784. *The Hydrolysis of Some Chloro*-1,3,5-*Triazines: Mechanism: Structure and Reactivity.*

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The stepwise hydrolysis of cyanuric chloride and of 2-arylamino-4,6-dichloro- and 2,4-diarylamino-6-chloro-1,3,5-triazines in acid, neutral, and alkaline solutions has been studied kinetically, the compounds isolated on successive replacement of chlorine by hydroxyl being used for the later steps. An S_N2 mechanism is proposed for alkaline and neutral hydrolysis, modified in the case of arylaminodichlorotriazines by an acidic dissociation. Acid catalysis, observed in most cases, takes the form $k = k_0 + k_a[H^+]$. The reactivity of the chlorine atom(s) has been related to the basicity of other substituents of the triazine ring and to their state of dissociation. The solubility of cyanuric chloride in water and in aqueous acetone has been measured.

THE first technically successful range of reactive dyes for cellulosic fibres owe their reactivity to the presence of a 2,4-dichloro-1,3,5-triazinyl-group.[1] Others, less reactive, contain a 2-chloro-1,3,5-triazinyl-group.[2] Their aqueous alkaline solutions react with the fibre, presumably to form cellulose esters by a type of Schotten–Baumann reaction. At the same time, some hydrolysis of the reactive chlorine atoms occurs. We have therefore examined in detail the hydrolytic behaviour of some relatively simple 2-arylamino-4,6-dichloro- and 2,4-diarylamino-6-chloro-1,3,5-triazines, as well as of cyanuric chloride (2,4,6-trichloro-1,3,5-triazine).

Published information on the hydrolysis of cyanuric chloride is not extensive, and some of it is conflicting. Though the presence of intermediate chlorohydroxytriazines has several times been postulated, a recent (1959) text [3] records no clear evidence of their formation. A recent paper,[2] however, states, without details, that 2,4-dichloro-6-hydroxy-1,3,5-triazine has been prepared by selective hydrolysis of cyanuric chloride, and mentions some of its properties, its reaction with cellulose, and its use to prepare arylaminochlorohydroxytriazines. The isolation of 2-chloro-4,6-dihydroxy-1,3,5-triazine has not hitherto been reported. Only one paper [4] reports measurements of the rate of hydrolysis of cyanuric chloride, in an aqueous suspension of calcium carbonate.

[1] Vickerstaff, *Melliand Textilber.*, 1958, **39**, 905.

[2] Wegmann, *Melliand Textilber.*, 1958, **39**, 1006.

[3] Smolin and Rapoport, " *s*-Triazines and Derivatives " in the series " The Chemistry of Heterocyclic Compounds," Interscience Publ., Inc., New York, 1959.

[4] Fierz-David and Matter, *J. Soc. Dyers and Colourists*, 1937, **53**, 424.

It has long been recognised[3] that successive replacement of the three chlorine atoms in cyanuric chloride by amino-, or alkyl, or arylamino-groups progressively reduced the reactivity of the remaining chlorine atom(s), but no quantitative studies of the hydrolysis of these products have been found.

EXPERIMENTAL

Materials.—(*a*) Cyanuric chloride was technical material purified by crystallisation from light petroleum (b. p. 100—120°).

(*b*) 2-Arylamino-4,6-dichloro-1,3,5-triazines were prepared by the known method[4-7] of treating a suspension of cyanuric chloride (produced by adding an acetone solution to ice and water) with an aqueous solution or suspension of the arylamine containing an equivalent of alkali to neutralise the hydrochloric acid liberated, the solution remaining slightly acid throughout. The products were isolated by filtration, after salting if necessary, dried *in vacuo* at laboratory temperature, and, when possible, recrystallised from an organic solvent. The following 1,3,5-triazines were prepared by this method:

2-Anilino-4,6-dichloro-,[4,5] m. p. 136° (Found: C, 45·2; H, 2·6; Cl, 29·4; N, 23·2. Calc. for $C_9H_6Cl_2N_4$: C, 44·8; H, 2·5; N, 23·2; Cl, 29·4%).

2,4-Dichloro-6-*p*-chloroanilino-,[8,9] m. p. 191° [Found: C, 39·0; H, 1·9; N, 19·9; Hydrolysable Cl, 25·9. Calc. for $C_9H_5Cl_3N_4$: C, 39·2; H, 1·8; 2Cl, 25·8; N, 20·3%).

2,4-Dichloro-6-*p*-sulphoanilino- (Na salt)[5,7] (Found: Hydrolysable Cl, 20·4. Calc. for $C_9H_5Cl_2N_4NaO_3S$: Cl, 20·7%).

2,4-Dichloro-6-*m*-sulphoanilino- (Na salt), containing ~3% of sodium chloride and a little water (Hydrolysable Cl, ~95%; *M*, 343).

2,4-Dichloro-6-*o*-sulphoanilino- (Na salt), containing some water of hydration (Hydrolysable Cl, 94%; *M*, 343).

2,4-*Dichloro*-6-p-*nitroanilino*- (Found: C, 38·2; H, 2·0; Cl, 23·5; N, 26·6. $C_9H_5Cl_2N_5O_2$ requires C, 37·8; H, 1·75; Cl, 24·8; N, 24·5%) (no suitable solvent for recrystallisation was found).

2,4-Dichloro-6-(*N*-methyl-*m*-sulphoanilino)- (Na salt), containing 10% of sodium chloride (Hydrolysable Cl, 89%; *M*, 357).

2,4-Dichloro-6-(*N*-methyl-*p*-sulphoanilino)- (Na salt), containing 9% of sodium chloride (Hydrolysable Cl, 89%; *M*, 357).

2,4-Dichloro-6-(4-sulpho-1-naphthylamino)- (Na salt), containing 11% of sodium chloride (Hydrolysable Cl, 83%; *M*, 393).

2,4-*Dichloro*-6-(8-*sulpho*-1-*naphthylamino*)- (*K salt*) (Found: C, 38·6; H, 1·8; N, 13·7; Cl, 17·2; S, 7·8. $C_{13}H_8Cl_2N_4O_3S$ requires C, 38·2; H, 1·8; Cl, 17·35; N, 13·7; S, 7·8%).

In two cases, there was no reaction in slightly acid media, and the conditions were modified:

2,4-*Dichloro*-6-(*toluene*-p-*sulphonamido*)-1,3,5-*triazine*. Toluene-*p*-sulphonamide (0·4 mole) was dissolved in an equivalent of sodium hydroxide solution, and diluted to 3½ l. (pH 11·5) at room temperature. Cyanuric chloride (0·44 mole), dissolved in acetone, was added with agitation. The pH quickly fell, and a further equivalent of N-sodium hydroxide was added during 5—10 min. to maintain the pH at ~9. In another few minutes the pH fell below 7 and a further addition of N-sodium hydroxide (0·06 mole) restored the pH to 7. A small amount of undissolved cyanuric chloride was removed by filtration. The product was precipitated by addition of concentrated hydrochloric acid (30 c.c.) (pH 2·2), filtered off, washed with water, and dried *in vacuo* at room temperature over phosphorus pentoxide. After recrystallisation from toluene the *product* was a white solid, m. p. 209—209·5° (84 g., 66%) (Found: C, 37·8; H, 2·4; N, 17·7; Cl, 22·2. $C_{10}H_8Cl_2N_4O_2S$ requires C, 37·6; H, 2·5; N, 17·6; Cl, 22·3%).

2,4-*Dichloro*-6-[N-(p-*sulphophenyl*)*toluene*-p-*sulphonamido*]-1,3,5-*triazine* (*Na salt*). Sodium 4-toluene-*p*-sulphonamidobenzenesulphonate (0·05 mole), prepared through the pyridine salt,[10] was dissolved in an equivalent of sodium hydroxide in water (250 c.c.; pH 11·1) at room

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[5] Thurston, Dudley, Kaiser, Hechenbleikner, Schaeffer, and Holm-Hansen, *J. Amer. Chem. Soc.*, 1951, **73**, 2981.

[6] Soc. Chem. Ind. Basle, B.P. 221,843/1924.

[7] Fritzsche, Krummenacher, Gubler, and Kaiser, U.S.P. 1,625,530/1927.

[8] Curd, Landquist, and Rose, *J.*, 1947, 154.

[9] Cuthbertson and Moffat, *J.*, 1948, 561.

[10] Halberkann, *Ber.*, 1921, **54**, 1843.

temperature. Cyanuric chloride (0·054 mole) in acetone was added with vigorous stirring. N-Sodium hydroxide was added to maintain the pH between 6·5 and 7·5 (28 c.c. were required during 40 min.). The *product* (92%) was filtered off, washed with water, and dried *in vacuo* over phosphorus pentoxide. It was a white powder, free from sodium chloride (Found: Hydrolysable Cl, 98%; *M*, 497).

