

CCCCVII.—*The Halogenation of Phenolic Ethers and Anilides. Part III. The "Phase and Steric" Factor.*

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FROM the data relating to the problem of substitution in the benzene nucleus, no simple relation of even a roughly quantitative kind has yet been traced between any *single* characteristic of a directing atom or group and its effect on the substitution reactions of the nucleus to which it is attached. Further development of the problem requires the logical analysis of (a) the effects of the directing group as the resultant of two or more variables, and/or of (b) the velocity coefficients representing the rates of the reactions as the resultants of two or more variables.

Course (a) has been adopted by the majority of authors, including Flürscheim, Lapworth, Robinson, and Ingold, all of whom resolve the constitutional effect of the group into three components. Course (b) has been adopted by Bradfield and B. Jones (J., 1928, 1006. 3073; 1929, 2810), who, on the basis of the interpretation of the Arrhenius expression  $k = \alpha e^{-E/RT}$  provided by the kinetic activation theory of reaction velocity, resolve the observed velocity coefficients as the product of two factors, one of which,  $\alpha$ , has been written as *PSZ* as a reminder that it is a compound term which includes any factors determined by periodic disturbances within the molecule ("phase factor" = *P*), or by the shape of the molecule ("steric factor" = *S*), whilst in the other, *E* represents a threshold value of the kinetic energy which the reacting molecules must possess.

The main results hitherto achieved by the adoption of course (b) are: (i) The demonstration that for the nitration of mono- and di-substituted benzene derivatives the  $\alpha$  terms relating to the different positions are identical.\* (ii) On the assumption that the  $\alpha$  terms relating to similar positions in a series of *p*-substituted phenolic ethers are identical, when the ethers are chlorinated in 99% acetic acid, the demonstration that the quantity *E* may be represented as the sum of two terms, each representing the contribution of one group. (iii) A similar demonstration of an additive effect for the bromination reactions of the same substances in 50% acetic acid.

\* In a recently published book, "Theoretische Grundlagen der Organischen Chemie" (Leipzig, 1931), Hückel (Bd. 2, Kap. 18) appears to have overlooked completely the fact that Bradfield and B. Jones were the first to point out the significance of measurements of the effect of temperature on velocity rates from the point of view of the "steric factor."

The assumption in (ii) and (iii) was made, in the first place, by analogy from (i), but shortly afterwards (J., 1928, 3077) it was pointed out that three other simple hypotheses embodying alternative assumptions would equally well account for the observed effects, and a method of distinguishing between these hypotheses was developed based on the study of the temperature coefficients of the reactions. A preliminary test with the then-available data failed to distinguish clearly between these hypotheses. The results of a long series of measurements now to be considered definitely show the original hypothesis to be correct, and exclude the alternative hypotheses.

Data are now given relating to the original series of phenyl ethers of the type  $\text{RO} \begin{array}{c} \diagup \\ \text{X} \\ \diagdown \end{array} \text{X}$ , and to a new series of tolyl ethers of the type  $\text{RO} \begin{array}{c} \diagup \\ \text{X} \\ \diagdown \end{array} \text{CH}_3$ . For the purpose of discussion it is convenient to consider the two sets of data in separate sections.

### 1. *Phenyl Ethers.*

The first hypothesis (I) of Bradfield and Jones, based on the assumption stated in (ii) above, leads to the relation

$$\log (k_1/k_2)_{T_1} = T_2/T_1 \cdot \log (k_1/k_2)_{T_2} \quad . \quad . \quad . \quad (1)$$

as an expression of the effect of temperature on the relative rates of two reactions. The second hypothesis (II) alternatively suggests that in the series of ethers the energy of activation is constant, the variations in rates of reaction arising from effects which cause a change in magnitude of the factor represented by  $\alpha$ . The relative rates of two reactions are then unaltered by change of temperature, *i.e.*,

$$\log (k_1/k_2)_{T_1} = \log (k_1/k_2)_{T_2} \quad . \quad . \quad . \quad (2)$$

The distinction which may be made between these hypotheses depends in the first instance on the accuracy with which the velocity coefficients are known (estimated to be within about 3%), and secondly on the temperature interval between the two sets of measurements. In practice, the diminishing solubility of the ethers in the acetic acid medium as the temperature decreases, and the freezing point of the acetic acid solutions set a lower limit, whilst an upper limit is set by the diminution in solubility of the chlorine with increase in temperature, and only the comparatively narrow range of 20—35° is available.

