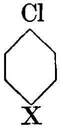
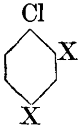
CXLII.—*The Comparative Effects of the Nitro-, Carboxyl, and Sulphonic Acid Groups on the Hydrolysis of Aryl Halides.*

By WILLIAM DAVIES and EDNA SWALLOW WOOD.

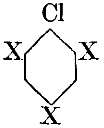
THE almost complete lack of activity of chlorine in 1 : 3-dichlorobenzene-4 : 6-disulphonic acid as compared with its great activity in 1 : 3-dichloro-4 : 6-dinitrobenzene has already been noticed (J., 1927, 1122). The effect of the nitro-group on *o*- and *p*-halogen atoms is great and well known (compare Kenner, J., 1914, **105**, 2717; Holleman and collaborators, *Rec. trav. chim.*, 1921, **40**, 67). Partly from a consideration of their activating effects on other atoms or groups in the same molecule, the carboxyl and the sulphonic acid groups, like the nitro-group, have been classified as positive (Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 2). However, the chief and almost the only experimental investigation of the activating effects of these two groups on halogen atoms in the benzene nucleus has been carried out by Schöpff and his collaborators, who deduced the following rule from their results (*Ber.*, 1891, **24**, 3784, where references to previous experimental work are given) :—
" Das Halogenatom des Benzolkernes ist bei gleichzeitiger Anwesenheit zweier negativer Gruppen in o- und p- Stellung, der gleich oder ungleich sein konnen, leicht durch andere zu ersetzen; ist nur eine negative Gruppe vorhanden, so findet keine Umsetzung statt, ausser bei der Nitrogruppe." One of the results of the rule has been the adoption in preparative work of precautions against hydrolysis in compounds of the type examined by Schöpff (see p. 1126).



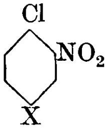
(I.)



(II.)



(III.)



(IV.)

This paper records a comparison of the effects of the groups mentioned in the title on the reaction $RCl + 2KOH = ROK + KCl + H_2O$.

Martinsen (*Z. physikal. Chem.*, 1907, **59**, 605) has shown that the speeds of nitration of nitrobenzene, benzenesulphonic acid, and benzoic acid are

CO_2H ($K = 100$)$>SO_3H$($K = 26{\cdot}0$)$>NO_2$($K = 1{\cdot}5$) . Series A.

Since benzoic acid (19·8%), benzenesulphonic acid (10%), and nitrobenzene (about 6·5%) undergo under similar conditions ortho-para-nitration to the extents indicated in parenthesis (Holleman, " Die direkte Einführung von Substituenten in den Benzolkern," pp. 124, 75, and 71 respectively), it is evident that no very exact quantitative meaning can be assigned to Martinsen's figures, which refer to total and not merely meta-nitration. Nevertheless Martinsen's results may be accepted as indicating in a roughly quantitative way the activation of meta-standing hydrogen.

The experiments now to be described show that the order of activation of the chlorine atom in (I), (II), (III), and (IV) produced by X (CO_2H, SO_3H or NO_2) is

$$NO_2 > SO_3H > CO_2H \quad . \quad . \quad . \quad . \quad \text{Series B.}$$

The activating powers of the three groups are, however, very different. So great is that of the nitro-group in comparison with the other two groups that only extremely rough figures can be given. In compounds of type (II) the chlorine in the nitro-compound is more than 70,000 times as reactive as that in the sulphonic acid and more than 200,000 times as reactive as that in the carboxylic acid. These figures merely represent lower limiting values as is explained on page 1131, and the nitro-compounds are in reality far more reactive than they indicate.

p-Chlorobenzenesulphinic acid also has been compared with the analogous substances (I) examined: the chlorine atom is slightly more mobile than that in *p*-chlorobenzenesulphonic acid. The experiments, however, necessitated temperatures above 100°, and it is possible that some of the sulphinic acid changed to *p*-chlorophenyl disulphoxide (compare Otto, *Annalen*, 1868, **145**, 323), which might possibly be much more reactive than the original sulphinic acid. In any event, it is clear that the sulphinic acid group confers the same order of activity as the sulphonic acid and the carboxyl group.

