IX.—*The Chlorination of Anilides. Part VI. The Rates of* N-*Chlorination of Acetanilides and Acetobenzylamides and the Effects of Substituents upon Side-chain Reactivity.*

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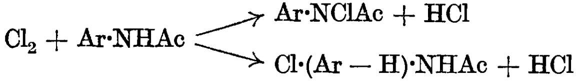
IN a previous paper (Orton, Soper, and Williams, J., 1928, 998) a method was described for measuring the rates of reaction of anilides with chlorine in aqueous acetic acid media and Wegscheider's test was applied to show that *N*-chlorination and *C*-chlorination proceed simultaneously, so that, under these conditions, the reactions may be represented thus,



$$Cl_2 + Ar\cdot NHAc \begin{array}{l} \nearrow Ar\cdot NClAc + HCl \\ \searrow Cl\cdot(Ar - H)\cdot NHAc + HCl \end{array}$$

The ratio k_N/k_C (where k_N and k_C are the velocity coefficients for

N- and *C*-chlorination respectively) is constant for each anilide throughout the reaction, but varies widely for different anilides, having the values 0·00873, 0·0548, 0·850, 10·40 for acetanilide and *m*-, *p*-, and *o*-chloroacetanilides respectively in 40% acetic acid, whilst *N*-chlorination predominates in nitroacetanilides and acetobenzylamides with almost complete exclusion of simultaneous *C*-chlorination. The object of this paper is to consider the influence of the substituents NO_2, Cl, and CH_3 upon the rates of these reactions, with special reference to the *N*-chlorination which takes place in 40% acetic acid and aqueous media (Soper, *J. Physical Chem.*, 1927, **31**, 1192) but is absent under the conditions prevailing in other investigations of the rates of chlorination of anilides (Orton and King, J., 1911, **99**, 1369; Orton and Bradfield, J., 1927, 986). The influence exerted by substituents in the benzene nucleus upon side-chain reactivity is closely allied to the general problem of orientation, and the above substituents have been chosen so as to furnish a contrast in orienting activities, those of NO_2 and CH_3 being opposed, whilst the action of Cl depends upon whether its "tautomeric" or its "inductive" influence has the greater scope.

Table I gives the results for 22 anilides. Each value is the average of three or more experiments * and the mean deviation from the mean is estimated, in general, at ± 2—3%; it is often less than this (see Orton, Soper, and Williams, *loc. cit.*) and never more than 5%. Where no value is given for k_C, nuclear chlorination is too slow in comparison with *N*-chlorination to be distinguished with certainty from accidental loss of chlorine. The figures in parentheses are subject to qualifications discussed in the experimental section.

TABLE I.

Temp. 18° (± 0·02°). Medium, 40% acetic acid (6·90*N*).

	k_N.	k_C.		k_N.
Acetanilide	96	11,000	Acetobenzylamide	172
Substituent :			Substituent :	
o-NO_2	550	—	*o*-NO_2	16·1
m-NO_2	87	—	*m*-NO_2	32·9
p-NO_2	60	—	*p*-NO_2	27·7
†2 : 4-Di-NO_2	—	—		
o-Cl	286	28	*o*-Cl	28·9
m-Cl	172	3,140	*m*-Cl	63·5
p-Cl	115	135	*p*-Cl	99
2 : 4-Di-Cl	504	—		
o-CH_3	140	1,390		
m-CH_3	(150)	(50,000)		
p-CH_3	2540	18,500	*p*-CH_3	(285)
Aceto-β-phenylethylamide				205
Acetamide				(237)

† Chloroamine equilibrium unsuitably placed.

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* I am indebted to Mr. S. P. Hughes, B.Sc., for help in checking values for three substances.

The electronic theory has recently been applied to the classification of benzene side-chain reactions (*Ann. Reports*, 1927, 1928) and, with certain reservations (see below), it may be used to interpret Table I, which illustrates the effects of substituents upon the speed of *N*-chlorination *for a particular set of conditions.* To this end, Table II has been constructed so as to investigate (*a*) how far the effects of substituents are consistent in a number of side-chain reactions; (*b*) whether, if consistency is found, it is such as to support the electronic schemes; (*c*) to determine whether *N*-chlorination finds a place in the scheme; (*d*) to seek analogies in other reactions for certain peculiarities observed in *N*-chlorination.