A graphical method of comparison of the experimental data with the predictions of these hypotheses has been employed, both because of its simplicity and because it tends to eliminate the effect of errors in individual measurements. It will be seen that if the logarithms of the ratios of the velocity coefficients for pairs of ethers at the one

temperature be plotted against the logarithms of the ratios at the second temperature, according to Hypothesis I the points should lie on a straight line passing through the origin and of slope =  $T_2/T_1$ , whilst according to Hypothesis II, they should lie on a straight line through the origin of slope = 1. Lines corresponding to equations (1) and (2) are shown in Fig. 1, together with the experimental points. Since  $T_2/T_1 = 1.051$ , the lines are not very divergent, and the portion of the diagram for values of  $\log(k_1/k_2) < 1$  has been omitted, since for these lower values no clear distinction between the hypotheses is obtained. It will be seen that Line I corresponding to Hypothesis I is, on the whole, in good agreement with the experimental points, while Hypothesis II (Line II) fails completely to represent the facts.

To indicate the stringency of the test and the distinction obtained, it may be stated (1) that about 50 experimental points are shown in the figure, (2) that in order to bring the points on to Line II it would be necessary to alter the experimental values of  $(k_1/k_2)_{T=35}$  by about 10% for points at the lower left end of the diagram, and by about 30% at the upper right portion—changes which are quite outside the estimated experimental error.

The two hypotheses discussed above represent two extremes. In addition, two equally simple intermediate hypotheses were formulated in which the magnitude of  $\alpha$  is considered to be determined by one group, either X or OR, whilst  $E$  is determined by the other. For the purpose of testing Hypothesis III, in which the group X is considered to determine  $\alpha$ , pairs of ethers are taken such that the  $p$ -position in the one is occupied by, say, Cl, and in the other by  $\text{NO}_2$ . For such pairs, Hypothesis III leads to the following relation for the temperature effect :

$$\log(k_1/k_2)_{T_1} = T_2/T_1 \cdot \log(k_1/k_2)_{T_2} + (T_2 - T_1)/T_1 \cdot \log \xi \quad (3)$$

where  $\xi$  is a constant. The numerical value of  $\xi$  is equal to the reciprocal of the ratio of the velocity coefficients for pairs of ethers in which  $R_1 = R_2$ . This hypothesis is therefore represented by a straight line of slope  $T_2/T_1$ , cutting the  $y$ -axis at a point  $y = (T_2 - T_1)/T_1 \cdot \log \xi$ . A distinction between this hypothesis and Hypothesis I is only obtained when  $\xi$  is greatly different from unity, a condition which is satisfied with the present data when  $X_1 = \text{Cl}$  or Br and  $X_2 = \text{NO}_2$ .\* Fig. 2 shows that this hypothesis is definitely incorrect.

\* Since  $p$ -chloro- and  $p$ -bromo-ethers with the same R are chlorinated at almost identical rates, the straight lines drawn for ratios of the types  $k_{\text{Cl}}^{\text{OR}}/k_{\text{NO}_2}^{\text{OR}}$  and  $k_{\text{Br}}^{\text{OR}}/k_{\text{NO}_2}^{\text{OR}}$  are practically coincident, and are shown by a single line (Line III). Similarly in the discussion of Hypothesis IV,  $k_{\text{Cl}}^{\text{OR}}/k_{\text{Br}}^{\text{OR}}$  is treated as unity.

FIG. 1.

Ordinates:  $\log_{10} (k_{X_1}^{OR_1} / k_{X_2}^{OR_2})_{20^\circ}$ .

Abscissæ:  $\log_{10} (k_{X_1}^{OR_1} / k_{X_2}^{OR_2})_{35^\circ}$ .

For Hypothesis I, all points should lie on Line I.

For Hypothesis II, all points should lie on Line II.