No doubt the unique character of the nitro-group depends on or is closely connected with the fact that aromatic nitro-compounds (compare *s*-trinitrobenzene and picric acid) readily form addition compounds (compare Kenner, *loc. cit.*; Kenner and Parkin, J., 1920, **117**, 852), whereas sulphonic and carboxylic acids have this tendency very slightly, if at all, developed. Not only does the nitro-group make a suitably placed chlorine atom reactive, but it seems to put the molecule into a reactive phase, and enables a suitably placed sulphonic or carboxylic acid group to produce an enormously greater effect than it does in the molecule without a nitro-group. For example, the activity of the chlorine in *p*-chlorobenzenesulphonic or *p*-chlorobenzoic acid is so small that it cannot be measured at ordinary pressures in a reasonable time. But in compounds of type (IV) the chlorine atom in the sulphonic acid is about 16, and that in the carboxylic acid about 4·4, times as reactive as the chlorine in *o*-chloronitrobenzene (see Series II). This great increase in the effect of the weaker groups in conjunction with a nitro-group seems to show that the nitro-group may owe its unique activating power to its ability to form intermediate compounds, of which the other groups, when in the same molecule, may take advantage.

The significance of the fact that the order in Series A is the reverse of that in Series B will be dealt with in a later communication. Meanwhile it may be noted that Schöpff's rule is on the whole correct, though the relatively extraordinarily great effect of the nitro-group is not indicated. The carboxyl or sulphonic acid group alone has too small an activating power at moderate temperatures to justify such precautions to prevent hydrolysis as those referred to on p. 1126. At high temperatures, however, the weaker activating groups show considerable effect, as, *e.g.*, in the preparation of diphenylamine-2 : 4 : 6-trisulphonanilide (p. 1125).

EXPERIMENTAL.

The Preparation and Purification of Materials.—*o*- and *p*-Chloronitrobenzenes are recrystallised from methylated spirit until they melt sharply at 32° and 83°, respectively.

Sulphonic acids. The sulphonyl chloride is boiled with methylated spirit for 2 hours and then water is gradually added at intervals to the boiling solution until the ester first formed is completely hydrolysed, as shown by no precipitation occurring on further addition of water. The solution, after being freed from hydrochloric acid by repeated evaporation nearly to dryness with suitable additions of water (it is also free from sulphate), is filtered, diluted to a convenient concentration, and standardised by titration with potassium hydroxide. The purity of the sulphonic acid is checked by an analysis of the potassium salt.

Chlorobenzene-*p*-sulphonic acid. Chlorobenzene sulphonated by Baxter and Chattaway's method (J., 1915, **107**, 1815) gives even under these mild conditions a moderate amount of the sulphone (m. p. 149°), which is easily separated from the acid. The barium salt gives a good yield of chlorobenzene-*p*-sulphonyl chloride (m. p. 53°) when heated with phosphorus pentachloride (Found in the anhydrous potassium salt : K, 16·8. Calc. : K, 16·95%).

