XIX.—*Nitrogen Halogen Derivatives of the Sulphonamides.*

By Frederick Daniel Chattaway.

The study of nitrogen halogen derivatives, that is, of compounds containing halogen directly attached to nitrogen, has yielded many valuable scientific results. Perhaps the most notable members of this class of substances are the bromoamides, which, on heating with caustic alkalis yield primary amines, and the acylphenyl-chloro- and -bromo-amides, which, under the influence of hydrogen chloride or bromide, undergo an intramolecular rearrangement whereby the halogen enters into the phenyl nucleus. Both these classes of derivatives, however, so readily undergo isomeric change that they are not well adapted for a study of the behaviour of halogen when attached to nitrogen.

It seemed possible that a number of syntheses which have failed when tried with somewhat unstable nitrogen halogen derivatives might succeed if attempted with stable compounds not liable readily to undergo isomeric change. Such substances are found in the nitrogen halogen derivatives of the sulphonamides, and the present paper contains a description of a number of these compounds, the various reactions of which are being further investigated.

The sulphonamides are distinguished by the great readiness with which they form well-crystallised derivatives in which all the aminic hydrogen is replaced by halogen when acted upon by hypochlorous acid at the ordinary temperature, for example:

$$C_6H_5\cdot SO_2\cdot NH\cdot CH_3 + HOCl \rightleftarrows C_6H_5\cdot SO_2\cdot NH(CH_3)\!<\!\begin{matrix}OH\\Cl\end{matrix} \rightleftarrows C_6H_5\cdot SO_2\cdot N(CH_3)Cl + H_2O.$$

The sulphonchloroamides so produced exhibit great stability when compared with other chloroamides, for example, the reverse change only takes place very slowly even on boiling with a large excess of water. Those containing two chlorine atoms attached to the nitrogen melt without decomposition and can frequently be heated considerably above their melting points without undergoing any change; they explode when heated by a direct flame, the tetrachloroamides derived from the disulphonamides resembling nitrogen chloride itself in the violence with which they detonate. When similarly heated, the sulphonalkylchloroamides do not detonate, but decompose rapidly with the evolution of gas.

They all readily take part in those characteristic reactions which distinguish the nitrogen halogen from the carbon halogen linking, the halogen being in every case replaced by hydrogen and the sulphonamide regenerated; for example, they liberate chlorine when heated with hydrochloric acid, iodine chloride or iodine when treated with an equivalent quantity or an excess of hydriodic acid, and set free sulphur when treated with hydrogen sulphide; when heated with alcohol, they form ethyl hypochlorite, which at once breaks down into aldehyde and hydrogen chloride,

$$C_6H_5\cdot SO_2\cdot NCl_2 + 2C_2H_5\cdot OH = C_6H_5\cdot SO_2\cdot NH_2 + 2C_2H_5\cdot OCl,$$

and with hydrogen cyanide they form cyanogen chloride.

The sulphondichloroamides dissolve readily in warm aqueous solutions of the alkaline hydroxides, forming salts of the sulphonmonochloroamides, which separate as the liquids cool in large crystals containing water of crystallisation, for example:

$$C_6H_5\cdot SO_2\cdot NCl_2 + 2KOH = C_6H_5\cdot SO_2K{:}NCl + KOCl + H_2O.$$

These salts are very easily soluble in water and are comparatively stable in aqueous or alkaline solution; they are, however, slowly hydrolysed when boiled for some hours with aqueous alkalis, the original sulphonamide being regenerated. The water of crystallisation is lost when the crystals are heated to 100° or when they are kept in a vacuum over phosphoric oxide. The anhydrous salts are very stable; when heated, they do not melt, but explode at temperatures varying with the nature of the substance, and to some extent with the rapidity with which they are heated.

There is every reason to believe that in the salts of the bromoamides the metal is not attached to nitrogen * but to oxygen, and that they are in reality salts of the bromo*iso*amides. Although it has not been directly proved, there are similar reasons for believing that the salts obtained from the sulphondichloroamides are derivatives of the sulphon*iso*chloroamides, $RSO(OH){:}NCl$, and have a constitution represented by the general formula $RSO(OM){:}NCl$.

On acidifying aqueous solutions of these salts one would expect to obtain the sulphon*iso*chloroamides or the sulphonmonochloroamides produced from them by intramolecular rearrangement; such compounds, however, have not yet been obtained. On adding acetic acid to such solutions, white, crystalline solids are precipitated, which, on recrystallisation, prove to be the sulphondichloroamides, whilst equivalent quantities of the sulphonamides remain in solution. This is probably due to a progressive hydrolysis of the sulphon*iso*chloroamides first formed, and the production, by the agency of the hypochlorous acid so formed, of the much more sparingly soluble sulphondichloroamides:

$$RSO(OH){:}NCl + H_2O = RSO_2\cdot NH_2 + HOCl.$$

$$RSO(OH){:}NCl + HOCl = RSO(OH){:}NCl_2\cdot OH = RSO_2\cdot NCl_2 + H_2O.$$

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* Hantzsch and Dollfuss, *Ber.*, 1902, **35**, 249.

All the aromatic sulphonamides easily yield very stable substituted nitrogen bromides, which show the typical behaviour of this type of compound, as they do not readily undergo isomeric change. A few sulphondibromoamides have been studied by Hoogewerff and van Dorp (*Rec. Trav. Chim.*, 1887, **6**, 373), and were described in their researches upon the action of potassium hypobromite on amides: among others, benzenesulphondibromoamide and benzene-*m*-disulphontetrabromoamide. These chemists, however, did not prepare them by a very convenient method or one capable of giving a good yield.

The method of preparing substituted nitrogen bromides by means of hypobromous acid, which has been applied with success in many other cases, is similarly successful here. All the sulphonamides and alkyl sulphonamides readily react with this reagent, which replaces all the aminic hydrogen by bromine, and a number of typical derivatives of the aromatic sulphonamides have been prepared in this way. For example:

$$C_6H_5\cdot SO_2\cdot NH\cdot CH_3 + HOBr \rightleftharpoons C_6H_5\cdot SO_2\cdot NH(CH_3){<}^{Br}_{OH} \rightleftharpoons$$
$$C_6H_5\cdot SO_2\cdot N(CH_3)Br + H_2O.$$

The yields are theoretical.

The sulphondibromoamides resemble the sulphondichloroamides; they crystallise well and behave similarly on heating. They are, however, bright yellow in colour. Although they are unusually stable as compared with nitrogen bromides generally, they slowly decompose on keeping, bromine being liberated. They interact with hydrochloric acid, hydriodic acid, hydrogen sulphide, and alcohol in the manner characteristic of nitrogen bromides, the sulphonamide in each case being regenerated.

Although hydrolysed when heated with water or with somewhat dilute acetic acid, they are remarkable among nitrogen bromides for the slowness with which these actions take place.

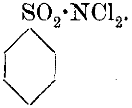
As has been noted by Hoogewerff and van Dorp (*loc. cit.*) in the case of the compounds which they prepared, the sulphondibromoamides interact readily with a solution of sodium or potassium hydroxide, salts of the sulphonmonobromoamides being produced. These salts are pale yellow, stable substances which readily dissolve in water and crystallise beautifully with varying amounts of water of crystallisation, the latter being lost when the salts are exposed over phosphoric oxide under reduced pressure. The anhydrous salts do not melt, but decompose explosively when strongly heated. It is probable that they are similar in constitution to the analogous salts derived from the sulphondichloroamides, and that they are derivatives of the unknown sulphon*iso*bromoamides, $R\cdot SO(OH)\colon NBr$. The latter compounds are not obtained on acidifying solutions of these salts, sulphondibromoamides and sulphonamides being produced in equivalent amount, probably in the manner suggested to explain the similar behaviour of the chloro-compounds.