Table II gives the effects of the substituents NO_2, Cl, and CH_3 upon 36 reactions, the rates for each reaction being calculated relative to that for the unsubstituted compound as unity. Only those reactions are included in which more than one substituent has been investigated.

The electronic theory suggests that it should be possible to group side-chain reactions in two main classes accordingly as they are favoured by accession of electrons to the point of reaction or by recession from that point. The influence of CH_3 should be in the opposite sense to that of NO_2 and Cl (if its inductive influence is predominant), and superimposed on these general effects there should be alternating effects where the substituent can initiate covalency changes. Table II shows that a general measure of consistency exists in the effects of groups in accelerating or retarding side-chain reactions and that the reactions tabulated fall into two main groups; 19 are in Group A with the nitro-group accelerating and the methyl group retarding, and 12 are in Group B, in which the reverse holds. It has been observed in drawing up the table that other substituents fall into line with those tabulated, the same sharp contrast existing between those which are *op*- and those which are *m*-directing in the usual substitution reactions. Five reactions (Group C) cannot be allotted with certainty to either class.

In the following scheme the alternating effects suggested by theory are compared with those observed :

	Group A.		Group B.	
	$-NO_2>H>-CH_3$.	Agreement.	$-CH_3>H>-NO_2$.	Agreement.
For $-NO_2$	*m*-<(*o*)*p*-	7 out of 9	*m*->(*o*)*p*-	7 out of 8
For $-CH_3$	*m*->(*o*)*p*-	7 out of 9	*m*-<(*o*)*p*-	8 out of 9

There are also many instances, not included in Table II, of alternating effects in the expected sense when only one substituent has been investigated. In Group C of Table II, also, the alternating effects for a given substituent are generally as anticipated. It is seen in

TABLE II.

	o-NO_2.	m-NO_2.	p-NO_2.	o-Cl.	m-Cl.	p-Cl.	H.	o-CH_3.	m-CH_3.	p-CH_3.	Medium.
Group A.											
5	—	—	—	1·8	1·2	1·6	1		Small?		Glacial acetic acid
6	—	3·01	—	—	—	—	1	—	—	0·726	Aq. acetone
7	—	1·85	—	—	—	—	1	—	—	0·917	Aq. alcohol
12	—	17·2	17·7	3·44	3·17	1·74	1	3·32	—	0·567	Alcohol
13	Large	1·37	Large	1·05	1·00	1·02	1	0·389	0·857	0·953	Water
14	,,	1·70	,,	0·97	1·03	0·96	1	0·222	0·981	0·972	,,
16	—	11·7	—	5·00	1·40	1·59	1	0·962	1·42	0·713	,,
18	8·20	5·90	3·45	8·84	6·09	7·78	1	(0·378	0·485	0·494)	Alcohol
26	1·08	3·27	2·48	1·16	—	1·71	1	0·506	1·01	0·946	Methyl alcohol
27	1·99	3·82	4·07	—	—	1·16	1	0·089	—	0·370	,, ,,
28	—	—	—	1·13	1·98	1·19	1	0·412	0·465	0·446	,, ,,
29		Very large		2·89	8·94	3·83	1	0·247	0·746	0·507	Alcohol
30	5·71	62·1	104	1·92	7·41	4·33	1	—	0·704	0·467	Aq. alcohol
31	—	—	7·19	—	—	2·55	1	—	—	0·917	,,
32	—	—	—	—	—	1·50	1	—	—	—	,,
33	8·00	7·52	9·80	1·99	—	2·02	1	—	—	0·709	,,
35	(0·554)	5·61	6·67	0·518	—	1·91	1	0·054	0·797	0·660	Water
37	—	—	—	—	—	4·93	1	—	—	0·518	Alcohol
38	1·90	—	10·0	—	—	1·53	1	—	—	0·64	*iso*Propyl alcohol
Group B.											
1	5·73	0·906	0·625	2·98	1·79	1·20	1	1·46	(1·56)	26·5	40% Acetic acid
2	0·0936	0·191	0·161	0·168	0·369	0·575	1	—	—	(1·66)	,, ,,
3	0·084	0·090	0·074	0·35	0·24	0·62	1	4·84	1·39	10·58	Aq. alcohol
4	0·134	0·152	0·134	0·392	0·300	0·830	1	3·24	1·15	4·15	,,
8	—	0·064	—	—	—	0·50	1	—	—	3·00	Benzene
11	—	—	—	0·0095	0·045	0·42	1	2·86	2·06	18·76	Alcohol
15	0·000455	0·00264	0·00623	—	—	—	1	2·73	2·91	0·114	Water
17	0·099	0·167	0·122	0·136	0·196	0·173	1	0·189	1·21	2·09	Alcohol
19	0·0356	0·156	0·0635	0·507	0·493	0·527	1	1·10	1·25	1·36	,,
20	0·0466	0·203	0·100	0·666	0·573	0·560	1	1·04	1·11	1·35	,,
21	—	—	—	0·476	0·396	0·560	1	1·03	1·15	1·31	,,
36	—	—	—	1·21	0·63	1·05	1	2·89	1·11	2·26	Water
Group C.											
9	1·77	6·93	11·5	1·46	1·46	0·85	1	Large	1·46	2·89	Aq. acetone
10	—	—	—	1·09	1·38	1·95	1	2·53	1·12	1·58	Alcohol
24	0·0654	0·692	0·610	—	—	—	1	0·259	1·10	0·563	,,
25	0·050	0·559	0·673	—	—	—	1	—	—	—	,,
34	0·0258	0·940	1·13	0·153	—	0·959	1	0·105	0·926	0·844	Water

