CCCCIII.—*The Chlorination of Anilides. Part V. The Significance of Velocity Measurements in Relation to the Problem of Benzene Substitution* (continued).

By ALAN EDWIN BRADFIELD and BRYNMOR JONES.

1. *The Critical Energy Increments for the Reactions of* p-*Disubstituted Benzenes.*

IN an attempt to link qualitative theories of the mechanism of nuclear activation with the kinetic theories of reaction which have found expression in the conception of the critical energy increment, the authors recently considered (this vol., p. 1006) the application to aromatic substitution reactions of the equation for reaction velocity $k = PSZe^{-E/RT}$ (where Z is the collision number, E the critical increment, and S and P are probability terms depending on the shapes and the "phase conditions" of the molecules). Expressions of the type $\log (k_o/2k_p)_{T_1} = (T_2/T_1) \log (k_o/2k_p)_{T_2}$ were deduced and employed to calculate the effect of temperature on the proportions of isomerides formed by further substitution of mono- and di-substituted benzene derivatives.* The success of our calculation warranted the provisional rejection of phase factors (P) and steric factors (S), the product of which differed for the alternative points of entrance of the substituent, and justified the adoption of the hypothesis that the ratio of the isomerides formed is governed entirely by the difference of energy of activation of the positions

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* The authors regret that at the time they were completely unaware that, so long ago as 1913, in a paper of which no abstract appeared in the *Chemisches Zentralblatt*, and which appears to have been generally overlooked by those interested in the problem of benzene substitution (compare, *e.g.*, the discussion of the effect of temperature by Holleman, *Chem. Reviews*, 1924, **1**, 221; Lapworth and Robinson, *Mem. Manchester Phil. Soc.*, 1928, **72**, 43), Scheffer (*Proc. K. Akad. Wetenschap. Amsterdam*, 1913, **15**, 1118) had not only deduced exactly the same expression from a thermodynamic standpoint, and carried out a similar calculation, but had also anticipated the authors in pointing out that Holleman's empirical "product rule" implies the addition of energies of activation. They now wish to direct attention to Scheffer's undisputed priority in this connexion.

concerned. As a result of extending this hypothesis to a series of closely related ethers p-RO·C_6H_4·X, to the rate of chlorination of which relations of the type* $k^{OR_1}_{X_1}/k^{OR_1}_{X_2} = k^{OR_2}_{X_1}/k^{OR_2}_{X_2}$ apply, we were led to the conclusion that the groups already present contribute additively to the energy of activation of the position in which the new substituent will enter. By a similar treatment of velocity ratios, Hückel (*Ber.*, 1928, **61**, 1517) has recently shown, *inter alia*, that the different rates of saponification of esters of *cis*- and *trans*-isomeric substituted *cyclo*hexanols find no reasonable explanation in "steric hindrance," thus affording indirect support for our hypothesis.

According to the theory of kinetic activation, the energy condition which must be satisfied before the molecules A and B can react in a given medium is that the sum of the kinetic energies of translation, $E_A + E_B$, of the two colliding molecules should exceed E, the critical energy increment, and conclusions which appear to be of some importance may be reached by a more detailed examination of the significance of E. It is to be remembered that E is not a characteristic of either one substance or the other, but of the reaction between the two. It would seem, however, that this amount of energy E is the minimum required to bring about some essential change in the sub-atomic structure of both A and B before the molecules can become articulated to form an intermediate complex which, by a rearrangement of electronic orbits, breaks down to the new molecules C and D. A fraction, ε_1, then, of E represents the energy required to "activate" A, whilst ε_2 is required to "activate" B, there being no necessity to assume any fixed relationship between ε_1 and E_A, and ε_2 and E_B. For the reaction of A with a second reagent M, similarly

$$\varepsilon_1' + \varepsilon_2' = E' \gtreqless E_A' + E_M$$

and again there need be no other relationship between ε_1' and E_A', and ε_2 and E_M than that expressed above. Further, there is no *a priori* reason to suppose there is any simple relationship between ε_1 and ε_1'.