(*c*) 2-Chloro-4,6-diarylamino-1,3,5-triazines were prepared by the known method[5,6] of treating a suspension of cyanuric chloride in aqueous acetone with an equivalent of the first arylamine and of alkali, at 0—5°, in slightly acid media, and treating the product, usually without isolation, with an equivalent of the second arylamine and of alkali, under similar conditions, but at temperatures between 10° and 40°. The products were isolated by filtration, after salting if necessary, and dried *in vacuo* at room temperature. This gave 2-anilino-4-chloro-6-*p*-sulphoanilino- (Na_2 salt), containing 7·5% of sodium chloride (Hydrolysable Cl, and N, 91%; *M*, 349·5), and 2-chloro-4,6-di-(*N*-methyl-*p*-sulphoanilino)-1,3,5-triazine (Na salt), containing 10·5% of sodium chloride (Found: C, 34·5; H, 2·8; N, 11·0; S, 10·7; Cl, 6·0. Calc. for 89·5% $C_{17}H_{14}ClN_5Na_2O_6S_2$: C, 34·5; H, 2·4; N, 11·8; S, 10·7; Cl, 6·0%).

2-*Anilino*-4-*chloro*-6-(*toluene*-p-*sulphonamido*)-1,3,5-*triazine*. 2,4-Dichloro-6-toluene-*p*-sulphonamido-1,3,5-triazine (0·05 mole) was ground with an equivalent of sodium hydrogen carbonate and dissolved in water (100 c.c.) at room temperature. Aniline (0·05 mole) in water (200 c.c.) was added dropwise during 2 hr. with simultaneous addition of N-sodium hydroxide, (48 c.c.) to maintain pH 6·5—7·5. After being kept overnight, the suspension was diluted to 1 l. and filtered. The solid was dried (crop 1; 11·5 g.). The filtrate was titrated with hydrochloric acid to a fairly sharp end-point at pH 4·9. The precipitate was filtered off, washed, and dried (crop 2; 6·4 g.). Crop 1 was purified by dissolving it in sodium carbonate solution, neutralising the solution to pH 7·5, filtering it, with addition of Filtercel, and titrating the filtrate with hydrochloric acid to a fairly sharp end-point at pH 4. The precipitate was filtered off, washed, dried, and added to crop 2 (total yield, 13·6 g., 72%). The *product* was a white powder, m. p. 226·5—227° (Found: C, 51·3; H, 3·8; N, 18·2; S, 8·9; Cl, 9·4. $C_{16}H_{13}ClN_5O_2S$ requires C, 51·2; H, 3·7; N, 18·7; S, 8·5; Cl, 9·45%).

2-*Chloro*-4,6-*di*-(N-p-*sulphophenyltoluene*-p-*sulphonamido*)-1,3,5-*triazine* (*Na_2 salt*). This was prepared by the method used for chlorodiarylaminotriazines, but the replacement of the second chlorine atom was slow and was incomplete even after 9 hr. at 60° and pH 7·5. The product was filtered off at this stage, washed, and dried (yield 69%). 10 g. were dissolved in 550 c.c. of water at 50° and, after filtration, recovered by addition of salt (25 g.) at 0° (yield 86%). The *product* was a white solid containing 0·1% of sodium chloride (Found: C, 42·9; H, 3·0; N, 8·7; Cl, 4·4; S, 15·2; Sulphated ash 18·5. $C_{29}H_{22}ClN_5Na_2O_{10}S_4$ requires C, 43·0; H, 2·75; N, 8·7; Cl, 4·4; S, 15·8; Sulphated ash, 17·7%).

2-*Chloro*-4-*hydroxy*-6-(m-*sulphoanilino*)-1,3,5-*triazine* (*Na_2 salt*).—2,4-Dichloro-6-*m*-sulphoanilino-1,3,5-triazine (Na salt) (0·1 mole) was dissolved in water (400 c.c.) containing sodium hydroxide (0·3 mole). After 18 hr. at room temperature the solution was titrated with hydrochloric acid (0·1 mole required) to pH 8·0—8·2. The *product* was precipitated by addition of salt (100 g.), filtered off, washed, and dried *in vacuo* at room temperature (yield, 55%). The product was a white powder containing 3·3% of sodium chloride (Found: Hydrolysable Cl, 92·5%; *M*, 346·5). Owing to its hydroxyl group the compound titrated as an acid of p*K* 5·4 (titre corresponded to 93·4%). A sample recrystallised from water was analysed (Found: C, 30·9; H, 1·8; N, 15·7; Cl, 10·1; S, 9·4. $C_9H_5ClN_4Na_2O_4S$ requires C, 31·2; H, 1·45; N, 16·2; Cl, 10·25; S, 9·25%).

2,4-*Dihydroxy*-6-m-*sulphoanilino*-1,3,5-*triazine* (*Na salt*). Sodium metanilate (0·1 mole) was treated with cyanuric chloride as described above. The solution of the dichlorotriazine was hydrolysed by addition of sodium hydroxide as in the last preparation. The solution of the chlorohydroxytriazine was acidified with hydrochloric acid and left at room temperature overnight. The excess of hydrochloric acid was neutralised with sodium hydroxide to pH 3·5. The *product* (61%) was precipitated by addition of salt, filtered off, washed, and dried. Recrystallised from water (Found: C, 34·0; H, 2·9; N, 17·7; S, 10·4. $C_9H_7N_4NaO_5S,\frac{1}{2}H_2O$ requires C, 34·3; H, 2·55; N, 17·8; S, 10·2%), the compound titrated as a monobasic acid of p*K* 6·3.

2,4-*Dichloro*-6-*hydroxy*-1,3,5-*triazine* (*Na salt*) A solution of cyanuric chloride (0·1 mole) in acetone was poured into a dilute phosphate buffer solution (pH 7) and filtered rapidly, and the solid was added at once to stirred dilute phosphate buffer (pH 7) (500 c.c.) at room temperature. N-Sodium hydroxide was added continuously to maintain the pH at 7 (2 equiv. during ~2 hr.). After removal of a small amount of insoluble matter the solution was diluted to 1 l. It contained 0·1 mole $l.^{-1}$ of chloride ion and 0·2 mole $l.^{-1}$ of hydrolysable chlorine, and, on acid hydrolysis, produced 0·1 mole $l.^{-1}$ of cyanuric acid. The solution changed little during 2—3 weeks, but eventually there was a sudden precipitation of cyanuric acid.

From a similar preparation in more concentrated solution the product was precipitated by addition of salt, filtered off, and dried *in vacuo* at room temperature over phosphorus pentoxide. The white solid contained 22·5% of sodium chloride and 5·3% of mixed sodium mono- and di-hydrogen phosphate (Found: C, 12·6; H, 1·5; N, 14·3; Hydrolysable Cl, 24·0. Calc. for 64% $C_3Cl_2N_3NaO$: C, 12·3; N, 14·3; Cl, 24·2; including 8% of water and the phosphates, H, 1·4%). The hydroxyl group confers fairly strong acid properties (pK <3). An unbuffered solution, when evaporated *in vacuo* at room temperature, decomposed suddenly with evolution of hydrogen chloride.

2-*Chloro*-4,6-*dihydroxy*-1,3,5-*triazine* (*Na salt*). Cyanuric chloride (technical, fine powder; 0·1 mole) was added in portions to a stirred, cooled solution of sodium hydroxide (0·5 mole) in water (500 c.c.) at <25°. When nearly all had dissolved the solution was still alkaline to Titan Yellow paper (pH >12). Further sodium hydroxide (0·3 mole) was added, followed by cyanuric chloride (0·1 mole), and so on until 0·5 mole of cyanuric chloride and 1·7 mole of sodium hydroxide had been added. Finally, 0·3 mole of sodium hydroxide was added. The solution was filtered and set aside at room temperature overnight. It was then faintly alkaline to Titan Yellow paper. A sample tested by the pyridine–sodium hydroxide reagent (see below) showed the presence of only about 0·01 mol. of dichlorotriazine. The solution was adjusted with concentrated hydrochloric acid to pH 8 (~0·5 mole required), the product being precipitated as *monosodium salt.* After collection, it was recrystallised from water (250 c.c.) and dried *in vacuo* at room temperature over potassium hydroxide (Found: C, 17·5; H, 2·5; N, 20·4; Cl, 17·2; Sulphated ash, 34·0; loss *in vacuo* at 100°, 17·3. $C_3HClN_3NaO_2,2H_2O$ requires C, 17·5; H, 2·4; N, 20·4; Cl, 17·3; Sulphated ash, 34·5; H_2O, 17·5%). The anhydrous salt was very hygroscopic. The compound titrated as a salt of a dibasic acid (pK 3·2 and 11·1).