References.

(1) and (2) *N*-Chlorination re-calculated from Table I.

(3) Hydrolysis of benzyl chlorides at 83°, Olivier *et al.*, *Rec. trav. chim.*, 1922—1926.

(4) Reciprocals of times of half completion of hydrolysis of benzyl bromides at 76° and 60°, Lapworth, Shoesmith, *et al.*, J., 1922—1926.

(5) Same data for reduction of benzyl bromides by HI at 101° and 25°; refs. as (4).

(6) and (7) Hydrolysis of benzenesulphonyl chlorides at 25° in 1 : 1 acetone–water and alcohol–water respectively, Berger and Olivier, *Rec. trav. chim.*, 1927, **46**, 516.

(8) Friedel–Crafts reaction with same compounds, *Rec. trav. chim.*, 1914, **33**, 244; 1927, **46**, 605.

(9) Hydrolysis of benzoyl chlorides at 0°, Berger and Olivier, *loc. cit.*

(10) Benzyl chlorides and sodium ethoxide at 30°, Franzen and Rosenberg, *J. pr. Chem.*, 1921, **101**, 333.

(11) k_1 for diphenylchloromethanes and ethyl alcohol at 25°, Norris, *Z. physikal. Chem.*, 1927, **130**, 662.

(12) Same for benzoyl chlorides at 0°.

(13) k_2 for hydrolysis of formanilides by NaOH at 100°, Davis, J., 1909, **95**, 1397; *Z. physikal. Chem.*, 1912, **78**, 353, 369.

(14) Same data for acetanilides.

(15) Decomposition of diazo-compounds, Cain and Nicoll, J., 1902, **81**, 1412; 1903, **83**, 206.

(16) Diazotisation of anilines at 0°, Böeseken, Brandsma, and Schoutissen, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 249; compare Tassilly, *Bull. Soc. chim.*, 1920, **27**, 19.

(17) Anilines and 1-chloro-2 : 4-dinitrobenzene at 7°, change % after 15 hrs., Linke, *Ber.*, 1923, **56**, 848.

(18) Saponification of phenylsuccinimides at 25°, Sanna, *Gazzetta*, 1927, **57**, 761; $-CH_3$ results not directly comparable, Miolatti and Longo, *Atti R. Accad. Lincei*, 1895, **1**, 351.

(19) k_1 for sodium phenoxides and ethylene oxide at 70·4°, Boyd *et al.*, J., 1914, **105**, 2117; 1919, **115**, 1239.

(20) Same data for propylene oxide.

(21) Modified k_2 for sodium phenoxides and ethyl iodide at 42·5°, Goldsworthy, J., 1926, 1254.

(22) Phenols and acetic anhydride at 100° (Panoff, A., 1903, ii, 357), in non-polar medium (benzene). Figures only for $-CH_3$. Not quoted in table.