Chlorobenzene-2 : 4-disulphonic acid. Since, owing to the tendency to sulphone formation, chlorobenzene cannot conveniently be disulphonated, phenol is disulphonated and the hydroxyl group then replaced by chlorine. This process is based on that of Pollak, v. Fiedler, and Roth (*Monatsh.*, 1918, **39**, 179), who obtained a mixture of chlorobenzene di- and tri-sulphonyl chlorides. It is more convenient to mono- and di-sulphonate phenol, and the corresponding chlorobenzene-mono- and -di-sulphonyl chlorides can be separated by distillation under very low pressure. Phenol (499 g.) is heated with 96% sulphuric acid (870 c.c.) in the water-bath for 4 hours, 50 c.c. of fuming sulphuric acid (10% SO_3) are added, and the mixture is heated for 5 hours in a brine bath at 108—110° (the temperature of the sulphonating mixture is 101—103°). Under these conditions the phenol is largely disulphonated without being trisulphonated. The sulphonic acids are converted into their calcium and thence into their sodium salts, and these, when heated with phosphorus pentachloride at 140—150°, give the mixed sulphonyl chlorides of chlorobenzene, which are washed with hot water and dried in a vacuum (440 g.; m. p. 77—80°). Distillation at 1 mm. gives a small fraction boiling below 180°, but the main fraction (240 g.) boils at 180—190° and melts at 81—89°. After crystallisation from light petroleum, the product is obtained in needles melting sharply at 89°. Pollak records m. p. 87—88°. The *potassium* salt is extremely soluble in cold water, and sparingly soluble in alcohol, which precipitates it in very fine prisms (Found in material dried at 155°: K, 22·6. $C_6H_3O_6ClS_2K_2$ requires K, 22·4%). The *amide* is readily soluble in hot alcohol and in water, slightly soluble in the cold solvents, and separates in minute needles, m. p. 206—207° (Found: N, 10·5. $C_6H_7O_4N_2ClS_2$ requires N, 10·4%).

Chlorobenzene-2 : 4 : 6-trisulphonic acid is most conveniently obtained, not according to Pollak, v. Fiedler, and Roth (*loc. cit.*), but by the preparation of phenol-2 : 4 : 6-trisulphonyl chloride by the action of chlorosulphonic acid on phenol at 145—155° after Pollak, Gebauer-Fülnegg, and Riesz (*Monatsh.*, 1926, **46**, 383). The phenol trisulphonyl chloride, when heated with phosphorus pentachloride, gives about a 10% yield of crude chlorobenzenetrisulphonyl chloride, m. p. 152—162°; this crystallises from light petroleum (b. p. 80—100°) in needles, m. p. 170° (recorded m. p., 170—171°) (Found: C, 17·5; H, 0·6. Calc.: C, 17·6; H, 0·5%). The *potassium* salt forms colourless needles, which are excessively soluble in water and sparingly soluble in alcohol (Found: K, 25·3. $C_6H_2O_9ClS_3K_3$ requires K, 25·1%). *Diphenylamine-*2 : 4 : 6-*trisulphonanilide* is made by boiling the sulphonyl chloride and an excess of aniline together for 1 hour. Aniline hydrochloride is removed; the residue crystallises from nitrobenzene in light grey needles which darken on keeping, m. p. 227° (decomp.). When heated with sodium, it gives a fine violet colour (Found: C, 56·4; H, 4·1. $C_{30}H_{26}O_6N_4S_3$ requires C, 56·8; H, 4·1%).

1-Chloro-2-nitrobenzene-4-sulphonic acid is best obtained pure, not by nitrating the chlorobenzenesulphonic acid (compare Fischer, *Ber.*, 1891, **24**, 3188), but as follows: A mixture of chlorobenzene-*p*-sulphonyl chloride (20 g.), nitric acid (20 c.c.; *d* 1·50), and concentrated sulphuric acid (80 c.c.) is stirred and warmed initially at 35°, when the reaction begins, and then for 5 hours at 25—30°. The product is precipitated by water, washed free from acid, and crystallised from light petroleum (b. p. 40—60°); it then has the correct m. p., 39—40°. The yield is 17 g. The *potassium* salt forms long, colourless needles readily soluble in hot, moderately easily soluble in cold water (Found in dry salt: K, 14·2. $C_6H_3O_5NClSK$ requires K, 14·2%).