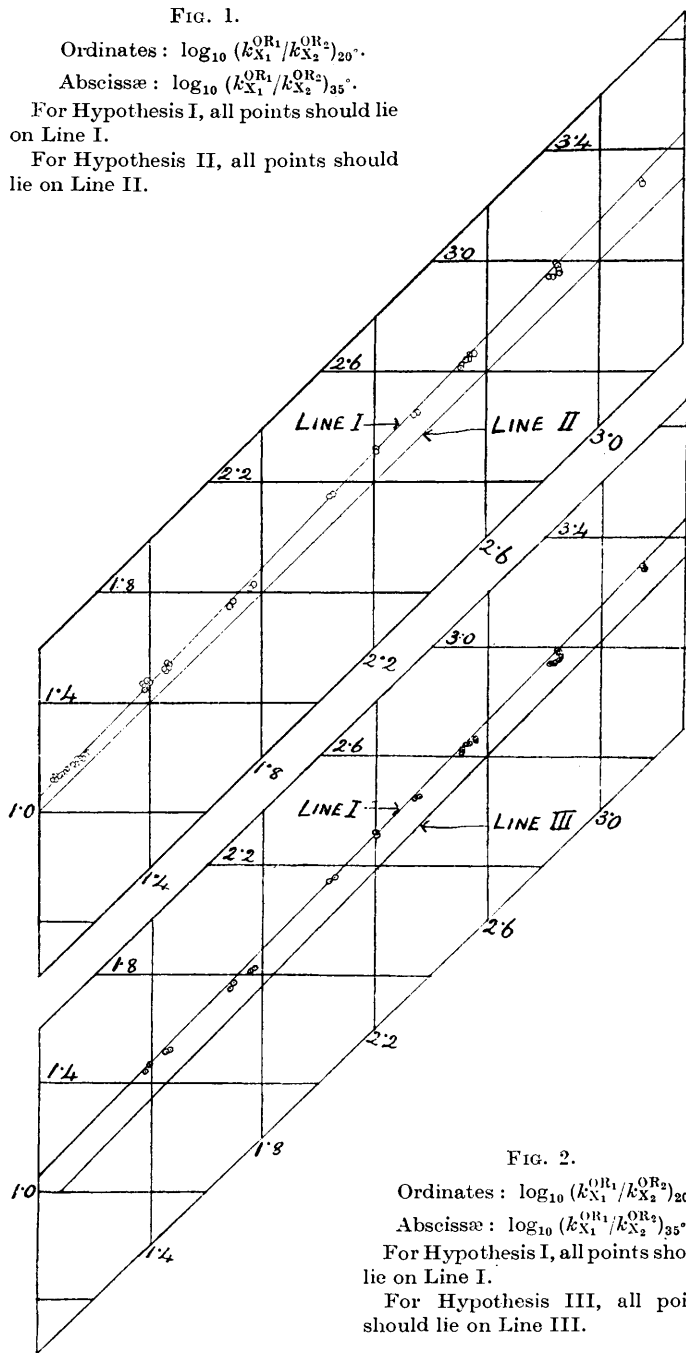


FIG. 2.

Ordinates:  $\log_{10} (k_{X_1}^{OR_1} / k_{X_2}^{OR_2})_{20^\circ}$ .

Abscissæ:  $\log_{10} (k_{X_1}^{OR_1} / k_{X_2}^{OR_2})_{35^\circ}$ .

For Hypothesis I, all points should lie on Line I.

For Hypothesis III, all points should lie on Line III.

Fig. 3.

Ordinates :  $\log_{10} (k_{X_1}^{OR_1} / k_{X_2}^{OR_2})_{20^\circ}$ .

Abscissæ :  $\log_{10} (k_{X_1}^{OR_1} / k_{X_2}^{OR_2})_{35^\circ}$ .

For Hypothesis I, all points should lie on Line I.

For Hypothesis IV, points plotted  $\blacksquare$  should lie on Line II.

For Hypothesis IV, points plotted  $+$  should lie on Line IVa or IVb.

