CXXXVIII.—*The Chlorination of Anilides. The Directing Influence of the Acylamido-group.*

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Proportions of the Isomerides formed by Chlorination.

IN 1909, Orton and W. Jones (J., 1909, **95**, 1056) showed that the chlorination of acetanilide, in acetic acid solution, by the addition of the calculated quantity of bleaching powder solution yielded some 40% of *o*-chloroacetanilide, the remainder of the acetanilide being converted into the *p*-isomeride. This investigation was extended to other acylanilides by Orton and King (J., 1911, **99**, 1377). These authors aimed at an actual separation of the products of chlorination by a process of crystallisation of the anilides and fractional steam distillation of the anilines obtained by hydrolysis, and estimated the proportions of the isomerides formed from the yields of pure substances obtained. In addition, Orton and King (J., 1911, **99**, 1369) measured the velocity coefficients for the reaction between various anilides and chlorine.

On reviewing these results subsequently, it was felt that some uncertainty would attach to any deduction, bearing on the problem of the directing influence of the acylamido-group on nuclear substitution, made by a correlation of these two series of measurements, since the estimate of the proportions of the isomerides formed was not so satisfactory as could be desired, for the reasons stated below. First, the method of chlorination involves the gradual dilution of the acetic acid medium by the bleaching powder solution used for chlorination, so that in the experiments referred to the medium varied from 100% to 50% acetic acid as the chlorination progressed. The results obtained by Holleman, Hartogs, and van der Linden (*Ber.*, 1911, **44**, 704) showing the marked effect of medium on the nitration of anilides suggest that the values obtained for the proportions of *o*- and *p*-chloro-compounds may actually represent a kind of average for more or less dilute acetic acid medium. Secondly, the actual isolation of the isomerides in a pure state involves a number of processes, which from their nature cannot be carried out in an exactly quantitative way. A re-determination was therefore undertaken.

In the present series of experiments, the composition of the chlorination product of acetanilide was determined by the freezing-point method, without any attempt at preliminary separation, and confirmed by a quantitative separation by sublimation of the *o*- and *p*-chloroacetanilides, a process which is very readily carried out.

In experiments on other acylanilides, these were first hydrolysed, and the anilines acetylated for analysis.

The delicate method of chlorination introduced by Orton and King (J., 1911, **99**, 1185), based on the reversible reaction between a chloroamine and hydrochloric acid,

$$>NCl + HCl \rightleftharpoons Cl_2 + >NH,$$

lends itself admirably to the present purpose. With many chloroamines, in glacial acetic acid, the equilibrium lies almost entirely to the right, and since the equilibrium is attained almost instantaneously, the addition of hydrochloric acid to a solution of a chloroamine results in the liberation of an exactly measured quantity of chlorine at the moment required. Moreover, since nucleus chlorination results in the liberation of hydrochloric acid equivalent to the chlorine used, the addition of a trace of hydrochloric acid suffices for complete chlorination, thus avoiding a high concentration of chlorine at any period of the reaction and the formation of anilide hydrochlorides in anhydrous solutions.

For the chlorination of acetanilide, the chloroamine most suitable as a source of chlorine is that of acetanilide itself, *i.e.*, the reaction is most readily carried out by allowing *N*-chloroacetanilide to undergo the so-called " transformation " (Orton, *Brit. Assoc. Reps.*, 1910, 85):

$$C_6H_5{\cdot}NClAc \longrightarrow C_6H_4Cl{\cdot}NHAc\ (o\text{-} + p\text{-}).$$

The possibility presents itself that at the moment of liberation of chlorine from *N*-chloroacetanilide, the acetanilide molecule may be in a special " reactive " state, and that the proportions of the isomerides formed may differ from those formed when the chlorine is not generated in this way. This, however, is not the case, as is seen from Table I, where the mean values from several experiments for the percentage of *p*-chloroacetanilide formed by the " transformation " of *N*-chloroacetanilide and by the chlorination of acetanilide by chlorine derived from another chloroamine are given for different media. The remainder of the product is the ortho-compound in each case.

TABLE I.

Chlorination at 20°.