The E terms for the expression for the velocity coefficients for the chlorination of p-MeO·C_6H_4·X and p-EtO·C_6H_4·X given in Part IV may now be expanded on these lines, thus :

$$\log_e(k^{OMe}_{p\text{-}X}/2Z) = -(\varepsilon_{OMe} + E_{p\text{-}X} + \varepsilon_{Cl_2})/RT$$
$$\log_e(k^{OEt}_{p\text{-}X}/2Z) = -(\varepsilon_{OEt} + E_{p\text{-}X} + \varepsilon'_{Cl_2})/RT$$

where $(\varepsilon_{OMe} + E_{p\text{-}X})$ is the energy required to activate the ortho-carbon atom, ε_{OMe} representing the effect of the methoxyl group, and $E_{p\text{-}X}$ representing the modifying influence of the para-atom X;

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* For notation, see Bradfield and Jones (*loc. cit.*).

$(\varepsilon_{\text{OEt}} + E_{p\text{-X}})$ has a similar significance. $\varepsilon_{\text{Cl}_2}$ and $\varepsilon'_{\text{Cl}_2}$ represent the energy required to activate the chlorine molecule for the reaction with the first and second substances respectively. The experimental work discussed in Part IV requires that (1) $E_{p\text{-X}}$ is the same in both cases, and (2) $(\varepsilon_{\text{OMe}} + \varepsilon_{\text{Cl}_2})$ and $(\varepsilon_{\text{OEt}} + \varepsilon'_{\text{Cl}_2})$ are independent of the chemical nature of X, for then

$$\log_e k^{\text{OEt}}_{p\text{-X}}/k^{\text{OMe}}_{p\text{-X}} = \{(\varepsilon_{\text{OMe}} - \varepsilon_{\text{OEt}}) + (\varepsilon_{\text{Cl}_2} - \varepsilon'_{\text{Cl}_2})\}/RT \quad . \quad . \quad (1)$$

is independent of the nature of X.

Consider now the equations for the rates of nitration of 4-ethoxyanisole in positions 2 and 3 respectively :

$$\log_e(k_2/2Z) = -(\varepsilon'_{\text{OMe}} + E_{p\text{-OEt}} + \varepsilon_{\text{HNO}_3})/RT$$
$$\log_e(k_3/2Z) = -(\varepsilon'_{\text{OEt}} + E_{p\text{-OMe}} + \varepsilon'_{\text{HNO}_3})/RT$$

where $(\varepsilon'_{\text{OMe}} + E_{p\text{-OEt}})$ is the energy required to activate carbon atom 2, $\varepsilon'_{\text{OMe}}$ and $E_{p\text{-OEt}}$ representing respectively the effects of the methoxy- and the ethoxy-group. A similar significance attaches to $\varepsilon'_{\text{OEt}}$ and $E_{p\text{-OMe}}$. $\varepsilon_{\text{HNO}_3}$ and $\varepsilon'_{\text{HNO}_3}$ are the energies required to activate the nitric acid molecule in order that it may react with carbon atoms 2 and 3 respectively. Hence

$$\log_e k_3/k_2 = \{(\varepsilon'_{\text{OMe}} - \varepsilon'_{\text{OEt}}) + (E_{p\text{-OEt}} - E_{p\text{-OMe}}) + (\varepsilon_{\text{HNO}_3} - \varepsilon'_{\text{HNO}_3})\}/RT \quad (2)$$

No theoretical grounds exist for supposing that there is any simple relation between the values $k^{\text{OEt}}_{p\text{-X}}/k^{\text{OMe}}_{p\text{-X}}$ and k_3/k_2 determined by equations (1) and (2) respectively.