When solutions of these salts in caustic alkalis are heated, they readily undergo hydrolysis; the yellow colour of the solution disappears as the action proceeds, and a solution of the sulphonamide in the caustic alkali together with alkaline bromide and bromate are formed.

The sulphonalkylbromoamides, $RSO_2{\cdot}NR'Br$, are prepared by the same method with equal ease. They are pale yellow, well-crystallised compounds which, in virtue of the halogen attached to the nitrogen, resemble other nitrogen bromides in chemical behaviour. They are comparatively stable substances, which, however, decompose with reddening and evolution of gas on heating above their melting points. As with the corresponding chlorine derivatives, those containing the benzyl group are the least stable, and decompose slowly even when kept in a dry atmosphere screened from light. Various reactions of these compounds are being investigated.

I. *Sulphondichloroamides and Sulphonalkylchloroamides.*

Benzenesulphondichloroamide,



$SO_2{\cdot}NCl_2$.

This substance was first mentioned by Kastle (*Amer. Chem. J.*, 1895, **17**, 704), who suggested its use instead of chlorine water as a reagent for bromine and iodine; it was subsequently briefly described by Kastle, Keiser, and Bradley (*Amer. Chem. J.*, 1896, **18**, 491). They obtained it by leading chlorine into a solution of benzenesulphonamide in caustic potash, heating the solid which separated with hot water, and subsequently dissolving the residue in alcohol and precipitating the dichloroamide by water as pearly-white laminæ which melted at 70°. These methods of preparation and purification are, however, not the most suitable.

Benzenesulphondichloroamide and all other sulphondichloroamides are most conveniently prepared by adding the corresponding sulphonamide to an excess of a saturated solution of bleaching powder, in which they all readily dissolve, and then slowly pouring acetic acid into the cooled solution. The sulphondichloroamides at once separate as oily liquids which solidify quickly to white, crystalline solids. These may be filtered off, and are practically pure dichloroamides. As, however, these solids are not easily and conveniently dried, it is best to add to the acid liquid sufficient chloroform to dissolve them completely. It is advisable to shake the chloroform solution with a further small quantity of fresh acidified bleaching powder solution to ensure the absence of any trace of unchanged sulphonamide. The chloroform solution is then separated, dried over fused calcium chloride, and the solvent driven off on the water-bath in a current of air, taking care that the temperature of the evaporating liquid does not rise much above 20°. The dichloroamides are then left as beautifully crystalline white solids, which may be recrystallised from chloroform, or, better, by dissolving them in warm chloroform and adding a little warm petroleum, when, on cooling, they separate in colourless crystals with a scarcely perceptible yellow tint.

Benzenesulphondichloroamide is easily soluble in chloroform or in acetic acid, and crystallises from these solvents in transparent, colourless plates with a very faint yellow tint. It is sparingly soluble in petroleum and water. It is hydrolysed on prolonged boiling with water or somewhat diluted acetic acid; the action is, however, very slow, and from such partly hydrolysed solutions the dichloroamide still remaining separates on cooling in a nearly pure state, as its solubility in these solvents is less than that of benzenesulphonamide. It melts at 76°, and when heated above this point remains for some time unchanged, but decomposes with ebullition at about 200°, giving off chlorine, nitrogen, hydrogen chloride, and benzenesulphonic chloride. When heated rapidly in a flame, it decomposes with a feeble explosion. This and the other chloroamides described in the paper were analysed by dissolving them in acetic acid, adding excess of potassium iodide, and titrating the liberated iodine with a standard solution of sodium thiosulphate.

0·3905 liberated I = 69·2 c.c. $N/10$ I. Cl as NCl = 31·41.

$C_6H_5O_2NCl_2S$ requires Cl as NCl = 31·37 per cent.

When benzenesulphondichloroamide is added to a somewhat dilute cold solution of caustic potash or soda, it dissolves forming a pale yellow liquid from which, on the addition of a saturated solution of the alkali hydroxide, salts of benzenesulphonmonochloroamide containing water of crystallisation slowly separate in long, colourless, flattened prisms. These are still more readily obtained by cautiously dissolving the sulphondichloroamide in a warm 10 per cent. solution of sodium or potassium hydroxide; on slowly cooling the pale yellow liquid, the salts crystallise out well in glittering, transparent, colourless, flattened prisms. If, after the dichloroamide has dissolved, the solution is heated nearly to boiling, a very vigorous reaction accompanied by violent ebullition sets in, and if much of the dichloroamide has been used the salt may separate out in small crystals even while the solution is hot. This behaviour seems to indicate that the alkali hydroxide first combines with the sulphondichloroamide, the salt of the sulphon*iso*chloroamide being formed from this additive product by a splitting off of alkaline hypochlorite, some of the heat being derived from the rapid transformation of the latter into chloride and chlorate.

Identical salts are precipitated on passing chlorine in limited amount into solutions of the sulphonamides in excess of strong caustic alkalis, but this method of preparation is not a convenient one. These salts, which are probably derivatives of benzenesulphon*iso*chloroamide, $C_6H_5\cdot SO(OH){:}NCl$, are very stable in presence of alkalis, and considerable heating is needed to effect complete hydrolysis, which, however, takes place with the formation of the original sulphonamide and alkaline chloride and chlorate when a solution in aqueous alkali is heated for some hours at 100°. No transformation of these salts has hitherto been observed to take place under these conditions. They are very easily soluble in water, although with some slight hydrolysis, and are again precipitated from solution on adding strong alkali. Similar results are obtained by warming the sulphondichloroamides with a solution of calcium or barium hydroxide.

Potassium benzenesulphonchloroamide, $C_6H_5\cdot SO_2K{:}NCl,H_2O$.

This salt was prepared as above described by dissolving benzenesulphondichloroamide in an excess of a warm 10 per cent. solution of potassium hydroxide. On cooling, the pale yellow solution deposited the salt in long, colourless, transparent prisms; these were filtered off, rapidly washed with a little cold water, pressed between filter paper, and dried for a short time in the air. A quantity of this salt was analysed by dissolving it in a solution of potassium iodide, acidifying with acetic acid, and titrating the liberated iodine with sodium thiosulphate.

0·4185 liberated I = 34·2 c.c. *N*/10 I. Cl as NCl = 14·48.

A further quantity was exposed in a vacuum over phosphoric oxide for four days until its weight became constant.

0·4349 lost 0·0310 H_2O. H_2O = 7·13 per cent.

A quantity similarly dried was analysed as before.

0·2937 liberated I = 25·5 c.c. *N*/10 I. Cl as NCl = 15·39.

$C_6H_5O_2NClSK,H_2O$ requires Cl as NCl = 14·31. H_2O = 7·27.

$C_6H_5O_2NClSK$ requires Cl as NCl = 15·43 per cent.

The salt is very soluble in water, giving a pale yellow solution; it is less soluble in a strong solution of potassium hydroxide, and crystallises easily from this in colourless, transparent, glittering, long prisms, apparently six-sided with domed ends.

When heated rapidly, the dry salt does not melt, but explodes some what violently with decomposition and liberation of a black solid, probably carbon, at about 140—145°. The temperature of decomposition depends, however to some extent on the rapidity with which the salt is heated

Sodium benzenesulphonchloroamide, $C_6H_5\cdot SO_2Na{:}NCl,3H_2O$.

This compound was prepared exactly as the potassium salt, than which it is somewhat more sparingly soluble in water; it crystallises in long, colourless, transparent, flattened prisms with domed ends. It is very easily soluble in water giving a pale yellow solution, less easily in a solution of sodium hydroxide.

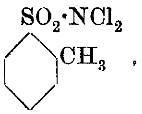
0·2632 liberated I = 19·7 c.c. $N/10$ I. Cl as NCl = 13·27 per cent.

