

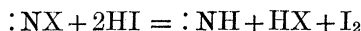
The Action of Chlorine upon Urea whereby a Dichloro Urea is produced.

By FREDERICK DANIEL CHATTAWAY, F.R.S.

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Although a few of the more familiar substances containing halogen attached to nitrogen, as, for example, nitrogen chloride, have been known for a long period, it is only within the last 10 years that such compounds have been systematically studied. They form, however, a group of extraordinary interest and play an all important part in many complex reactions; to illustrate this it is only necessary to refer to the substitution of halogen in anilides and to the well-known method for obtaining amines from amides. I have shown in a series of investigations that hydrogen attached to nitrogen in compounds of the most varied characters may be replaced with ease by chlorine or bromine if suitable conditions are observed and it may be said, speaking generally, that this can always be done, although the nitrogen halogen derivatives produced may react or undergo isomeric change so readily that they can only with difficulty be isolated.

All compounds in which halogen is directly attached to trivalent nitrogen can take part in certain well-defined reactions characteristic of the linkage. One of the most striking of these group reactions is that with hydriodic acid, whereby at the ordinary temperature the halogen is replaced by hydrogen and iodine is liberated quantitatively. This reaction, which may be expressed by the general equation



affords an easy method of analysing these compounds.

Such a nitrogen halogen derivative is formed as an intermediate product in a reaction with urea, the course of which has never hitherto been explained although it has received an unusual amount of attention on account of its furnishing a ready method of estimating the quantity of this substance present in a liquid.

When urea is added to a solution of an alkaline hypochlorite or hypobromite it is at once decomposed, nitrogen and carbon dioxide being set free; if an excess of alkali is used the carbon dioxide is fixed and the nitrogen, which alone escapes, should thus afford a measure of the amount of urea. The reaction is generally represented by the equation:—



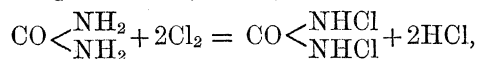
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which throws no light upon its nature; indeed it obscures it, as it makes it appear to be a case of oxidation. It does not even express quantitatively what takes place, for all chemists who have investigated the decomposition have noted that the amount of nitrogen liberated is invariably less than that contained in the urea used. When the operations are carried out under specified conditions this loss of nitrogen, which may amount to as much as half of the total, is very constant and so can be allowed for by adding a definite fraction of the whole to the gas actually measured. The method can thus be made to give results sufficiently accurate for clinical purposes and since it is easy to carry out it has received very general application. It is not known what becomes of the nitrogen which does not appear as gas, for all the suggestions that have been made hitherto wholly fail to account for more than a small fraction of the quantity that disappears.

If urea be added instead of to an alkaline solution of a hypochlorite to one acidified by acetic acid, that is to a solution of hypochlorous acid no gas is evolved, nor is any gas liberated if chlorine itself is passed into a solution of urea in acetic acid. Action, however, takes place in each case and a nitrogen chloride is produced; for although the hypochlorous acid or chlorine disappears, the resulting solution liberates iodine in large quantity from hydriodic acid.

The isolation of the substance produced from such a solution is not practicable, since the method of extraction by chloroform which often serves for the separation of substituted nitrogen chlorides cannot be used, as the chloro urea formed is easily soluble in water but almost insoluble in chloroform. It is, however, less soluble in water than urea itself and crystallises out in a pure condition when chlorine in excess is passed rapidly through a cooled sufficiently strong aqueous solution of urea. The action which takes place is represented by the equation



two only of the four hydrogen atoms of the urea being replaced by chlorine.

This dichloro derivative appears to be the only stable nitrogen chloride which urea is capable of forming. The crystals which separate from the solution of urea have this composition from the first and chlorine seems to have no further substituting action upon them.

Dichloro urea, having regard to its mode of formation, as well as to the structure of urea itself, has most probably the constitution represented by

the formula $\text{O}:\text{C} \begin{smallmatrix} \text{N} < \text{Cl} \\ & \text{H} \\ \text{N} < \text{H} \\ & \text{Cl} \end{smallmatrix}$, which explains its formation and such of its

reactions as have yet been studied.