Chlorobenzene-*p*-sulphinic acid was prepared in excellent yield by reduction of the corresponding sulphonyl chloride with sodium sulphide after the method of D.R.-P. 224019 and purified by conversion into the sparingly soluble ferric salt and crystallisation of the moderately soluble *ammonium* salt (shining plates). The acid melts at 100—102° (Otto and Brummer, *Annalen*, 1867, **143**, 113, give m.p. 88—90°) (Found for the ammonium salt dried over phosphoric oxide: N, 6·6; loss at 100°/40 mm., 8·4. $C_6H_8O_2NClS,H_2O$ requires N, 6·6; H_2O, 8·5%).

Carboxylic acids. Commercial *p*-chlorobenzoic acid was purified until the correct melting-point was attained. It was finally found more convenient, in order to obtain a pure specimen (m. p. 243° in a sealed tube), to prepare it from pure *p*-chlorotoluene. The 4-chloro-3-nitrobenzoic acid (Schuchardt) melted at 182° before and after purification.

4-Chloro*iso*phthalic acid is best prepared by the oxidation of 4-chloro-*m*-xylene (b. p. 181—185°) as described for the preparation of chlorotrimesic acid below. It is not essential in this case to extract the acid with ether, as it is only slightly soluble in cold water (Found: equiv., 100·6. Calc.: equiv., 100·25). It melts at 295°, the m. p. recorded by Ullmann and Uzbachian (*Ber.*, 1903, **36**, 1799). No improvement in the yield followed the use of magnesium sulphate in the oxidation, which these authors advocate in order to minimise the hydrolysis of the chlorine atom in the chloro*iso*phthalic acid as the latter is produced.

1-Chlorotrimesic acid has already been prepared by the action of phosphorus pentachloride on hydroxytrimesic acid (Ost, *J. pr. Chem.*, 1877, **15**, 308), but is much more conveniently made as follows: Chloromesitylene is prepared by the chlorination of mesitylene in presence of antimony trichloride at 10—30°, and the fraction boiling at 204—206° (15·5 g.) is oxidised with potassium permanganate (95 g. in 2200 c.c. of water) for 22 hours. The solution is concentrated, the unchanged chloromesitylene distilling over in the process, sulphur dioxide is passed in until the manganese dioxide has disappeared, and the carboxylic acid is collected after cooling. The filtrate is extracted with ether, and the total yield is 15·5 g. (63·5%) of anhydrous acid, m. p. 285° (Ost gives 278°). It is very readily soluble in cold (contrast Ost) and excessively soluble in hot water (Found: equiv., 81·8. Calc.: equiv., 81·5). The oxidation was carried out also in presence of excess of magnesium sulphate, but there was no improvement in the yield. The hydrolysis without magnesium sulphate must have been very minute, since it could not be detected by a colour reaction with ferric chloride solution.

Details of the Methods used in Estimating the Amount of Hydrolysis.

All the reagents, organic and inorganic, were proved to be free from halogen. No halogen is detectable in Merck's guaranteed potassium hydroxide. The vessels were boiled with pure potassium hydroxide solution until all adventitious halogen was removed.

An aqueous-alcoholic solution was used (except where stated otherwise), because a medium was required which would dissolve both nitro-compound and potassium salt. Absolute alcohol, practically free from acetaldehyde, was diluted with the required amount of $N/2$-potassium hydroxide until the solution contained 60% of alcohol by volume on the assumption that no change in volume had occurred during mixing. Such a solution boils at about 82°. Richardson (J., 1926, 525, 528) has shown that in the prolonged treatment of *p*-chloronitrobenzene with alcoholic potassium hydroxide the nitro-group as well as the chlorine atom is apt to be attacked to form some dichloroazoxybenzene. However, the use of this reagent was continued, because the nitro-compounds (picryl chloride and 2 : 4-dinitrochlorobenzene) through which comparisons were made with sulphonic and carboxylic acids were heated for a relatively short time (15 minutes).