	Percentage of para.	
Medium.	Chlorination of acetanilide.	Transformation of *N*-chloroacetanilide.
Chloroform	68·8	69·8
Acetic acid	67·5	66·8
50% Acetic acid	60·7	57·3
Methyl alcohol	60·6	—

It is seen from the above table that the medium has only a small effect on the proportions of *o*- and *p*-isomerides. No explanation is at present offered to account for the differences between the values for 50% acetic acid, which seem to be rather greater than the experimental error involved.

In Table II is shown the percentage of the isomerides formed by the chlorination of several anilides. The most striking feature of these results is that although the acids corresponding to the acyl groups differ so largely in strength as measured by their ionisation constants, in molecular weight, and in "space-filling power," yet the proportions of the isomerides are practically the same in each case.

TABLE II.

Chlorination in acetic acid, m. p. 16°, at 20°.

Anilide.	% ortho.	% para.
Formanilide	30·1	69·9
Acetanilide	32·5	67·5
Benzanilide	30·4	69·6
Benzenesulphonanilide	35·0	65·0

Similarly, the nitration of formanilide, acetanilide, and benzanilide under the same conditions yields approximately the same proportions of *o*- and *p*-nitroanilides (Holleman, Hartogs, and van der Linden, *loc. cit.*).

Velocity of Chlorination of Anilides.

Orton and King (*loc. cit.*) found it possible to employ their method of chlorination for the measurement of the velocity of the reaction between chlorine and anilides in acetic acid solution, a reaction which is found to be of the simple bimolecular type. Their measurements are for an acetic acid containing 0·14% of water, as a medium, at a temperature of 16°. The velocity of chlorination is found to be very sensitive to the medium effect of water, increasing rapidly as the proportion of water is increased.

The experiments described above on the proportions of the isomerides formed were carried out at 20°, in an acetic acid, m. p. 16°, *i.e.*, containing about 0·3% of water. The velocity determinations have been repeated at 20°, in a medium containing 1% of water, the errors due to slight variation in the water content being thereby minimised. Column 1 of Table III gives the velocity coefficients at 20° for perfectly standard conditions, namely, anilide and chlorine both initially at 0·0025 mol./litre; hydrochloric acid 0·0125 mol./litre; medium, acetic acid with 1% of water. In column 2 are Orton and King's values for these and other anilides, and in column 3 the ionisation constants of the acids $R{\cdot}CO_2H$, corresponding to the groups $R{\cdot}CO{\cdot}NH^-$, are given for reference.

TABLE III.

Velocity coefficients.

Anilide.	O. and B. (H_2O = 1%).	O. and K. (H_2O = 0·14%).	Ionisation constant of $R{\cdot}CO_2H$. $K \times 10^5$.
Formanilide	9·2	4·95	21·4
Acetanilide	62·2	40·0	1·86
Propionanilide	—	72·0	1·34
Butyranilide	—	64·5	1·49—1·75
*iso*Valeranilide	—	57·0	1·67—1·73
Benzanilide	69·1	42·0	6·8
Benzenesulphonanilide	42·7	—	—

The amount of hydrochloric acid employed produces an appreciable effect on the velocity of chlorination, the effect on acetanilide being a decrease in speed as the hydrochloric acid is increased, although with formanilide and benzenesulphonanilide this effect is reversed (see Table IV). The validity of the correlation of the velocity measurements under standard conditions with the measurements of the proportions of the isomerides formed remains unimpaired by the slight differences in medium in the two sets of experiments, since the latter values are but little affected by large variations in the medium.

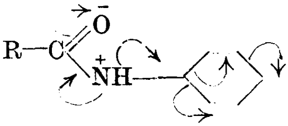
TABLE IV.

Chlorination in 99% acetic acid at 20°.

Molar proportions of HCl added :—	1·5	5	10	20
k for :				
Formanilide	8·9	9·2	—	10·2
Acetanilide	66·5	62·2	59·6	55·7
Benzanilide	—	69·1	—	—
Benzenesulphonanilide	41·5	42·7	44·4	46·9

Discussion of Results.

