75. *The Halogenation of Phenolic Ethers and Anilides. Part XII. Some Arrhenius Activation Energies.*

By Brynmor Jones.

A kinetic study is described of the nuclear chlorination at temperatures between 15° and 35° of 21 ethers of the type *p*-OR·C_6H_4X, where R is generally a simple alkyl or substituted benzyl group and X is either F, Cl, COPh, O·COPh, or NO_2. Analysis of the results on the basis of the equation $k = PZe^{-E/RT}$ confirms the original conclusion that changes in the velocity of chlorination resulting from modifications in OR and X are due to changes in the energy of activation, which, in the ethers studied, varies from 9,850 to 14,650 cals.

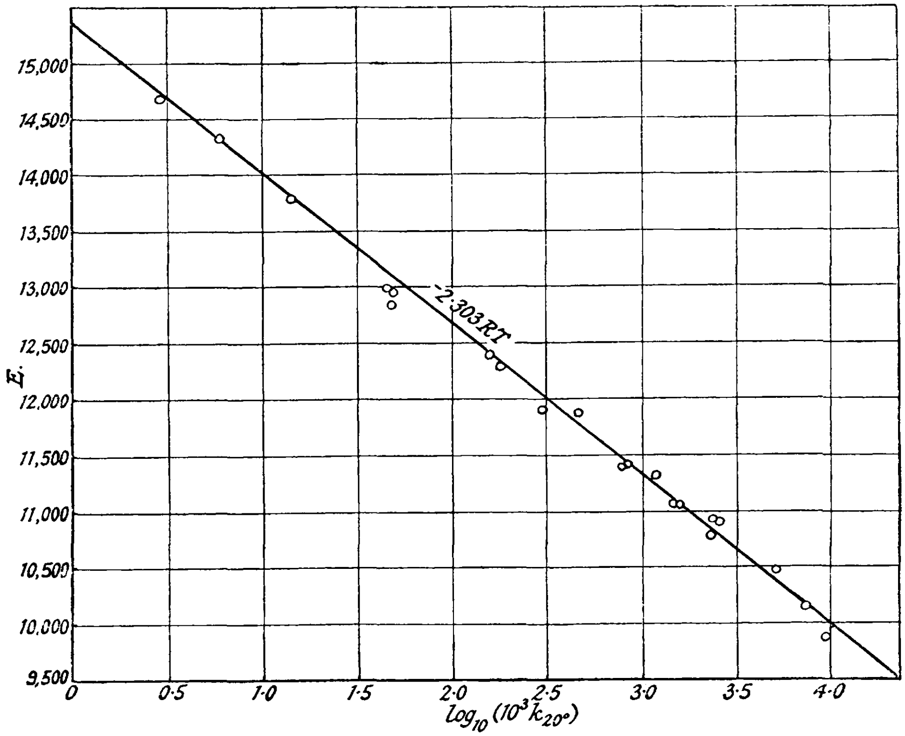
It has been demonstrated that in the chlorination of a number of phenolic ethers the P term of the expression $k = PZe^{-E/RT}$ is approximately constant, and consequently the observed regularities in the relative influence of substituent groups on nuclear reactivity find their simplest explanation on the assumption that the groups contribute characteristic quota to the activation energy (J., 1928, 1006, 3073; 1931, 2907). Since the range of ethers to which this conclusion may be applied has been greatly extended (J., 1935, 1831, 1835; 1936, 1854; 1938, 1414; 1941, 267; *Trans. Faraday Soc.*, 1941, 37, 726), it is necessary to strengthen the experimental evidence for the essential constancy of P throughout.

The present measurements are of ethers of the simple type *p*-OR·C_6H_4X, examples being selected to cover as wide a range of speeds and activation energies as possible. To increase precision, measurements have been made in many cases at 5° intervals over the range 15—35°, representing the practical limits imposed by the freezing of the medium on the one hand and the loss of chlorine to the vapour phase on the other.

The velocity coefficients, the energies of activation, and the values of log PZ are summarised in the following table. The rate constants were calculated from the usual expressions for a bimolecular reaction, the time being in mins. and the concentrations in g.-mols./l. The values of E were obtained by plotting log k against $1/T$, a straight line being obtained in all cases. From these values of E and the velocity coefficients at 20°, values of log PZ were calculated as usual. It is clear from the figure that when $\log_{10}(10^3k_{20°})$ for each ether is plotted against E all the points fall on or very near to a line of slope $-2{\cdot}303RT$, the intercept of which on the log k axis when $E = 0$ gives a value for log PZ of 8·46. This result confirms the original conclusion set out above.