(*d*) In much of the kinetic work an empirical colorimetric method, due to Dr. R. Sause,[11] was used to follow the changes in concentration of compounds containing the dichlorotriazinyl group. Such compounds, in a solution of pyridine (1160 c.c.) and sodium hydroxide (9·4 g.) in water (840 c.c.), produce a yellow colour which develops to maximum intensity and then slowly fades. The time, and temperature, of maximum development must first be determined for each compound. A solution of the dichlorotriazinylamine (0·1 g.) in water (1 l.) was prepared. A 100 c.c. graduated flask containing 85 c.c. of the reagent was allowed to reach equilibrium in a thermostat-bath at 25°. A solution (2 c.c.) of the compound was added, the volume was made up to 100 c.c. with distilled water, and the whole rapidly mixed. At intervals of a few minutes for a fast reaction, or several hours for a slow one, the absorption density of the mixture was measured in a spectrophotometer (*e.g.*, Unicam S.P. 600) at the wavelength of maximum absorption (~450 mμ). If the time of maximum development was inconvenient it was altered by development at a lower or higher temperature. When the wavelength, time, and temperature of maximum absorption were known for each compound examined, the relation of maximum density to concentration was checked by similar tests with 1, 2, 3, 4, and 5 c.c. of the sample solution. Beer's law was obeyed in every case. The reaction was not given by monochloromonohydroxytriazinylamines, or, generally, by monochlorodiarylaminotriazines.

In the remainder of the kinetic work, the reaction was followed either by titration of the chloride ion produced with silver nitrate, after acidification of a sample, the simplified potentiometric method with a " bottled end-point "[12] being used, by acid–alkali titration, or by ultraviolet spectrophotometry.

RESULTS

Hydrolysis of Cyanuric Chloride.—This reaction was followed in the first place by adding a solution of 1·85 g. of it in acetone (12 c.c.) to 0·1N-nitric acid (100 c.c.) with stirring and titrating the mixture continuously with silver nitrate, the titre being noted as a function of

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[11] R. Sause, Imperial Chemical Industries Limited, Dyestuffs Division, Dyehouse Department, personal communication.

[12] Goodall and Mellor, *Analyt. Chim. Acta*, 1952, **6**, 373.

time, at 0·5°, 10°, and 20°. The graphs of titre against time were sigmoid, as would be expected from the reaction sequence $C_3N_3Cl_3 \longrightarrow C_3N_3Cl_2{\cdot}OH \longrightarrow C_3N_3Cl(OH)_2 \longrightarrow C_3N_3(OH)_3$.

In the next series, only the first step in this sequence was measured. A suspension was sampled at intervals through a filter and the total of cyanuric chloride in solution plus its hydrolysis products was determined by complete hydrolysis of the sample. A large excess (3 g. or 5 g.) of cyanuric chloride was dissolved in acetone (14, 35, 70, 105, or 140 c.c.) and added quickly to the aqueous solution (700 c.c.) (water or 0·001N- or 0·1N-nitric acid) which was vigorously stirred in a 1-l. Dewar flask fitted with a thermometer and a sampling tube with a sintered-glass filter tip. Samples (at least 4) were withdrawn at intervals of about 2 min. 50 c.c. of each sample were acidified if necessary, hydrolysed completely in a boiling-water bath for 2 hr., and titrated with silver nitrate. For each ratio acetone : water, experiments were carried out at a number of temperatures in the range 0—25°.

In all cases the graph of titre against time had a finite intercept at zero time, which could be identified with the solubility of cyanuric chloride in the acetone–water mixture, and in all cases the graphs were linear, indicating a constant rate of hydrolysis, as would be expected if the solution remained saturated throughout. The rate constant of the hydrolysis was then given by the slope divided by the intercept. The experimental conditions had been chosen to ensure as far as possible that the solution remained close to saturation at least for the short time during which samples were taken. The amount of cyanuric chloride in suspension was large compared with the amount hydrolysed during the experiment. Variation in the amount (3 g. or 5 g.) gave results falling on the same curve. The dispersion produced was finely divided, with a resultant large solid-surface area and the agitation was vigorous. Moreover, even in the much faster hydrolyses in buffer solutions (see below), which were followed by the same method, the graphs of titre against time were still linear, which would hardly be the case if rate of solution had seriously limited the slower hydrolyses. The method used, however, inevitably approached the solubility equilibrium from one side only, that of supersaturation. Hydrolysis prevented an approach from the other side. It is possible, therefore, that the intercepts may slightly overestimate the solubility.

For each acetone : water ratio the solubility results were plotted in the form log *s* against $1/T$. They showed no significant variation between the three aqueous media. Up to 1 : 10 v/v acetone–water these graphs were linear. At 1·5 : 10 and 1 : 5 v/v acetone–water, however, the graphs appeared to consist of two intersecting lines; this has not yet been explained, but may be connected with the extent of initial supersaturation.

From the graphs, the solubilities at 5° intervals from 0° to 25° were read. These are plotted against the volume of acetone per 100 c.c. of water in Fig. 1. These graphs are again linear up to 10% acetone. Their intercepts give the solubility of cyanuric chloride in water (or dilute acid) at each temperature, as shown in Table 1.

TABLE 1.

Solubility of cyanuric chloride in water.

Temp.	0°	5°	10°	15°	20°	25°
10^{-3} mole l.$^{-1}$	1·73	1·9	2·05	2·2	2·4	2·65
g./100 c.c.	0·032	0·035	0·038	0·041	0·044	0·049

The slope of the graph, log *s* against $1/T$, corresponds to a heat of solution of 2·6 kcal. mole^{-1}.

In the graphs of log (first-order rate constant) against $1/T$, the points for 2, 5, and 10 c.c. of acetone per 100 c.c. of water, where the aqueous medium was water or 0·001-N- or 0·1N-nitric acid, all fell close to one line. A fit by the method of least squares gave $\log k = 12{,}485 - (3{\cdot}434 \times 10^{-3}/T)$ (see Table 2) corresponding to an activation energy of 15·7 kcal. mole^{-1}. These results show the absence of acid catalysis up to 0·1N-mineral acid.

TABLE 2.

Hydrolysis of cyanuric chloride in water.

Temp.	0°	5°	10°	15°	20°	25°
k (hr.$^{-1}$)	0·825	1·39	2·27	3·70	5·91	9·27

By the same method the rate constants in buffer solutions at 5° were: pH 6·0 (phosphate) 2·4. pH 7·0 (phosphate) 3·95, pH 9·0 (borate) 11·1 hr.$^{-1}$. At higher pH the hydrolysis was very fast. The results quoted may represent reaction with buffer anions rather than with hydroxyl ions since the rate does not increase, in this region, as rapidly as the hydroxyl-ion concentration.

In phthalate buffers, of pH 4·0, at two concentrations, the rate constants were 4·52 (0·01 mole l.$^{-1}$) and 16·8 (0·05 mole l.$^{-1}$) at 7°. These points, together with the water rate, correspond fairly closely to the line $k = 1{\cdot}7 + 300[\text{Phthalate}]$. A single result in an acetate buffer corresponded, if a similar linear relation is assumed, to $k = 1{\cdot}7 + 860[\text{Acetate}]$, in hr.$^{-1}$, at 7°. In 0·1N-acetic acid the rate was practically the same as in 0·1N-nitric acid or in water. The rates in the acetate and the phthalate buffers are greater than those in the phosphate buffers of higher pH.

The first product of the hydrolysis of cyanuric chloride, $C_3N_3Cl_2\cdot OH$, exists in neutral or alkaline solution as the anion $C_3N_3Cl_2\cdot O^-$. In neutral solution its hydrolysis was slow. Alkaline hydrolysis was followed by the pyridine colour reaction. A typical experiment is recorded in Table 3.

TABLE 3.

Alkaline hydrolysis of dichlorohydroxytriazine at 25°.

0·002M-Dichlorohydroxytriazine; 0·098M-sodium hydroxide.

2 c.c. samples were measured by the pyridine reaction in a 0·5 cm. cell.

Time		Absorption density	log 10*D*	
Min.	Sec.	(λ 444 mμ)	Obs.	Calc.
2	5	0·404	0·606	0·613
10	54	0·354	0·549	0·549
25	23	0·277	0·443	0·443
45	18	0·199	0·299	0·302
65	45	0·144	0·158	0·156
85	30	0·102	0·009	0·013
105	48	0·074	$\bar{1}$·869	$\bar{1}$·868

Slope −0·431/hr. $k = 0{\cdot}99$ hr.$^{-1}$.

In dilute sodium hydroxide solution the results were represented by k (hr.$^{-1}$) = 10·5[OH$^-$] (mole l.$^{-1}$) at 25° and ionic strength of 0·15 mole l.$^{-1}$. There was a small increase with increasing ionic strength. In alkaline buffer solutions the results, compared with those calculated from this equation, were: pH 11·19 (carbonate) $1{\cdot}8 \times 10^{-2}$ (calc., $1{\cdot}6 \times 10^{-2}$), pH 9·22 (borax) $3{\cdot}2 \times 10^{-4}$ (calc., $1{\cdot}7 \times 10^{-4}$). The last may include a significant contribution from the "neutral" rate.