The nitration in acetic acid of certain quinol ethers of the type p-RO·C_6H_4·OMe has been studied by Robinson and Smith (J., 1926, 392) and by Clarke, Robinson, and Smith (J., 1927, 2647), and the ratios k_3/k_2 have been determined. The values obtained are compared in the following table with the ratios $k^{\text{OR}}_{p\text{-X}}/k^{\text{OMe}}_{p\text{-X}}$ for the chlorination of ethers p-RO·C_6H_4·X, given in Part IV.

R.	Nitration. k_3/k_2.	Chlorination. $k^{\text{OR}}_{p\text{-X}}/k^{\text{OMe}}_{p\text{-X}}$.
Et	1·63	1·99
Pr^a	1·80	2·20
Bu^a	1·86	2·22
p-NO_2·C_6H_4·CH_2	0·38	0·143

An obvious parallelism exists, and certain simplifying assumptions will now be made in an attempt to connect equations (1) and (2).

The first assumption is that $\varepsilon_{\text{Cl}_2} = \varepsilon'_{\text{Cl}_2}$ and $\varepsilon_{\text{HNO}_3} = \varepsilon'_{\text{HNO}_3}$, and the second that in compounds of the type R_1O·C_6H_4·OR_2, the effect of RO in modifying the amount of energy required to activate carbon atom 3 is proportional to its effect on carbon atom 2, *i.e.*, $E_{p\text{-OR}_1} = n\varepsilon'_{\text{OR}_1}$, and that n is a constant independent of R_1 and R_2.

The third assumption is that $m(\varepsilon_{OR_1} - \varepsilon_{OR_2}) = (\varepsilon'_{OR_1} - \varepsilon_{OR_2})$ where m is a constant. Equations (1) and (2) then become

$$\log_e k^{OEt}_{p\text{-}X}/k^{OMe}_{p\text{-}X} = (\varepsilon_{OMe} - \varepsilon_{OEt})/RT_1 \quad . \quad . \quad . \quad (1')$$

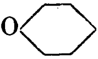
$$\log_e k_3/k_2 = \{m(\varepsilon_{OMe} - \varepsilon_{OEt}) - mn(\varepsilon_{OMe} - \varepsilon_{OEt})\}/RT_2 . \quad (2')$$

whence

$$\log_{10} k^{OEt}_{p\text{-}X}/k^{OMe}_{p\text{-}X} = \frac{T_2}{m(1-n)T_1}\log_{10} k_3/k_2 . \quad . \quad . \quad (3)$$

Unfortunately, there is no means of determining either m or n separately, or the product $m(1 - n)$. The arbitrary value 0·6278 has been assigned to $m(1 - n)$ and the calculation of the proportions of the isomerides formed by the nitration of 4-ethoxy-, 4-propoxy-, and 4-butoxy-anisole at 0°, and of 4-*p*-nitrobenzyloxyanisole at 24° * from the data for chlorination at 20° of the ethers $RO{\cdot}C_6H_4{\cdot}X$ has been carried out by means of (3), and the results are compared with the observed values in Table I. The agreement is fairly satisfactory.

TABLE I.

Nitration of ROOMe.

R.	3-Nitro-derivative, % Found.	3-Nitro-derivative, % Calc.
Et	62·2	61·4
Pr^α	64·3	63·0
Bu^α	65·0	63·1
p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$	27·6	23·1

The existence of additive relationships for the critical increments for the chlorination of ethers of the type p-$RO{\cdot}C_6H_4{\cdot}X$ has been demonstrated (Bradfield and Jones, *loc. cit.*), but the above calculations would have rested on a surer foundation if it were also known that similar relationships obtain for the nitration of the ethers p-$R_1O{\cdot}C_6H_4{\cdot}OR_2$. A satisfactory kinetic method for studying nitration does not appear to have been developed, but in this particular case, static measurements, *viz.*, the determination of the final ratio of isomerides formed, can be utilised to provide a test, since Holleman's " product rule " may be applied to the data for the nitration of the two compounds p-$R_1O{\cdot}C_6H_4{\cdot}OR_2$ and p-$R_3O{\cdot}C_6H_4{\cdot}OR_2$ to calculate the ratio of the isomerides formed by