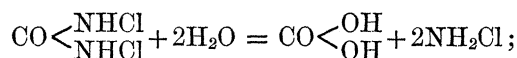
If this constitution be granted it seems probable that the reaction between urea and chlorine takes place in two stages and that the amino groups are substituted successively, but the monochloro derivative does not crystallise out, possibly owing to its solubility being not far removed from that of urea itself. Either of two causes may prevent the formation of a ter- or tetrachloro derivative; the hydrochloric acid which is formed in the reaction may prevent that addition of chlorine to the nitrogen which must precede further substitution, or the more highly substituted urea may be hydrolysed so easily that it breaks up as soon as it is formed. Dichloro urea is so much more easily hydrolysed than urea itself that the latter is the more probable cause.

Although two molecules of hydrogen chloride are formed when urea is substituted by chlorine, very little heat is developed, dichloro urea must therefore be an endothermic compound and might be expected to be highly explosive. When heated, however, it does not explode itself but decomposes with liberation of nitrogen chloride which, if heated a few degrees above the temperature at which it is set free, may detonate with great violence.

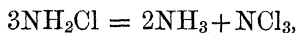
Dichloro urea gives all the characteristic reactions of a typical nitrogen chloride; for instance, it liberates iodine from hydriodic acid, chlorine from hydrochloric acid, and reacts with alcohol, forming ethyl hypochlorite, urea being in each case re-formed.

It is distinguished from most other substituted nitrogen chlorides by the readiness with which it is hydrolysed in presence of water, nitrogen chloride, carbon dioxide, a little nitrogen and ammonium chloride being formed. If the compound is dissolved in water or kept in a moist atmosphere, this hydrolysis takes place slowly at the ordinary temperature and becomes very rapid at about 30° C.

It is probable that in this reaction a mono-substituted ammonia is first produced thus:—



but if so it apparently can only exist momentarily, as nitrogen chloride is at once liberated. The formation of the end products of the reaction can be explained by assuming that this monochloro ammonia at once breaks up into ammonia and nitrogen chloride,

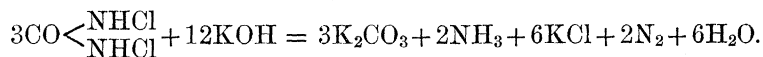


which then to some extent react, forming nitrogen and hydrogen chloride, the latter at once combining with the free ammonia and allowing the remaining

nitrogen chloride to escape, as this does not react with ammonium chloride. Both acids and alkalis accelerate the rate of hydrolysis and also alter the nature of the end products by hindering or furthering the secondary reaction between the ammonia and the nitrogen chloride.

In presence of dilute acids the ammonia is at once fixed and the reaction between it and the nitrogen chloride with its accompanying liberation of nitrogen is prevented, all the chlorine contained in the dichloro urea is therefore liberated as nitrogen chloride. In presence of alkalis, on the other hand, the reaction between the ammonia and the nitrogen chloride goes on to completion, since the hydrochloric acid formed in it is at once fixed; no nitrogen chloride, therefore, is set free, since twice as much ammonia is formed as is required to decompose it.

The reaction between dichloro urea and a solution of caustic potash is instantaneous: nitrogen is liberated with violent effervescence, the excess of ammonia and the alkaline carbonate formed remaining dissolved in the liquid. The action, which is quantitative, is expressed by the equation



The behaviour of dichloro urea with alkalis affords an explanation of the course of the reaction which occurs when urea is decomposed either by an excess of alkaline hypochlorite or hypobromite. The urea is, without doubt, converted into dichloro or dibromo urea,* which is at once hydrolysed in the manner above described. In presence of the excess of hypochlorite or hypobromite, the mono-substituted ammonia formed in the hydrolysis may be further substituted to a greater or less extent, nitrogen being evolved quantitatively only when this takes place under such conditions that the amount of hydrogen attached to nitrogen in the reacting system is always sufficient to react completely with the chlorine attached to nitrogen.

Preparation of Dichloro Urea.—The preparation of dichloro urea should be carried out at a low temperature and as rapidly as possible, since, in presence of the hydrochloric acid formed at the same time, hydrolysis so readily occurs and so much nitrogen chloride is produced that if it is carried out at the ordinary temperature, or its duration is unnecessarily prolonged, a poor yield is obtained. It is best, therefore, to work with small quantities, to cool thoroughly, and to pass the chlorine as rapidly as possible.

* It is possible that in absence of free acid, and in presence of excess of hypochlorite or hypobromite, a tri- or tetra- substitution product may be produced, the formation and decomposition of which can be formulated easily, but this does not affect the essential character of the reaction, which is one of halogen substitution followed by hydrolysis of the substituted urea and interaction between the resulting compounds.