The hydrolysis of this compound in acid solution was difficult to follow. Neither the pyridine colour reaction nor chloride titration gave reproducible results. A dilute solution of the compound was adjusted to pH 5, so that the first stage of the hydrolysis $C_3N_3Cl_2\cdot ONa \longrightarrow C_3N_3Cl(OH)\cdot ONa + HCl$, would release one equivalent of acid, whilst the second stage $C_3N_3Cl(OH)\cdot ONa \longrightarrow C_3N_3(OH)_3 + NaCl$ would not. Standard hydrochloric acid sufficient to produce the desired acidity was added quickly, and, after an interval, an exactly equivalent amount of sodium hydroxide was added quickly to stop the reaction. The acidity produced was then determined by titration to pH 5 with 0·1N-sodium hydroxide. The experiment was repeated 4—5 times with times ranging from one to several minutes. The 4—5 points, for a given acidity, gave a fairly good first-order plot, and over a range of hydrogen-ion concentration from ~0·025 to 0·08M the rate constants were approximately given by k (hr.$^{-1}$) = 110[H$^+$] (mole l.$^{-1}$), though some points departed appreciably from this relation.

The second product of hydrolysis, $C_3N_3Cl(OH)_2$, a dibasic acid with pK ~3·2 and 11·1, was hydrolysed very slowly in neutral solution: little change was detected in one month at pH 7 and 25°. Its hydrolysis in alkaline solution was followed by ultraviolet spectrophotometry where the product, cyanuric acid, had much less intense absorption, or by chloride titration. At 25°, the rate constants in 0·1N- and 0·2N-sodium hydroxide were both 10^{-3} hr.$^{-1}$ and at pH 11 (carbonate) it was $3{\cdot}8 \times 10^{-4}$ hr.$^{-1}$. Hydrolysis in acid solution (0·01—0·18N-nitric acid) was followed by continuous chloride titration. The rate constants were close to the line given by k (hr.$^{-1}$) = 23·4[H$^+$] (mole l.$^{-1}$). Hydrolysis in acetate buffer solutions was followed by chloride titration of acidified samples. In equimolar acetic acid–sodium acetate solutions from 0·05 to 0·2 mole l.$^{-1}$, at a total ionic strength of 0·2M, the rate constants were given by k (hr.$^{-1}$) = 0·65[Acetate] (mole l.$^{-1}$) at 25°.

Hydrolysis of Arylaminodichlorotriazines.—This reaction was followed by addition of the compound to the appropriate aqueous acid, alkali, or buffer solution in a thermostat-bath, with sampling at intervals for analysis by the pyridine colour reaction or by titration with silver nitrate (after acidification). Since the product in alkaline or neutral solution was, wholly or in part, the monochloromonohydroxytriazine which was hydrolysed rapidly in dilute acid, the chloride titrations in these cases were timed with a stop-clock and extrapolated to zero time. In a constant medium, first-order rate constants were found. Preliminary results with sodium dichloro-*m*-sulphoanilinotriazine showed that hydrolysis in neutral solution was very slow, but that the rate increased in acid or alkali. The general pattern is shown in Fig. 2.

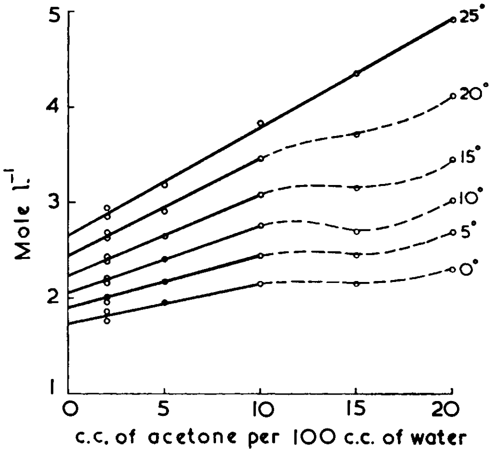

FIG. 1. Solubility of cyanuric chloride in aqueous acetone.

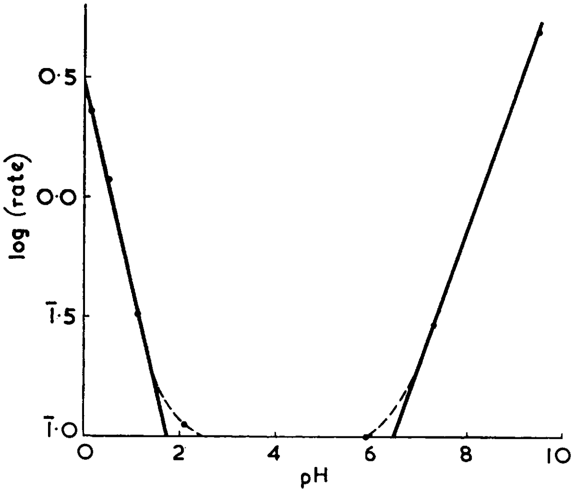

FIG. 2. Hydrolysis of 2,4-dichloro-6-*m*-sulphoanilino-1,3,5-triazine.

In acid solution both chlorine atoms were hydrolysed since the second stage $C_3N_3Cl_2 \cdot NHR \longrightarrow C_3N_3Cl(OH) \cdot NHR \longrightarrow C_3N_3(OH)_2 \cdot NHR$ was faster than the first (see below). The results, by either method of analysis, thus gave the rate constant of the first stage. With most of the compounds examined, the results accorded with the linear equation $k = k_0 + k_a[H]$, where [H] is the concentration of mineral acid.

A typical experiment is shown in Table 4, and the values of the constants of the linear equations for a number of the compounds are given in Table 5.

In most cases the fit of the points (Table 5) to the line gave a correlation coefficient $>0{\cdot}99$. A single result for the compound R = Me, X = m-C_6H_4 was close to that for the *p*-sulpho-compound.

2,4-Dichloro-6-(toluene-*p*-sulphonamido)-1,3,5-triazine gave $10^3k = 12$ in 0·001N-acid with

TABLE 4.

Acid hydrolysis of 2,4-dichloro-6-*p*-sulphoanilinotriazine at 25°.

Triazine 0·0048M; HNO_3 0·3M.

100 c.c. samples were titrated with 0·1N-$AgNO_3$.

Time				log (Total − *x*)	
Hr.	Min.	Titre (*x*)	Total − *x*	Obs.	Calc.
1	55	0·16	9·48	0·977	0·979
3	42	0·33	9·31	0·969	0·970
20	0	1·59	8·05	0·906	0·906
27	0	2·10	7·54	0·877	0·877
44	0	3·25	6·39	0·806	0·809
68	0	4·55	5·09	0·707	0·706

Slope = $-3·94 \times 10^{-3}$ hr. $k = 9·07 \times 10^{-3}$ hr.$^{-1}$.

TABLE 5.

Acid hydrolysis of 2,4-dichloro-6-sulphoarylamino-1,3,5-triazines, $C_3N_3Cl_2{\cdot}NR{\cdot}X{\cdot}SO_3H$. at 25°.

R	H	H	H	Me	H	H
X	*m*-C_6H_4	*p*-C_6H_4	*o*-C_6H_4	*p*-C_6H_4	1,4-$C_{10}H_6$	1,8-$C_{10}H_6$
10^3k_0 (hr.$^{-1}$)	1	1	1·5	0·35	2	3
10^3k_a (l. mole^{-1} hr.$^{-1}$)	25	27	35	20	29	64

irregular results above 0·1N-acid. If the linear relation is assumed in this case, 10^3k_a would be $\sim 4 \times 10^3$ l. mole^{-1} hr.$^{-1}$ at 25°.

2,4-Dichloro-6-(*N*-*p*-sulphophenyltoluene-*p*-sulphonamido)-1,3,5-triazine gave a nearly constant value of $10^3k = \sim 40$ hr.$^{-1}$ from 0·01N- to 0·4N-acid, with a slight fall at the higher acidity.

The second step in the acid hydrolysis was followed by measurements on only one intermediate arylaminochlorohydroxytriazine (the *p*-sulphoanilino-compound. From 0·01N- to 0·04N-nitric acid, k (hr.$^{-1}$) = $64[H^+]$, a value >2000 times that for the arylaminodichlorotriazine.

In " neutral " solution (pH 3—7) the rates of the two steps were comparable. Chloride titration, therefore, did not give a simple measure of either, but the pyridine colour reaction measured the first. Measurements of the very slow hydrolysis in some buffer solutions in this pH region gave results of the same order as the values of k_0 in Table 5, suggesting that in most cases the minimum value is $0·5—1 \times 10^{-3}$, but in phosphate buffers of pH 7 the values were sometimes 2—3 times as great. In acetate (pH 4·7) or phthalate (pH 4·0) buffers the rates were much faster. With dichloro-*m*-sulphoanilinotriazine, for example, the measured first-order rate constant was given by $10^3k = 1 + 100$[Acetate] and $1 + 20$[Phthalate] at 25°. The active species were the carboxylate ions; the carboxylic acids alone had no effect.

The " neutral " rate of the second step, measured with 2-chloro-4-hydroxy-6-*m*-sulphoanilinotriazine was $\sim 2 \times 10^{-4}$ hr.$^{-1}$. In *NN*-diethylmetanilate buffers, the rate constant at pH 6, where 20% of the hydroxyl group was undissociated, was 3×10^{-4} hr.$^{-1}$ and at pH 5 (70% undissociated) it was $9·5 \times 10^{-4}$ hr.$^{-1}$. In alkaline solution (pH >8) the first step of the hydrolysis was fairly fast and the second step very slow. Either chloride titration or the pyridine colour reaction could thus be used to follow the first step.

