CCCCVI.—*The Halogenation of Phenolic Ethers and Anilides. Part II. Additional Velocity Measurements in 99% Acetic Acid.*

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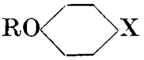
THE velocity coefficients for the chlorination at 20° of additional phenolic ethers and for a few phenol esters in " 99% acetic acid " have been determined by the method previously described (Orton and King, J., 1911, **99**, 1360; Bradfield and Jones, J., 1928, 1006, 3073). In the following tables are given the mean values obtained. Further work has shown that the value previously recorded for *p*-chlorophenyl *m*-nitrobenzyl ether is about 7% too high, and a revised value is now given. In Table I, square brackets denote concentrations in g.-mols. per litre.

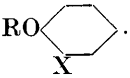
Comparison of the ratios of the velocity coefficients given in Tables II and III with those given in previous papers shows that the new results are in harmony with, and give further support to, the theory which has been developed on the basis of the activation theory of reaction velocity, *viz.*, that the critical energy increments for the reaction of aromatic ethers with chlorine may be expressed as the sum of the characteristic individual contributions of the groups attached to the benzene nucleus.

In addition, several new ratios are obtained. As would be anticipated from general experience, there is little difference between the rates of chlorination of corresponding bromo- and chloro-ethers, the ratio being 103 : 100 for *p*-halogeno-ethers and 120 : 100 for *o*-substituted compounds. In the latter compounds, two positions are available for the entering chlorine atom, and for a complete interpretation of the velocity measurements it is essential to know the rate of entry at each position, *i.e.*, the proportions of the isomeric substitution products formed must also be known. From the velocity coefficients it is not possible to deduce the relative amounts

TABLE I.

Velocity coefficients for chlorination in 99% acetic acid.

(1) *Substances of the type* 

and 

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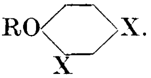
[Cl_2] = 0·0075; [ether] = 0·0225; [HCl] = 0·0375.

X =	R =	*k*.	X =	R =	*k*.
p-Br	CH_3	1·256	*p*-Br	*m*-NO_2·C_6H_4·CH_2	0·2006
,,	C_2H_5	2·514	*o*-Br	CH_3	5·457
,,	*n*-C_3H_7	2·847	,,	*p*-NO_2·C_6H_4·CH_2	0·7503
,,	*iso*-C_3H_7	5·506	*p*-Cl	*m*-NO_2·C_6H_4·CH_2	0·1947
,,	C_6H_5·CH_2	0·8496	*p*-CO_2Me	CH_3	0·7308
,,	*p*-NO_2·C_6H_4·CH_2	0·1768	*p*-CO_2Et	CH_3	0·8387

(2) *Substances of the type* 

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[Cl_2] = 0·04; [ether] = 0·12; [HCl] = 0·05.

X =	R =	*k*.	X =	R =	*k*.
Cl	C_2H_5	0·005714	Br	CH_3	0·0039
,,	C_6H_5·CH_2	0·001960	,,	C_2H_5	0·0080
			,,	C_6H_5·CH_2	0·0025

(3) *Phenolic esters.*

[Cl_2] = 0·02; [ester] = 0·20; [HCl] = 0·05.

Ester.	*k*.
Phenyl benzoate	0·002025
**p*-Chlorophenyl benzoate	0·000015
*Phenyl *p*-toluenesulphonate	0·00013
*†*p*-Chlorophenyl ethyl carbonate	0·00007

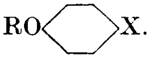
* Maximum values. † [Cl_2] = 0·0075; [ester] = 0·0225; [HCl] = 0·0375.

TABLE II.

Relative directive effects of the groups –OR in *o*- and *p*-bromo-ethers, and dihalogeno-ethers. Values of $100k_X^{OR}/k_X^{OMe}$.

					CH_2·C_6H_4·A		
	R =				A =		
	Me.	Et.	Prα.	Prβ.	H.	*p*-NO_2.	*m*-NO_2.
X = *p*-Br	100	200	227	438	67·7	14·1	16·0
o-Br	100	—	—	—	—	13·8	—
2 : 4-Dibromo	100	205	—	—	64	—	—
2 : 4-Dichloro	—	199	—	—	68·0	—	—

TABLE III.

Relative directive effects of Br and Cl in compounds 

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R =	$100k_{Br}^{OR}/k_{Cl}^{OR}$.	R =	$100k_{Br}^{OR}/k_{Cl}^{OR}$.
CH_3	102·5	C_6H_5·CH_2	101·5
C_2H_5	103	*p*-NO_2·C_6H_4·CH_2	101·5
n-C_3H_7	103·4	*m*-NO_2·C_6H_4·CH_2	103
iso-C_3H_7	102·4		