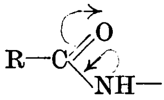
The bearing of modern theories on the rates of entrance of chlorine into a given position, either ortho or para, for the different anilides may be briefly examined. According to Allan, Oxford, R. Robinson, and Smith (J., 1926, 403) and Ingold and Ingold (*ibid.*, p. 1311), the directing influence of the acylamido-group is to be attributed to the tendency of the nitrogen atom to act as an electron source, as modified by a betaine-like electronic conjugation with the oxygen of the carbonyl group :

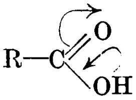


Both these processes result in the acquirement of a positive charge by the nitrogen atom. The tendency for the nitrogen to act as an electron source towards the nucleus is said to be the greater the more negative (or less positive) it is originally.

The process I (below) is exactly analogous to the process leading to the ionisation of the corresponding carboxylic acid (Allan, Oxford, Robinson, and Smith, *loc. cit.*, p. 405; Lea and Robinson, *ibid.*, p. 2352), so that whatever effect R may have on (II) should also be manifest to a greater or lesser extent in (I), that is, the greater the strength of the acid (II) the greater the tendency of the nitrogen in (I) to acquire a positive charge by this process, and hence the lesser tendency of the nitrogen atom to act as an electron source toward the nucleus. Hence the directing effect of the group R·CO·NH· should decrease with increase in the ionisation constant of the acid $R{\cdot}CO_2H$.

(I.)





(II.)

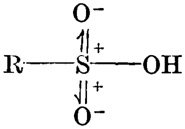
According to Allan, Oxford, Robinson, and Smith (*loc. cit.*, p. 407), in comparing the directive powers of groups it may be considered that what is being compared is the number of occasions in unit time that effectual polarisations take place, *i.e.*, the velocity of substitution at a given carbon atom is the measure of the directive power of a group. In the present case, since the different acyl groups do not alter the proportions of the isomerides appreciably, the velocity coefficients given in Table III, column 1, may be taken directly as a comparative measure of the directing effects of the groups concerned on either the ortho- or the para-position. These are seen to be in the order $C_6H_5{\cdot}CO{\cdot}NH^- > CH_3{\cdot}CO{\cdot}NH^- > H{\cdot}CO{\cdot}NH^-$, whereas from the foregoing theoretical considerations the order should be $CH_3{\cdot}CO{\cdot}NH^- > C_6H_5{\cdot}CO{\cdot}NH^- > H{\cdot}CO{\cdot}NH^-$.

If it be assumed, as would appear to be reasonable, that the proportions of the isomerides formed by the chlorination of propionanilide, butyranilide, and *iso*valeranilide are not very different from those formed by the chlorination of acetanilide, the velocity coefficients obtained by Orton and King lead to the series :

$$C_2H_5{\cdot}CO{\cdot}NH^- > \begin{matrix} C_3H_7{\cdot}CO{\cdot}NH^- \\ C_4H_9{\cdot}CO{\cdot}NH^- \end{matrix} > C_6H_5{\cdot}CO{\cdot}NH^- >$$
$$CH_3{\cdot}CO{\cdot}NH^- > H{\cdot}CO{\cdot}NH^-$$

corresponding with the theoretical sequence, except that again the group $C_6H_5{\cdot}CO{\cdot}NH^-$ should follow $CH_3{\cdot}CO{\cdot}NH^-$, instead of preceding it.

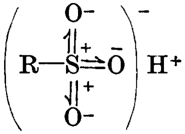
The benzenesulphonamido-group requires special consideration, since here no betaine-like process of electronic conjugation takes place. The ionisation of a sulphonic acid may be attributed to the effect of the positive charges on the sulphur atom, which tend to loosen the binding between the hydroxyl oxygen and the hydrogen atom,



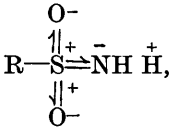
$$R-\overset{\overset{\textstyle O^-}{\uparrow\!\|\,+}}{\underset{\underset{\textstyle O^-}{\downarrow\!\|\,+}}{S}}-OH$$

In a similar way, the nitrogen atom of a sulphonanilide is rendered somewhat positive, and although perhaps it is not justifiable to compare the effect of the sulphonyl group with that of a carboxyl group, since a different mechanism is called into play, from the consideration of the strength of a sulphonic acid, it is rather surprising to find the benzenesulphonamido-group nearly as strongly directing as the acetamido-group.