(23) Benzoylation of phenols; all results not directly comparable and not included in table; Bernoulli and Goar, *Helv. Chim. Acta*, 1926, **9**, 730; compare van Duin, *Rec. trav. chim.*, 1927, **46**, 189.

(24) Esterification by 2% HCl at 25°, Goldschmidt, *Ber.*, 1895, **28**, 3218.

(25) Esterification in alcohol with 0·3333*M*-HCl and 0·05*M*-water, Kailan, *Monatsh.*, 1906—1907; *Annalen*, 1907, **351**, 186.
(26) Esterification in absence of added catalyst at 135°, % change after 5 hrs., Michael *et al.*, *Ber.*, 1909, **42**, 310, 317.
(27) Saponification of methyl benzoates at 25°; % changed after 2 hrs.
(28) Same after 65 mins., Kellas, *Z. physikal. Chem.*, 1897, **24**, 221.
(29) Saponification of ethyl benzoates at 30°, McCombie and Scarborough, J., 1915, **107**, 156.
(30) Hydrolysis of ethyl benzoates by NaOH at 30°, Kindler, *Annalen*, 1926, **450**, 1; 1927, **452**, 90; 1928, **464**, 278. Figures also for compounds of types (31) $Ar{\cdot}CH_2{\cdot}CO_2Et$, (32) $Ar{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$, (33) $Ar{\cdot}CH{=}CH{\cdot}CO_2Et$.
(34) and (35) Hydrolysis of benzamides by HCl and baryta respectively, Reid, *Amer. Chem. J.*, 1899, **21**, 284; 1900, **24**, 397.
(36) Reduction of phenylhydrazines by stannous chloride and HCl, Franzen, *J. pr. Chem.*, 1918, **97**, 61.
(37) Addition of hydrogen sulphide to nitriles at 60·6° and 1·75 atm. with NaSH as catalyst. Ref. as (30).
(38) Benzoyl chlorides and *iso*propyl alcohol at 25°; ref. as (12) and also Norris and Gregory, *J. Amer. Chem. Soc.*, 1928, **50**, 1813.

the table that the effect of chlorine is in almost all reactions in the same sense as that of the nitro-group, its inductive influence thus predominating. Analysis of the superposed alternating effects shows that here the results are complex. It may be noted that there is little evidence in Table II for the occurrence of " steric hindrance " due to a single ortho-substituent, though there are indications in reactions in which a carbonyl group is involved (24—35; compare Olivier, *Rec. trav. chim.*, 1929, **48**, 227). Another instance is recorded by Pfeiffer, Engelhardt, and Alfuss (*Annalen*, 1928, **467**, 158) in the esterification of benzonitriles.

In considering, now, the place to be taken by the results of Table I, we see that *N*-chlorination of acetobenzylamides falls unequivocally into Group B. With acetanilides, the results are more complex. When the acetamido-group is directly attached to the nucleus it can act as a strong *op*-directing group, and, in fact, with acetanilide, *N*-chlorination comprises less than 1% of the total reaction. The allocation of *N*-chlorination to Group B of Table II suggests that it is a reaction which is facilitated by flux of electrons towards the nitrogen, so that *N*- and *C*-chlorination are competing processes. Factors tending to obstruct the sharing of electrons between the nitrogen atom and the nucleus will assist *N*- as against *C*-chlorination; thus acetobenzylamide is *N*-chlorinated twice as fast as acetanilide, and *C*-chlorinated at a negligible rate. The results show that in the acetanilides, the introduction of chlorine atoms into the nucleus also reduces the preponderance of *C*-chlorination, an effect only partially offset in *m*-chloroacetanilide by the mutual reinforcement of the *op*-directing activities of the two groups. Indeed, in the acetanilides, chlorine in all positions accelerates *N*-chlorination. This may be ascribed in the *o*- and *p*-compounds to a dominant tautomeric influence by the halogen atom, but the result with the *m*-compound is unexpectedly high. At the same time, chlorine retards the reaction with the acetobenzylamides in all positions without alternation, the inductive effect of the halogen atom presumably dominating the situation, owing to the methylene group's intervening between the nitrogen atom and the nucleus. The nitro-group depresses reactivity in both series, but, somewhat unexpectedly, far more effectively in the acetobenzylamides than in the acetanilides. The high value for *o*-nitroacetanilide is unexpected, as is also the extraordinarily high rate of reaction of aceto-*p*-toluidide. The *p*-methyl group produces no such effect in the acetobenzylamides, but it may be noted that it has marked effects in reactions 3, 11, and 15 of Table II. There seems to be no analogy in Table II for the special effect of the *o*-nitro-group, unless it be in reaction 35, where it appears to upset the normal reaction completely. (For " ortho-effects," compare also van Duin, *Rec. trav. chim.*, 1927, **46**, 256; Kindler, *Annalen*, 1928, **464**, 278.)