When dried for several days over phosphoric oxide until no further loss in weight occurred, the crystals did not fall to powder, but became opaque, retaining, to a certain extent, their crystalline shape.

0·2052 liberated I = 19·1 c.c. $N/10$ I. Cl as NCl = 16·49.
$C_6H_5O_2NClSNa,3H_2O$ requires Cl as NCl = 13·25.
$C_6H_5O_2NClSNa$ requires Cl as NCl = 16·59 per cent.

When heated rapidly, the anhydrous salt does not melt, but explodes with violence at about 180—185°.

Toluene-o-sulphondichloroamide,



Toluene-*o*-sulphonamide was powdered and dissolved in an excess of a cooled solution of bleaching powder. On adding acetic acid slowly, the dichloroamide separated as an oil which did not solidify even on strongly cooling. It was therefore extracted by chloroform, the solution in chloroform again shaken with acidified bleaching powder, and afterwards removed, dried, and the solvent evaporated off in a current of air on a water-bath. A pale yellow, oily liquid was left which slowly solidified to a beautifully crystalline, colourless mass. It is very soluble in chloroform and freely soluble in petroleum. It crystallises from light petroleum in clusters of slender, colourless plates which melt at 33°.

0·2694 liberated I = 44·9 c.c. $N/10$ I. Cl as NCl = 29·54.
$C_7H_7O_2NCl_2S$ requires Cl as NCl = 29·53 per cent.

Potassium toluene-o-*sulphonchloroamide*, $CH_3{\cdot}C_6H_4{\cdot}SO_2K{:}NCl,H_2O$.

This salt was prepared as previously described, using a 10 per cent. solution of potassium hydroxide; it crystallises in glittering, transparent, colourless prisms.

0·3688 liberated 28·1 c.c. *N*/10 I. Cl as NCl = 13·50.
$C_7H_7O_2NClSK,H_2O$ requires Cl as NCl = 13·54 per cent.

The hydrated salt loses its water of crystallisation when kept for some days in a vacuum over phosphoric oxide, but alters very little in appearance.

0·2590 liberated I = 21·1 c.c. *N*/10 I. Cl as NCl = 14·44.
$C_7H_7O_2NClSK$ requires Cl as NCl = 14·54 per cent.

The anhydrous salt explodes feebly when heated to about 145°.

Sodium toluene-o-*sulphonchloroamide*, $CH_3{\cdot}C_6H_4{\cdot}SO_2Na{:}NCl,2H_2O$.

This salt crystallises in long, colourless, transparent, somewhat flattened prisms.

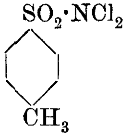
0·2130 liberated I = 16·5 c.c. *N*/10 I. Cl as NCl = 13·73.
$C_7H_7O_2NClSNa,2H_2O$ requires Cl as NCl = 13·44 per cent.

When dried over phosphoric oxide in a vacuum or heated on a water-bath, the crystals lose their water of crystallisation and become opaque.

0·2005 liberated I = 17·7 c.c. N/10 I. Cl as NCl = 15·65.
$C_7H_7O_2NClSNa$ requires Cl as NCl = 15·57 per cent.

The anhydrous salt does not melt, but explodes with some violence when heated to about 170—175°.

Toluene-p-*sulphondichloroamide*,



This was first obtained by Kastle, Keiser, and Bradley (*loc. cit.*), but no analysis was published; they give its melting point as 80°, and state that it crystallises in smaller crystals than the benzene derivatives and is rather more difficult to obtain pure and dry.

It is easily prepared by the general method described above. It is moderately soluble in chloroform, sparingly so in petroleum; and crystallises from chloroform mixed with a little petroleum, in very long, colourless, flattened, four-sided prisms terminated by short pyramids (m. p. 83°).

0·2190 liberated I = 36·5 c.c. *N*/10 I. Cl as NCl = 29·54.
$C_7H_7O_2NCl_2S$ requires Cl as NCl = 29·53 per cent.

Potassium toluene-p-*sulphonchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2K\colon NCl, H_2O$.

This salt, prepared from a 10 per cent. solution of potassium hydroxide, crystallises in large, colourless, four-sided plates, often elongated into long, flattened prisms. The salt dried in air gave the following numbers on analysis:

0·3564 liberated I = 27·2 c.c. *N*/10 I. Cl as NCl = 13·53 per cent.

A quantity was kept for some days over phosphoric oxide in a vacuum until its weight was constant; the crystals became opaque.

0·4839 lost 0·0335. H_2O = 6·92 per cent.

A further quantity similarly dried was analysed:

0·3043 liberated I = 24·8 c.c. *N*/10 I. Cl as NCl = 14·44.
$C_7H_7O_2NClSK, H_2O$ requires Cl as NCl = 13·54. H_2O = 6·88.
$C_7H_7O_2NClSK$ requires Cl as NCl = 14·54 per cent.

When heated rapidly, the anhydrous salt does not melt, but explodes with violence at about 160—165°.

Sodium toluene-p-*sulphonchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2Na\colon NCl, 3H_2O$.

This salt crystallises in long, flattened, colourless, transparent prisms.

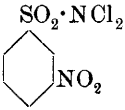
0·4806 liberated I = 34·3 c.c. Cl as NCl = 12·65.
$C_7H_7O_2NClSNa, 3H_2O$ requires Cl as NCl = 12·58 per cent.

When exposed over phosphoric oxide in a vacuum for some days, or when heated on a water-bath for a short time, the salt loses its water of crystallisation; the crystals become opaque, but retain roughly their original shape.

0·3082 liberated I = 27·1 c.c. Cl as NCl = 15·59.
$C_7H_7O_2NClSNa$ requires Cl as NCl = 15·57 per cent.

The anhydrous salt explodes with violence when heated to about 175—180°.

Nitrobenzene-m-*sulphondichloroamide*,



This compound crystallises from chloroform, in which it is moderately soluble, in colourless, glittering, six-sided plates with a faint yellow tint (m. p. 121°).

0·2952 liberated $I = 43·7$ c.c. $N/10$ I. Cl as $NCl = 26·24$.
$C_6H_4O_4N_2Cl_2S$ requires Cl as $NCl = 26·15$ per cent.

Potassium nitrobenzene-m-*sulphonchloroamide*,

$$NO_2 \cdot C_6H_4 \cdot SO_2K \colon NCl, x(H_2O),$$

crystallises from a strongly alkaline solution in very small, pale yellow, transparent plates, which, on drying over phosphoric oxide in a vacuum, lose water of crystallisation and become opaque. The water of crystallisation was not estimated, as, owing to the smallness of the crystals, it was found difficult to remove all adhering water. The anhydrous salt was analysed:

0·2056 liberated $I = 14·7$ c.c. $N/10$ I. Cl as $NCl = 12·67$.
$C_6H_4O_4N_2ClSK$ requires Cl as $NCl = 12·9$ per cent.

The anhydrous salt explodes with incandescence and deposition of carbon at about 155°. Although the dry salt can be heated on a water-bath for a short time without decomposition, if its solution in caustic potash is heated, it darkens in colour, heat is evolved, and a violent action occurs, resulting in the formation of a purple solution from which acids precipitate tarry substances the nature of which has not yet been determined. All the salts of the two sulphonchloroamides containing a NO_2 group which have been investigated behave in this manner.

Sodium nitrobenzene-m-*sulphonchloroamide*,

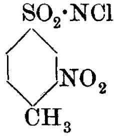
$$NO_2 \cdot C_6H_4 \cdot SO_2Na \colon NCl, x(H_2O),$$

crystallises in small, very pale yellow plates. These, like those of the potassium salt, were too small to be satisfactorily dried by pressing between paper in order to determine the water of crystallisation. When dried over phosphoric oxide in a vacuum, they lose their water of crystallisation and become opaque, forming a nearly white, crystalline powder.