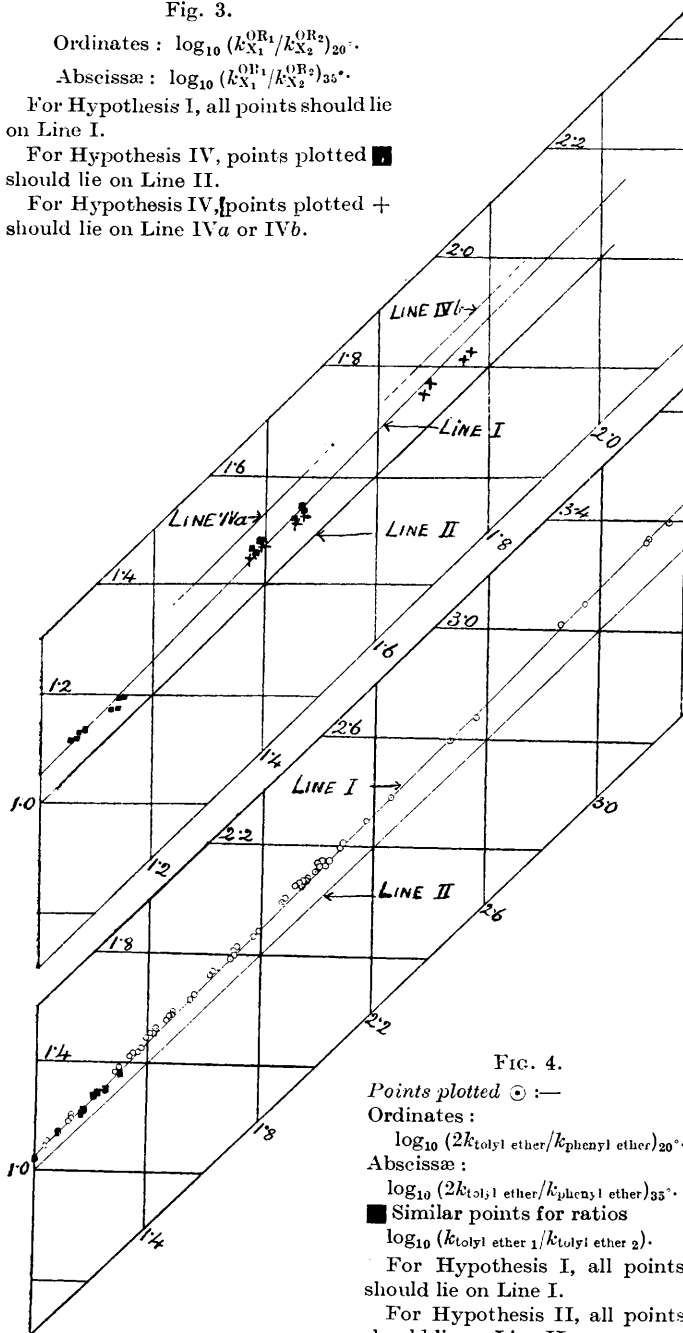


FIG. 4.

Points plotted  $\odot$  :-

Ordinates :

$\log_{10} (2k_{\text{tolyl ether}} / k_{\text{phenyl ether}})_{20^\circ}$ .

Abscissæ :

$\log_{10} (2k_{\text{tolyl ether}} / k_{\text{phenyl ether}})_{35^\circ}$ .

■ Similar points for ratios

$\log_{10} (k_{\text{tolyl ether 1}} / k_{\text{tolyl ether 2}})$ .

For Hypothesis I, all points should lie on Line I.

For Hypothesis II, all points should lie on Line II.

In order to test the fourth hypothesis, in which the group R is assumed to determine the magnitude of  $\alpha$ , pairs of ethers are taken in which R<sub>1</sub> and R<sub>2</sub> are fixed whilst X is varied, and the temperature effect is again considered. The relation obtained is of the form of expression (3), but the value of  $\xi$  is now given by the reciprocal of the ratio of the velocity coefficients for a pair of ethers with the same X. In order that the spacing of the lines representing Hypotheses I and IV may be well outside the experimental error, the only pairs of ethers considered in the graphical representation are those in which R<sub>1</sub> = C<sub>2</sub>H<sub>5</sub> or CH<sub>3</sub> and R<sub>2</sub> = *m*- or *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>. When X<sub>1</sub> = X<sub>2</sub>, this hypothesis is not differentiated from the second hypothesis, and points corresponding to such pairs, represented ■ in Fig. 3, should lie on Line II, whereas when X<sub>1</sub> and X<sub>2</sub> are different the corresponding points (plotted as +) should lie on Lines IV*a* and IV*b*, which correspond to equation (3), with the appropriate values of  $\xi$ . This hypothesis is seen to lead to conclusions contrary to experiment, and the first hypothesis remains as the only one capable of representing the experimental facts.

In Bradfield and Jones's derivation of expressions (1), (2), and (3), quoted above, it is tacitly assumed that  $Z$ , the collision number, is a constant which may be cancelled out. Although this is not strictly true, the error introduced is inappreciable.  $Z$  may be written as  $\pi \left( \frac{\sigma_1 + \sigma_2}{2} \right)^2 n_1 n_2 \sqrt{u_1^2 + u_2^2}$ , where  $\sigma_1$  and  $\sigma_2$  are molecular diameters,  $u_1^2$  and  $u_2^2$  the mean-square velocities of the molecules, and  $n_1$  and  $n_2$  the numbers of molecules of reactants per c.c.; also  $u_1^2$  and  $u_2^2$  may be written  $3RT/M_1$  and  $3RT/M_2$ , respectively, where  $M_1$  and  $M_2$  are the molecular weights of the reactants. According to Norrish and Smith (J., 1928, 129), the effective volumes and therefore the values of  $\sigma$  are practically identical for most organic molecules in solution. Hence, for the chlorination of two ethers of molecular weight  $M_A$  and  $M_B$

$$Z_B/Z_A = \sqrt{(M_{Cl} + M_B)M_A / (M_{Cl} + M_A)M_B}$$

and the equation corresponding to (1) above (for example) becomes, on retaining the  $Z$  terms:

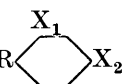
$$\log(k_1 Z_B / k_2 Z_A)_{T_1} = T_2 / T_1 \cdot \log(k_1 Z_B / k_2 Z_A)_{T_2} \quad (1a)$$

With *p*-chloroanisole and *p*-chlorophenyl *p*-nitrobenzyl ether, for which the difference in molecular weights is almost a maximum among the pairs of ethers considered here, substitution of the calculated value of  $Z_B/Z_A$  and the appropriate values of  $k_1$  and  $k_2$  at 20° in equation (1a) gives the calculated value of the ratio at 35° as

0.1504, whereas by equation (1) it is 0.1510. The difference is negligible.