The arylaminodichlorotriazines were weak acids, dissociating according to the equation $C_3N_3Cl_2{\cdot}NHR \rightleftharpoons C_3N_3Cl_2{\cdot}\overset{-}{N}R + H^+$. Those which were insoluble in water (R = Ph, *p*-$Cl{\cdot}C_6H_4$, *p*-$NO_2{\cdot}C_6H_4$) dissolved readily in dilute sodium hydroxide solution. Those which were soluble in water could be titrated (rapidly) with sodium hydroxide. Approximate p*K* values so determined are shown in Table 6.

TABLE 6.

Dissociation constants of dichlorosulphoarylaminotriazines at 25°.

Aryl	*o*-C_6H_4	*m*-C_6H_4	*p*-C_6H_4	1,4-$C_{10}H_6$	1,8-$C_{10}H_6$
p*K*	10·7 (10·3 at μ 0·5)	10·6 (10·4 at μ 0·5)	10·5	9·4 (9·06 at μ 1·0)	>12

In dilute sodium hydroxide solution (usually 0·1—0·5N), at a constant ionic strength of 0·5, the compounds gave first-order rate constants. A representative example is shown in Table 7.

TABLE 7.

Alkaline hydrolysis of anilinodichlorotriazine at 25°.

Triazine 0·06 g.l.$^{-1}$; NaOH 0·1M; NaCl 0·4M.

5 c.c. samples were measured by the pyridine reaction.

Time (min.)	10	20	30	40	50	60	70	80
D (λ 452 mμ)	0·681	0·516	0·389	0·289	0·218	0·161	0·117	0·085
log 10*D*: obs.	0·833	0·713	0·590	0·461	0·339	0·207	0·068	$\bar{1}$·929
calc.	0·840	0·713	0·585	0·457	0·327	0·200	0·070	$\bar{1}$·942

Slope = −0·780/hr. k = 1·80 hr.$^{-1}$.

The rate constants increased with increasing hydroxide-ion concentration in accordance with the linear equation $k = k' + k''[OH^-]$. A typical example is shown in Fig. 3. The values of the constants are shown in Table 8.

TABLE 8.

Hydrolysis of arylaminodichlorotriazines, $C_3N_3Cl_2{\cdot}NHR$, in sodium hydroxide solution at 25°

R	k' (hr.$^{-1}$)	k'' (l. mole^{-1} hr.$^{-1}$)	R	k' (hr.$^{-1}$)	k'' (l. mole^{-1} hr.$^{-1}$)
Ph	1·74	0·62	m-$HO_3S{\cdot}C_6H_4$ ...	0·66	0·71
p-C_6H_4Cl	0·98	0·65	p-$HO_3S{\cdot}C_6H_4$	0·60	0·98
p-$NO_2{\cdot}C_6H_4$	0·21	3·2	4,1-$HO_3S{\cdot}C_{10}H_6$ ...	0·06	0·71
o-$HO_3S{\cdot}C_6H_4$	0·85	0·19	8,1-$HO_3S{\cdot}C_{10}H_6$ ...	2·2 *	0·0 *

* At 0°.

Owing to the feeble acidity of the NH group in the last compound of Table 8, the results in more dilute sodium hydroxide solution obeyed a different relationship (see p. 4143). From 0·01N to 0·1N-alkali, they were given by $1/k = 0{\cdot}0184 + 0{\cdot}002[OH^-]$ at 25° (Fig. 4) or $1/k = 0{\cdot}32 + 0{\cdot}022[OH^-]$ at 0°.

Compounds $C_3N_3Cl_2{\cdot}NMeR$, which could not dissociate, were hydrolysed rapidly. The rate was of the first order in each reactant. In 0·0025—0·05N-sodium hydroxide the second-order rate constants (l. mole^{-1} hr.$^{-1}$) were: R = *m*-sulphophenyl 260 (15°), 750 (25°); R = *p*-sulphophenyl 75 (0°), 760 (25°).

Dichlorotoluene-*p*-sulphonamidotriazine, which at pH >7 is completely in the dissociated form $C_3N_3Cl_2{\cdot}\overset{-}{N}{\cdot}SO_2{\cdot}C_6H_4Me$, behaved like the NMeR compounds. The constants (l. mole^{-1} hr.$^{-1}$) were ~17 (0°) and 130 (25°). With this, and the NMeR, compounds there was a small increase in the rate constant with increasing alkali concentration which did not appear to be wholly due to the increase in ionic strength.

The compound $C_3N_3Cl_2{\cdot}N(SO_2{\cdot}C_6H_4Me){\cdot}C_6H_4{\cdot}SO_3^-$, which also could not dissociate, was hydrolysed very rapidly even in 0·005N-sodium hydroxide at 25°. A very appropriate rate constant was $2{\cdot}5 \times 10^4$ l. mole^{-1} hr.$^{-1}$ (25°).

In alkaline buffer solutions, in the region of the p*K* values, the compounds $C_3N_3Cl_2{\cdot}NHR{\cdot}SO_3^-$ gave first-order constants which were approximately in accord with the equation $1/k = a + bH$, where $H = 10^{-pH}$. A curve for one of them is shown in Fig. 5. The constants, at an ionic strength of 0·5, are given in Table 9.

TABLE 9.

Hydrolysis of dichlorosulphoarylaminotriazines, $C_3N_3Cl_2{\cdot}NHR{\cdot}SO_3^-$, in alkaline buffer solutions at 25° ($1/k = a + b.10^{-pH}$).

R	o-C_6H_4	m-C_6H_4	p-C_6H_4
a	1·12 (1·0)	1·6	1·62
$10^{-10}\,b$	1·1 (2·0)	1·1	0·85

In all these cases the first-order constant increased to some extent, at constant pH and ionic strength, with increasing concentration of buffer ion. The results were mainly obtained with

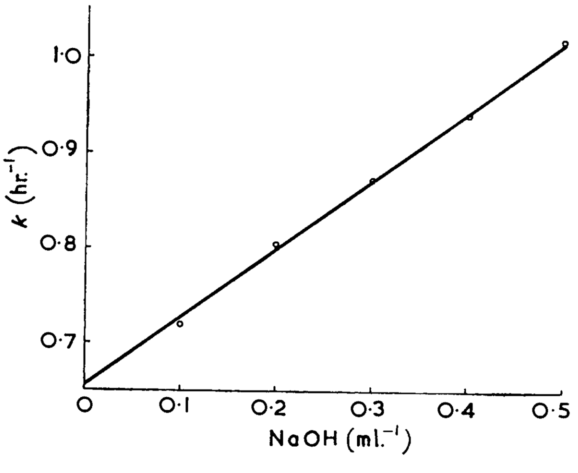

FIG. 3. Alkaline hydrolysis of 2,4-dichloro-6-*p*-sulphoanilino-1,3,5-triazine at 25°.

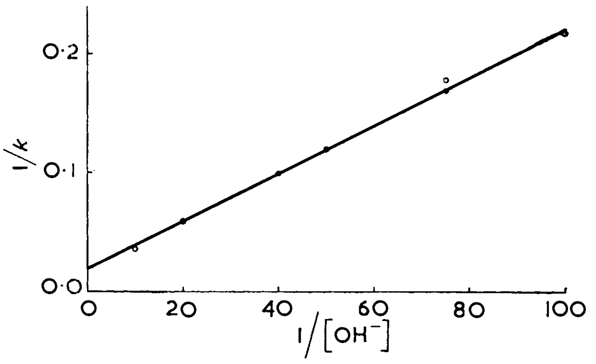

FIG. 4. Alkaline hydrolysis of 2,4-dichloro-6-(8-sulpho-1-naphthylamino)-1,3,5-triazine at 25°.

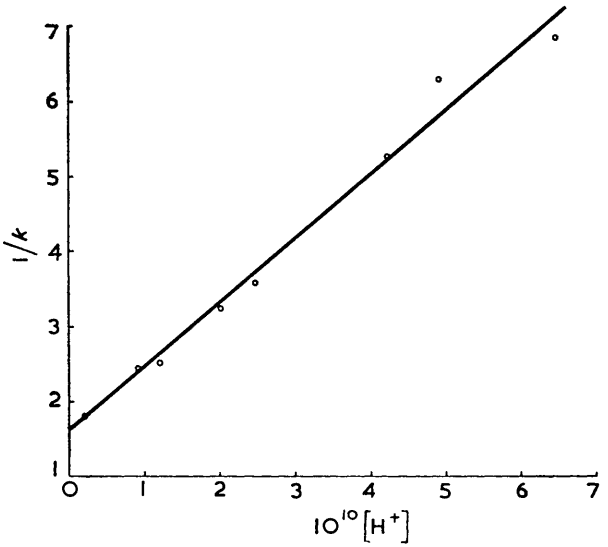

FIG. 5. Hydrolysis of 2,4-dichloro-6-*m*-sulphoanilino-1,3,5-triazine in alkaline buffers at 25°.