Velocity coefficients for the chlorination of ethers of the type p-$OR{\cdot}C_6H_4X$ *in* 99% *acetic acid.*

R.	X.	$k_{15°}$.	$k_{20°}$.	$k_{25°}$.	$k_{30°}$.	$k_{35°}$.	E (cals.).	log PZ.
$CHMe_2$	F	7·10	9·50	12·5	16·6	21·7	9,850	8·34
Me	O·COPh	5·50	7·40	—	13·25	17·3	10,100	8·45
$CHMe_2$	Cl	3·80	5·15	6·92	9·48	12·4	10,500	8·55
Et	Cl	1·66	2·33	—	4·27	5·68	10,800	8·43
C_5H_{11}	COPh	1·83	2·56	—	4·76	6·45	10,900	8·55
Et	COPh	1·73	2·40	3·17	4·43	—	10,950	8·56
Et	$CO{\cdot}C_6H_4Cl$ (*p*)	1·16	1·60	—	3·00	4·08	11,050	8·45
CH_2Ph	F	1·07	1·48	2·03	—	3·73	11,050	8·42
Me	Cl	0·844	1·20	1·64	2·28	3·10	11,350	8·55
CH_2Ph	Cl	0·557	0·786	1·51	—	2·04	11,400	8·41
$CH_2{\cdot}C_6H_4Cl$ (*p*)	F	0·613	0·850	—	1·63	2·23	11,450	8·47
$CH_2{\cdot}C_6H_4Cl$ (*p*)	Cl	0·322	0·467	0·646	0·902	1·26	11,900	8·55
$CH_2{\cdot}C_6H_4{\cdot}NO_2$ (*p*)	F	—	0·300	—	0·590	0·810	11,950	8·40
$CH_2{\cdot}C_6H_4{\cdot}NO_2$ (*m*)	Cl	—	0·182	—	0·365	0·506	12,300	8·44
$CH_2{\cdot}C_6H_4{\cdot}NO_2$ (*p*)	Cl	—	0·157	0·225	0·321	0·446	12,400	8·45
$CH_2{\cdot}CO_2Et$	Cl	—	0·048	—	—	0·141	12,850	8·28
$CH_2{\cdot}CO_2H$	Cl	—	0·049	—	—	0·146	12,950	8·36
$CH_2{\cdot}CO_2Me$	Cl	0·031	0·046	—	0·094	0·132	13,000	8·37
$CHMe_2$	NO_2	—	0·0141	—	0·031	0·0443	13,800	8·45
Et	NO_2	—	0·0059	—	—	0·0196	14,350	8·48
Me	NO_2	—	0·00287	—	—	0·00978	14,650	8·40



EXPERIMENTAL.

Materials.—The majority of the ethers were pure crystalline specimens prepared for earlier investigations and these were recrystallised before use. The liquids (*p*-chloroanisole, b. p. 88°/18 mm.; *p*-chlorophenetole, b. p. 98°/17 mm.;

p-chlorophenyl *iso*propyl ether, b. p. 101°/17 mm.; and *p*-fluorophenyl *iso*propyl ether, b. p. 73°/18 mm.) were prepared from carefully purified *p*-chlorophenol and *p*-fluorophenol, considerable head and tail fractions being neglected in each case. *p*-Chlorophenoxyacetic acid and its methyl and ethyl esters were obtained by standard methods, and after repeated crystallisations had m. p.'s 156°, 39°, and 50°, respectively. The acetic acid was purified by distillation from chromic anhydride and acetic anhydride as described by Orton and Bradfield (J., 1927, 983).

Measurements.—The procedure for the measurements at 15° and 20° was the same as that employed for those at 20° in earlier parts of this series, three 10-c.c. titres only being withdrawn from 100-c.c. of reaction mixture in which the molecular proportions of ether : chlorine : hydrochloric acid were in most cases 3 : 1 : 1·5. In the measurements at 25°, 30°, and 35° a slight modification in this procedure was introduced because of the greater loss of chlorine from the reaction mixture as titres were withdrawn. Three flasks, each of 25 c.c. capacity, were used for each velocity determination and one portion only was removed for titration from each flask. The pipettes used were stored in a jacket in the thermostat, and a microburette graduated in 0·02 c.c. was employed for the titrations. Owing to the extensive number of measurements, the original large batch of purified acetic acid became exhausted, and in order to avoid possible errors due to a slight variation in the water content of the old and the new stock, all measurements on any one ether were done with the same batch of acid.

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