2. *Tolyl Ethers.*

Particular interest attaches to the directive effect of the methyl group, for whilst, like the halogens, it normally behaves as a weak *op*-directing group in contrast to the hydroxy- and amino-groups (compare, however, Brady, Quick, and Welling, J., 1925, 127, 2264), yet, like the last two groups and unlike the halogens, it appears to raise the general level of reactivity of the nucleus to which it is attached (Orton and King, J., 1911, 99, 1369; Wibaut, *Rec. trav. chim.*, 1915, 34, 241; Ingold and Shaw, J., 1927, 2918). In this respect the methyl group in *p*-tolyl ethers behaves normally, as is evident from the following table showing the rates of chlorination in acetic acid of phenyl and tolyl ethers, together with corresponding data for anilides and toluidides for comparison.

Rates of chlorination of R 

	X <sub>1</sub> = H,			X <sub>1</sub> = Cl,		
	X <sub>2</sub> = Cl.	H.	CH <sub>3</sub> .	X <sub>2</sub> = Cl.	H.	CH <sub>3</sub> .
R = OCH <sub>3</sub> .....	1.23	ca. 900	ca. 2000	0.0030	4.44	5.29
NHAc .....	0.21	40	77	v. slow	0.073	9

As a result of the activating effect of the methyl group, *p*-tolyl ethers are chlorinated too rapidly for accurate measurement under the conditions employed. Ethers in which one of the ortho-positions is filled by halogen or by the nitro-group were therefore studied, although this involves a departure from the type of ether mainly studied hitherto.

With these ethers, when measurements are made with equal initial concentrations of ether and chlorine, the velocity coefficients calculated from the usual formula for bimolecular reactions show a steady rise of about 10% over the range 35—65% of change, but when the ether/chlorine ratio is increased to 3 : 1, constant values are obtained which are not altered by further increase in the proportion of ether (beyond the normal drift with concentration; compare Bradfield and Jones, *loc. cit.*), as may be seen from the following figures :

*3-Bromo-p-tolyl benzyl ether at 20°.*

Mol. ratio, [ether]/[Cl <sub>2</sub> ].	Calculated <i>k</i> and % change.			Mean <i>k</i> .
1 : 1	4.08 (38.6%)	4.41 (56.1%)	4.71 (64.9%)	—
3 : 1	3.77 (34.9%)	3.73 (54.5%)	3.76 (64.7%)	3.75
10 : 1	3.58 (35.9%)	3.53 (50.4%)	3.54 (64.3%)	3.55

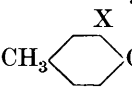
The main series of measurements were therefore made with the ratio 3 : 1.

*Ad hoc* experiments have so far failed to disclose the nature of the disturbing effect in the 1 : 1 experiments. It does not appear to be due to further chlorination of the primary product, for 3 : 5-dichloro-*p*-tolyl ether scarcely reacts with chlorine under the conditions employed, the velocity coefficient being not greater than 1/500 of the value for the primary reaction.

The relative effects of the alkyl groups on the rate of chlorination of the tolyl ethers are interesting when compared with the values for the phenyl ethers (see Table I). When a nitro-group occupies the position ortho to the alkoxy-group, the ratio Me : Et : Pr<sup>a</sup> is that found previously, but when the nitro-group is replaced by halogen, the relative effects are appreciably different from the values in the phenyl series. So far as the nitrotolyl ethers are concerned, the similarity of the results to those obtained in the phenyl series suggests that the conclusions already drawn apply, *mutatis mutandis*, to these compounds.

TABLE I.

Relative directive effects of the groups OR in compounds of the type

		Values of the ratio $100k_X^{OR}/k_X^{OMe}$ .				
		OR = OMe.	OEt.	OPr <sup>a</sup> .	O-CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub> .	O-CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub> ( <i>p</i> -)
X = Cl	.....	100	187	213	59	11.0
Br	.....	100	181	211	58	11.0
NO <sub>2</sub>	.....	100	203	226	—	—
Phenyl ethers	.....	100	200	225	68	13.7

Relative directive effect of bromine compared with chlorine in tolyl ethers.