The following procedure gives a good result:—Dissolve 20 grammes of urea in 40 c.c. of water and cool to about -10° C. in a mixture of alcohol and crushed ice.* Pass in as rapidly as practicable a stream of chlorine made by dropping strong hydrochloric acid upon bleaching powder. So little heat is evolved in the reaction that with proper cooling the temperature never rises above zero, however rapid the stream of chlorine. Nitrogen chloride is produced from the first and can be recognised by its characteristic smell, but it remains in solution, the liquid, owing to its presence, becoming bright yellow in colour. After passing the chlorine for a considerable time, white crystals make their appearance, at first usually on the surface of the liquid; these increase in amount till the whole becomes a pulp of thin colourless plates. When these no longer appear to increase in amount, filter off, separating the acid mother liquor as completely as possible; wash once or twice with a little water and when as much of the latter as possible has been removed wash the crystals several times with dry chloroform. Dichloro urea is not appreciably soluble in cold chloroform and a good deal of adhering moisture is thus got rid of. Press finally between filter paper, spread out in a thin layer on a clock glass, and free from the last traces of water by exposing for about half an hour over phosphoric oxide in a vacuum.

A further crop of crystals can be obtained by again passing chlorine through the cooled mother liquor and this can be repeated as long as any separate. Nothing besides dichloro urea and the products of its hydrolysis are formed in the reaction; if the acid mother liquor is evaporated down, carbon dioxide is given off and nitrogen chloride escapes in quantity; later, as the liquid becomes concentrated, hydrogen chloride is expelled, and finally ammonium chloride is left.

Although the final result of the action which takes place is the substitution of two atoms of hydrogen by two atoms of chlorine, as in other similar cases, this is without doubt effected by the addition of four atoms of chlorine to the nitrogen followed by the elimination of two molecules of hydrogen chloride.

The yield of dichloro urea is not very large, so much being hydrolysed during the process: in a well conducted experiment it reaches about 25 per cent. of the theoretical, the weight of pure dry product obtained amounting as a rule to rather more than half the weight of the urea used. The loss, although largely due to the hydrolysis of the compound, is much increased by the

* It is not absolutely necessary to use a freezing mixture, the temperature, owing to the urea dissolving, falls at once to below zero, and if the flask in which the operation is carried out is cooled by tap-water, a moderate amount of the compound can be obtained, but the yield is much better at a lower temperature.

circumstance that dichloro urea is very soluble in water and consequently a considerable amount does not crystallise out from the mother liquor.

Dichloro urea reacts with an aqueous solution of hydriodic acid in the way characteristic of nitrogen chlorides; urea is reformed and iodine quantitatively liberated. It was analysed by taking advantage of this reaction: a known weight was added to an excess of a solution of potassium iodide made acid by acetic acid and the iodine liberated estimated by a standard solution of sodium thiosulphate.

0.5112 gramme liberated iodine = 158.6 c.c. N/10 I.

Cl, as :NCl = 54.99 per cent.

CON₂H₂Cl₂ requires Cl, as :NCl = 54.96 per cent.

Dichloro urea cannot be kept for any length of time without change. When damp it hydrolyses exactly as when dissolved in water. To obtain it pure, therefore, it must be dried very rapidly over phosphoric oxide in a vacuum. When only freed from adhering water as far as possible by a pump, it is slowly hydrolysed by the retained moisture even though placed in a desiccator over strong sulphuric acid, and this often occurs to such an extent that the mass becomes quite yellow from the nitrogen chloride mechanically retained by the crystals. To show the amount of hydrolysis which takes place under these conditions a quantity of the pure substance freed from all but adhering water thus was kept over strong sulphuric acid, and analysed from time to time, the nitrogen chloride formed being allowed occasionally to escape. In two days the percentage of chlorine as :NCl had fallen to 43.79 and in seven days to 13.33.

Even when dried and kept over phosphoric oxide it slowly decomposes, nitrogen chloride being evolved. A quantity of the pure dry compound thus preserved in a vacuum over phosphoric oxide was analysed at intervals; after 12 hours the percentage of Cl as :NCl had fallen to 54.67, after two days to 52.97, and after nine days to 47.87 per cent.