On an alternative view, the ionisation of a sulphonic acid may be attributed to the tendency of a sulphur atom to act as the positive end of a semipolar bond, a tendency which is satisfied in its higher valency states. Hence we have in a sulphonic acid, and in a sulphonamide, the tendency towards the following :



$$\left(R-\overset{\overset{\textstyle O^-}{\uparrow\!\|\,+}}{\underset{\underset{\textstyle O^-}{\downarrow\!\|\,+}}{S}}\overset{-}{\rightleftharpoons}O\right)^- H^+$$



$$R-\overset{\overset{\textstyle O^-}{\uparrow\!\|\,+}}{\underset{\underset{\textstyle O^-}{\downarrow\!\|\,+}}{S}}\overset{-}{\rightleftharpoons}NH\,\overset{+}{H},$$

a tendency which, with the sulphonamide, is fulfilled when salt formation takes place (compare Clarke, Kenyon, and Phillips, J., 1927, 188). In the sulphonanilide, then, the nitrogen atom is tending to become negative, but forming a dipole arrangement (Goss, Ingold, and Wilson, J., 1926, 2440; Baker and Ingold, *ibid.*, p. 2462) with the proton. Although it is difficult to foresee the extent to which this dipole arrangement affects the tendency of the group to act as an electron source towards the nucleus, nevertheless this view appears more in harmony with the fact that the rate of chlorination of benzenesulphonanilide is more rapid than that of formanilide.

An extension of this investigation to other compounds containing the groups $^-$NRR and $^-$OR is in progress.

EXPERIMENTAL.

Analysis of Mixtures of o- *and* p-*Chloroacetanilides.—Melting-point method.* The melting point of the chlorination product of acetanilide was determined by the method described by G. Owen (J., 1923, **123**, 3394) and the composition read off from a curve constructed from the data given by Orton and G. Owen (J., 1924, **125**, 766) for the melting points of mixtures of *o*- and *p*-chloroacetanilides. In some of the earlier experiments the eutectic point was determined, after the addition of a known quantity of the ortho-compound to bring the composition of the mixture to the region where the eutectic point could be realised, to demonstrate the absence of a third substance. The method, however, lacks accuracy, and was not employed after the development of the sublimation method of obtaining an independent check on the composition of the chlorination product.

Sublimation method. The difference between the vapour pressures of *o*- and *p*-chloroacetanilides (Sidgwick and Rubie, J., 1921, **119**, 1013) would suggest that at least a partial separation of the isomerides could be obtained by sublimation. It is found that the separation is quantitative when the sublimation is carried out in the following way. The finely powdered mixture of *o*- and *p*-chloroacetanilides is spread in a thin layer on a watch glass which is placed on the top of an air-oven, and a wide funnel clamped over it in an inverted position so that the edge of the funnel just clears the watch glass.

The internal temperature of the oven is maintained at 110°, the temperature of the solid on the watch glass probably being about 50—60°. The *o*-chloroacetanilide sublimes and condenses to some extent on the sides of the funnel, although part escapes through the stem (dimensions of funnel employed : width 10 cm., length 17 cm.). The watch glass and contents are weighed from time to time, and after 12—15 hours' heating are at a constant weight. In a control experiment, a mixture containing 62·4% of *p*-chloroacetanilide gave, by this method, (*a*) 62·3%, (*b*) 61·8% of the para-compound. The residual solid melted sharply at 178°, and was therefore completely free from the ortho-compound. The presence in the mixture to be analysed of any *m*-chloroacetanilide, which is non-volatile under these conditions, shows itself by the lowering of the melting point of the solid remaining, whilst unchanged acetanilide or 2 : 4-dichloroacetanilide volatilises so slowly that when 3—4% is present a constant weight is not attained even after 36 hours' heating. In no case did the sublimation method of analysis give any indication of a third substance in the chlorination products here described.