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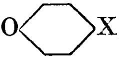
* In the experiments of Robinson and Smith, and of Clarke, Robinson, and Smith (*loc. cit.*), the temperatures were not kept rigidly constant, but these values appear to be approximately the temperatures during the nitrations. Further, the relative proportions of ether : acetic acid : nitric acid were not the same for the nitration of 4-*p*-nitrobenzyloxyanisole as for the other nitrations, so the figures for this ether are not strictly comparable with the others.

nitration of p-$R_1O{\cdot}C_6H_4{\cdot}OR_3$, and agreement between the observed and calculated ratios would indicate the additivity of the energies of activation. For example, from Robinson and Smith's data for 4-ethoxy- and 4-p-nitrobenzyloxy-anisole, the proportion of 2-nitro-compound formed by nitration of 4-p-nitrobenzyloxy-phenetole at 0° is calculated to be 82·2% (compare, however, footnote, p. 3076); there appear, however, to be no data available to test this calculation.

2. *Phase and Steric Factors.*

The isothermal condition $k_{X_1}^{OR_1}/k_{X_2}^{OR_1} = k_{X_1}^{OR_2}/k_{X_2}^{OR_2}$, derived from the experimental results given in Part IV, has been interpreted as indicating additivity of energies of activation for the chlorination of ethers of the type $RO{\cdot}C_6H_4{\cdot}X$, by extending to these reactions the hypothesis that the product of the phase and steric factors is constant. Nevertheless, other equally simple hypotheses would satisfy this condition, and the following analysis (for which the more detailed subdivision of the E-terms is unnecessary) indicates how some of these hypotheses may be differentiated by a measurement of the change of the ratio of the velocity coefficients with temperature.

First Hypothesis.—That the product of the phase and steric factors is the same for different substances of the type ROX, *under the same conditions, the groups* RO *and* X *then contributing additively to the energy of activation.* This is the hypothesis already promulgated. Suitable algebraic manipulation of the expressions for the velocity coefficients (given in Part IV) derived from this hypothesis, gives the relation

$$k_{X_1}^{OR_1}/k_{X_2}^{OR_2} = e^{\{(E_{X_2}-E_{X_1})+(E_{OR_2}-E_{OR_1})\}/RT}$$

whence, for two different temperatures,

$$\log\,(k_{X}^{OR_1}/k_{X_2}^{OR_2})_{T_1} = (T_2/T_1)\log(k_{X_1}^{OR_1}/k_{X_2}^{OR_2})_{T_2} \quad . \quad . \quad (4)$$

Second Hypothesis.—That the energy of activation is the same for all compounds of the type under discussion, and that a replacement of R_1 *by* R_2 *alters the product* PS *to* P′S′, *whilst a replacement of* X_1 *by* X_2 *brings about an* n*-fold increase or decrease in* PS *or* P′S′. The equations for the velocity coefficients then become

$$k_{X_1}^{OR_1} = 2PSZe^{-E/RT} \qquad k_{X_1}^{OR_2} = 2P'S'Ze^{-E/RT}$$
$$k_{X_2}^{OR_1} = 2nPSZe^{-E/RT} \qquad k_{X_2}^{OR_2} = 2nP'S'Ze^{-E/RT}$$

whence $k_{X_1}^{OR_1}/k_{X_2}^{OR_1} = 1/n = k_{X_1}^{OR_2}/k_{X_2}^{OR_2}$, as required, and

$$(k_{X_1}^{OR_1}/k_{X_2}^{OR_2})_{T_1} = PS/nP'S' = (k_{X_1}^{OR_1}/k_{X_2}^{OR_2})_{T_2} \quad . \quad . \quad (5)$$