0·05M-carbonate buffers adjusted with hydrochloric acid. The results in parentheses refer to buffers containing initially 0·01M-sodium carbonate.

Dichloro-(8-sulpho-1-naphthylamino)triazine behaved in alkaline buffer solutions like the $C_3N_3Cl_2$·NMeR compounds. At pH 10—11 the measured first-order constants (hr.$^{-1}$) were close to the line log $k = \bar{1}$·97 + 0·96 (pH − 11), at 25°. The corresponding second-order constants, $k_2 = k/[OH^-]$, calculated by taking pH = −log $[H^+]f_H$ and assuming $f_H = f_{OH}$, ranged from 650 to 770 l. mole^{-1} hr.$^{-1}$. Similar results for the NMeR compounds were: R = *p*-sulphophenyl, log k = 0·22 + (pH − 11) (25°) shown in Fig. 6, from pH 8·6 to 11·3, giving values of k_2 ranging from 1000 to 1500 l. mole^{-1} hr.$^{-1}$ (the line corresponds to k_2 = 1300); R = *m*-sulphophenyl, k_2 of 650 and 700 l. mole^{-1} hr.$^{-1}$ in borate buffers (μ <0·1) and 1350 and 1500 l. mole^{-1} hr.$^{-1}$ in phosphate and carbonate buffer (μ = 0·5), at 25°.

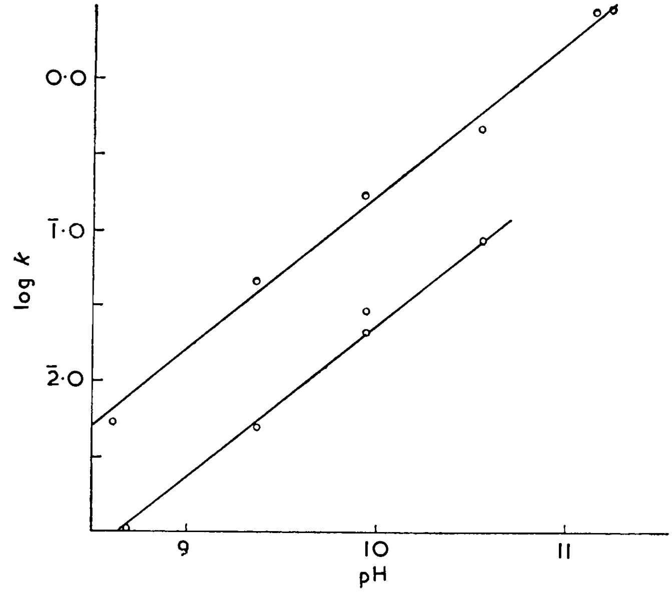

FIG. 6. Hydrolysis of (a) 2,4-dichloro-6-(*N*-methyl-*m*-sulphoanilino)-1,3,5-triazine and (b) 2,4-dichloro-6-toluene-*p*-sulphonamido-1,3,5-triazine in alkaline buffers at 25°.

Dichloro(toluene-*p*-sulphonamido)triazine, at pH 8·6—10·6 (Fig. 6) gave log k = 0·36 + (pH − 12), k_2 from 160—200 l. mole^{-1} hr.$^{-1}$, at 25°.

The hydrolysis of $C_3N_3Cl_2$·N(C_6H_4·SO_3^--*p*)·SO_2·C_6H_4Me was still fast at pH 9 and 10. Again, Δlog k was approximately equal to ΔpH, and values of k_2 were 5·8 and 4·5 × 10^4 l. mole^{-1} hr.$^{-1}$ at 25°.

Hydrolysis of 4,6-*Diarylamino*-2-*chloro*-1,3,5-*triazines*.—This reaction was much slower than that of the corresponding dichlorotriazines. In acid solution 2-anilino-4-chloro-6-*m*-sulphoanilino-1,3,5-triazine showed acid catalysis. First-order constants at 40° were 0·7 and 2·8 × 10^{-3} hr.$^{-1}$ in 0·001N- and 0·01N-nitric acid, respectively. In neutral solution there was little change in 3 days at 40°.

2-Chlorodi-(*N*-*p*-sulphophenyltoluene-*p*-sulphonamido)triazine, on the other hand, did not show acid catalysis, but was hydrolysed in neutral solution at a rate comparable with those of the arylaminodichlorotriazines. Rate constants, at 25°, were 3·5 × 10^{-4} hr.$^{-1}$ in 0·1N-acid and 5·4 × 10^{-4} hr.$^{-1}$ at pH 7.

In alkaline solution, dissociation of the NHR groups was not detected in the compounds $C_3N_3Cl(NHR)_2$. These, as well as those in which the hydrogen was replaced by methyl or toluenesulphonyl, were hydrolysed at rates proportional to the concentrations of the compound and of hydroxyl ion. C_3N_3Cl(NHPh)NH·SO_2·C_6H_4Me, where the NH·SO_2 group was fully dissociated above pH 8, behaved in the same way. The results are shown in Table 10.

The first of these compounds in Table 10, 2-anilino-4-chloro-6-*m*-sulphoanilino-1,3,5-triazine, gave, from 20° to 80°, in the same units, log k = 14·24 − (4·32 × $10^3/T$), corresponding to an activation energy of 19·8 kcal./mole.

TABLE 10.

Alkaline hydrolysis of diaminochlorotriazines, $C_3N_3Cl(NR^1R^2)NR^3R^4$, at 25°.

R^1	H	Me	H	p-$C_6H_4{\cdot}SO_3^-$
R^2	Ph	p-$C_6H_4{\cdot}SO_3^-$	Ph	$SO_2{\cdot}C_6H_4Me$
R^3	H	Me	H	p-$C_6H_4{\cdot}SO_3^-$
R^4	m-$C_6H_4{\cdot}SO_3^-$	p-$C_6H_4{\cdot}SO_3^-$	$SO_2{\cdot}C_6H_4Me$	$SO_2{\cdot}C_6H_4Me$
k (l. mole^{-1} hr.$^{-1}$)	0·5	0·4	0·077	420

DISCUSSION

The hydrolysis of cyanuric chloride, $C_3N_3Cl_3$, of dichlorohydroxy-1,3,5-triazine, $C_3N_3Cl_2{\cdot}OH$, and of arylaminodichloro-1,3,5-triazines, occurs in steps, each involving the replacement of one chlorine atom, with relative rates depending on the acidity or alkalinity of the medium. In all these cases, and in those of the derived chlorohydroxy-compounds, a slow hydrolysis in the region of neutrality increases with either increasing alkalinity or increasing acidity, or with each.

The suggested mechanism for alkaline hydrolysis, for neutral hydrolysis, and for buffer-ion catalysis is, like the reaction with other nucleophilic reagents, a direct attack by a base (hydroxide ion, water, or buffer anion) on an electron-deficient carbon atom with replacement of chlorine, a process kinetically of the first order in each reactant.

The first step in the alkaline hydrolysis of cyanuric chloride has not been investigated at pH >9. The rate increases rapidly with rising pH. The second step, measured with the isolated dichlorohydroxytriazine, present in solution as the anion $C_3N_3Cl_2{\cdot}O^-$, showed the expected first-order dependence on the compound and on hydroxide ion. The third step, measured with the isolated chlorodihydroxytriazine, was more complex since the ionisation of the second hydroxyl group occurs from pH 9 upwards, leading to the less reactive form $C_3N_3ClO_2^-$. There are then two simultaneous hydrolyses:

$$C_3H_3Cl(OH){\cdot}O^- + OH^- \longrightarrow C_3N_3(OH)_2{\cdot}O^- + Cl^-$$

$$C_3N_3Cl(O^-)_2 + OH^- \longrightarrow C_3N_3(OH)_2O^- + Cl^-$$

of which the second will be much the slower. In the change from 0·1N- to 0·2N-sodium hydroxide the fraction of the chlorotriazine present as the monoanion is very nearly halved, whilst the hydroxide ion concentration is doubled. The rate is therefore nearly the same, as was found. Even at pH 11, where the fraction present as the monoanion is ~0·5 and the hydroxide ion concentration is only 10^{-3}, the product of the two is still as high as half its value at pH 13, so that the rate in 0·1N-sodium carbonate is about half that in 0·1N-sodium hydroxide. From these results, if we ignore the reaction of the dianion, the rate constant for the monoanion $C_3H_3Cl(OH){\cdot}O^-$ can be estimated to be ~0·9 l. mole^{-1} hr.$^{-1}$ at 25°, compared with 10 for the monoanion $C_3N_3Cl_2{\cdot}O^-$.