0·2772 liberated $I = 21·3$ c.c. $N/10$ I. Cl as $NCl = 13·62$.
$C_6H_4O_4N_2ClSNa$ requires Cl as $NCl = 13·7$ per cent.

When heated rapidly, the dry salt explodes with incandescence and deposition of carbon at about 175°.

2-Nitrotoluene-p-*sulphondichloroamide*,



This compound crystallises from chloroform, in which it is moderately soluble, in very pale yellow, transparent, four-sided prisms (m. p. 101°).

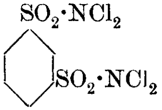
0·3082 liberated I = 43·5 c.c. *N*/10 I. Cl as NCl = 25·02.
$C_7H_6O_4N_2Cl_2S$ requires Cl as NCl = 24·87 per cent.

Potassium 2-nitrotoluene-p-*sulphonchloroamide*,
$C_6H_3Me(NO_2)\cdot SO_2K{:}NCl,x(H_2O)$,
crystallises in small, pale yellow, transparent plates, which lose water of crystallisation and become opaque when dried in a vacuum over phosphoric oxide.

0·2121 liberated I = 14·4 c.c. *N*/10 I. Cl as NCl = 12·03.
$C_7H_6O_4N_2SClK$ requires Cl as NCl = 12·27 per cent.

The anhydrous salt, when heated to about 160°, explodes. The sodium salt resembles this substance; both behave like the salts of nitrobenzene-*m*-sulphonchloroamide when heated with aqueous caustic alkali.

Benzene-m-*disulphontetrachloroamide*,

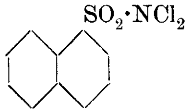


This compound is easily soluble in chloroform; it crystallises from a mixture of this solvent and light petroleum in colourless, transparent rhombs (m. p. 128°).

0·1694 liberated I = 36·1 c.c. *N*/10 I. Cl as NCl = 37·77.
$C_6H_4O_4N_2Cl_4S_2$ requires Cl as NCl = 37·91 per cent.

When strongly heated, the melted substance explodes with a violence recalling the explosion of nitrogen chloride itself, carbon being deposited. It readily dissolves in a warm solution of potassium or sodium hydroxide, forming salts of benzene-*m*-disulphondichloroamide, which, however, are so soluble that they have not been satisfactorily isolated.

Naphthalene-1-*sulphondichloroamide*,

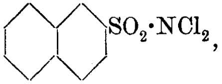


This compound crystallises from a mixture of chloroform and petroleum in large, transparent plates of a pale yellow colour; this colour, which is more marked than is usual in nitrogen chlorides derived from colourless amides, appears to be the real colour of the compound and not to be due to impurity; its solution in chloroform is also much deeper yellow than that of other similar compounds; it melts at 91°.

0·3280 liberated I = 47·4 c.c. *N*/10 I. Cl as NCl = 25·61.
$C_{10}H_7O_2NCl_2S$ requires Cl as NCl = 25 68 per cent.

Potassium and *sodium naphthalene*-1-*sulphonchloroamides* crystallise out in small, colourless plates when a solution of the dichloroamide in warm caustic potash or soda is allowed to cool. When dried over phosphoric oxide, their composition is represented by the formulæ $C_{10}H_7\cdot SO_2K{:}NCl$ and $C_{10}H_7\cdot SO_2Na{:}NCl$.

Naphthalene-2-*sulphondichloroamide*,



is somewhat difficult to obtain crystalline as it is very soluble in all solvents; it slowly crystallises from light petroleum containing a very little chloroform in thick, colourless, transparent plates (m. p. 68°).

0·3514 liberated I = 50·2 c.c. *N*/10 I. Cl as NCl = 25·32.
$C_{10}H_7O_2NCl_2S$ requires Cl as NCl = 25·68 per cent.

Potassium naphthalene-2-*sulphonchloroamide*, $C_{10}H_7\cdot SO_2K{:}NCl,3H_2O$, which is comparatively sparingly soluble, crystallises in large, very thin, transparent, pearly-white plates.

0·3868 liberated I = 22·9 c.c. *N*/10 I. Cl as NCl = 10·49.
$C_{10}H_7O_2NClSK,3H_2O$ requires Cl as NCl = 10·62 per cent.

When dried for some days over phosphoric oxide in a vacuum, the crystals give up their water of crystallisation and lose their transparency.

0·1873 of the anhydrous salt liberated I = 13·2 c.c. *N*'10 I. Cl as NCl = 12·49.
$C_{10}H_7O_2NClSK$ requires Cl as NCl = 12·67 per cent.

When heated, the dry salt explodes feebly at about 170° with deposition of carbon.

Sodium naphthalene-2-sulphonchloroamide, $C_{10}H_7\cdot SO_2Na\colon NCl,H_2O$, is also sparingly soluble; it crystallises from a solution of sodium hydroxide in large, pearly-white, thin, transparent plates.

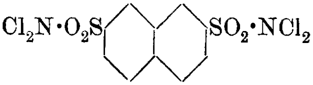
0·2546 liberated I = 17·5 c.c. *N*/10 I. Cl as NCl = 12·18.
$C_{10}H_7O_2NClSNa,H_2O$ requires Cl as NCl = 12·58 per cent.

On standing over phosphoric oxide in a vacuum for some days, the water of crystallisation is lost, but the crystals change very little in appearance.

0·1392 of the anhydrous salt liberated I = 10·5 c.c. *N*/10 I. Cl as NCl = 13·37.
$C_{10}H_7O_2NClSNa$ requires Cl as NCl = 13·44 per cent.

The dry salt does not melt, but explodes feebly at about 180° with deposition of carbon.

Naphthalene-2 : 7-*disulphontetrachloroamide*,



This compound is moderately soluble in chloroform and crystallises from this solvent in clusters of short, colourless, transparent pyramids which melt at 165°. The melted substance explodes with great violence when strongly heated.

0·2530 liberated I = 47·3 c.c. *N*/10 I. Cl as NCl = 33·14.
$C_{10}H_6O_4N_2Cl_4S_2$ requires Cl as NCl = 33·44 per cent.

The potassium and sodium salts of naphthalene-2 : 7-disulphondichloroamide crystallise in long, colourless, hair-like crystals. When dried over phosphoric oxide, their composition is represented by the formulæ $C_{10}H_6(SO_2K\colon NCl)_2$ and $C_{10}H_6(SO_2Na\colon NCl)_2$. They decompose explosively with the formation of brown, earthy-looking powders at about 145—150° and 165—170° respectively.

Anthraquinone-2-sulphondichloroamide, $C_{14}H_7O_2\cdot SO_2\cdot NCl_2$, crystallises from chloroform, in which it is moderately soluble, in clusters of bright yellow, transparent plates (m. p. 177°).

0·2554 liberated I = 28·2 c.c. *N*/10 I. Cl as NCl = 19·57.
$C_{14}H_7O_4NCl_2S$ requires Cl as NCl = 19·91 per cent.

Arylsulphonalkylchloroamides.

Compounds of this nature are produced with great readiness by the action of an aqueous solution of hypochlorous acid on the sulphonalkylamides. They are most conveniently prepared by dissolving the corresponding sulphonalkylamide in chloroform and shaking the solution for some minutes with a solution of hypochlorous acid made by adding an excess of potassium hydrogen carbonate to a *N*/10 solution of sodium hypochlorite. It is best to shake finally for a few minutes with a fresh quantity of hypochlorous acid solution, then to separate, dry the chloroform solution over fused calcium chloride, and drive off the solvent in a current of air. The sulphonalkylchloroamides are left as white, crystalline solids or as pale yellow, viscid oils, which can be made to solidify by cooling and stirring with a little light petroleum. They can be recrystallised from chloroform or petroleum, or, as a rule, better from a mixture of the two solvents. They all crystallise particularly well.

