behaviour of ortho-substituted phenols came to light, and it appeared desirable to extend the observations so as to confirm, if possible, the generalisations which had suggested themselves. The present paper therefore includes experimental data for the velocity constants of three additional alkyl substituted phenols, namely, *o*-4-xenol, *m*-6-xenol, and mesitol. In all, results for eighteen phenols are dealt with. The facts are summarised in the accompanying diagram, where the velocity constants for the ethylene oxide reaction are plotted against the values for the percentage of hydrolysis of the sodium phenoxides in aqueous solution. A reference to this diagram will show that the velocity constants for phenol and

its *meta*- and *para*-substitution products lie approximately along a straight line, whilst the constants for the alkyl substituted phenols containing one alkyl group in an *ortho*-position lie approximately on a second straight line which runs nearly parallel with the first and some distance below it.

It appears, therefore, that whilst in general the speed of the ethylene oxide reaction increases approximately in proportion to the degree of hydrolysis of the sodium phenoxide, a retarding influence makes itself felt in those cases where an *ortho*-placed alkyl group is present in the phenol molecule. This retarding influence, it will be observed, is superimposed on the factor which in the main determines the speed of the reaction. It becomes apparent only as the result of such an analysis of the phenomena as is here suggested. A comparison of the actual magnitude of the velocity constant for phenol with that of the constant for any of the alkyl *ortho*-substituted phenols reveals no such retardation. Thus thymol, in the molecule of which an *isopropyl* radicle is present in the *ortho*-position to the hydroxyl group, has a velocity constant one and a half times as great as that of phenol. Mesityl, with two *ortho*-placed methyl groups, has a constant nearly twice as great as that of phenol. None the less, the retarding influence of the *ortho*-placed alkyl groups is operating in both instances. The case of mesitol is of particular interest in this connexion. Since in mesitol two *ortho*-placed methyl groups occur, the retardation might be expected to be more pronounced than in cases where only one such group is present. A consideration of the diagram shows that this anticipation is fully borne out by the experimental results.

On the other hand, the position of the *o*-chlorophenol constant, and more especially of that for 2:4:6-trichlorophenol, indicates that negative substituents—or at least chlorine atoms—in the *ortho*-position act in an exactly opposite way, the velocity of combination being accelerated by their presence; and it is noteworthy that just as two *ortho*-placed alkyl groups cause a very pronounced retardation of the speed, so two *ortho*-placed chlorine atoms have an accelerating effect much more powerful than that due to a single chlorine atom.

Whilst it is natural to attribute to steric hindrance the retarding influence of the *ortho*-placed alkyl groups, a final decision on the question is not yet possible in view of the quite different effect produced by *ortho*-situated chlorine atoms. Further experimental evidence is also required to decide whether the accelerating influence of the chlorine atom should be ascribed to its residual affinity or to its polar quality. In the meantime, it may be pointed out that in the case of guaiacol, which contains an *ortho*-

1242 VELOCITIES OF COMBINATION OF SODIUM DERIVATIVES, ETC.

situated group of ill-defined polar character, the velocity constant lies some distance above the line for phenols containing ortho-groups of well-marked positive type.

EXPERIMENTAL.

The velocity constants for *o*-4-xynol, *m*-6-xynol, and mesitol were determined at 70.4° in 98 per cent. alcohol according to the method previously described (T., 1914, 105, 2117). It was found necessary to employ a mixture of light petroleum with ether (1:1) in separating glycol *m*-6-xynyl ether from unchanged *m*-6-xynol, since this phenol is not completely extracted from an ethereal

Percentage hydrolysis of sodium phenoxides in aqueous solution at 25°.

solution by repeated shaking with aqueous potassium hydroxide. The same method had to be employed in the case of the mesityl ether.

Summary of Results.

	Percentage yield of glycol ether.			$\frac{1}{t} \log \frac{100}{100-x}$
	2 hours.	1 hour.	Maximum.	
<i>o</i> -4-Xynol.	75.3	51.0	98.5	0.3050
	75.1	—	—	—
<i>m</i> -6-Xynol.	74.5	58.5	98.9	0.3005
	74.8	—	—	—
Mesitol.	82.3	—	99.0	0.3745
	81.8	—	—	—
	82.5	—	—	—

Glycol o-xylyl ether, $C_8H_9 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, is a colourless oil boiling at $159^\circ/18$ mm. Its *p-nitrobenzoate* crystallises from alcohol in pale yellow plates melting at 225° :

0.1518 gave 6.5 c.c. N_2 (moist) at 23° and 762 mm. $N=4.82$.

$C_{17}H_{17}O_5N$ requires $N=4.62$ per cent

Glycol m-xylyl ether, $C_8H_9 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, was obtained as a white solid, which, after recrystallisation from light petroleum, melted at 57° :

0.1621 gave 0.4289 CO_2 and 0.1252 H_2O . $C=72.16$; $H=8.58$.

$C_{10}H_{14}O_2$ requires $C=72.23$; $H=8.51$ per cent.

Glycol mesityl ether, $C_9H_{11} \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, separates from light petroleum in glistening, white crystals which melt at 60° :

0.1556 gave 0.4196 CO_2 and 0.1263 H_2O . $C=73.54$; $H=9.02$.

$C_{11}H_{16}O_2$ requires $C=73.25$; $H=8.97$ per cent.

THE UNIVERSITY COLLEGE
OF SOUTHAMPTON.

[Received, July 23rd, 1919.]