A similar case occurs in the hydrolysis of arylaminodichlorotriazines, $C_3N_3Cl_2{\cdot}NRR'$, which have been studied in greater detail. Where neither R nor R′ is a hydrogen atom capable of dissociation, the first step of the hydrolysis is again kinetically of the first order in each reactant, and the reaction is fast. When R = H, the compounds are weak acids dissociating at pH 8 upwards, and the reaction is relatively slow. The postulated mechanism then is:

$$C_3N_3Cl_2{\cdot}NHR \rightleftharpoons C_3N_3Cl_2{\cdot}NR^- + H^+ \qquad (1)$$

$$C_3N_3Cl_2{\cdot}NHR + OH^- \longrightarrow C_3N_3Cl(OH){\cdot}NHR + Cl^- \qquad (2)$$

$$C_3N_3Cl(OH){\cdot}NHR \rightleftharpoons C_3N_3Cl(O^-){\cdot}NHR + H^+ \qquad (2a)$$

$$C_3N_3Cl_2{\cdot}NR^- + OH^- \longrightarrow C_3N_3Cl(O^-){\cdot}NHR + Cl^- \qquad (3)$$

The dissociation constant for step (2a) is 10^{-5}—10^{-6}, so that in alkaline solution the product is fully dissociated and the total reaction consumes two equivalents of alkali. Let K be the dissociation constant of step (1) and k_2 and k_3 be the (second-order) rate constants of steps (2) and (3), respectively. Let the initial concentration of dichlorotriazine be a and the concentration of chloride ion at a given time be x. Then, in a constant medium, $\mathrm{d}x/\mathrm{d}t = k[a - x]$, where k is the measured first-order constant. The dissociation constant of step (1) is given by:

$$K = [\mathrm{H}^+][\mathrm{A}^-]f_{\mathrm{H}}f_{\mathrm{A}}/[\mathrm{HA}]f_{\mathrm{HA}}, \qquad (4)$$

where brackets denote concentrations and f activity coefficients. Let $10^{-\mathrm{pH}} = H$. pH scales are chosen so that in suitably simple and dilute solutions $H = [\mathrm{H}^+]f_{\pm}$, where $f_{\pm}$ is the mean activity coefficient of a uni-univalent strong electrolyte and is arbitrarily equated to f_{H}. If this assumption is extended to the working solutions, the value of K given by titration is Kf, where $f = f_{\mathrm{HA}}/f_{\mathrm{A}}$, and the proportions of the undissociated and the dissociated form present are given by $\mathrm{H}/[\mathrm{H} + Kf]$ and $Kf/[\mathrm{H} + Kf]$, respectively. The total rate of hydrolysis is thus given by:

$$\mathrm{d}x/\mathrm{d}t = k_2[a - x]\mathrm{H}[\mathrm{OH}^-]/[\mathrm{H} + Kf] + k_3[a - x]Kf[\mathrm{OH}^-]/[\mathrm{H} + Kf]; \qquad (5)$$

and, from equations (4) and (5), the measured first-order constant is

$$k = \{k_2K_{\mathrm{W}}'f_{\mathrm{H}} + k_3Kf[\mathrm{OH}^-]\}/[\mathrm{H} + Kf], \qquad (6)$$

where K_{W}' is the ion-product of water ($[\mathrm{H}^+][\mathrm{OH}^-]$).

Equation (6) can be simplified in three distinct cases:

(i) When $\mathrm{H} \ll \mathrm{K}$,

$$k = k_2K_{\mathrm{W}}'f_{\mathrm{H}}/Kf + k_3[\mathrm{OH}^-]. \qquad (7)$$

With pK values between 9 and 11, this condition is satisfied in dilute sodium hydroxide solution, where k was linear in $[\mathrm{OH}^-]$ with a slope giving k_3 directly. k_2 could be calculated from the intercept if Kf was known by titration at the same ionic strength. For this purpose $K_{\mathrm{W}}'f_{\mathrm{H}}$ was taken as $\sqrt{K_{\mathrm{W}}K_{\mathrm{W}}'}$, with the assumption that $f_{\mathrm{H}} = f_{\mathrm{OH}}$. Values of K_{W}' were taken at the appropriate ionic strength and temperature.[13]

(ii) When $\mathrm{H} \approx K$,

$$k[\mathrm{H} + Kf] = k_2K_{\mathrm{W}}'f_{\mathrm{H}} + k_3Kf[\mathrm{OH}^-]. \qquad (8)$$

If, in addition, $k_3 \ll k_2$, and $Kf[\mathrm{OH}^-]$ is comparable with K_{W}', as was the case in the pH region 9—11, the last term in equation (8) is negligible, and the equation simplifies to

$$1/k = Kf/k_2K_{\mathrm{W}}'f_{\mathrm{H}} + \mathrm{H}/k_2K'_{\mathrm{W}}f_{\mathrm{H}}. \qquad (9)$$

In this region $1/k$ was, approximately, linear in H. The intercept of equation (9) is the reciprocal of that of (7). Their product should thus be unity. Actual values are shown in Table 11. The value in parentheses refers to the more dilute carbonate buffers.

TABLE 11.

Comparison of intercepts (7) and (9) for dichlorosulphophenylaminotriazines, $C_3N_3Cl_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3^-$.

SO_3^-	*o*	*m*	*p*
Intercept product	0·96 (0·85)	1·00	1·00

Now, k_2 can be calculated from the slope, or, if Kf is known, from the intercept. Alternatively, Kf = intercept/slope. Values of Kf so calculated are compared with titration values in Table 12. Again the value in parentheses refers to the more dilute carbonate buffers. The divergences between the values in the other pairs are probably mainly due to the fact that measured rates include contributions from buffer-ion catalysis.

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[13] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," 3rd edn. Reinhold, New York, 1958.

It follows from Table 11 that nearly identical values of k_2 will be obtained from the intercepts of equations (7) and (9), whilst Table 12 shows that values from the slope of equation (9) will differ from these by a factor between 2 and 4. Values from the intercepts have been preferred since in dilute alkali (equation 7) there are, at least, no buffer ions.

TABLE 12.

Dissociation constants for dichlorosulphophenylaminotriazines, $C_3N_3Cl_2{\cdot}NHC_6H_4{\cdot}SO_3^-$, at 25°.

SO_3^-	*o*	*m*	*p*
p_{Kf}; Eqn. 9	10·0 (10·3)	9·8	9·7
p_{Kf}; expt.	10·3	10·4	10·2

For one compound, dichloro-(8-sulpho-1-naphthylamino)triazine, where, owing to hydrogen bonding between NH and SO_3^- in the *peri*-positions, the p*K* value was greater than 12, the conditions (ii) were satisfied in the more dilute sodium hydroxide solutions. In such a case

$$1/k = Kf/k_2K_W'f_H + 1/k_2[OH^-], \qquad (10)$$

and $1/k$ was linearly related to $1/[OH^-]$, which was directly known. The slope of this line then leads to k_2 directly.

(iii) When $K \leqslant H$,

$$kH = k_2K_W'f_H$$

or

$$\log k = \log k_2 + \log\,[K_W'f_H] + pH. \qquad (11)$$

Here, log *k* is linear in pH, with unit slope. This condition was not met with most of the compounds $C_3N_3Cl_2{\cdot}NHR$ until the pH was so low that neutral hydrolysis made a considerable contribution. With the 8-sulpho-1-naphthylamino-compound, however, it was met in a higher pH range. The condition, of course, corresponds to those in which dissociation (1), and consequently reaction (3), are negligible, or in which (1) is complete and (2) is negligible, and in which the alkaline hydrolysis is simply of the first order in the compound and in hydroxyl ion. Equation (11) thus described the behaviour, throughout the alkaline buffer range, of the compounds $C_3N_3Cl_2{\cdot}NRR'$, which could not dissociate, and also of compound $C_3N_3Cl_2{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4Me$ where dissociation (1) was complete. In these cases there was again evidence of some buffer-ion catalysis, so that agreement with equation (11) was only approximate. Values of the second-order constants calculated from hydrolysis in dilute alkali and mean values in alkaline buffer solutions are compared in Table 13.

The variation of the reactivity of the chlorine atoms with the constitution of the group NRR′ (where R may be H) or ^-NR is shown by the collected results in Table 14, which are all in the form of second-order rate constants and relate to the hydrolysis in alkaline solution of one chlorine atom only.

TABLE 13.

Rate constants (l. mole^{-1} hr.$^{-1}$) for alkaline hydrolysis of aminodichlorotriazines, $C_3N_3Cl_2{\cdot}NRR'$, at 25°.

R	H	Me	Me	$SO_2{\cdot}C_6H_4Me$	H
R′	$1,8\text{-}C_{10}H_6{\cdot}SO_3^-$	*m*-$C_6H_4{\cdot}SO_3^-$	*p*-$C_6H_4{\cdot}SO_3^-$	*p*-$C_6H_4{\cdot}SO_3^-$	$SO_2{\cdot}C_6H_4Me$
k_2 (hydroxide)	500	750	760	$2{\cdot}5 \times 10^4$	130
k_2 (buffers)	700	700,* 1250	1300	5×10^4	180

* More dilute buffers.

The results show the marked dependence of the reactivity of the chlorine atoms on the magnitude of the negative charge on the amino-nitrogen atom, which is conjugated

TABLE 14.

Alkaline hydrolysis of aminodichlorotriazines.