The view that *N*-chlorination is a reaction favoured by factors tending to produce a crowding of electrons at the nitrogen atom is supported by the fact that the rates for acetamide, aceto-β-phenylethylamide, acetobenzylamide, and acetanilide lie in a continuous decreasing series; for the phenyl group acts as an " electron sink " towards the nitrogen atom, since (*a*) these substances are chlorinated or nitrated in positions *op*- to the nitrogen atoms, and (*b*) the approach of the phenyl group towards the nitrogen atom lowers the basic properties. Since *N*-chlorination cannot proceed by the separation of an anion, it seems probable that the vital stage is the attraction of the positive component of an incipiently ionised chlorine molecule, much as in the process of nuclear chlorination.

Nuclear Chlorination.—Table I contains two new results for nuclear chlorination—those for *m*-chloroacetanilide, mentioned above, and for aceto-*m*-toluidide. The latter, as we should expect, is *C*-chlorinated far more rapidly than acetanilide. On the other hand, the high rate of *C*-chlorination of the para-isomeride is another unexpected effect of the *p*-methyl group. This effect has been observed before, as is shown by Table III, which gives the relative values of k_{C} in glacial acetic acid (Orton and King, *loc. cit.*), in 40% acetic acid, and also in water (Soper, 1927, *loc. cit.*). The figures in parentheses are the values of $k_{\mathrm{N}}/k_{\mathrm{C}}$.

TABLE III.

	Acetanilide.					
Medium.	Abs.	Rel.	*o*-Cl.	*p*-Cl.	*o*-CH_3.	*p*-CH_3.
Glacial acetic ...	40	1	0·0018	0·0053	0·23	1·93
40% Acetic ...	11,000	1 (0·0087)	0·0025 (10·4)	0·0123 (0·85)	0·126 (0·101)	1·68 (0·137)
Water	17,000	1 (0·0076)	0·0026 (13·6)	0·0124 (0·91)	—	—

Limitations of Solvents—It is to be noted in Table III that a parallelism in the values of k_{C} exists in spite of the change in medium, and also despite the intrusion of simultaneous *N*-chlorination in the aqueous media. The change in solvent is, however, comparatively slight, and it should also be observed that in all the reactions in Table II, *the solvents are very similar*, only one being non-polar. This fact limits the generality of the conclusions to be drawn from the experiments. The results shown in Tables I and II are based upon experiments in which a standard substance is made to react with a series of compounds having various substituents inserted at positions remote from the point of reaction; a connexion is then traced between the changes in the reaction rate and the influence supposed to be exerted by the inserted groups upon the bond actually concerned in the reaction (*e.g.*, compare Norris, *Z. physikal. Chem.*, 1927, **130**, 662; Norris *et al.*, *J. Amer. Chem. Soc.*, 1925—1929). The electronic theory permits clearer definition since it ascribes the effects of substituents to their varying "electron affinities," which modify electronic configurations at the reacting atom, and external physical evidence (*e.g.*, from electric moments) is sometimes available as to the quality of the electron affinities. Consequently the process is now sometimes inverted, and the mechanism of a reaction is inferred from the effects of substituents on its speed (see above, also *Ann. Reports*, 1927, 1928). But these comparative experiments are usually made with solutions, wherein reaction velocity is notoriously susceptible to the influence of environment, the action of which may be *specific* to each reacting substance (Christiansen, *Z. physikal. Chem.*, 1924, **113**, 35; McCombie, Scarborough, and Smith, J., 1927, 802; Norrish and Smith, J., 1928, 129; Richardson and Soper, J., 1929, 1873). Hence, although identical conditions of solvent, vessel, and temperature are employed, so that the only variable is the constitution of one reactant, yet, owing to variations of environmental influences with constitution, the resulting series of reaction rates may fail to register the effects of substituents upon the point of reaction in the molecule. Little information is available on the effect of changing the medium upon comparative rates of reaction of a series of compounds with a standard substance, but this view is supported by the fact that changes of solvent alter the order of the relative rates of reaction of benzyl chloride and its nitro-derivatives with trimethylamine (McCombie, Scarborough, and Smith, *loc. cit.*), and similar effects were observed in other reactions by Berger (*Rec. trav. chim.*, 1927, **46**, 856), by Menschutkin (*Z. physikal. Chem.*, 1900, **34**, 157), and by Blakey, McCombie, and Scarborough (J., 1928, 2863).