A number of compounds derived from various methyl, ethyl, propyl, and benzyl derivatives of the sulphonamides have been obtained. Those containing methyl, ethyl, and propyl groups are comparatively stable, whereas those in which benzyl occurs undergo spontaneous decomposition after a few hours, even when kept in dry air; chlorine and hydrogen chloride are liberated, while an odour resembling that of benzaldehyde becomes apparent.

When rapidly heated, they all decompose with evolution of gas, but without explosion.

Benzenesulphonmethylchloroamide, $C_6H_5\cdot SO_2\cdot NCl\cdot CH_3$, crystallises from a mixture of chloroform and petroleum in colourless, short rhombs (m. p. 81°).

0·4819 liberated I = 47·1 c.c. *N*/10 I. Cl as NCl = 17·32.

$C_7H_8O_2NClS$ requires Cl as NCl = 17·24 per cent.

Benzenesulphonethylchloroamide, $C_6H_5\cdot SO_2\cdot NCl\cdot C_2H_5$, colourless plates (m. p. 52°).

0·4248 liberated I = 39 c.c. *N*/10 I. Cl as NCl = 16·27.

$C_8H_{10}O_2NClS$ requires Cl as NCl = 16·14 per cent.

Benzenesulphonbenzylchloroamide, $C_6H_5\cdot SO_2\cdot NCl\cdot CH_2\cdot C_6H_5$, colourless, slender prisms (m. p. 109°).

0·3042 liberated I = 21·5 c.c. *N*/10 I. Cl as NCl = 12·53.

$C_{13}H_{12}O_2NClS$ requires Cl as NCl = 12·59 per cent.

This substance is comparatively unstable; on keeping in a desiccator over phosphoric oxide, it slowly decomposed, giving off chlorine and hydrogen chloride, while a strong odour resembling that of benzaldehyde was noted. In two days, the percentage of Cl as NCl fell to 11·60 per cent.

Toluene-p-*sulphonmethylchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl \cdot CH_3$, crystallises in colourless prisms which melt at 82°.

0·4530 liberated I = 41·5 c.c. *N*/10 I. Cl as NCl = 16·24.
$C_8H_{10}O_2NClS$ requires Cl as NCl = 16·14 per cent.

Toluene-p-*sulphonethylchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl \cdot C_2H_5$, crystallises in colourless, six-sided plates (m. p. 86°).

0·4862 liberated I = 41·8 c.c. *N*/10 I. Cl as NCl = 15·24.
$C_9H_{12}O_2NClS$ requires Cl as NCl = 15·17 per cent.

Toluene-p-*sulphonpropylchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl \cdot C_3H_7$, is very readily soluble in chloroform and in light petroleum; it crystallises in colourless plates (m. p. 58°).

0·5844 liberated I = 46 c.c. *N*/10 I. Cl as NCl = 13·95.
$C_{10}H_{14}O_2NClS$ requires Cl as NCl = 14·31 per cent.

Toluene-p-*sulphonbenzylamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot CH_2 \cdot C_6H_5$.

This and a number of similar compounds not hitherto described have been prepared by adding the calculated quantity of the amine, either anhydrous or in aqueous solution, to the sulphonic chloride, either solid or dissolved in ether or chloroform. Vigorous action as a rule took place and much heat was generated. After standing for some hours to complete the action, the calculated quantity of potassium hydrogen carbonate dissolved in water was added, the whole being finally warmed for a time on the water-bath. The solid thus obtained was then recrystallised, except when otherwise stated, from alcohol.

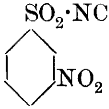
Toluene-*p*-sulphonbenzylamide crystallises in colourless, transparent, six-sided prisms terminated by pyramids (m. p. 116°).

Toluene-p-*sulphonbenzylchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl \cdot CH_2 \cdot C_6H_5$. This compound crystallises in colourless, six-sided plates (m. p. 136°).

0·3359 liberated I = 22·8 c.c. *N*/10 I. Cl as NCl = 12·03.
$C_{14}H_{14}O_2NClS$ requires Cl as NCl = 11·99 per cent.

Nitrobenzene-m-*sulphonmethylamide*, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot CH_3$, very pale yellow, flattened prisms (m. p. 125°).

Nitrobenzene-m-*sulphonmethylchloroamide*,



forms pale yellow, transparent, four-sided plates (m. p. 136°).

0·3958 liberated I = 31·6 c.c. *N*/10 I. Cl as NCl = 14·15.
$C_7H_7O_4N_2ClS$ requires Cl as NCl = 14·14 per cent.

Nitrobenzene-m-*sulphonethylamide*, $NO_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_2H_5$, small, colourless plates with a faint tinge of yellow (m. p. 81°).

Nitrobenzene-m-*sulphonethylchloroamide*, $NO_2\cdot C_6H_4\cdot SO_2\cdot NCl\cdot C_2H_5$, forms large, very pale yellow, four-sided plates (m. p. 84°).

0·5097 liberated I = 38·7 c.c. *N*/10 I. Cl as NCl = 13·45.
$C_8H_9O_4N_2ClS$ requires Cl as NCl = 13·39 per cent.

Nitrobenzene-m-*sulphonbenzylamide*, $NO_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot CH_2\cdot C_6H_5$, colourless plates with a faint tinge of yellow (m. p. 101°).

Nitrobenzene-m-*sulphonbenzylchloroamide*,

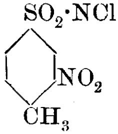
$$NO_2\cdot C_6H_4\cdot SO_2\cdot NCl\cdot CH_2\cdot C_6H_5,$$

crystallises from chloroform, in which it is moderately soluble, in colourless, slender prisms with the faintest perceptible yellow tint (m. p. 142°).

0·4280 liberated I = 26·3 c.c. *N*/10 I. Cl as NCl = 10·89.
$C_{13}H_{11}O_4N_2ClS$ requires Cl as NCl = 10·85 per cent.

2-*Nitrotoluene*-p-*sulphonmethylamide*, $NO_2\cdot C_6H_3Me\cdot SO_2\cdot NH\cdot CH_3$, very pale yellow prisms (m. p. 93°).

2-*Nitrotoluene*-p-*sulphonmethylchloroamide*,



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crystallises from chloroform, in which it is moderately soluble, in very pale yellow, transparent, four-sided prisms (m. p. 90°).

0·3160 liberated I = 23·8 c.c. *N*/10 I. Cl as NCl = 13·35.
$C_8H_9O_4N_2ClS$ requires Cl as NCl = 13·39 per cent.

2-*Nitrotoluene*-p-*sulphonethylamide*, $NO_2\cdot C_6H_3Me\cdot SO_2\cdot NH\cdot C_2H_5$, short, thick, very pale yellow prisms (m. p. 87°).

2-*Nitrotoluene*-p-*sulphonethylchloroamide*,

$$NO_2\cdot C_6H_3Me\cdot SO_2\cdot NCl\cdot C_2H_5,$$

crystallises in pale yellow, four-sided plates (m. p. 76°).

0·4192 liberated I = 30·2 c.c. $N/10$ I. Cl as NCl = 12·77.
$C_9H_{11}O_4N_2ClS$ requires Cl as NCl = 12·72 per cent.

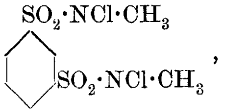
2-*Nitrotoluene*-p-*sulphonbenzylamide*, $NO_2{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$, slender, colourless plates with the faintest possible yellow colour (m. p. 94°).

2-*Nitrotoluene*-p-*sulphonbenzylchloroamide*, $NO_2{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}NCl{\cdot}CH_2{\cdot}C_6H_5$, crystallises from chloroform, in which it is moderately soluble, in slender, flattened prisms, almost colourless, but with the faintest perceptible shade of yellow (m. p. 144°).