Amino-group	Parent amine pK_a	k (25°) (l. mole^{-1} hr.$^{-1}$)	Amino-group	Parent amine pK_a	k (25°) (l. mole^{-1} hr.$^{-1}$)
8,1-$HO_3S\cdot C_{10}H_6\cdot N^-$	5·03 *	V. small	8,1-$HO_3S\cdot C_{10}H_6\cdot NH$ ...	5·03	500
$Ph\cdot N^-$	4·62 *	0·62	*m*-$HO_3S\cdot C_6H_4\cdot NMe$	3·72	750
p-$C_6H_4Cl\cdot N^-$	3·81 *	0·65	*p*-$HO_3S\cdot C_6H_4\cdot NMe$	3·25	760
m-$HO_3S\cdot C_6H_4\cdot N^-$	3·74 †	0·71	*m*-$HO_3S\cdot C_6H_4\cdot NH$	3·74	2000
p-$HO_3S\cdot C_6H_4\cdot N^-$	3·23 ‡	0·98	*p*-$HO_3S\cdot C_6H_4\cdot NH$	3·23	2800
4,1-$HO_3S\cdot C_{10}H_6\cdot N^-$	2·81 *	0·71	4,1-$HO_3S\cdot C_{10}H_6\cdot NH$ ...	2·81	3500
o-$HO_3S\cdot C_6H_4\cdot N^-$	2·46 §	0·19	*o*-$HO_3S\cdot C_6H_4\cdot NH$	2·46	3200
p-$NO_2\cdot C_6H_4\cdot N^-$	1·0 *	3·2	*p*-$C_6H_4Me\cdot SO_2$ *p*-$HO_3S\cdot C_6H_4$ >N	—	25,000
p-$Me\cdot C_6H_4\cdot N^-$	V. low	130			

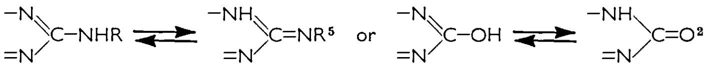
* Brown, McDavid, and Häflinger in Braude and Nachod's " Determinations of Organic Structures by Physical Methods," Academic Press, Inc., New York, 1955, chapter 14. † McCoy and Swinehart, *J. Amer. Chem. Soc.*, 1954, **76**, 4708. ‡ Maclaren and Swineheart, *ibid.*, 1951, **73**, 1822. § Diebel and Swinehart, *J. Phys. Chem.*, 1957, **61**, 333.

with the triazine ring. The first eight results, for compounds with, substantially, a unit charge, are sharply distinguished from the remainder. In the ninth compound, where the negative charge is diminished by the strongly electron-attracting toluene-*p*-sulphonyl group directly attached to the nitrogen, the reactivity is considerably increased, whilst the undissociated compounds are all more reactive, and again the large effect of a toluene-*p*-sulphonyl group is seen. Conversely, replacement of hydrogen on this nitrogen atom by the feebly electron-repelling methyl group reduces the reactivity of the chlorine atoms, but to a smaller extent.

Within each set, changes in the (substituted) aryl group have smaller effects, but in the same direction. Broadly, the reactivity increases with increase in the electron-attracting power of the group, as indicated, for example, by the pK_a value of the parent amine.

Similar effects are seen with the diaminochlorotriazines (Table 10).

Some authors have postulated tautomerism, *e.g.*,



to explain qualitative differences in the stability to hydrolysis of different chlorotriazines. On this view, the compounds $C_3N_3Cl_2\cdot NMeR$ and $C_3N_3Cl_2\cdot NR\cdot SO_2\cdot C_6H_4Me$ should be more stable than compounds $C_3N_3Cl_2\cdot NHR$. In fact, their alkaline hydrolysis is much faster, but if the comparison is made with the undissociated NHR compounds, the *N*-methyl compounds are hydrolysed somewhat more slowly and the *N*-toluenesulphonyl compounds much faster. The hypothesis, applied to dichlorohydroxytriazine, takes no account of the fact that this compound is completely ionised in neutral or alkaline solution. It is, of course, possible, both for compounds $C_3N_3Cl_2\cdot NR^-$ and for compounds $C_3N_3Cl_2\cdot O^-$, formally to place the negative charge of the ion on any of the three ring-nitrogen atoms instead of on the substituent nitrogen or oxygen atom, but the essential factor is the presence of an electron-donating substituent, of which the ionic groups NR^- and O^- are extreme examples. Other basic substituents, NHR or NRR′, exert their expected effects whether it is possible to write tautomeric forms or not.

The arylaminodichlorotriazines are all undissociated in neutral solution, and their hydrolytic rate constants (first step) do not vary much from 10^{-3} hr.$^{-1}$ (25°) except for $C_3N_3Cl_2\cdot N(SO\cdot C_6H_4Me)\cdot C_6H_4\cdot SO_3^-$ for which the value rises to 4×10^{-2} hr.$^{-1}$. On the other hand, the ion $C_3N_3Cl_2\cdot \bar{N}\cdot SO_2\cdot C_6H_4Me$, formed by dissociation, gave a value less than 10^{-3} hr.$^{-1}$. The effects of structure in neutral hydrolysis are thus similar to those in alkaline hydrolysis.

For neutral solutions the rate constants for the hydrolysis of ions $C_3N_3Cl_2{\cdot}O^-$ and $C_3N_3Cl(OH){\cdot}O^-$ have not been measured, but they are unlikely to exceed 10^{-4} hr.$^{-1}$, compared with nearly 10 hr.$^{-1}$ for cyanuric chloride at 25°.

Commencing with cyanuric chloride, replacement of one chlorine atom by NHR (R = aryl) reduces the rate of neutral hydrolysis (attack by H_2O) by a factor of about 10^4, and replacement by O^- reduces it by a factor probably rather higher. In alkaline hydrolysis (attack by OH^-) the relative rates are: $NHR \approx 10^2 \times O^-$; $O^- \approx 10 \times NR^-$. Replacement of a second chlorine by O^- or NHR causes further reductions in reactivity of similar magnitudes.

Buffer-ion catalysis has not been thoroughly investigated, but many of the results give evidence of its occurrence and in some cases a linear relation between the measured first-order rate constant and the buffer-ion concentration, of the form $k = k_o + k_b[B^-]$, has been observed. Few values of the constant k_b are available. Values for acetate ions are higher than those for phthalate ions, but both appear more effective than phosphate ($H_2PO_4^-$ or HPO_4^{2-}) or borate ions, though possibly not than carbonate ions. In short, the results do not suggest that k_b increases regularly with increasing base strength of the anion. Again, of course, replacement of chlorine in cyanuric chloride by basic (OH or NHR) groups markedly reduced the reactivity towards buffer anions.

The ready and complete hydrolysis of cyanuric chloride to cyanuric acid by cold aqueous sodium acetate is known.[14] It is thus surprising that refluxing cyanuric chloride with glacial acetic acid has been recommended [3] as a convenient preparation of cyanuric acid.

The acid-catalysed hydrolysis of the chlorotriazines generally accords with the equation $k = k_o + k_a[H^+]$, where k_o is the neutral rate constant. Cyanuric chloride itself did not show acid catalysis in up to 0·1N-acid, but this appeared as soon as one chlorine atom had been replaced by OH or NHR. The suggested mechanism of acid catalysis is the uptake of a proton by the triazine ring, followed by the hydrolysis, by water, of the protonated molecule. If the fraction protonated is small, this leads to the observed linear equation with $k_a = k_a'/K$, where k_a' is the rate constant for the hydrolysis of the protonated species and K is its dissociation constant. As, in alkaline medium, a substituent with a negative charge markedly decreased the reactivity, so, in acid medium, the uptake of a proton would be expected markedly to increase it. k_a' should thus always be high. The replacement of a chlorine atom in cyanuric chloride by a basic group would be expected to reduce both K and k_a'. The two effects have not been separated, but the former clearly predominates. The most striking feature of the results is the much more marked acid catalysis when one, or two, chlorine atoms are replaced by hydroxyl compared with that when the replacing group is NHR. For $C_3N_3Cl_2(OH)$, k_a is about 100, for $C_3N_3Cl(OH)_2$ 23, and for $C_3H_3Cl(OH){\cdot}NHR$ 64, whilst for $C_3N_3Cl_2{\cdot}NHR$ (or ·NMeR) it is 0·02—0·06. This difference may be due to tautomerism in the case of the hydroxyl groups, but not in the case of the amino-groups. Its absence in the latter case is illustrated by the small difference in the values of k_a for $C_3N_3Cl_2NH{\cdot}C_6H_4{\cdot}SO_3H$ and the corresponding NMe compound. In the corresponding *N*-(toluenesulphonyl) compound, the basicity of the molecule is so reduced (K increased) that acid catalysis disappears.

The acidity of the arylaminodichlorotriazines shows that the dichloro-1,3,5-triazinyl group is strongly electron-withdrawing, though not quite so strongly as the toluene-*p*-sulphonyl group. The approximate pK values for the compounds $X{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3^-$ (*m* or *p*) are 10—10·5 when X = dichlorotriazinyl, and 8 when X = toluene-*p*-sulphonyl.

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[14] Ullmann, " Encyklopädie der technischen Chemie," Urban and Schwarzenberg, München-Berlin, 3rd edn., 1954, Vol. V, p. 623.