Third Hypothesis.—That the energy of activation is determined solely by the nature of the group OR, *replacement of the group* X_1 *by*

X_2 *causing an* n-*fold increase or decrease of the product* PS, *only.* The equations for the velocity coefficients become

$$k^{OR_1}_{X_1} = 2PSZe^{-E_{OR_1}/RT} \qquad k^{OR_2}_{X_1} = 2PSZe^{-E_{OR_2}/RT}$$

$$k^{OR_1}_{X_2} = 2nPSZe^{-E_{OR_1}/RT} \qquad k^{OR_2}_{X_2} = 2nPSZe^{-E_{OR_2}/RT}$$

whence $k^{OR_1}_{X_1}/k^{OR_1}_{X_2} = 1/n = k^{OR_2}_{X_1}/k^{OR_2}_{X_2}$, as required, and $nk^{OR_1}_{X_1}/k^{OR_2}_{X_2} = e^{(E_{OR_2}-E_{OR_1})/RT}$, whence

$$\log (nk^{OR_1}_{X_1}/k^{OR_2}_{X_2})_{T_1} = (T_2/T_1) \log (nk^{OR_1}_{X_1}/k^{OR_2}_{X_2})_{T_2} . \quad . \quad (6)$$

Fourth Hypothesis.—That the energy of activation is determined by the oxygen atom attached to one carbon atom, as modified by the group X, *replacement of* R_1 *by* R_2 *causing an* n-*fold increase or decrease of the product* PS *only.* The equations then become

$$k^{OR_1}_{X_1} = 2PSZe^{-(E_0+E_{X_1})/RT} \qquad k^{OR_2}_{X_1} = 2nPSZe^{-(E_0+E_{X_1})/RT}$$

$$k^{OR_1}_{X_2} = 2PSZe^{-(E_0+E_{X_2})/RT} \qquad k^{OR_2}_{X_2} = 2nPSZe^{-(E_0+E_{X_2})/RT}$$

whence $k^{OR_1}_{X_1}/k^{OR_1}_{X_2} = e^{(E_{X_2}-E_{X_1})/RT} = k^{OR_2}_{X_1}/k^{OR_2}_{X_2}$, as required, and $nk^{OR_1}_{X_1}/k^{OR_2}_{X_2} = e^{(E_{X_2}-E_{X_1})/RT}$, whence

$$\log (nk^{OR_1}_{X_1}/k^{OR_2}_{X_2})_{T_1} = (T_2/T_1) \log (nk^{OR_1}_{X_1}/k^{OR_2}_{X_2})_{T_2} . \quad . \quad (7)$$

A distinction may be drawn between these hypotheses by measuring the ratio $k^{OR_1}_{X_1}/k^{OR_2}_{X_2}$, at different temperatures, and comparing the change in the ratio with temperature with that calculated by means of expressions 4, 5, 6, and 7, respectively. The fineness of this distinction depends on the experimental accuracy, which, unfortunately, for a decisive result requires to be very much greater that is at present attainable, but Table II shows the agreement between the observed values of $k^{OMe}_{CO_2H}/k^{OEt}_{NO_2}$ at 30° and those calculated from the observed values at 20°.

TABLE II.

	$(k^{OMe}_{CO_2H}/k^{OEt}_{NO_2})_{T_1}$.	$(k^{OMe}_{CO_2H}/k^{OEt}_{NO_2})_{T_2}$. Found.	Calc.	Difference.
Hypothesis 1	74·22	68·82	64·42	−4·40
,, 1 (" corrected ")	66·8	61·93	58·22	−3·71
,, 2	74·22	68·82	74·22	+5·40
,, 3	74·22	68·82	75·94	+7·12
,, 4	74·22	68·82	62·97	−5·85