0·3525 liberated I = 20·8 c.c. $N/10$ I. Cl as NCl = 10·46.
$C_{14}H_{13}O_4N_2ClS$ requires Cl as NCl = 10·40 per cent.

Benzene-m-*disulphon*-s-*dimethylamide*, $C_6H_4(SO_2{\cdot}NH{\cdot}CH_3)_2$, small, colourless plates (m. p. 132°).

Benzene-m-*disulphon*-s-*dimethyldichloroamide*,



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crystallises from chloroform, in which it is sparingly soluble, in colourless, transparent prisms (m. p. 135°).

0·3776 liberated I = 45·3 c.c. $N/10$ I. Cl as NCl = 21·26.
$C_8H_{10}O_4N_2Cl_2S_2$ requires Cl as NCl = 21·28 per cent.

When heated rapidly above its melting point, it decomposes violently with blackening.

Naphthalene-1-*sulphonmethylamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}CH_3$, small, colourless plates (m. p. 137°).

Naphthalene-1-*sulphonmethylchloroamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NCl{\cdot}CH_3$, is very easily soluble in chloroform; it crystallises from a mixture of chloroform and light petroleum in transparent, short, colourless, six-sided prisms (m. p. 78°).

0·3412 liberated I = 25·9 c.c. $N/10$ I. Cl as NCl = 13·45.
$C_{11}H_{10}O_2NClS$ requires Cl as NCl = 13·86 per cent.

Naphthalene-1-*sulphonethylamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}C_2H_5$, very pale yellow, thick plates (m. p. 93°).

Naphthalene-1-*sulphonethylchloroamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NCl{\cdot}C_2H_5$, crystallises in glittering, transparent, very pale yellow, short prisms terminated by pyramids (m. p. 77°).

0·4602 liberated I = 34·1 c.c. *N*/10 I. Cl as NCl = 13·13
$C_{12}H_{12}O_2NClS$ requires Cl as NCl = 13·14 per cent.

Naphthalene-1-*sulphonbenzylamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$, pale yellow, six-sided prisms (m. p. 137°).

Naphthalene-1-*sulphonbenzylchloroamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NCl{\cdot}CH_2{\cdot}C_6H_5$, crystallises in short, very pale yellow prisms (m. p. 94°).

0·3534 liberated I = 21·3 c.c. *N*/10 I. Cl as NCl = 10·68.
$C_{17}H_{14}O_2NClS$ requires Cl as NCl = 10·69 per cent.

Naphthalene-2-*sulphonmethylamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}CH_3$, thin, colourless plates (m. p. 111°).

Naphthalene-2-*sulphonmethylchloroamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NCl{\cdot}CH_3$, crystallises in short, colourless prisms (m. p. 91°).

0·3012 liberated I = 23·1 c.c. *N*/10 I. Cl as NCl = 13·59.
$C_{11}H_{10}O_2NClS$ requires Cl as NCl = 13·86 per cent.

Naphthalene-2-*sulphonpropylamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}C_3H_7$, colourless, pearly, thin, transparent plates (m. p. 77°).

Naphthalene-2-*sulphonpropylchloroamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NCl{\cdot}C_3H_7$, crystallises in clusters of glittering, transparent, colourless plates (m. p. 86°).

0·3731 liberated I = 26·3 c.c. *N*/10 I. Cl as NCl = 12·49.
$C_{13}H_{14}O_2NClS$ requires Cl as NCl = 12·49 per cent.

Naphthalene-2-*sulphonbenzylamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$, is readily soluble in chloroform, and on adding light petroleum crystallises in small, colourless plates (m. p. 124°).

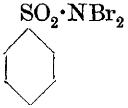
Naphthalene-2-*sulphonbenzylchloroamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NCl{\cdot}CH_2{\cdot}C_6H_5$, crystallises in clusters of glittering, transparent, very pale yellow plates (m. p. 117°).

0·4394 liberated I = 25·7 c.c. *N*/10 I. Cl as NCl = 10·37.
$C_{17}H_{14}O_2NClS$ requires Cl as NCl = 10·69 per cent.

The sulphondichloroamides and the sulphonalkylchloroamides are being further studied as they are very reactive and, being easily soluble and very stable, promise to be of considerable value in organic syntheses. Moreover, the sulphondichloroamides are so readily prepared and analysed, and the ease with which they crystallise is so much affected by admixture, that they should prove of considerable use in the investigation of sulphonic acids.

II. *Sulphondibromoamides and Sulphonalkylbromoamides.*

Benzenesulphondibromoamide,



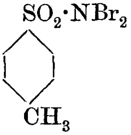
This compound was first prepared by Hoogewerff and van Dorp (*Rec. Trav. Chim.*, 1877, 6, 373) by dissolving benzenesulphonamide in an excess of alkaline hypobromite and adding acetic acid; a yield of about 60 per cent. of the theoretical was obtained. It can be obtained with much greater ease and in theoretical amount by the action of hypobromous acid on benzenesulphonamide. The best method of procedure is described later. The compound can be obtained perfectly pure, melting at 116°, by one crystallisation from chloroform. A specimen so prepared gave the following numbers on analysis:

0·3874 liberated I = 49·2 c.c. *N*/10 I. Br as NBr = 50·77.

$C_6H_5O_2NBr_2S$ requires Br as NBr = 50·76 per cent.

This and other similar sulphondibromoamides are far more stable towards hydrolysing agents than is usually the case among nitrogen bromides. Two grams of benzenesulphondibromoamide were dissolved in 50 c.c. of 90 per cent. acetic acid and the solution gently boiled for four hours, during which time bromine vapour was very slowly evolved. The solution remained yellow after standing at the ordinary temperature for three days, and on diluting with water about half a gram of pure dibromoamide separated out, the more soluble benzenesulphonamide remaining in solution. Similarly, on boiling 2 grams of the compound with half a litre of water, the melted substance, which at first remained largely undissolved as a heavy oil, slowly dissolved, while a vapour was given off which turned starch paper moistened with potassium iodide blue. After four hours' boiling, the liquid was still yellow, and slowly deposited about 0·4 gram of pure dibromoamide, which crystallised out in large, transparent, yellow plates.

*Toluene-*p*-sulphondibromoamide,*



This compound was prepared by the action of an aqueous solution of hypobromous acid on toluene-*p*-sulphonamide. The following procedure was adopted in the preparation of this and other similar compounds described in this paper. The finely-powdered sulphonamide was added to a well cooled solution of hypobromous acid * containing about twice the theoretical quantity of the latter and shaken together for some minutes in a large separating funnel; a quantity of chloroform, sufficient to dissolve the sulphondibromoamide, was then added and the shaking continued for a few minutes. To ensure the absence of unchanged sulphonamide, the chloroform solution was again shaken for a short time with a further small quantity of freshly made hypobromous acid solution. The chloroform solution, after separation and drying over fused calcium chloride, deposited the sulphondibromoamide in yellow crystals on driving off the solvent in a current of air. The yield is theoretical. The compound crystallises from chloroform, in which it is moderately soluble, in transparent, orange-coloured plates (m. p. 104°).

0·3192 liberated I = 38·8 c.c. *N*/10 I. Br as NBr = 48·59.
$C_7H_7O_2NBr_2S$ requires Br as NBr = 48·59 per cent.

When the melted substance is heated rapidly, it decomposes explosively, liberating bromine and toluene-*p*-sulphonic bromide.

Potassium toluene-p-*sulphonbromoamide*, $CH_3 \cdot C_6H_4 \cdot SO_2K{:}NBr,2H_2O$.