The equation $RCl + 2KOH = ROK + KCl + H_2O$ requires two mols. of potassium hydroxide. Three mols. were taken (except in Series III and IV, where only two were employed) in order to have a large excess of alkali always present; in the case of the nitro-compounds this was particularly necessary, as the speed of hydrolysis was so great.

The chloro-compound was refluxed with the potassium hydroxide solution in a Duroglass bromine flask adequately protected from acid fumes, and the amount of potassium chloride produced was estimated as silver chloride. The chlorine in chlorobenzene-*p*-sulphonic acid and in *p*-chlorobenzoic acid was not reactive enough at ordinary pressures, and high temperatures and sealed tubes were resorted to (Series I). The di- and tri-substituted chlorobenzene derivatives gave, after prolonged refluxing, sufficient chloride to be estimated by the micro-method.

Estimation of Chlorine.—After the reaction had proceeded for the desired time, the potassium hydroxide solution was acidified with concentrated nitric acid and filtered cold through a halogen-free Hirsch funnel and filter-paper, which retained certain products from the glass and also any unchanged precipitated carboxylic acid. A micro asbestos filter tube was then prepared after Pregl, but in addition the asbestos was thoroughly washed with hot aqueous ammonia solution, and then consecutively with water, dilute nitric acid, and alcohol. The chloride produced in the reaction was collected as silver chloride in the filter tube after Pregl. The silver chloride was often violet and was sometimes mixed with a relatively large amount of unchanged carboxylic acid, especially *p*-chlorobenzoic acid, the solubility of which in water at the ordinary temperature is less than 0·02. The substance in the filter was treated with a definite amount (which should be the same in all these cases) of hot 3% pure ammonia solution, and then the filtrate with water, dilute nitric acid, and alcohol. The precipitated silver chloride now coagulated more rapidly than before, and was again collected and weighed. (It is not easy to make micro asbestos filter tubes perfectly constant in weight to washing with ammonia, but any errors introduced through this are of the second order.) This gravimetric process, though tedious, is preferable to the volumetric methods for the estimation of several mg. of chloride.

SERIES I. Compounds of formula (I).

Activating group (X).		Temp.	Time (hrs.).	G.-mol. of subs.	G. of AgCl or c.c. of $AgNO_3$ soln.	% Conversion.	Ratio (CO_2H = 1).
NO_2		82°	6	0·0100	0·2548	17·8	
,,		82	6	0·0100	36·89 c.c.	18·4	
SO_3H	(a)	160—170	5	0·0100	0·0600	4·18	1·935
,,	(b)	140—165	10	0·004816	9·51 c.c.	3·94	2·03
,,	(c)	100—170	36	0·005 *	0·00622	0·868	2·765
,,	(d)	100—150	36	0·005 *	0·00246	0·3433	3·1
SO_2H	(a)	160—170	5	0·0100	0·1217	8·48	3·93
,,	(b)	140—165	10	0·005	17·82 c.c.	7·11	3·66
,,	(c)	100—170	36	0·003 *	0·00731	1·70	5·41
CO_2H	(a)	160—170	5	0·0100	0·0309	2·156	1
,,	(b)	140—165	10	0·005	4·76 c.c.	1·94	1
,,	(c)	100—170	36	0·00566 *	0·00255	0·3143	1
,,	(d)	100—150	36	0·00671 *	0·00106	0·1103	1

* In aqueous solution.

0·01994*N*-Silver nitrate was used with thiocyanate, except in the second experiment, where 0·05003*N*-silver nitrate was used with potassium chromate as indicator.

In experiments (a) and (b) macroanalysis was used.

Except in the first two experiments (with *p*-chloronitrobenzene), the reactants were heated in red-line Jena glass tubes in a Lothar Meyer bomb furnace at temperatures varying from 100° to 170°. The temperatures varied very considerably owing to changes in the gas pressure, but this is immaterial, as the tubes were always in the furnace together. No doubt there were slight inequalities in the heating of the furnace, but the tubes were arranged in the furnace in different order in different experiments without causing great variations in the amount of hydrolysis. The experiments clearly show that there is a detectable order in the activation due to the different groups.