A possible objection to the above calculation is that the data for anisic acid and for *p*-nitrophenetole, owing to experimental exigencies, do not refer to identical conditions of concentration, and the observed values of the velocity coefficients depend to some extent on the initial concentrations. However, examination of the data indicates that the velocity coefficient for anisic acid would be slightly lower if it were possible to measure it at the same concentration as that to which the data for *p*-nitrophenetole apply, and that this

" correction " would not amount to more than 10% of the value of k. The value calculated by expression (4) for the ratio at 30° has been recalculated on the assumption that the " corrected " values of the velocity coefficients at 20° and 30° are 10% lower than the observed values, and it is seen that the result is but little affected. This calculation also shows that a small *systematic* error throughout the measurements would lead to little difference in the result.

That the solvent is not without effect on the velocity of reaction is shown by Norrish and Smith (this vol., 129), and it is implicit in all the foregoing that it affects these similar reactions to a similar extent, and that the term representing its effect, which should be introduced into the expression for k, cancels out when ratios are taken. This assumption is in some degree justified by a calculation by Norrish and Smith's method, employing their approximations, of the ratio of the number of effective collisions to the number of collisions fulfilling the energy condition for the chlorination of anisic acid, p-nitrophenetole, and ω-trichloroacetanilide, and is of the order 10^{-5} in each case. This factor includes, of course, any P or S terms.

Examination of Table II now shows that the first hypothesis is, *at least*, as correct as the others. The purpose of this discussion will have been served if it has been shown that the data considered here, and in Part IV, find a quantitative explanation within the limits of experimental error, by the single assumption that the different rates of entrance of a given substituent at different points in the same molecule or in similar molecules under identical conditions are determined by the differences of the critical energy increments, without invoking phase or steric factors. An extensive test of this hypothesis on the lines indicated has been begun in these laboratories.

3. *Structure and Reactivity.*

From the new data for the chlorination of anilides in 99% acetic acid, it is seen that the value 0·580 for the velocity coefficient of ω-trichloroacetanilide falls into place in the series acetanilide ($k = 62{\cdot}2$), formanilide ($k = 9{\cdot}2$), trichloroacetanilide, showing the general parallel between the rate of chlorination of anilides of the type $C_6H_5{\cdot}NH{\cdot}CO{\cdot}R$ and the strength of the acid $R{\cdot}CO_2H$. On the other hand, p-toluenesulphonanilide chlorinates even more rapidly than benzenesulphonanilide.

The effect of replacing the imino-hydrogen atom of acetanilide by a methyl group in reducing the rate of chlorination roughly to one two-thousandth, is striking. An obvious explanation would be that substitution in the acetanilide nucleus proceeds both by a direct route, and by an indirect one involving the intermediate formation of a chloroamide, the former process being the slower, whilst for methylacetanilide only the direct route is available. For reasons summarised in Part III of this series, the authors regard this explanation as unlikely, and in addition, qualitative observations of solubility and ease of hydrolysis by aqueous acids indicate that the marked difference in properties of these two substances is not confined to speed of chlorination. *N*-Methylation of *p*-toluenesulphonanilide produces a similar but much smaller effect.

A gap in the series of alkyl groups investigated has been filled by a determination of the velocity coefficients for p-*chlorophenyl* iso*butyl ether* and p-iso*butoxybenzoic acid.* The mean value of the ratio $100k_{p\text{-X}}^{\text{OBu}^{\beta}}/k_{p\text{-X}}^{\text{OMe}}=216$ for these ethers is of the expected order of magnitude. No attempt can be made at present to connect quantitatively the reactivity of these compounds with their structure, but it is noteworthy that the results so far obtained find a simple qualitative explanation in terms of the modern theories of benzene substitution developed by Robinson and Ingold (see summary, *Ann. Reports,* 1926 and 1927).

EXPERIMENTAL.