This salt can be obtained either directly from the sulphonamide by dissolving it in a warm solution of potassium hydroxide, adding the theoretical quantity of bromine, and cooling, or, more easily, by dissolving finely-powdered toluene-*p*-sulphondibromoamide in a warm 20 per cent. solution of potassium hydroxide and allowing the bright yellow solution to cool. The potassium salt then crystallises out in beautiful, transparent, pale yellow, six-sided plates containing 2 molecules of water of crystallisation.

0·5242 liberated I = 32·2 c.c. *N*/10 I. Br as NBr = 24·56.
$C_7H_7O_2NBrSK,2H_2O$ requires Br as NBr = 24·65 per cent.

When kept for some days over phosphoric oxide in a vacuum, the crystals lose their water of crystallisation and become opaque. The water is also lost when the salt is heated nearly to 100°.

0·4201 of the anhydrous salt liberated I = 29·1 c.c. *N*/10 I. Br as NBr = 27·69.
$C_7H_7O_2NBrSK$ requires Br as NBr = 27·74 per cent.

When heated, the dry salt does not melt, but decomposes with a feeble explosion at about 145—150°.

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* This solution was made by shaking bromine with precipitated mercuric oxide suspended in water.

Sodium toluene-p-*sulphonbromoamide*, $CH_3 \cdot C_6H_4 \cdot SO_2Na\!:\!NBr, 3H_2O$.

This compound, like the potassium salt, can either be obtained by adding bromine to a solution of the sulphonamide in sodium hydroxide or by dissolving the sulphondibromoamide in a warm 20 per cent. solution of sodium hydroxide. It separates from the warm alkaline solution in long, transparent, pale yellow, flattened prisms, which contain 3 molecules of water of crystallisation.

0·4437 liberated I = 27·3 c.c. $N/10$ I. Br as NBr = 24·60.

$C_7H_7O_2NBrSNa, 3H_2O$ requires Br as NBr = 24·51 per cent.

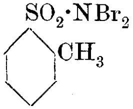
When dried over phosphoric oxide in a vacuum or at 100°, it loses its water of crystallisation, and the crystals, while retaining their outward shape, become opaque.

0·4094 of the anhydrous salt liberated I = 30·1 c.c. $N/10$ I. Br as NBr = 29·39.

$C_7H_7O_2NBrSNa$ requires Br as NBr = 29·38 per cent.

When heated, the anhydrous salt does not melt, but decomposes with a feeble explosion at about 145—150°.

Toluene-o-*sulphondibromoamide*,



This substance was prepared exactly as the para-derivative; it is readily soluble in chloroform and very slightly in petroleum. When dissolved in warm chloroform and a little warm light petroleum added, it separates, on cooling, in transparent, orange-coloured, four-sided rhombic plates (m. p. 80°).

0·5444 liberated I = 66·2 c.c. $N/10$ I. Br as NBr = 48·62.

$C_7H_7O_2NBr_2S$ requires Br as NBr = 48·59 per cent.

When heated rapidly above its melting point, it decomposes explosively.

Potassium toluene-o-*sulphonbromoamide*, $CH_3 \cdot C_6H_4 \cdot SO_2K\!:\!NBr, H_2O$, was prepared from a 20 per cent. solution of potassium hydroxide; it crystallises in pale yellow, six-sided plates.

0·3370 liberated I = 21·9 c.c. $N/10$ I. Br as NBr = 25·98.

0·2427, when dried for 6 days over phosphoric oxide in a vacuum, lost 0·0135 H_2O. H_2O = 5·56.

$C_7H_7O_2NBrSK, H_2O$ requires Br as NBr = 26·11. H_2O = 5·88 per cent.

When the dry salt is heated, it decomposes at about 130—135°.

*Sodium toluene-*o-*sulphonbromoamide*, $CH_3 \cdot C_6H_4 \cdot SO_2Na{:}NBr,H_2O$, was prepared from a 20 per cent. solution of sodium hydroxide; it crystallises in long, slender, pale yellow, flattened prisms.

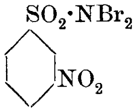
0·1908 liberated I = 12·9 c.c. *N*/10 I. Br as NBr = 27·03.
$C_7H_7O_2NBrSNa,H_2O$ requires Br as NBr = 27·55 per cent.

This salt loses its water of crystallisation with extreme slowness over phosphoric oxide, but on heating at 100° water is driven off, although the salt also suffers a slight decomposition, as these bromo-derivatives are not so stable as the salts of the chloroamides.

0·3210, when heated at 100° for 2 hours, lost 0·0247 H_2O. H_2O = 7·69.
$C_7H_7O_2NBrSNa,H_2O$ requires H_2O = 6·21 per cent.

When heated, the anhydrous salt does not melt, but decomposes explosively at about 135—140°.

*Nitrobenzene-*m-*sulphondibromoamide*,

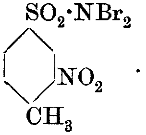


In the preparation of this compound, a large quantity of chloroform must be used on account of its sparing solubility. If a small quantity only of the solvent is used, the greater part of the dibromoamide remains undissolved. It is moderately soluble in boiling chloroform and crystallises from the solvent in transparent, orange rhombs, which melt at about 157° with some decomposition, the melted substance reddening and evolving some gas. When rapidly heated to a high temperature, as by placing a small quantity in a melting-point tube into a flame, it decomposes explosively.

0·4382 liberated I = 48·6 c.c. *N*/10 I. Br as NBr = 44·34.
$C_6H_4O_4N_2Br_2S$ requires Br as NBr = 44·41 per cent.

When warmed with solutions of potassium and sodium hydroxides, it dissolves, forming salts which crystallise out, on cooling the solutions, in pale yellow, glittering plates containing water of crystallisation. When anhydrous, they have the composition $NO_2 \cdot C_6H_4 \cdot SO_2[K,Na]{:}NBr$, and decompose explosively when heated.

2-*Nitrotoluene*-p-*sulphondibromoamide*,



This dibromoamide was prepared exactly as the preceding compound, which it closely resembles in solubility and properties. It crystallises from boiling chloroform, in which it is sparingly soluble, in short, orange-coloured, four-sided, transparent prisms; these melt with decomposition at 142—143°.

0·8035 liberated I = 85·4 c.c. $N/10$ I. Br as NBr = 42·49.
$C_7H_6O_4N_2Br_2S$ requires Br as NBr = 42·74 per cent.

When heated quickly to a high temperature, it decomposes explosively; it dissolves in a solution of sodium or potassium hydroxide, forming salts of the monobromoamide, which crystallise in pale yellow plates.

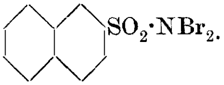
Benzene-m-*disulphontetrabromoamide*, $C_6H_4(SO_2{\cdot}NBr_2)_2$.

This compound was first prepared with some difficulty by Hoogewerff and van Dorp (*Rec. Trav. Chim.*, 1889, **8**, 173) by adding a dilute solution of silver nitrate to a complex salt, which they obtained as a yellow precipitate on adding acetic acid to a solution of benzene-*m*-disulphonamide in alkaline potassium hypobromite. It also can be prepared quantitatively and with the greatest ease by the action of a solution of hypobromous acid on the amide. On adding a saturated aqueous solution of benzene-*m*-disulphonamide to an excess of a well cooled solution of hypobromous acid, benzene-*m*-disulphontetrabromoamide separates almost at once as an orange-yellow, crystalline powder, which can be filtered off, washed, and dried, first by pressing between filter paper, and finally over phosphoric oxide in a vacuum. The following analysis of a specimen so prepared shows that it is perfectly pure.

0·3370 liberated I = 48·8 $N/10$ I. Br as NBr = 57·89.
$C_6H_4O_4N_2Br_4S_2$ requires Br as NBr = 57·93 per cent.

The compound may be recrystallised from chloroform, in which it is sparingly soluble.

