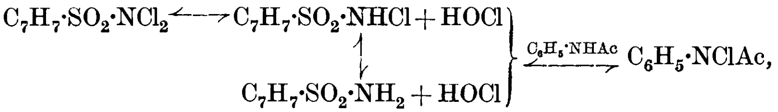
XX.—*The Effect of the Constitution of a Chloroamine on its Hydrolysis Constant.*

By Frederick George Soper and Gilbert Freeman Smith.

The methods available for the measurement of the hydrolysis constants of chloroamines have been described previously (J., 1924, **125**, 1899; 1925, **127**, 98). In the present investigation, 20% aqueous acetic acid (20 g. of acid in 100 c.c. of solution) was used as medium owing to its greater solvent power, which permitted determination of the hydrolysis constants over a much wider range of concentration than is possible in water. The primary and secondary hydrolysis constants of the standard chloroamine, *p*-toluenesulphondichloroamide, had to be redetermined in the new solvent, and the method was modified because the hydrolysis constant of chlorine therein was unknown.

The procedure adopted was to determine the ratio of the primary and secondary hydrolysis constants, K_1 and K_2, as before from the apparent solubility of the dichloroamide in solutions of the sulphonamide (*loc. cit.*, 1924, p. 1903); here, a, b, and c, are the concentrations in mols. per litre of unhydrolysed dichloroamide, monochloroamide, and free sulphonamide, respectively, and $K_1/K_2 = b^2/ac$. The hydrolysis constant of *N*-chloroacetanilide was then determined by distillation (*loc. cit.*, 1925, p. 101), allowance being made for the volatility of the unhydrolysed chloroamine. This knowledge, combined with determinations of the increased solubility (S) of the dichloroamide in acetanilide solutions, allowed of the calculation of K_1 and K_2 in the following way. If the equilibria existing in a saturated solution of *p*-toluenesulphondichloroamide in aqueous acetanilide are represented by



$$\left.\begin{array}{r} C_7H_7\cdot SO_2\cdot NCl_2 \rightleftarrows C_7H_7\cdot SO_2\cdot NHCl + HOCl \\ \updownarrow \\ C_7H_7\cdot SO_2\cdot NH_2 + HOCl \end{array}\right\} \xrightleftharpoons{C_6H_5\cdot NHAc} C_6H_5\cdot NClAc,$$

the thiosulphate titre, T_1, of the solution is given by

$$T_1 = 4[C_7H_7\cdot SO_2\cdot NCl_2] + 2[C_7H_7\cdot SO_2\cdot NHCl] + 2[C_6H_5\cdot NClAc] + 2[HOCl]$$

or, neglecting the last term, for reasons given in J., 1925, **127**, 100,

$$T_1 = 4a + 2b + 2x,$$

$$i.e., \ (T_1 - 4a)/2 = x + b = S \quad . \quad . \quad . \quad . \quad (1)$$

where x is the concentration of the *N*-chloroacetanilide. The determination of K_1/K_2 from the solubility determination in the sulphonamide solution gives

$$b^2/ac = 13{\cdot}13, \text{ where } a = 0{\cdot}634 \times 10^{-3}\,M \quad . \quad . \quad (2)$$

whilst the relation between the concentrations of sulphonamide and sulphonchloroamide requires that

$$x = b + 2c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence from (1), (2), and (3)

$$b^2 + 8{\cdot}324 \times 10^{-3}\,b - 4{\cdot}162 \times 10^{-3}\,S = 0 \quad . \quad . \quad (4)$$

This allows of the calculation of b, c, and x and also of [HClO] from the hydrolysis constant of *N*-chloroacetanilide,

$$[\mathrm{HClO}]\,(d - x)/x = 6{\cdot}70 \times 10^{-7} \quad . \quad . \quad . \quad . \quad (5)$$

where d is the initial concentration of anilide, and hence of $K_1 = [\mathrm{HClO}]c/x$.

The values of K_1 and K_2 obtained in this way in 20% acetic acid are $5{\cdot}17 \times 10^{-7}$ and $3{\cdot}94 \times 10^{-8}$, respectively, whilst in water they were $8{\cdot}0 \times 10^{-7}$ and $4{\cdot}9 \times 10^{-8}$. From these values the hydrolysis constants of other chloroamines can be determined from the apparent solubility of the dichloroamide in solutions of the requisite anilide (*loc. cit.*, 1925, p. 99). [A correction should be made in equation (4) of that paper (p. 100) which should read $2[C_7H_7{\cdot}SO_2{\cdot}NH_2] = x - b$. The alteration has no appreciable effect on the constants given therein, since the sulphonamide concentration is always very slight.] The constants measured in water are in satisfactory agreement with the values now obtained in aqueous acetic acid over a much wider concentration range. The constant for *N*-chloro-*p*-toluidide is an exception and the relatively high value obtained in water has been traced to a further decomposition and oxidation which readily occurs in neutral aqueous solutions (see Chattaway and Orton, J., 1900, **77**, 792).