of the isomerides formed, except by an application of Holleman's "product rule" ("Die direkte Einführung von Substituenten in der Benzolkern," p. 482). The equivalent of this in the present case is to assume that the effect of a given group X is the same whether it occupies the position ortho or para to the group OR. From this premise it may easily be shown that $r = k^{\mathrm{OR}}_{p\text{-}\mathrm{X}}/2k^{\mathrm{OR}}_{o\text{-}\mathrm{X}}$, where r is the fraction of the product which consists of the 2 : 6-compound, and the symbols $k^{\mathrm{OR}}_{p\text{-}\mathrm{X}}$ and $k^{\mathrm{OR}}_{o\text{-}\mathrm{X}}$ have the significance explained in earlier papers. However, the product rule also leads to a relation between the known velocity coefficients for dihalogeno-ethers and the corresponding para-substituted compounds, *viz.*,

$$k^{\mathrm{OR}}_{2:4\text{-di-Br}} = k^{\mathrm{OR}}_{2:4\text{-di-Cl}}\,(k^{\mathrm{OR}}_{p\text{-Br}}/k^{\mathrm{OR}}_{p\text{-Cl}})^2$$

The values of $k^{\mathrm{OEt}}_{2:4\text{-di-Br}}$ and $k^{\mathrm{OCH_2Ph}}_{2:4\text{-di-Br}}$ calculated by substituting appropriate values in the right-hand side of this relation are 0·00605 and 0·00202 respectively. The observed velocity coefficients for these dibromo-ethers, *viz.*, 0·0080 and 0·0025, are subject to an unavoidable error: nevertheless, the lack of concordance is, we think, sufficient to cast grave doubts on the applicability of the product rule.

The error referred to above arises from the fact that in the reaction between 2 : 4-dibromo-ethers and chlorine, in addition to the main reaction leading to substitution in position 6, replacement of bromine by chlorine occurs, and free bromine (or bromine chloride) appears. This side reaction appears to be accelerated by sunlight. A similar replacement of bromine by chlorine in dibromoanilines has been observed by Orton and Reed (J., 1907, **91**, 1543).

The figures for the unsubstituted and *p*-chloro-esters bring out clearly the already well-known fact that the esterification of a hydroxyl group greatly diminishes its directive power. Indeed, with the *p*-chloro-esters only about 5—10% of the chlorine disappears in 3 days, and it can only be claimed that the velocity coefficients calculated during this period of the reaction represent maximum limiting values. On the other hand, esterification of the carboxyl group of anisic acid increases slightly the rate of chlorination, the relative rates for this substance and its methyl and ethyl esters being 100 : 165 : 189.

The next stage in the application of the experimental and theoretical methods which have been developed by the authors is the study of the effects of change of medium and/or reagent. Without entering into its theoretical significance until more data are available, it may be pointed out that the relation between the relative rates of bromination of *p*-chloro- and *p*-bromo-ethers in 50% acetic acid (Bradfield and Jones, J., 1929, 2810) and of chlorination in 99% acetic acid may be expressed with some accuracy by the equation

$$0{\cdot}775 \log (k^{OR_1}_{p\text{-}X}/k^{OR_2}_{p\text{-}X})_{\text{Bromination}} = \log (k^{OR_1}_{p\text{-}X}/k^{OR_2}_{p\text{-}X})_{\text{Chlorination}}$$

For instance, the experimental values for bromination are 1·00 : 2·31 : 7·11 for the methoxyl, ethoxyl, and *iso*propoxyl groups, and from them the values 1·00 : 1·91 : 4·57 may be calculated for chlorination, agreeing within about 4% with the observed values 1·00 : 1·99 : 4·40.

EXPERIMENTAL.

The velocity measurements were carried out in the manner previously described in an acetic acid medium containing 1 c.c. of water in 100 c.c. of reaction mixture. Dichlorophenol, m. p. 43°, was prepared from *p*-chlorophenol by Orton and King's method of chlorination (J., 1911, **99**, 1185). The ethers were prepared from the phenols and alkyl iodides or benzyl chlorides by standard methods. *p*-Bromophenyl *p*-nitrobenzyl ether and 2 : 4-dichlorophenyl benzyl ether have m. p.'s 114·5° and 62° respectively, these values being in each case about 2° higher than those recorded in the literature. The following ethers do not appear to have been prepared previously. p-*Bromophenyl* n-*propyl ether*, b. p. 126° (bath temp.)/11 mm.; $n_D^{25°}$ 1·5386 (Found : Br, 37·2. $C_9H_{11}OBr$ requires Br, 37·2%). p-*Bromophenyl* m-*nitrobenzyl ether*, after recrystallisation from alcohol and acetic acid, melts at 89·3° (Found : Br, 26·2. $C_{13}H_{10}O_3NBr$ requires Br, 25·9%). p-*Chlorophenyl* m-*nitrobenzyl ether* melts at 73·8° (Found : Cl, 13·4. $C_{13}H_{10}O_3NCl$ requires Cl, 13·5%). o-*Bromophenyl* p-*nitrobenzyl ether* has m. p. 111·4° (Found : Br, 25·9. $C_{13}H_{10}O_3NBr$ requires Br, 25·9%). 2 : 4-*Dibromophenyl benzyl ether* melts at 67·8° (Found : Br, 47·1. $C_{13}H_{10}OBr_2$ requires Br, 46·7%).

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