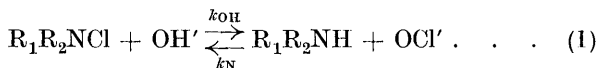


CCVIII.—*The Direct Interchange of Chlorine in the Interaction of p-Toluenesulphonamide and N-Chloroacetanilide.*

By DAVID REGINALD PRYDE and FREDERICK GEORGE SOPER.

ON the mechanism advanced for the formation of chloroamines from hypochlorous acid and acylamines (previous paper), the fundamental hydrolysis equilibrium of a chloroamine is



The equilibrium constant, K_h' , of this reaction is related to the hydrolysis constant, $K_h = [HOCl][:NH]/[:NCl]$, determined for a number of chloroamines (J., 1925, **127**, 98; 1928, 138) by the expression

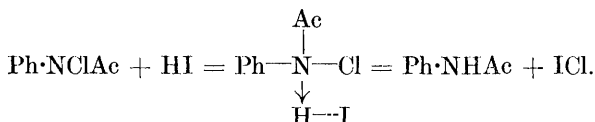
$$K_h' = K_h[OCl']/[HOCl][OH'] = K_h/K_h^{NaOCl} \quad . \quad . \quad (2)$$

For *N*-chloroacetanilide, $K_h = 6.7 \times 10^{-7}$, and K_h^{NaOCl} , the hydrolysis constant of sodium hypochlorite, is 1.0×10^{-6} (J., 1924, **125**, 2227), giving the value 0.67 for K_h' , which is also the ratio of the velocity coefficients, k_{OH} and k_N , of hydrolysis and of formation respectively. Since k_N has been found to be 1,020, $k_{OH} = 7 \times 10^2$ and the velocity of hydrolysis in neutral solution at unit concentration = 7×10^{-5} mol./min. This speed corresponds to a 50% hydrolysis of *N*-chloroacetanilide in about 7 days or to 1% hydrolysis in 2.3 hours:

The rate of production of hypochlorous acid from *N*-chloroacet-

anilide in neutral solution thus appears to be slow. This is confirmed by observation. In neutral solution, a mixture of *N*-chloroacetanilide and *p*-cresol, which reacts rapidly with hypochlorous acid, shows no appreciable fall in titre over a period of 4 hours. In alkaline solution ($p_{\text{OH}} = 2$), the hydrolysis is, as would be anticipated, very rapid, and is attended by other decomposition in which 99% of the chlorine appears as chloride, with simultaneous coloration of the mixture and formation of carbylamine. It is possible, however, by pouring a freshly prepared mixture of chloroamine and alkali into phenol and excess of *N*/10-hydrochloric acid solution, which removes the hypochlorite and in which the chloroamine is sufficiently stable, to show that the equilibrium concentrations required by equation (2) are satisfactorily complied with from whichever side the equilibrium is approached.

In view of the slow formation of hypochlorous acid from *N*-chloroacetanilide in neutral solution, many of the reactions of chloroamines, *e.g.*, that with iodides, must be regarded as direct and not as dependent on the intermediate formation of hypochlorous acid :



Other experiments indicate that such direct interaction of the chloroamine is not confined to interaction with the halogen acids. In the presence of *p*-toluenesulphonamide, *N*-chloroacetanilide is converted into acetanilide, *p*-toluenesulphonchloroamide is formed, and the sulphonchloroamide separates if the initial concentration of the *N*-chloroacetanilide is not too small. A fairly rapid interchange of chlorine occurs until equilibrium is attained, which, from the known hydrolysis constants, would correspond to 95% of sulphonchloroamide.

To demonstrate the presence of *p*-toluenesulphonmonochloroamide in solution, use may be made of its relatively rapid rate of hydrolysis into hypochlorous acid. Unlike *N*-chloroacetanilide, *p*-toluenesulphonchloroamide, when mixed with *p*-cresol in neutral solution, shows a rapid fall in iodine titre. This fall in titre is independent of the concentration of the cresol and therefore measures the rate of hydrolysis of the sulphonchloroamide rather than of a possible direct interaction with cresol. The velocity coefficients obtained are shown in Table I. The chloroamines of acetanilide and of *p*-toluenesulphonamide may thus be differentiated in solution by their behaviour in the presence of *p*-cresol.

TABLE I.

Hydrolysis of *p*-toluenesulphonchloroamide at 25° and $p_H = 7.0$.

[<i>p</i> -Cresol] = 0.02 <i>M</i> .			[<i>p</i> -Cresol] = 0.06 <i>M</i> .		
Time.	[R·SO ₂ ·NHCl].	<i>k</i> .	Time.	[R·SO ₂ ·NHCl].	<i>k</i> .
0	0.00434	—	0	0.00350	—
3.20	0.00311	0.104	2.00	0.00280	0.113
5.10	0.00245	0.110	4.00	0.00225	0.110
6.80	0.00214	0.104	5.80	0.00190	0.106
8.00	0.00191	0.102	8.20	0.00147	0.105
11.00	0.00155	0.103	9.60	0.00126	0.106

When a neutral aqueous solution of *N*-chloroacetanilide and *p*-toluenesulphonamide was kept at 25.0°, no change in the amount of titratable chlorine was observed over a period of 1 hour, but on introduction of *p*-cresol to test whether the sulphonchloroamide had been formed, a rapid fall in titre was observed, the velocity coefficients shown in Table II being similar to those obtained for the hydrolysis of *p*-toluenesulphonchloroamide.

