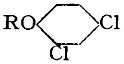
140. *The Halogenation of Phenolic Ethers and Anilides. Part XIII. Arrhenius Activation Energies for Di- and Poly-substituted Aromatic Ethers.*

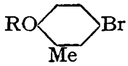
By Brynmor Jones.

The kinetic study of the nuclear chlorination of aromatic ethers at temperatures between 15° and 35° has been extended to di- and poly-substituted ethers which contain activating as well as deactivating substituents. In each case there is only one position available for substitution. Analysis of the results on the basis of the equation $k = PZe^{-E/RT}$ shows that the variations in the P term are small and within the error of experiment, while the energy of activation varies from 9,900 to 14,350 cals.

A RECENT detailed investigation of the rates of nuclear chlorination of 21 ethers of the type *p*-OR·C_6H_4X at temperatures between 15° and 35° showed that the *P* term of the expression $k = PZe^{-E/RT}$ is constant within the limits of experimental error, while *E* varies from 9,850 to 14,650 cals. (this vol., p. 418). This result confirms the original view, first put forward in 1928, that the observed regularities in the relative influences of substituent groups on the rates of nuclear chlorination of these ethers are simply and adequately accounted for by assuming that each group contributes a characteristic quota to the energy of activation. The results of a limited number of measurements are now recorded for certain di- and poly-substituted aromatic ethers, and the same conclusion is reached. In these series the range of suitable compounds is more restricted, but members of the following four types have been investigated :



(I.)



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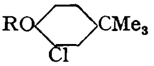

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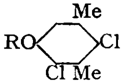


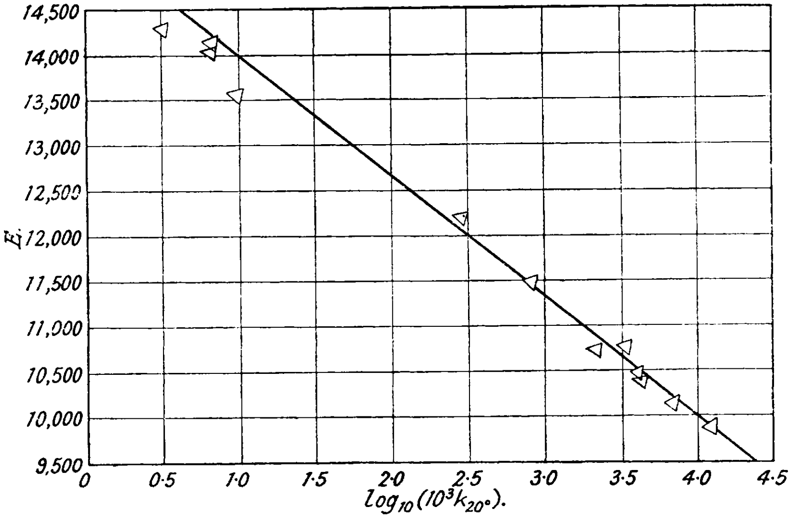
(IV.)

The results are summarised in the table. Where measurements were made at more than two temperatures the values of *E* were obtained by plotting log *k* against $1/T$; in other cases they were calculated from the usual expression. Values of log *PZ* were derived from these values of *E* and the velocity coefficients at 20°.

Velocity coefficients for the chlorination of di- and poly-substituted aromatic ethers in 99% *acetic acid.*

Type.	R.	$k_{15°}$.	$k_{20°}$.	$k_{30°}$.	$k_{35°}$.	*E* (cals.).	log *PZ*.
IV	Me	9·52	12·50	—	29·1	9,900	8·49
IV	CH_2Ph	—	7·14	—	16·7	10,150	8·43
IV	$CH_2{\cdot}C_6H_4Cl(p)$	3·19	4·37	—	10·34	10,400	8·40
II	Me	—	4·10	7·45	9·85	10,500	8·46
IV	$CH_2{\cdot}C_6H_4Cl(m)$	2·45	3·38	6·22	8·44	10,800	8·59
II	CH_2Ph	—	2·18	4·01	5·35	10,750	8·36
IV	$CH_2{\cdot}CO_2H$	—	0·836	1·60	2·19	11,500	8·50
III	$CH_2{\cdot}C_6H_4{\cdot}NO_2(p)$	—	0·291	—	0·811	12,250	8·63
I	$CHMe_2$	—	0·0095	—	0·0296	13,600	8·12
I	CH_2Et	—	0·0067	0·0150	0·0216	14,150	8·39
I	Et	—	0·00636	—	0·0206	14,050	8·29
I	Me	—	0·0031	—	0·0103	14,350	8·20