On the other hand, it may happen that for a series of related substances, the effects of environment are sufficiently similar to justify drawing the desired inferences connecting the reaction rates directly with the influence of constitution upon reactivity (see Bradfield and Jones, J., 1928, 1006, 3073; also Hückel, *Ber.*, 1928, **61**, 1517; 1929, **62**, 2040). Bearing in mind this possibility, together with (*a*) the inevitable variation in precision in the different measurements quoted in Table II, and (*b*) the possibility of unsuspected wall effects in certain cases (Bailey, J., 1928, 1204), the general measure of consistency observed in Table II suggests that the only positive conclusion which can be drawn from the available data is that comparative velocity measurements can be used as indications of the effects of substituents upon the point of reaction in the molecule when an assembly of reactions can be examined. Individual anomalies in particular reactions (such as those observed in *N*-chlorination) may be genuine effects of the substituent upon the position of attack in the molecule, or may, at least in part, be due to the imperfect separation of environmental factors as indicated in the foregoing discussion.

EXPERIMENTAL.

Materials.—Acetanilides were prepared by acetylation of purified anilines, and repeatedly recrystallised from alcohol or dilute acetic acid. Aceto-β-phenylethylamide (from the amine) and acetamide were purified by two distillations at 0·5 mm. Benzylamine and its monochloro- and mononitro-substituted derivatives were made (as hydrochlorides) from the corresponding benzyl chlorides by the method of Ing and Manske (J., 1926, 2348), *m*-chlorobenzyl chloride being prepared by chlorination of *m*-chlorotoluene at its boiling point (Kenner and Witham, J., 1921, **119**, 1460). The acetobenzylamides were obtained by acetylation of the benzylamine hydrochlorides by warming with excess of acetic anhydride and sodium acetate. In each case, the excess of acetic anhydride was hydrolysed with water, the solution made alkaline with potassium hydroxide, and the (partly precipitated) acetyl derivative extracted with chloroform and recrystallised several times, usually from alcohol or hot water. The following compounds could not be traced in the literature : *Aceto*-p-*chlorobenzylamide*, m. p. 109·5°, after crystallisation from hot water until of constant m. p. (Found : Cl, 19·1. $C_9H_{10}ONCl$ requires Cl, 19·3%); *aceto*-m-*chlorobenzylamide*, m. p. 38°, purified by distillation at 0·5 mm. (Found : Cl, 19·0%). The low m. p. of the *m*-compound as compared with its isomerides is in accord with the rule for disubstituted benzenes (*Ann. Reports*, 1926, 144). (I am indebted to Messrs. W. O. Jones, B.Sc., and G. I. Davies, B.Sc., for the analyses.)

p-Methylbenzylamine was made by reducing *p*-toluonitrile with sodium and alcohol, and the other materials required—reaction medium, chlorine, etc.—were prepared as described by Orton, Soper, and Williams (*loc. cit.*).

Velocity Measurements.—The experimental method employed, the precautions taken, and the control experiments applied were those described previously, alternate portions of the reaction mixture being analysed at known time intervals (*a*) for chlorine by titration with *N*/500-sodium thiosulphate, and (*b*) for chloroamine by removal of chlorine with saturated aqueous *p*-cresol and subsequent titration. The initial concentrations of chlorine and of anilide were of the order 0·0005—0·0010*M* and 0·001—0·005*M* respectively, and, as before, hydrochloric acid was always present in 0·01*M* concentration in order to suppress the hydrolysis of chlorine. In view of the more strongly basic character of the acetobenzylamides as compared with the acetanilides, it was considered advisable to test the effect of hydrogen chloride upon the rate of *N*-chlorination. With 0·01*M*-, 0·05*M*-, and 0·10*M*-hydrochloric acid present, the values of k_N for acetobenzylamide were respectively 170, 176, and 173, showing that there is no appreciable effect over this range of concentration. The heat of reaction was shown to be negligible.