TABLE II.

[Ph·NClAc] = 0.01*M*; [C₇H₇·SO₂·NH₂] = 0.05*M*; $p_H = 7.0$.

Time, mins.	0	53	60	61.7	65.1	80.7
Titre of 10 c.c.	16.5	16.50	(cresol added; calc. titre = 13.95)	7.80	5.40	3.12
<i>k</i>	—	—	—	—	0.103	0.102

Further indication of the conversion of *N*-chloroacetanilide into acetanilide in a period of 1 hour, during which time only 0.45% of the chloroamine normally hydrolyses, is possible by adding one equivalent of chlorine in *N*/50-solution, to which both *N*-chloroacetanilide and *p*-toluenesulphonamide are stable. The chlorine is immediately removed, showing that the stable *N*-chloroacetanilide has been replaced by some other substance which is readily *C*-chlorinated.

Since the rate of hydrolysis of the *p*-toluenesulphonchloroamide in neutral solution is rapid, it is possible to estimate the rate at which this substance is formed by observing the rate at which hypochlorous acid can be removed from the mixture. By using *p*-cresol for this purpose, the bimolecular velocity coefficient of the formation of the sulphonchloroamide from *N*-chloroacetanilide and the sulphonamide was found to be 0.47 :

*Rate of interaction of C₇H₇·SO₂·NH₂ and Ph·NClAc.*Initial concs. : [·NCl] = 0.01*M*; [R·SO₂·NH₂] = 0.05*M*; [*p*-Cresol] = 0.02*M*.

Time, mins.	0	6.0	14.3	22.0
Titre of 10 c.c.	14.62	12.70	10.55	8.95
<i>k</i> ₁	—	0.0235	0.0228	0.0223
<i>k</i> ₂ = <i>k</i> ₁ /0.05	—	0.470	0.456	0.446

This rate of formation of *p*-toluenesulphonchloroamide appears to be approximately the same in *N*/10-hydrochloric acid although the hydrogen-ion concentration is 10^6 times greater. Since the sulphonchloroamide reacts with hydrochloric acid to give chlorine more rapidly than does *N*-chloroacetanilide, the effect of the presence of *p*-toluenesulphonamide on the rate of formation of chlorine from *N*-chloroacetanilide and hydrochloric acid is to increase it owing to the formation of the sulphonchloroamide. Since the sulphonchloroamide is not removed immediately it is formed, the reaction exhibits a period of induction, illustrated by the following results, in which the titre is that of 10 c.c. of solution against *N*/100-sodium thiosulphate :

Rate of formation of chlorine from N-chloroacetanilide and N/10-hydrochloric acid.

Time	0	31	47	60	75.5	90	131
In the absence of sulphonamide :							
Titre	19.98	—	18.88	—	18.55	—	17.03
In presence of 0.02 <i>M</i> -sulphonamide :							
Titre	19.95	19.55	18.07	15.99	13.53	11.07	8.33

The time of half reaction due to the simultaneous formation of the sulphonchloroamide is approximately 140 mins. Were the sulphonchloroamide so reactive with hydrochloric acid that it was removed as soon as it was formed, the time of half reaction, as calculated from the rate of formation in neutral solution, would be 148 mins.

Unless the sulphonamide exerts some very powerful catalytic effect on the hydrolysis of *N*-chloroacetanilide, this substance can *N*-chlorinate *p*-toluenesulphonamide some 10^4 times faster than it can form hypochlorous acid. This suggests that, when chlorine or hypochlorous acid results in nuclear chlorination, a chloroamine may be of use in the chlorination of side chains.

Summary.

1. The estimated rate of hydrolysis of *N*-chloroacetanilide into hypochlorous acid and acetanilide in neutral solution at 25° is 50% in 7 days, and is confirmed by the observed stability of aqueous solutions of this substance in the presence of phenols which remove rapidly hypochlorous acid.
2. 50% Hydrolysis of *p*-toluenesulphonmonochloroamide, under similar conditions, occurs in 7 minutes.
3. *p*-Toluenesulphonamide catalyses strongly the formation of hypochlorous acid from *N*-chloroacetanilide. This is interpreted in terms of a direct interchange of chlorine, whereby *p*-toluenesulphonmonochloroamide is formed.

4. A similar interchange of chlorine, and at approximately the same rate, occurs in acid solution, accounting for an increase in the rate of production of chlorine from *N*-chloroacetanilide and hydrochloric acid. The effect of *p*-toluenesulphonamide on the latter rate is quite distinct from that of acetanilide and phenols (*J. Physical Chem.*, 1927, **31**, 1192), which also cause an increment in the apparent rate.

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