The measurements of the velocity of chlorination of the following anilides and phenolic ethers were carried out by the method already described (Orton and Bradfield, J., 1927, 986; Bradfield and Jones, *loc. cit.*), the medium being purified acetic acid (Orton and Bradfield, J., 1924, **125**, 960; 1927, 983) containing a total of 1 c.c. of water per 100 c.c. of reaction mixture, previously adopted as standard. Since the reproducibility of the observed velocity coefficients has been sufficiently illustrated in the earlier papers, it will suffice to give in tabulated form the mean values of *k*.

Velocity Coefficients for the Chlorination of Anilides at 20°.

Concentration of chlorine = 0·0025 g.-mol./litre.
,, ,, HCl = 0·0125 ,,

	Conc. of anilide (g.-mol./litre).			
	0·0025.	0·0075.	0·025.	0·075.
p-Toluenesulphonanilide	65·11	—	—	—
p-Toluenesulphonmethylanilide	2·61	2·48	2·396	—
Trichloroacetanilide	—	0·5778	0·582	—
Methylacetanilide	—	—	—	0·0338*

* Conc. of chlorine = 0·005 g.-mol./litre.

Chlorination of Trichloroacetanilide at 30°.

Anilide : chlorine : HCl = 0·0075 : 0·0025 : 0·0125 g.-mol./litre.
$k_{30^\circ} = 1{\cdot}081$; $k_{30^\circ}/k_{20^\circ} = 1{\cdot}871$.

Chlorination of iso*Butyl Ethers at* 20°.

Ether : chlorine : HCl = 0·0225 : 0·0075 : 0·0375 g.-mol./litre.
p-Chlorophenyl *iso*butyl ether, $k = 2{\cdot}701$; *p*-*iso*butoxybenzoic acid, $k = 0{\cdot}935$.

Temperature Coefficients for Ethers.

Anisic acid.

Ether : chlorine : HCl = 0·0225 : 0·0075 : 0·0375 g.-mol./litre.
$k_{30^\circ} = 0{\cdot}8898$; $k_{20^\circ} = 0{\cdot}444$; $k_{30^\circ}/k_{20^\circ} = 2{\cdot}004$.

p-*Nitrophenetole.*

Ether : chlorine : HCl = 0·20 : 0·02 : 0·05 g.-mol./litre.
$k_{30^\circ} = 0{\cdot}01293$; $k_{20^\circ} = 0{\cdot}005983$; $k_{30^\circ}/k_{20^\circ} = 2{\cdot}16$.

p-iso*Butoxybenzoic acid* was prepared from *p*-hydroxybenzoic acid by a modification of Ladenburg and Fitz's method for the alkylation of hydroxybenzoic acids (*Annalen*, 1867, **141**, 254): 19·4 g. (1 mol.) of *p*-hydroxybenzoic acid were dissolved in a solution of 15·8 g. (2 mols.) of potassium hydroxide in the smallest possible quantity of water, and refluxed at 120° for 7 hours with 26 g. (1·1 mols.) of *iso*butyl iodide and 2 c.c. of *iso*butyl alcohol; 10% potassium hydroxide (1 mol.) was then added, and the refluxing continued for another hour to hydrolyse any ester formed. The product was dissolved and suspended in 50 c.c. of water and just acidified with concentrated hydrochloric acid. The precipitated solid was filtered off, repeatedly washed with water until free from hydrochloric acid, and crystallised from acetic acid; m. p. 136·5° (*M*, by titration, 193·4. Calc.: *M*, 194·2).

p-*Chlorophenyl* iso*butyl ether* was prepared from *p*-chlorophenol, sodium, *iso*butyl alcohol, and *iso*butyl iodide by the usual method, and purified by distillation under 3 mm. pressure (bath temp. 95—97°). The form of the apparatus used did not permit of an accurate determination of the b. p., the velocity coefficient itself being taken as the standard of purity, as described in Part IV; $n_D^{25^\circ} = 1{\cdot}5090$ (Found: Cl, 19·4. $C_{10}H_{13}OCl$ requires Cl, 19·3%).

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