Method of Chlorination.—The selection of a chloroamine for use as a source of chlorine (Orton and King, *loc. cit.*) is in the present case guided by the following considerations : (1) The chloroamine must be stable, and readily obtained in a state of purity, (2) a quantitative separation of the parent substance from the chlorinated product must be possible. Two chloroamines fulfil these requirements, chloroacetamide, the acetamide being readily soluble in water, and *p*-toluenesulphondichloroamide, "dichloramine T," the sulphonamide being readily soluble in alkali, whilst the chloroanilides are almost insoluble in water or alkali.

Dichloramine T was prepared as follows (compare Chattaway, J., 1905, **87**, 145; Kraus and Crede, *J. Amer. Chem. Soc.*, 1917, **39**, 2720). 10 G. of *p*-toluenesulphonamide are dissolved in 100 c.c. of acetic acid, and 120 c.c. of a 2·5*N*-solution of bleaching powder slowly run in with shaking and cooling. The fine crystalline powder is collected, and without drying dissolved in 75 c.c. of hot acetic acid, and reprecipitated by the addition of 37 c.c. of *N*/10-bleaching powder solution. Yield, 15 g. (Found : Cl, by titration, 29·43. Calc. : Cl, 29·53%).

Preparation of Chloroacetamide (compare Hofmann, *Ber.*, 1882, **15**, 407; Hantzsch and Dollfuss, *Ber.*, 1902, **35**, 252; Mauguin, *Ann. Chim. Phys.*, 1911, **22**, 297; Boismenu, *Compt. rend.*, 1911, **153**, 1482).—A good yield is obtained by dissolving 35 g. of acetamide in 80 c.c. of water, and adding 50 g. of sodium bicarbonate. A fairly rapid current of chlorine is led in, the solution being kept cool. After a time, the bulky mass of chloroacetamide and sodium chloride is filtered off, and after the addition of a further quantity of sodium bicarbonate to the filtrate the passage of chlorine is continued. The combined solid products are dried and extracted with warm chloroform, the sodium chloride is filtered off, and on cooling, the chloroacetamide separates. Yield, 34 g. (Found : Cl, by titration, 38·01. Calc. : Cl, 37·97%).

Chlorination of Acetanilide in Chloroform.—The chloroform used was washed with water, kept over lime, and filtered before use. In early experiments, about 10 g. of acetanilide together with the requisite quantity of chloroacetamide were dissolved in chloroform, and about 1/10 molar proportion of hydrochloric acid was added. When chlorination was complete, as indicated by titration, the chloroform was removed by distillation and the residue extracted with a small quantity of water. The solid so obtained melted to a dark-coloured liquid and rapidly became dark-coloured in air, and it would appear that some by-product, presumably an oxidation product, is formed during chlorination. The following process, involving a purification of the crude product, was therefore adopted. 2·7 G. (1 mol.) of acetanilide and 2·4 g. of dichloramine T (0·5 mol.) were dissolved in 50 c.c. of chloroform and placed in a thermostat at 20°, hydrochloric acid (0·09 mol.) being added in the form of a concentrated aqueous solution. After 5 hours, chlorination was complete and the chloroform was removed by distillation. The solid residue in the flask was boiled under reflux with 50 c.c. of 10% sulphuric acid for 2 hours, the whole dissolving to a straw-coloured solution, which was made alkaline and distilled in steam. The anilines passing over were collected with chloroform and acetylated by the addition of acetic anhydride to the chloroform solution, the chloroform being allowed to boil away during the acetylation. The excess acetic anhydride and acetic acid formed were removed in a vacuum desiccator over sodium hydroxide. That this method of purification and isolation effects no noteworthy alteration in the proportion of the isomerides is shown by a control experiment, in which a mixture of *o*- and *p*-chloroacetanilides, m. p. 149·7°, after being put through the complete process melted at 149·2°.

The yield and analytical data for duplicate experiments are appended.

(*a*) Yield 96·8%, m. p. 157·7° = 69·5% para. Eutectic point 76·6°, from curve 77°. Sublimation gave 68·3%, 68·1% para.