When an aqueous solution is kept at the ordinary temperature the dichloro urea is slowly hydrolysed; carbon dioxide, a little nitrogen and nitrogen chloride escape and ammonium chloride remains in solution. Hydrolysis by water takes many days to complete unless the aqueous solution is warmed, when it is much more rapid; at about 20° bubbles of gas are freely evolved and rapid effervescence sets in at about 40°, the nitrogen chloride escaping without explosion.

Dichloro urea prepared as described above is a soft, white, crystalline powder with a pearly lustre. Under the microscope it is seen to consist of thin transparent plates somewhat irregular in shape. It can be recrystallised

from water, in which it is easily soluble and from which it separates in similar but larger plates, by cooling an aqueous solution saturated at about 15° C. though with some loss owing to hydrolysis. Its aqueous solution is at first colourless but becomes yellow as hydrolysis proceeds, owing to the liberation of yellow nitrogen chloride which remains dissolved in the water. It is easily soluble in alcohol and ether, very slightly soluble in chloroform and insoluble in petroleum ether. When its alcoholic solution is heated it reacts in the way characteristic of nitrogen chlorides, urea is reformed and ethyl hypochlorite is produced, the latter very easily breaking down into aldehyde and hydrogen chloride.

Its behaviour with acids is complicated by the circumstance that it is so readily hydrolysed; for example, when it is added to strong hydrochloric acid though chlorine is rapidly given off the amount of urea reformed is not very large. When placed in cold strong sulphuric acid it is hydrolysed and nitrogen chloride is liberated. The latter decomposes into its elements if the liquid be heated, its characteristic smell disappearing and being replaced by that of chlorine.

Dichloro urea is a compound of a marked acid character, it has an acid taste recalling that of hypochlorous acid and its aqueous solution strongly reddens litmus paper, which only becomes bleached after the lapse of some minutes. It acts very corrosively upon the skin, staining it yellow and destroying the tissues.

When heated, dichloro urea melts with decomposition at about 83° , nitrogen chloride being liberated. Although the substance appears not itself to explode, if the temperature of the bath in which the melting point is being taken is allowed to rise at all rapidly a few degrees above this point, the nitrogen chloride set free in the melting point tube may explode with considerable violence.

It can be decomposed without danger by throwing it into a porcelain dish heated to 100° on a water bath in quantities of not more than about half a gramme at a time. The white compound fuses and gives off nitrogen chloride as a yellow vapour which escapes quietly unless, through too large a quantity of material having been decomposed at once, some of the vapour is mechanically retained as bubbles in the semi-fused residue and thus becomes heated to the temperature at which it explodes. Hydrogen chloride is not set free when dichloro urea is thus decomposed by heat.

When an aqueous solution of the compound is added to a solution of caustic soda, vigorous effervescence, due to escape of nitrogen, occurs. The liquid remaining contains ammonia and potassium carbonate, the volume of carbon dioxide liberated when this is treated with an acid being to the volume of

nitrogen previously liberated in the ratio of 3 to 2. One-third of the nitrogen contained in the dichloro urea used is found as ammonia.

The investigation of dichloro urea, which is an extremely reactive body and promises to be of considerable use in organic synthesis, is being continued.

The thanks of the author are due to Dr. Baker for allowing him to use the Christ Church Laboratory, where this work has been carried out.

*Note on the Instability of Tubes subjected to End Pressure, and
on the Folds in a Flexible Material.*

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When a straight rod is subjected to end compression it is stable for small lateral displacements unless the compressing force exceeds a definite limit depending on the elastic constants of the material of the rod and its length and cross section dimensions.

If this limit is exceeded, the rod is unstable and the least departure from straightness grows under the action of the force, the axis of the rod then taking the form of one of the well-known elastic curves; and this is the only form which a solid rod can take in the circumstances.

With tubes and plates, however, the case is different, for with the tube the ratio of the thickness of the walls to the diameter of the tube has to be considered as well as the ratio of the diameter to the length. Thus a tube whose length is insufficient to produce instability involving a bending of the axis may become unstable by the crumpling up of the walls, the axis itself remaining straight.

In plates something of the same kind may take place. The edges of a rectangular plate may be constrained to remain straight and parallel to one another, but if pressure is applied to two opposite edges instability will ensue if it exceeds a critical value.

In the case of solid rods the governing condition is the constancy (to the first order) of the length of the axis; with tubes and plates it is the constancy to the same order of the area of the mid-wall surface. Considering the case of tubes in rather more detail, take the axis of the tube as z and let its unstrained radius be r_0 .