R =	$100k_{Br}^{OR}/k_{Cl}^{OR}$ .	R =	$100k_{Br}^{OR}/k_{Cl}^{OR}$ .
Me	123	C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub>	120
Et	118	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -CH <sub>2</sub>	123
Pr <sup>a</sup>	122		

The implication of the figures for the chloro- and the bromo-tolyl ethers considered by themselves is that here also the groups attached to the nucleus each contribute a characteristic quota to either the  $\alpha$  or the  $E$  term of the expression  $k = \alpha e^{-E/RT}$ , and hence the four hypotheses considered in Section (I) appear to be also applicable here. The data for the tolyl series of ethers are insufficient to provide a clear distinction between the first and the second hypothesis, but it is shown below that by combining them with the data for the phenyl series, a discrimination is reached in clear favour of Hypothesis I. It follows, from this proof that the  $\alpha$  term has the same value in both series, that the peculiar effects of the methyl group in tolyl ethers (and presumably in toluoides) do not arise from any alteration in the phase or steric factors.



Before considering Hypotheses I and II in more detail, it may be pointed out that Hypotheses III and IV cannot here be tested. With the tolyl ethers alone the facts are again insufficient, but now, in addition, combination with the data for phenyl ethers is inadmissible. For then Hypothesis III is no longer inductively true, since it requires that relative effects of the groups OR shall be independent of all other groups attached to the nucleus (compare Table I). Again, the test of Hypothesis IV requires that pairs of ethers possessing the same group X shall be available. This condition is obviously not satisfied with such pairs as *p*-chloroanisole and 3-chloro-*p*-tolyl methyl ether. It should be noted that there is nothing in Hypotheses I and II to preclude the joint consideration of two distinct series of compounds, provided that the effects of a given group OR or X are constant within each series.

Returning to Hypotheses I and II, the expressions for velocity coefficients for a tolyl and a phenyl ether respectively become :

$$k_1 = \alpha e^{-E/RT} \quad \text{and} \quad k_2 = 2\alpha e^{-E/RT}$$

the factor 2 being introduced in the second expression as there are two similar vacant positions in the phenyl ether. For the effect of temperature on the ratio ( $k_1$  for tolyl ether)/( $k_2$  for phenyl ether), equations similar to (1) and (2) above, except that  $k_1/k_2$  now becomes  $2k_1/k_2$  throughout, are easily deduced. The theoretical lines and the experimental points are shown in Fig. 4, and again Hypothesis I emerges successfully from the test.

In the above, the *ex cathedra* view is adopted that, where two similar positions are vacant, they are simultaneously available for substitution. Though it is not yet possible to prove it conclusively, some evidence can be brought to support this contention. First, consider the effect of temperature on the *o*:*p*-ratio. The two expressions

$$\log (k_o/2k_p)_{T_1} = T_2/T_1 \cdot \log (k_o/2k_p)_{T_2} \quad \dots \quad (4)$$

$$\log (k_o/k_p)_{T_1} = T_2/T_1 \cdot \log (k_o/k_p)_{T_2} \quad \dots \quad (5)$$

are obtained according as the two ortho-positions are, or are not, taken into account. In a typical case the calculation by the two expressions leads to similar results. For example, from the *o*:*p*-ratio for the nitration of chlorobenzene, *viz.*, 26.9 : 73.1 at  $-30^\circ$ , the values 30.7 : 69.3 and 29.1 : 70.9 at  $0^\circ$  are calculated by (4) and by (5) for comparison with the value 30.1 : 69.9 found. In the particular case of the nitration of toluene, arising from the fact that whereas the ratio  $k_o/2k_p < 1$ , yet the ratio  $k_o/k_p > 1$ , the changes calculated by (4) and (5) are not only numerically different, but opposite in direction : and here expression (4) is definitely in better agreement with experiment, as shown :

	-30°.	60°.
	<i>o</i> : <i>p</i> .	<i>o</i> : <i>p</i> .
Found.....	55.6 : 41.7	57.5 : 38.5
Calc. by (4) .....		57.4 : 38.6
„ (5) .....		53.2 : 42.9