The velocity coefficients were calculated as before from the equations for a bimolecular reaction following two courses simultaneously. The following experiment is typical of the results with benzylamides.

Expt. 133. Aceto-*m*-nitrobenzylamide = 0·004109*M*; chlorine = 0·001232*M*; HCl = 0·01*M*; thiosulphate = 0·949 × *N*/500.

Time (mins.)	0	1·10	3·10	5·00	5·90	8·10	10·20	13·40	15·10
Titre (c.c.) ...	1·44	11·98	4·81	11·90	6·80	11·75	8·62	11·62	9·72

From curves constructed with these figures, we have :

Time.	KI titre.	NCl titre.	Diff.	Change, %.	k.
0	12·08	1·44	10·64	18·0	—
1·00	12·03	2·73	9·30	28·3	35·3
3·10	11·93	4·81	7·12	45·1	35·0
5·90	11·83	6·80	5·03	61·2	35·4
10·20	11·71	8·62	3·09	76·1	35·2
13·40	11·62	9·38	2·24	82·8	34·5
				Mean	35·1

Corrected value for k_N = 33·5.

In experiments such as the above, in which the fall in potassium iodide titre is slight and may be due partly or wholly to accidental loss of chlorine, no reliance can be placed on the result for k_C; k_N is corrected for the fall of potassium iodide titre. Two methods of calculation are possible, on the assumptions (*a*) that the fall is due entirely to *C*-chlorination; (*b*) that it is due entirely to accidental loss, in which case there is no corresponding consumption of anilide. As, however, the anilide is always present in large excess, the two methods give results which do not differ greatly : in the above experiment, k_N as calculated by method (*b*) lies between 32·9 and 34·4. Method (*a*) has been used throughout, since *C*-chlorination does actually take place slowly with some of the anilides in question (unpublished work by Dr. B. Jones).

The results in parentheses in Table I are provisional only. That for aceto-*m*-toluidide is the mean of five experiments in which potassium iodide was added to the whole of the reaction mixture at a noted time, less than 0·1 min. after mixing. A trial of the method with acetanilide gave a result $k_C = 10{,}400$ compared with the previous value 11,000. The ratio k_N/k_C was found by a separate experiment (see Orton, Soper, and Williams, *loc. cit.*; method for acetanilide). The value given for acetamide is the mean of three concordant experiments, but certain other experiments suggest that complications may arise in the reaction with this substance. The figure for aceto-*p*-methylbenzylamide is the mean of two experiments only and awaits confirmation.

Measurements were also made with 2 : 4-dinitroacetanilide. One experiment is shown below. Zero time was about 1 min. after mixing.

Expt. 145. 2 : 4-Dinitroacetanilide = 0·001542*M*; chlorine = 0·000623*M*; HCl = 0·011*M*; thiosulphate = 0·972 × *N*/500.

Time (mins.)	0	1·00	1·85	2·75	3·80	4·70	6·40	7·50
Titre (c.c.)	6·30*	2·75	2·86	2·61	6·09*	2·87	2·76	5·81*

The titres marked * were those with potassium iodide alone; *p*-cresol was used with the others. *N*-Chlorination evidently takes place rapidly until the chloroamine concentration reaches a certain value, after which its titre remains constant, although there is still a large amount of free chlorine left. Moreover, the final chloroamine titre was lowered by increasing the intial hydrogen chloride concentration. It thus appears that the chloroamine equilibrium (Orton and Jones, J., 1909, **95**, 1456), $C_6H_3(NO_2)_2\cdot NHAc + Cl_2 \rightleftharpoons C_6H_3(NO_2)_2\cdot NClAc + HCl$, lies much further to the left in 40% acetic acid than with the other anilides examined. This observation with 2 : 4-dinitroacetanilide is in accord with the fact recorded by Soper and Smith (J., 1928, 138) that the introduction of a single nitro-group into the benzene nucleus greatly increases the hydrolysis constant of a chloroamine.

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