(*b*) Yield 93·2%, m. p. 156·4° = 68% para. Eutectic point 77°. Sublimation gave 67·4%, 67·4% para.

Chlorination in Acetic Acid.—The acetic acid used, after purification as described by Orton and Bradfield (J., 1924, **125**, 960), melted at 16°. After chlorination with dichloramine T in a manner exactly similar to that described above, the acetic acid was removed by distillation under 11 mm. pressure. The product was hydrolysed, distilled in steam, etc., as before.

(*a*) Yield 92%, m. p. 156·5° = 68% para. Sublimation gave 67·5%, 67·5% para.

(*b*) Yield 91%, m. p. 156·0° = 67·3% para. Sublimation gave 67·0%, 67·0% para.

Chlorination in 50% *Acetic Acid.*—As dichloramine T is only slightly soluble in 50% acetic acid, the use of a large bulk of liquid is avoided by the following procedure. 2·7 G. of acetanilide (1 mol.) were dissolved in 50 c.c. of 50% acetic acid, to which 0·09 mol. of concentrated hydrochloric acid was added, and placed in a bath at 20°. The calculated quantity of a solution of dichloramine T in glacial acetic acid was run in in small portions, simultaneous addition of water keeping the medium as nearly 50% as possible. The solution was evaporated to dryness under a pressure of 11 mm., and the product worked up as before.

(*a*) Yield 93·8%, m. p. 150·6° = 60·7% para. Sublimation gave 61·3%, 61·2% para.

(*b*) Yield 90·6%, m. p. 150·4° = 60·5% para. Sublimation gave 60·5% para.

Chlorination in Methyl Alcohol.—Methyl alcohol "free from acetone" is only slowly attacked by chlorine. Nevertheless, for the chlorination, which was carried out in the usual way, a 5% excess of dichloramine T was taken to compensate for that lost by reaction with the medium. When chlorination was complete, the methyl alcohol was distilled off under diminished pressure, and the product hydrolysed, etc., as before.

(*a*) Yield 89%, m. p. 150·2° = 60·2% para. Sublimation gave 61·2%, 61·1% para.

(*b*) Yield 91%, m. p. 150·5° = 60·5% para. Sublimation gave 60·5%, 60·6% para.

Transformation of N-*Chloroacetanilide.*—*N*-Chloroacetanilide was prepared by the method described by Chattaway and Orton (J., 1899, **75**, 1046), and the transformation effected in the various solvents by the addition of 1/10 molar proportion of hydrochloric acid, in a manner completely analogous to the chlorination experiments described above. The isolation of the product was also carried out in the same way. Analytical data :

Transformation of N-*chloroacetanilide in chloroform.* (*a*) Yield 90%, m. p. 158·0° = 69·8% para. Sublimation gave 69·9%, 69·6% para.

(*b*) Yield 89%, m. p. 157·8° = 69·6% para. Sublimation gave 70·0%, 70·0% para.

Transformation of N-*chloroacetanilide in acetic acid.* (*a*) Yield 89%, m. p. 155·7° = 67% para. Sublimation gave 67·5%, 67·5% para.

(*b*) Yield 89%, m. p. 155·0° = 66·0% para. Sublimation gave 66·4%, 66·7% para.

Transformation of N-*chloroacetanilide in* 50% *acetic acid.* (*a*) Yield 92·3%, m. p. 146·9° = 56·9% para. Sublimation gave 57·8%, 57·8% para.

(*b*) Yield 92·9%, m. p. 146·6° = 56·6% para. Sublimation gave 57·6%, 57·8% para.

Chlorination of Formanilide in Acetic Acid.—2·42 G. (1 mol.) of formanilide, m. p. 48°, and 2·4 g. (0·5 mol.) of dichloramine T were dissolved in 50 c.c. of acetic acid, maintained at 20°, and hydrochloric acid (0·09 mol.) was added. The acetic acid was removed under diminished pressure. The product was hydrolysed with a mixture of equal volumes of concentrated sulphuric acid and water, and the anilines were distilled in steam, collected as for acetanilide, and acetylated for analysis.