Temperatures higher than 170° were not employed, because at this temperature very minute traces of sulphuric acid were formed in the tubes containing sulphonic acid. In all the experiments involving sulphonic acids, the filtrate from the silver chloride was tested with barium nitrate : positive results for sulphuric acid were obtained only in the products from these high-temperature experiments.

SERIES II. Compounds of formula (IV).

r denotes the amount of first-hour conversion compared with that of *o*-chloronitrobenzene (X nil).

Activating group (X).	Time (hrs.).	G.-mol. of subs.	G. of AgCl or c.c. of $AgNO_3$ soln.	% Conversion.	Ratio (CO_2H = 1).	*r*.
Nil	1	0·0100	0·0215	1·50		1·0
,,	6	0·0100	0·1195	8·3		
,,	6	0·0100	0·1208	8·4		
NO_2	0·25	0·0100	1·4254	99·4		
,,	0·25	0·0100	1·4288	99·6		
SO_3H (a)	1	0·0101	0·3513	24·06	3·79	16
,, (b)	6	0·00567	0·5740	70·6	2·49	
,, (c)	6	0·0101	66·59 c.c.	66·4	2·67	
CO_2H (a)	1	0·0100	0·0910	6·35	1·0	4·4
,, (b)	6	0·0100	0·4061	28·35	1·0	
,, (c)	6	0·0100	25·02 c.c.	24·9	1·0	

All these experiments were done at 82° with aqueous-alcoholic potassium hydroxide. 0·0997*N*-Silver nitrate was used with thiocyanate, but the process was not satisfactory, as the colour of the organic solution somewhat masked that of the indicator.

The ratio 3·79 for 1 hour is in fair agreement with the ratio for 6 hours, for if 24% of the sulphonic acid and 6·3% of the carboxylic acid present are converted per hour, then 80·7% and 32·3%, respectively, are transformed after 6 hours. This gives the ratio after 6 hours as 80·7/32·3 = 2·50 (Found : 2·49 and 2·67). This method is obviously very rough, but does not assume the order of the reaction.

Similar experiments for 1 hour were done in aqueous potassium hydroxide solution at 100° : the percentage conversion of the sulphonic acid was 20·6 and 19·2, and of the carboxylic acid, 5·2. Notwithstanding the higher temperature, the velocity of reaction is less in water than in alcohol. Similar cases are recorded in the literature (compare Slator and Twiss, J., 1909, **95**, 99; Rheinlander, J., 1923, **123**, 3105).

SERIES III. Compounds of formula (II).

Activating groups (X).	Time (hrs.).	G.-mol. of subs.	AgCl formed (g.).	Conversion in 127 hours per 0·01 g.-mol.	Conversion per 100 hours.	% Conversion per 100 hours.	*s*.
$2SO_3H$ (a)	63·5	0·01	0·0052	0·0104	0·0082	0·57	2·7
,, (b)	127	0·005	0·007025	0·01405	0·01107	0·77	4·0
,, (c)	127	0·005	0·00308	0·00616	0·00485	0·34	2·8
$2CO_2H$ (a)	63·5	0·01	0·00191	0·00382	0·00302	0·21	1 (a)
,, (b)	127	0·005	0·001715	0·00343	0·00270	0·19	1 (b)
,, (c)	127	0·005	0·00106	0·00212	0·00168	0·12	1 (c)

SERIES IV. Compounds of formula (III).