Effect of the Acyl Radical on the Hydrolysis of the Chloroamine.—The hydrolysis constants of the *N*-chloro-derivatives of four acylanilides are given in Table I, together with the ionisation constants, K_a, of the corresponding acids. The magnitude of the ionisation constant of the acid will be governed by the degree of polarisation of

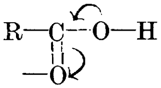
TABLE I.

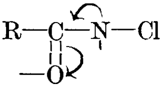
	$K_h \times 10^7$.	No. of determntns.		$K_a \times 10^4$.
N-Chloroformanilide	1·26 ± 0·04	4	Formic acid	2·14
N-Chloroacetanilide	6·70 *	—	Acetic acid	0·186
N-Chloropropionanilide	7·5 ± 0·27	3	Propionic acid	0·134
N-Chlorobutyranilide	7·0 ± 0·18	4	Butyric acid	0·149—0·175

* The mean deviation from the mean has not been inserted for this case, which is taken as standard. It is estimated to be correct to within 10%.

the molecule as indicated in (I) (Allan, Oxford, Robinson, and Smith, J., 1926, 405; Ingold and Ingold, *ibid.*, p. 1311), being connected

(I.)





(II.)

with the degree of positiveness of the carbonyl carbon atom. If bivalent oxygen and tervalent nitrogen transmit the influence of the carbonyl carbon atom in the same way (II), we should expect that the ionisation of the chloroamine into positive chlorine, and therefore the hydrolysis constant of the chloroamine, would be increased in proportion to the increase in the ionisation constant of the acid. Actually an increase in the ionisation constant of the acid is attended by a decrease in the hydrolysis constant of the chloroamine. Increase in the positiveness of the carbonyl carbon thus causes a decrease of the hydrolysis of the chloroamine.

The effect of substituents in the benzene ring on the positivity of a nuclear carbon atom is indicated by the ionisation constants of the phenols, benzoic acids, and anilines. When the effect of substituents in the benzene ring on the hydrolysis of the chloroamine, $NClAc{\cdot}C_6H_5$, is studied, it is found that an increase in this positivity of the nuclear carbon atom attached to the NClAc group causes an *increase* in the hydrolysis of the chloroamine. The results obtained for the effects of the nitro-, methyl, and chlorine groups are given in Table II.

TABLE II.

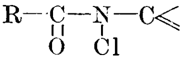
Substituent.	$K_h \times 10^7$.	No. of determs.	$K_a \times 10^{10}$ for Ph·OH.	$K_a \times 10^5$ for $Ph{\cdot}CO_2H$.	$K_b \times 10^{10}$ for $Ph{\cdot}NH_2$.
H	6·7		1·1	6·0	5·0
o-NO_2	112 ± 3	4	750	620	0·00015—0·0004 *
m-NO_2	99 ± 4	6	100	34·5	0·04
p-NO_2	324 ± 22	4	960	40·0	0·01
o-CH_3	1·11 ± 0·02	5	0·63	12·0	3·3
m-CH_3	2·61 ± 0·05	5	0·98	5·1	6·0
p-CH_3	3·48 ± 0·12	4	0·67	5·1	12—20
o-Cl	6·4 ± 0·30	5	7·7	132	0·044 *
m-Cl	23·0 ± 0·5	4		15·5	0·34
p-Cl	16·4 ± 0·3	4	4·0	9·3	0·99

* Unpublished work in collaboration with Dr. G. Williams.

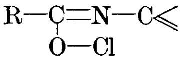
An explanation is thus required of the singular result that positiveness of the carbonyl carbon linked to nitrogen causes a decrease in the hydrolysis constant of the chloroamine, whilst positiveness of a nuclear carbon atom linked to nitrogen causes an increase in the hydrolysis constant of the chloroamine.

If one regards an acyl-chloroamine as represented either by the formula III, or by the possible formula IV (which is suggested by

(III.)



$\mathrm{R-\underset{\underset{O}{\|}}{C}-\underset{\underset{Cl}{|}}{N}-C{<}}$



$\mathrm{R-\underset{\underset{O-Cl}{|}}{C}{=}N-C{<}}$

(IV.)

unpublished work on the kinetics of the formation of acylchloroamines), then increase in the positivity of either the carbonyl or the nuclear carbon atom should have the same effect on the hydrolysis constant of the chloroamine, in that either an increase or a decrease in this constant results.

A possible explanation of the observations may be that a chloroamine in solution consists of a tautomeric mixture of the (III) and (IV) forms. The effect of the positiveness of the carbonyl carbon is then to increase the ease with which positive chlorine can separate from a nitrogen atom (III), but to decrease the ease with which a negative OCl′ ion can separate from the carbonyl atom (IV). Since the induced effect of a group decreases rapidly with the distance, the positivity of the carbonyl carbon will affect the ionisation of its attached OCl′ ion to a greater extent than it will the ionisation of the positive chlorine attached to nitrogen, with the result that the hydrolysis is decreased. Conversely, increase in the positivity of the nuclear carbon atom will result in an increase of the hydrolysis owing to the proximity of the NCl group.