Naphthalene-2-sulphondibromoamide,



This compound crystallises from warm chloroform, on adding a little light petroleum, in deep orange-coloured, four-sided plates. It melts with decomposition and evolution of gas at 90—95°.

0·3550 liberated I = 38·6 c.c. *N*/10 I. Br as NBr = 43·47.
$C_{10}H_7O_2NBr_2S$ requires Br as NBr = 43·80 per cent.

It dissolves in warm solutions of potassium and sodium hydroxides, forming salts of the monobromoamide which crystallise in small, pale yellow plates.

Arylsulphonalkylbromoamides.

The sulphonalkylbromoamides are very easily prepared by shaking a chloroform solution of the sulphonalkylamide with an excess of an aqueous solution of hypobromous acid and proceeding as before described. The presence of free bromine is best avoided, and when preparing compounds containing ethyl or benzyl a little precipitated mercuric oxide may with advantage be added to the solution of hypobromous acid, the chloroform solution of the bromoamide being filtered from this at the pump previous to separating and drying. It is also generally advisable to ensure the complete conversion of the amide by shaking a second time for a few minutes with freshly prepared hypobromous acid. A number of typical compounds have been prepared. The methyl compounds are the most stable and may be kept for a long time unchanged; the benzyl derivatives, on the other hand, rapidly decompose, even over phosphoric oxide, and when light is excluded. On heating strongly above their melting points, they all decompose with reddening and evolution of gas.

Benzenesulphonmethylbromoamide, $C_6H_5\cdot SO_2\cdot NBr\cdot CH_3$.—This compound is sparingly soluble in chloroform; it crystallises in beautifully brilliant, transparent, pale yellow plates, which appear to be flattened rhombs (m. p. 107°).

0·5338 liberated I = 42·7 c.c. *N*/10 I. Br as NBr = 31·98.
$C_7H_8O_2NBrS$ requires Br as NBr = 31·97 per cent.

Benzenesulphonbenzylbromoamide, $C_6H_5\cdot SO_2\cdot NBr\cdot CH_2\cdot C_6H_5$.—This compound crystallises in clusters of very pale yellow, four-sided prisms (m. p. 104°). On heating above its melting point, it decomposes with reddening and effervescence at about 140°.

0·3805 liberated I = 23·4 c.c. *N*/10 I. Br as NBr = 24·59.
$C_{13}H_{12}O_2NBrS$ requires Br as NBr = 24·52 per cent.

It slowly decomposes, even when kept excluded from the light in a dry atmosphere. To gain a rough idea of the rapidity of this change, a quantity of the pure compound was placed in a desiccator over phosphoric oxide. After two days, it had obviously slightly decomposed, a smell resembling benzaldehyde was noticed, and on analysis the percentage of Br as NBr was found to be 24·05 per cent.

Toluene-p-*sulphonmethylbromoamide*, $CH_3·C_6H_4·SO_2·NBr·CH_3$.—This compound crystallises from warm chloroform on adding a little petroleum in pale yellow, apparently four-sided prisms (m. p. 112°). When heated above its melting point, it decomposes with reddening and effervescence at about 160°.

0·4810 liberated I = 36·6 c.c. *N*/10 I. Br as NBr = 30·42.
$C_8H_{10}O_2NBrS$ requires Br as NBr = 30·27 per cent.

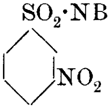
Toluene-p-*sulphonethylbromoamide*, $CH_3·C_6H_4·SO_2·NBr·C_2H_5$.—This compound crystallises in bright yellow, glittering, transparent, four-sided prisms (m. p. 113°). On heating further, it decomposes with reddening and evolution of gas at about 150°.

0·4856 liberated I = 35·1 c.c. *N*/10 I. Br as NBr = 28·89.
$C_9H_{12}O_2NBrS$ requires Br as NBr = 28·74 per cent.

Toluene-p-*sulphonbenzylbromoamide*, $CH_3·C_6H_4·SO_2·NBr·CH_2·C_6H_5$.—This compound forms clusters of transparent, four-sided, rhombic plates, having an exceedingly pale yellow colour; its solution in chloroform is, however, distinctly yellow. It melts at 149°. On heating a few degrees higher to about 156°, it decomposes with reddening and evolution of gas.

0·6705 liberated I = 39·4 c.c. *N*/10 I. Br as NBr = 23·49.
$C_{14}H_{14}O_2NBrS$ requires Br as NBr = 23·50 per cent.

Nitrobenzene-m-*sulphonmethylbromoamide*,



—This compound crystallises from chloroform, in which it is moderately soluble, in transparent, pale yellow, four-sided rhombic plates (m. p. 149°). When heated strongly, it decomposes with reddening and evolution of gas about 180°.

0·4923 liberated I = 33·2 c.c. *N*/10 I. Br as NBr = 26·96.
$C_7H_7O_4N_2BrS$ requires Br as NBr = 27·09 per cent.

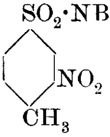
Nitrobenzene-m-*sulphonbenzylbromoamide*,

$NO_2\cdot C_6H_4\cdot SO_2\cdot NBr\cdot CH_2\cdot C_6H_5$.

—This compound is moderately soluble in warm chloroform, forming a distinctly yellow solution, from which it crystallises in clusters of very slender prisms having a faint yellow colour ; it melts at 147°.

0·3959 liberated I = 21·4 c.c. *N*/10 I. Br as NBr = 21·61.
$C_{13}H_{11}O_4N_2BrS$ requires Br as NBr = 21·54 per cent.

2-*Nitrotoluene*-p-*sulphonmethylbromoamide*,



—This substance crystallises from warm chloroform, in which it is moderately soluble, in yellow, transparent, short, six-sided prisms ; it melts at 117°. When heated further it darkens, becomes red, and decomposes with evolution of gas at about 180°, as does also the ethyl compound.

0·5158 liberated I = 33·2 c.c. *N*/10 I. Br as NBr = 25·73.
$C_8H_9O_4N_2BrS$ requires Br as NBr = 25·86 per cent.

2-*Nitrotoluene*-p-*sulphonethylbromoamide*,

$NO_2\cdot C_6H_3Me\cdot SO_2\cdot NBr\cdot C_2H_5$.

—This compound crystallises in glittering, transparent, pale yellow rhombs (m. p. 96°).

0·5774 liberated I = 35·9 c.c. *N*/10 I. Br as NBr = 24·86.
$C_9H_{11}O_4N_2BrS$ requires Br as NBr = 24·74 per cent.

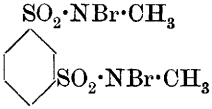
2-*Nitrotoluene*-p-*sulphonbenzylbromoamide*,

$NO_2\cdot C_6H_3Me\cdot SO_2\cdot NBr\cdot CH_2\cdot C_6H_5$.

—This compound crystallises from chloroform, in which it is only sparingly soluble, in clusters of extremely slender, flattened prisms, having a very faint yellow colour (m. p. 151°).

0·4421 liberated I = 23·1 c.c. *N*/10 I. Br as NBr = 20·89.
$C_{14}H_{13}O_4N_2BrS$ requires Br as NBr = 20·76 per cent.

Benzene-m-*disulphon*-s-*dimethyldibromoamide*,



—This compound crystallises from chloroform, in which it is sparingly soluble, in very pale yellow, four-sided plates.

0·3744 liberated I = 35·3 c.c. *N*/10 I. Br as NBr = 37·69.

$C_8H_{10}O_4N_2Br_2S_2$ requires Br as NBr = 37·87 per cent.

It melts at 176° with slight reddening; if maintained at this temperature for a few seconds, or heated a few degrees higher, it decomposes, becoming deep red in colour and liberating bubbles of gas.

Various reactions of the sulphondibromoamides and of the sulphonalkylbromoamides are being studied.

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