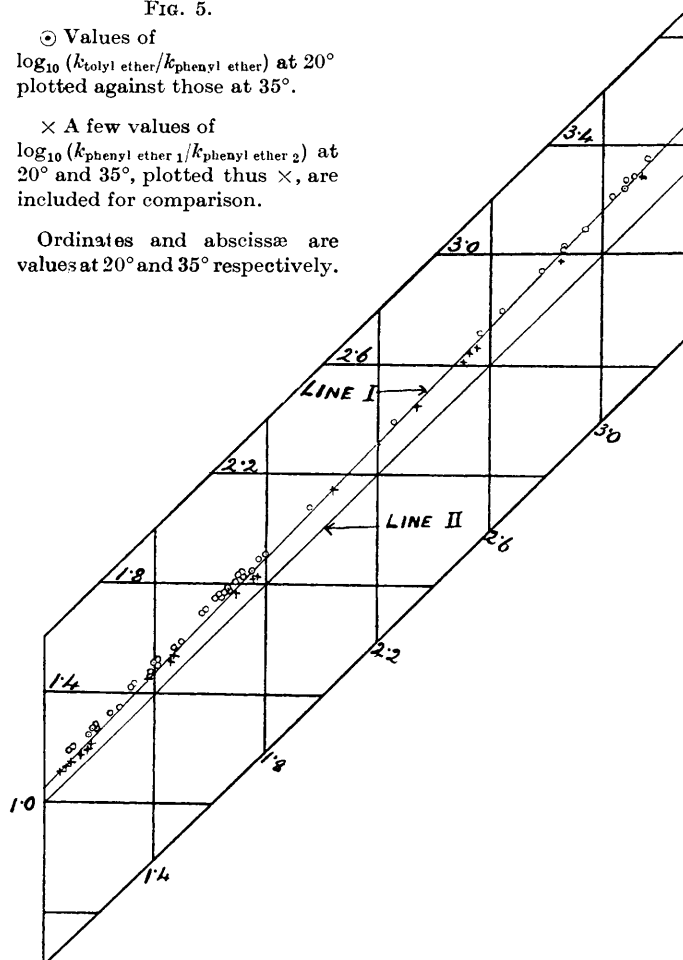
Secondly, in the joint consideration of the data for the phenyl and tolyl series of ethers, if only one of the ortho-positions in a

FIG. 5.

⊙ Values of  $\log_{10}(k_{\text{tolyl ether}}/k_{\text{phenyl ether}})$  at 20° plotted against those at 35°.

× A few values of  $\log_{10}(k_{\text{phenyl ether 1}}/k_{\text{phenyl ether 2}})$  at 20° and 35°, plotted thus ×, are included for comparison.

Ordinates and abscissæ are values at 20° and 35° respectively.



*p*-substituted phenyl ether be considered, by Hypothesis I it is now points with co-ordinates  $\log(k_1/k_2)_{T_1}$  and  $\log(k_1/k_2)_{T_2}$ , which should lie on Line I. The difference between Fig. 5, in which such points are plotted, and Fig. 4, in which the co-ordinates are  $\log(2k_1/k_2)_{T_1}$

and  $\log(2k_1/k_2)_{T_2}$ , is not very great, but on the whole the latter shows slightly better agreement between the experimental points and the theoretical line. The accuracy of the data does not permit of final decision in either of the cases considered, but certainly favours the view that the two similar positions are simultaneously available.

The results of the measurement of the relative effects of the alkyl groups when attached to oxygen in tolyl as compared with phenyl ethers represent the first departure from the strictly additive rule for the energies of activation which has been discovered. It is too early to discuss this anomaly, but the following observations may be made: (1) The effect is regular, and therefore can scarcely be due to lack of purity of the chloro- and bromo-tolyl ethers, which were prepared from a variety of materials by different methods. (2) On plotting the numerical values of the logarithms of the ratios of tolyl ethers with given alkyl groups against similar values for phenyl ethers, the points approximate to a straight line of slope 0.97. It may easily be shown that this result follows from the assumption that in the tolyl series the contribution of an alkyl group towards the total energy of activation is only 0.97 of the contribution made by it in the phenyl series.

#### EXPERIMENTAL.

The ethers were prepared by standard methods and purified by repeated crystallisation or vacuum-distillation. The recorded distillation temperatures are bath temperatures for distillation under 2 mm. pressure.

*3-Chloro-p-tolyl n-propyl ether*, prepared from 3-chloro-*p*-cresol and *n*-propyl iodide in the usual manner, distilled at 106° and had  $n_D^{25}$  1.5161 (Found: Cl, 19.3.  $C_{10}H_{13}OCl$  requires Cl, 19.3%). *3-Bromo-p-tolyl n-propyl ether* distils at 115°;  $n_D^{25}$  1.5362 (Found: Br, 35.0.  $C_{10}H_{13}OBr$  requires Br, 34.9%). *3-Chloro-p-tolyl benzyl ether*, prepared from the potassium salt of 3-chloro-*p*-cresol and benzyl chloride by the usual method, crystallises from alcohol as colourless needles, m. p. 50.5° (Found: Cl, 15.0.  $C_{14}H_{13}OCl$  requires Cl, 15.1%). *3-Chloro-p-tolyl p-nitrobenzyl ether*, prepared similarly, yields pale yellow needles from acetic acid, m. p. 132° (Found: Cl, 13.2.  $C_{14}H_{12}O_3NCl$  requires Cl, 12.8%). *3-Bromo-p-tolyl benzyl ether* crystallises in colourless needles from alcohol, m. p. 42.5° (Found: Br, 28.9.  $C_{14}H_{13}OBr$  requires Br, 28.9%). *3-Bromo-p-tolyl p-nitrobenzyl ether* crystallises in pale yellow needles from acetic acid, m. p. 131.5° (Found: Br, 24.7.  $C_{14}H_{12}O_3NBr$  requires Br, 24.8%). *3-Nitro-p-tolyl n-propyl ether*, from the silver salt of the nitrocresol and *n*-propyl iodide, is a golden-yellow oil which distils