Activating groups (X).	Time (hrs.).	G.-mol. of subs.	AgCl formed (g.).	Conversion in 127 hours per 0·01 g.-mol.	Conversion per 100 hours.	% Conversion per 100 hours.	*s*.
$3SO_3H$ (a)	63·5	0·005	0·00821	0·03284	0·02583	1·80	1·7
,, (b)	127	0·0025	0·00791	0·03164	0·02491	1·74	1·4
,, (c)	127	0·0025	0·01102	0·04408	0·03472	2·42	2·7
$3CO_2H$ (a)	63·5	0·0025	0·00246	0·01968	0·01553	1·08	1 (a)
,, (b)	127	0·0025	0·00572	0·02288	0·0180	1·26	1 (b)
,, (c)	127	0·0025	0·00411	0·01644	0·0129	0·090	1 (c)
		Alcoholic potassium hydroxide at 82°.					
$3SO_3H$	96	0·00679	0·0537			5·7	
Picryl chloride	0·25	0·01	1·4254	99·4% converted in 0·25 hour.			
,,	0·25	0·01	1·4288	99·6% converted in 0·25 hour.			

Weights of silver chloride, when given to the fourth decimal place only, were determined on a macro-balance.

It was found impossible to repeat, even approximately, the results of experiments carried out at different times, probably owing to differences in boiling point due to changes in barometric pressure, or to changes in the intensity of light. These difficulties were partly overcome by carrying out four experiments (each set labelled a, b, and c) at the same time in absence of bright light. The figures in the last column (*s*) give the ratio of chloride produced from a sulphonic acid to chloride produced from the corresponding carboxylic acid : *e.g.*, the first figure is obtained thus : $0·57/0·21 = 2·7$.

The agreement in the different series is poor and the analyst (W. D.) admits that the problem of carrying out reactions on a macro-scale and then estimating the minute quantity of product on a micro-scale has not yet been solved. Nevertheless a rough agreement among the results is discernible.

Discussion of Results.

A lower limiting value for the activation due to nitro-groups compared with that due to carboxyl or sulphonic acid groups can be obtained. It has been shown that the chlorine in chlorobenzene-2 : 4-disulphonic acid is hydrolysed to the extent of about 0·57% in 100 hours (estimation of the hydrolysis for one time interval from the amount produced during another is justifiable when the concentration of the reactants is, as here, practically unchanged) in aqueous potassium hydroxide solution. 2 : 4-Dinitrochlorobenzene, on the other hand, is more than 99% hydrolysed in 0·25 hour (see Series II) in alcoholic potassium hydroxide solution (which has been shown to have only a slightly greater hydrolytic power than the aqueous solution; see p. 1130 and Series IV). Then, a direct proportion gives about 70,000 hours as the time required for 99% hydrolysis of chlorobenzene-2 : 4-disulphonic acid. This of course ignores the immense retardation of hydrolysis as the concentration of the reactants becomes less, and the figure is much more probably at least of the order of 10^6 instead of about 10^5. Similarly, by using the value 0·2% hydrolysis per 100 hours for chlorobenzene-2 : 4-dicarboxylic acid, about 200,000 hours would be required for 99% hydrolysis. It may safely be said, then, that the nitro-groups in 2 : 4-dinitrochlorobenzene have more than 70,000 and 200,000 times the activating effect of the acigenic groups in chlorobenzene-2 : 4-disulphonic and chlorobenzene-2 : 4-dicarboxylic acids, respectively.

A comparison of the activating powers of the sulphonic and carboxylic acid groups is less indefinite. The first, third, and fourth series show the ratio of the effect of the sulphonic to that of the carboxylic acid groups to be 2—3, about 3, and about 2, respectively. The sulphinic acid group has been shown (Series I) to have about four times the effect of a carboxylic acid group under the same conditions. It is possible, however, that the relatively unstable sulphinic acid has decomposed in other directions to some extent. This possibility is advanced, since we isolated a very small quantity of *p*-chlorophenyl disulphoxide, m. p. 137° (Otto, *loc. cit.*, records 136—138°), during the purification of the *p*-chlorobenzenesulphinic acid with ammonia.

The authors wish to thank Dr. E. J. Hartung for helpful advice.

MELBOURNE UNIVERSITY. [*Received, September 19th,* 1927.]