When $\log_{10}(10^3k_{20°})$ for each ether is plotted against *E* (see figure), all the points fall on or near the same straight line, of slope $-2{\cdot}303\boldsymbol{R}T$, as did the ethers of the simpler type *p*-OR C_6H_4X. Hence, although the present series of measurements are limited to a smaller number of ethers, and in some cases to a narrower range of temperature, than were those for the ethers of the type *p*-OR·C_6H_4X, yet together with these they show clearly that the variations in the *P* term on passing from one series of ethers to another are insignificant in comparison with the variations in the energy of activation.*



There is one further point arising out of these results. In considering the nuclear reactivity of di- and poly-substituted ethers of the above types with those of the simpler type *p*-OR·C_6H_4X, it is reasonable to suppose that the *P* term for the latter includes an additional factor 2 resulting from the presence of two similar vacant

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* The variations (of the order of 15%) in the relative directive power of OR groups discussed in Part X (J., 1941, 275) may, as there suggested, indicate small changes in the probability factor, but the relatively wide limits of error necessarily involved in the computation of *P* by the present method of analysis render such small variations quite insignificant.

ortho-positions available for substitution. The existence of such a factor would require that values of log 2*k* rather than of log *k* for the di- and poly-substituted ethers should fall on the straight line shown in the figure. Inspection shows that, while values of log 2*k* for the four alkyl ethers of dichlorophenol would fall more closely on the line than the values of log *k* plotted, yet the corresponding values for the other eight ethers would all lie distinctly to the right of the line. It appears, therefore, that the present series of measurements are too restricted in scope to allow of a decision on this point. Evidence of another type for the existence of a purely statistical factor based on the number of positions available for substitution has been discussed previously (J., 1936, 1854).

EXPERIMENTAL.

Materials.—Pure crystalline specimens of several of the ethers were available from earlier investigations (J., 1941, 267). 2-Chloro-4-*tert*.-butylphenol was prepared in excellent yield from *p*-*tert*.-butylphenol (J., 1941, 363) by Orton and King's method of controlled chlorination, freshly-prepared chloroacetamide being used as the source of chlorine (J., 1911, **99**, 1185; Orton and Bradfield, J., 1927, 993). When all the chlorine had reacted, the acetamide was removed by addition of water, and the 2-chloro-4-*tert*.-butylphenol extracted with ether. The extract was washed with (*a*) aqueous sodium bicarbonate and (*b*) water, dried, and the solvent removed. The residue of 2-chloro-4-*tert*.-butylphenol distilled at 113—115°/8 mm. The p-*nitrobenzyl ether* was crystallised thrice from ethyl alcohol and separated as colourless plates, m. p. 90° (Found: N, 4·7. $C_{17}H_{18}O_3NCl$ requires N, 4·4%). Similarly 2 : 4-dichloro-3 : 5-dimethylphenol was prepared from 2-chloro-5-*m*-xylenol (cf. Part X, J., 1941, 275); 2 : 4-*dichloro*-3 : 5-*dimethylphenoxyacetic acid* after two crystallisations from benzene was recrystallised from acetic acid, from which it separated in colourless prisms, m. p. 146° (Found: Cl, 28·4; equiv., 252. $C_{10}H_{10}O_3Cl_2$ requires Cl, 28·5%; equiv., 249). The acetic acid was purified by distillation from chromic anhydride and acetic anhydride as described by Orton and Bradfield (J., 1927, 983).

Measurements.—The method of determining the velocity coefficients and the precautions taken to ensure accurate values were the same as in Part XII (this vol., p. 418).

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