(*a*) Yield 84%, m. p. 157·5° = 69·2% para. Sublimation gave 69·4%, 69·7% para.

(*b*) Yield 85%, m. p. 158·0° = 69·9% para. Sublimation gave 71·0%, 70·9% para.

Chlorination of Benzanilide in Acetic Acid.—Benzanilide, m. p. 162°, requires 200 c.c. of acetic acid to dissolve 3·94 g. Chlorination was effected in the above-described manner, the product hydrolysed with a mixture of 1 volume of concentrated sulphuric acid and 2 volumes of water, and the anilines were distilled in steam and acetylated for analysis.

(*a*) Yield 92%, m. p. 157·9° = 69·7% para. Sublimation gave 68·8%, 68·7% para.

(*b*) Yield 92%, m. p. 158·7° = 70·7% para. Sublimation gave 69·4%, 69·6% para.

Chlorination of Benzenesulphonanilide in Acetic Acid.—The chlorination of benzenesulphonanilide, m. p. 110°, was carried out in the usual way. Sulphuric acid of 60% strength is needed for the hydrolysis of the chloroanilides. The anilines obtained were acetylated for analysis.

(*a*) Yield 86·4%, m. p. 154° = 65% para. Sublimation gave 64·3%, 64·3% para.

(*b*) Yield 90%, m. p. 154·4° = 65·4% para. Sublimation gave 65·5%, 65·4% para.

Velocity Determinations.—The determination of the velocity of chlorination of the anilides was carried out by the method described by Orton and King (*loc. cit.*), who used *N* : 2 : 4-trichloroacetanilide as a source of chlorine. This chloroamine and dichloramine T were both used in the experiments now described, the same values for the coefficients being obtained whichever chloroamine was employed.

The anilide was dissolved in 40—50 c.c. of acetic acid, m. p. 16·2—16·4°, prepared as described by Orton and Bradfield (this vol., p. 983), in a 100 c.c. flask, and the required quantity of a freshly standardised solution of the chloroamine run in. The amount of water which, together with the water present in the acetic acid and that to be added with the hydrochloric acid (of which a constant-boiling solution was used), would make up 1 c.c. was added, and the solution made up with acetic acid nearly to the 100 c.c. mark. When the solution had attained the temperature of the thermostat, 20° ± 0·05°, the necessary amount of hydrochloric acid was added, the contents of the flask rapidly mixed by shaking, and the flask replaced in the thermostat. 10 C.c. were removed at intervals and run into potassium iodide solution, the time of half delivery of the pipette, which could be estimated to ± 2 sec., was noted, and the liberated iodine titrated with *N*/100-thiosulphate, with the usual precautions to secure a good end-point.

The loss of chlorine to the vapour phase, consequent upon increasing the air space in the flask, has an appreciable effect if more than three or four portions are removed in any one experiment, so that in these experiments measurements were limited to a few titres during the middle period of the reaction (35%—65% change). Further, since the object in view is to obtain figures which shall represent the relative speeds of chlorination under standard conditions, rather than to establish the true bimolecular nature of the reaction, measurements were only made with anilide and chlorine at the same initial concentration, which was 0·0025 mol./litre in every case.

The velocity coefficient, k, was calculated from the expression $k = x/at(a - x)$, the time being expressed in minutes. The values given above (Table IV) represent the mean values for at least two concordant experiments. As an example of the constancy of k in any one experiment, the following is quoted as typical :

Chlorination of benzenesulphonanilide.

a = 0·0025 mol./litre. HCl = 0·00375 mol./litre.

Time (±0·03 min.).	% changed.		k.
7·02	39·6		40·8
13·28	57·9		41·4
16·97	63·7		41·3
		Mean	41·2

The reproducibility of the values is shown by the following data for the velocity measurements for acetanilide :

Chlorination of acetanilide.

Molar proportions of HCl.	Mean values of k for individual experiments.	Mean k.
1·5	67·0, 66·0	66·5
5	62·8, 60·9, 62·8	62·2
10	59·5, 60·4, 57·9, 60·0, 60·2	59·6
20	55·6, 55·8	55·7

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