at 154°;  $n_D^{20}$  1.5301 (Found: C, 61.7; H, 6.9.  $C_{10}H_{13}O_3N$  requires C, 61.5; H, 6.7%). 3-Nitro-*p*-tolyl isopropyl ether is a golden-yellow oil distilling at 134°;  $n_D^{25}$  1.5242 (Found: C, 61.7; H, 6.9.  $C_{10}H_{13}O_3N$  requires C, 61.5; H, 6.7%).

The measurements of the velocity of chlorination at 20° and 35° were carried out by the method described previously (Orton and Bradfield, J., 1927, 986; Bradfield and Jones, *loc. cit.*), the medium being purified acetic acid containing a total of 1 c.c. of water per 100 c.c. of reaction mixture. A slight modification of the procedure was adopted, however, for a number of the measurements at 35°, to minimise the loss of chlorine to the vapour phase. Three flasks, either of 50 c.c. or of 25 c.c. capacity, were employed for each velocity determination and one portion only was removed for titration from each flask. Some difficulty was experienced initially in the measurements with tolyl ethers, owing to the return of the starch iodide blue colour after the end-point of the titration had been reached, with a consequent loss of sharpness. This difficulty was overcome by titrating in the presence of carbon tetrachloride, in which the organic substances remained dissolved and so were protected from the reducing action of the aqueous hydriodic acid.

The mean values of the velocity coefficients obtained are tabulated below. The diagrams given above are constructed from these data, together with those previously published, much of which has been checked by repetition. So far as possible, in taking ratios, the two values of the velocity coefficients employed were taken from two experiments in which the initial concentrations of the reactants were the same.

### Velocity Coefficients.

#### Ethers of *p*-chloro- and *p*-bromo-phenol.

		[Cl <sub>2</sub> ] = 0.0075; [HCl] = 0.0375.			
		20°.	35°.	20°.	35°.
[Ether] = 0.0075.		0.0075.	0.0225.	0.0075.	0.0075. 0.0225.
R =		Ethers of <i>p</i> -chlorophenol.		Ethers of <i>p</i> -bromophenol.	
Pr <sup>β</sup>	.....	5.778	13.69	5.845	15.54
Pr <sup>α</sup>	.....	—	—	—	—
Bu <sup>α</sup>	.....	2.926	7.320	—	—
Et	.....	2.637	6.334	2.626	6.398
Me	.....	—	—	—	—
*A·H	.....	—	—	—	—
<i>m</i> -A·NO <sub>2</sub>	.....	—	—	—	—
<i>p</i> -A·NO <sub>2</sub>	.....	—	—	—	—
			0.5478		0.5661
			0.4620		0.4796

\* A = CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>.

*Nitrophenyl and nitrotolyl ethers.*[Cl<sub>2</sub>] = 0.02; [HCl] = 0.05; [ether] = 0.20.

	20°.	35°.	20°.	35°
	Ethers of <i>p</i> -nitrophenol.		Ethers of 3-nitro- <i>p</i> -cresol.	
R = Pr <sup>a</sup> .....	—	—	0.04949	0.1273
Et .....	0.005983	0.01920	0.04437	0.1182
Me .....	0.002993	0.009602	0.02186	0.05941

*Chloro- and bromo-tolyl ethers.*[Cl<sub>2</sub>] = 0.0025; [HCl] = 0.0125.

	20°.		35°.	20°.		35°.
[Ether]	0.0075.	0.0125.	0.0075.	0.0075.	0.0125.	0.0075.
	3-Chloro- <i>p</i> -tolyl ethers.			3-Bromo- <i>p</i> -tolyl ethers.		
R = Pr <sup>a</sup> .....	11.25	—	23.67	13.69	—	28.56
Et .....	9.882	—	21.10	11.75	11.10	25.39
Me .....	5.283	—	11.72	6.490	—	14.27
A·H .....	3.137	2.849	7.058	3.754	3.549*	8.489
<i>p</i> -A·NO <sub>2</sub> .....	0.5841	0.5798	1.429	0.7163	0.6925	1.747

\* Conc. of ether = 0.025 mol./litre.

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