CLXII.—*The Velocities of the Reactions between Ethyl Iodide and the Sodium Salts of Various Substituted Phenols in Ethyl–alcoholic Solution.*

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ALTHOUGH much work has been done on the relation between the constitutions of different alkyl halides and their activities towards the sodium salts of phenol and of α- and β-naphthol (Segaller, J., 1913, **103**, 1154, 1421; 1914, **105**, 106, 112; Cox, J., 1918, **113**, 666, 821; 1920, **117**, 493; Shroder and Acree, J., 1914, **105**, 2583), the effects of the substituents in the phenolic substances on the velocities have not hitherto been studied. The object of the present investigation was to ascertain the effect of introducing methyl and chlorine in different positions in the molecule of sodium phenoxide, on the rate of reaction of this substance with ethyl iodide. It was hoped that the results might be of some value in reference to the general and induced polarity effects accompanying substitution in the benzene ring.

As Segaller and others have shown, the reactions between alkyl halides and sodium phenoxides are bimolecular but of a special type, the velocity coefficients being smaller the greater the initial concentrations of the reacting substances, in accordance with the equation $k_v = k_1 + a \log v$, where v is the volume containing 1 g.-mol. of the alkyl halide and sodium phenoxide. All the reactions studied in this investigation were therefore carried out in solutions of the same strength, *viz.*, seminormal, with a view to obtain comparable results.

The following are the mean values ($k \times 10^5$) of the observed velocity coefficients for the sodium salts of the cresols and chlorophenols: Concentrations of sodium salts and of ethyl iodide, $N/2$. Temp. 42·5°.

(Phenol	702)	*p*-Chlorophenol	393
p-Cresol	918	*o*- ,,	334
m- ,,	810	*m*- ,,	278
o- ,,	726	2 : 4-Dichlorophenol	196

The results resemble those obtained by Boyd and Marle (J., 1914, **105**, 2117) in their investigation on the reactivities of substituted sodium phenoxides towards ethylene and propylene oxides, the order of the reactivities of the cresols and chlorophenols towards ethyl iodide and ethylene oxide being identical.

A possible explanation of the order of the reactivities towards ethyl iodide is suggested by the results obtained by Shroder and Acree in the study of the reactions between sodium phenoxide and alkyl halides (J., 1914, **105**, 2582). They have shown that in a mixture of sodium phenoxide and ethyl iodide in alcoholic solution, the "ionic" and "molecular" reactions

$$\mathrm{Ph{\cdot}O'} + \mathrm{C_2H_5I} = \mathrm{Ph{\cdot}O{\cdot}C_2H_5} + \mathrm{I'}$$

and

$$\mathrm{Ph{\cdot}ONa} + \mathrm{C_2H_5I} = \mathrm{Ph{\cdot}O{\cdot}C_2H_5} + \mathrm{NaI}$$

occur simultaneously, the former being about five times as fast as the latter. The "ionic" reaction involves the transfer of an electron from the phenoxide ion to the iodine atom, a process which will be the more easily effected the weaker the tendency of the phenoxide ion to hold its electron—in other words, the smaller the ionisation constant of the phenol in question. We should expect, therefore, that the order of the reactivities of the phenoxides would be the inverse of the order of the ionisation constants of the corresponding phenols. The results, except in the case of sodium *o*-tolyl oxide, accord with this expectation, the ionisation constants increasing in the order *o*-, *p*-, and *m*-cresol, phenol, *p*-, *o*-, and *m*-chlorophenol, 2 : 4-dichlorophenol.* In the case of sodium *o*-tolyl oxide the retarding steric effect of the methyl group in the ortho-position may account for the unexpectedly low reactivity.

EXPERIMENTAL.

The ethyl alcohol used in these experiments was commercial absolute alcohol, carefully dried by digestion with lime and calcium. The ethyl iodide was purified by successive washings with dilute caustic soda solution and water, drying over calcium chloride, and distillation from silver powder. The cresols and chlorophenols, supplied by Kahlbaum, were purified by fractional distillation a few hours before use. All the instruments used were standardised against instruments carrying the certificate of the National Physical Laboratory.

The experiments were carried out at 42·5° ± 0·1° in a thermostat provided with an Ostwald toluene regulator and an efficient stirrer.

To a weighed quantity of the phenol was added a measured volume of an alcoholic solution containing an equivalent quantity of sodium ethoxide. The solution was then diluted to normal concentration by adding the calculated volume of alcohol. 50 C.c. of this solution

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* The ionisation constants of phenol and the cresols have been determined by Dawson and Mountford (J., 1918, **113**, 937). The order of the constants for *p*- and *o*-chlorophenols may be deduced from the measurements of the hydrolysis of their salts by Hantzsch and Farmer (*Ber.*, 1899, **32**, 3066, 3089). It is assumed from a consideration of the induced polarity effects that the ionisation constant of *m*-chlorophenol, for which data are not available, is greater than those of *o*- and *p*-chlorophenol.

were mixed quickly with an equal volume of a normal solution of ethyl iodide, and 10 c.c. of the mixture were introduced into each of eight small test-tubes, which had been steamed out previously. The test-tubes, provided with well-fitting rubber stoppers, were then placed in the thermostat. After 10 minutes, the contents of one of the tubes were transferred quickly to a beaker containing ice and an amount of standard acid nearly sufficient to neutralise the unchanged phenoxide. The titration was completed as quickly as possible, with lacmoid as indicator. Further titrations were carried out in a similar way at suitable intervals of time. The results were calculated from the equation $k = xy/ta(a - x)$, in which y, a, and $a - x$ represent the volume (in c.c.) of acid required to neutralise the phenoxide in 10 c.c. of the mixture before the commencement of the experiment, in the first titration (zero-time), and after t minutes, respectively.

In order to economise space the detailed results of only one experiment are shown, *viz.*, that in which the salt was sodium *m*-tolyl oxide, and $N/5$-hydrochloric acid was used for titration.

t.	$a-x$.	x.	$k \times 10^5$.	t.	$a-x$.	x.	$k \times 10^5$.
0	22·15	—	—	90	13·45	8·70	811
30	18·15	4·00	829	120	12·05	10·10	788
60	15·40	6·75	824	150	10·80	11·35	791
70	14·70	7·45	817				Mean 810.

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