EXPERIMENTAL.

Preparation of 20% *Aqueous Acetic Acid and its Stability to Chloroamines.*—Commercial glacial acetic acid was purified by distillation from chromic anhydride (Orton and Bradfield, J., 1924, **125**, 960). This acid was then diluted to approximately 20% with conductivity water and its strength adjusted after titration with 3*N*-caustic soda, until it contained 20 g. of acetic acid per 100 c.c. of solution at 15°. When shielded from light, *p*-toluenedichlorosulphonamide, *N*-chloroacetanilide, and hypochlorous acid are fairly stable in this medium, as is seen from Table III.

Measurement of the Hydrolysis of N-*Chloroacetanilide by Distillation.*—The apparatus used has been previously described (*loc. cit.*). The distillate, consisting of hypochlorous acid and chloroamine, obtained from an *M*/20-*N*-chloroacetanilide solution in 20% acetic acid was 0·002177*M* with respect to thiosulphate. In the presence

TABLE III.

Titre of 20 c.c. of solution (in c.c. of $N/500$-thiosulphate).

Time.	HOCl soln.	$C_6H_5\cdot NClAc$ soln.	$C_7H_7\cdot SO_2\cdot NCl_2$ soln.
0 hrs.	14·78 c.c.	17·12 c.c.	13·83 c.c.
12 ,,	14·55 ,,	17·07 ,,	13·70 ,,
21 ,,	14·25 ,,	17·00 ,,	13·59 ,,
34 ,,	13·50 ,,	16·68 ,,	13·59 ,,

of excess acetanilide, the distillate, now consisting of chloroamine only, was 0·001474M. The concentration of hypochlorous acid in the first distillate is therefore 0·000703M, corresponding to a concentration of 0·00183M-hypochlorous acid in the original solution. The latter deduction was made graphically from the results obtained on distillation of hypochlorous acid solution in 20% acetic acid (Table IV).

TABLE IV.

Distillation of hypochlorous acid solutions.

(*a*) C.c. of $N/500$-$Na_2S_2O_3$ required by 20 c.c. of solution	1·85	2·38	3·50	3·92	7·83	8·12
(*b*) C.c. of $N/500$-$Na_2S_2O_3$ required by 10 c.c. of distillate	3·55	4·43	7·05	7·29	13·10	13·24

From the concentration of free hypochlorous acid in the chloroamine solution, the hydrolysis constant can be calculated.

Solubility of p-*Toluenesulphondichloroamide.*—The solubility of *p*-toluenesulphondichloroamide in 20% acetic acid is $0\cdot6343 \times 10^{-3}$ mol. per litre. The solubilities in the various anilide solutions and in the solutions of the sulphonamide were measured in the manner already described (*loc. cit.*, 1925, p. 102). The results of two typical experiments are given in Table V.

TABLE V.

$d \times 10^3$.	$T_1 \times 10^3$.	$b \times 10^3$.	$x \times 10^3$.	$(d - x) \times 10^3$.	[HOCl] $\times 10^7$.	$K_h \times 10^7$.
			N-Chloro-*o*-chloroacetanilide.			
1	4·495	0·464	0·515	0·485	7·07	6·65
2	5·624	0·711	0·832	1·168	4·61	6·48
4	7·179	1·034	1·287	2·713	3·17	6·69
7	9·243	1·433	1·925	5·075	2·29	6·03
10	10·79	1·712	2·414	7·586	1·916	6·02
			N-Chloro-*o*-nitroacetanilide.			
3	3·667	0·274	0·291	2·709	12·0	111·4
5	3·975	0·346	0·373	4·627	9·48	117·6
7	4·305	0·422	0·463	6·537	7·77	109·8
10	4·665	0·502	0·562	9·438	6·54	109·8

Summary.

1. The hydrolysis constants of a number of acyl-chloroamines have been measured in 20% aqueous acetic acid.

2. Comparison of the hydrolysis constants of a series of chloroamines RR′NCl, in which R′ was constant, with the ionisation constants of the fatty acids, ROH, shows that an increase in the latter is associated with a decrease in the hydrolysis constant of the chloroamine.

3. When the acyl group R is kept constant and the aryl radical R′ is altered by the introduction of substituents, it is found that increase of the ionisation constant of the phenol, R′·OH, is attended by an *increase* in the hydrolysis constant of the chloroamine.

4. A possible explanation, based on the assumption that an acylchloroamine consists of a tautomeric mixture of the substances R·C(OCl):NR′ and R·CO·NClR′, is advanced.

In conclusion, we wish to express our appreciation of Professor K. J. P. Orton's continued interest in this work.

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