XLVIII. — *Chemistry of the Compounds of Thiourea and Thiocarbimides with Aldehyde-ammonias.*

By AUGUSTUS E. DIXON, M.D., Professor of Chemistry, Queen's College, Cork.

SOME years ago (Trans., 1888, 411), I laid before this Society an account of the interaction of the "mustard oils" with the aldehyde-ammonias, in which it was shown that the action is a generic one, at least for the thiocarbimides containing univalent hydrocarbon residues. Thus, it was found that, under similar conditions, 1 mol. of ethyl-, allyl-, phenyl-, benzyl-, and orthotolyl-thiocarbimides, respectively, combine with 2 mols. of acetaldehyde-ammonia, with elimination of both the oxygen atoms of the latter, in the form of water. Further, it was shown that phenyl- and benzyl-thiocarbimides combine readily with isovaleraldehyde-ammonia, yielding similar products.

The equations representing these interactions were provisionally formulated, thus:—

the valeraldehyde derivatives being considered as similar in type, namely, $\text{CS} \begin{smallmatrix} \text{NR}\cdot\text{CH}(\text{C}_4\text{H}_9) \\ \text{NH}\cdot\text{CH}(\text{C}_4\text{H}_9) \end{smallmatrix} \text{NH}$.

In this connection, attention was drawn to a compound obtained by Nencki (*Ber.*, 7, 162) from the interaction of thiourea itself with aldehyde-ammonia; and the suggestion was put forward that this substance, regarded by the discoverer "as an ammonia compound of diethylidenesulphourea" and formulated as $\left\{ \begin{smallmatrix} \text{CS} \\ (\text{C}_2\text{H}_4)_2 \end{smallmatrix} \right\} \text{N}_2\cdot\text{NH}_3$, might, perhaps, be similar in structure to the thiocarbimide derivatives already mentioned: representing, in fact, the parent type, of which the latter are the substitution products. On this view, the formation of the compound was provisionally explained as follows:—

The object of the present investigation was to endeavour to acquire some further knowledge of the chemistry of these substances, with a view, first, to ascertain whether Nencki's and the thiocarbimide compounds are really members of the same class; secondly, to gain, if possible, some information regarding their structure; and, thirdly, to learn whether the process of their formation can be extended to other varieties of thiocarbimides and aldehydes. Advantage has been taken of the opportunity to prepare the methyl derivative of the thiocarbimide series, and a homologue of Nencki's compound has been obtained. The experimental results are detailed below.

Thiourea and Aldehyde-ammonia.

Nencki (*loc. cit.*) obtained the compound by boiling an aqueous solution containing 2 mol. proportions of aldehyde-ammonia to 1 of the amide. Boiling water, however, so readily decomposes the product that the yield by this method always falls considerably below the theoretical. But if the aldehyde-ammonia, dissolved in cold or tepid water, be added to the thiourea solution near its boiling point, the addition of some crystals of the ready-formed compound, prepared by boiling a few drops of the mixture in a test-tube, at once determines the separation of a considerable quantity of the substance, though the temperature of the mixture be comparatively low. The liquid is now rapidly cooled, and the crystals removed by filtration; on boiling the filtrate, a second crop is obtained. By this means, the yield amounts to about 85 per cent. of the theoretical.

In its ready decomposability into its constituents on boiling the solution,* this substance resembles the thiocarbimide compounds; the latter can only be recrystallised with heavy loss, even from alcohol. The substance is, as Nencki states, very sparingly soluble in alcohol; it is practically insoluble in ether, benzene, and chloroform. 180° , the melting point recorded by him, is substantially correct; according to my experiments, the substance, when carefully purified by repeated recrystallisation, melts between 183° and 184° (uncorr.) to a deep, bromine-coloured liquid, which immediately decomposes with evolution of gas.

Picrate.—A compound with picric acid was obtained by mixing an alcoholic solution of it with a warm aqueous solution of the base. Fine, hair-like needles separated on cooling, which, on recrystallisation from hot water, were obtained in lemon-yellow prisms, several centimeters in length. This salt does not melt at 230° , but, when

* 100 parts (14 grams) of the compound, almost pure, gave on recrystallisation from boiling water only 42 parts.

heated over a gas flame, it darkens and decomposes, melting quietly, at a high temperature, to a blackish liquid with evolution of gas.

A portion, dried over sulphuric acid, gave the following results on analysis:—

0.1937 gram of substance, burnt with copper oxide, gave 37.9 c.c. nitrogen, measured at 17° and 748.6 mm.

	Calculated for $C_5H_{11}N_3S, C_6H_5(NO_2)_3 \cdot OH.$	Experiment.
N	22.51 per cent.	22.49 per cent.

Action of Silver Nitrate.—Equimolecular proportions of base and silver nitrate were mixed in cold aqueous solution. A bulky, white precipitate at once appeared, consisting of delicate, flexible, silky needles; it is very unstable, soon losing its lustrous appearance and becoming dark-coloured, even though the solutions be cooled to near the freezing point. It was drained on the filter-pump, rapidly washed with water, and dried over sulphuric acid.

As the filtrate was not acid to test-paper, it seemed unlikely that a silver substitution derivative was in hand. The substance was, in fact, easily shown to be an addition product, by boiling a portion with water and filtering from the silver sulphide thereby produced; the filtrate gave the reaction of nitric acid at once.

On analysis, the following data were obtained:—

0.4727 gram of substance, oxidised with nitric acid, yielded 0.2111 gram AgCl.

	Calculated for $C_5H_{11}N_3S, AgNO_3.$	Experiment.
Ag	34.24 per cent.	33.61 per cent.

A similar preparation was next made, using 2 mol. proportions of silver nitrate (alcoholic) to 1 of the aldehyde-ammonia compound. A silver determination gave the following result:—

0.3492 gram of substance, oxidised with nitric acid, yielded 0.1532 gram AgCl, or Ag = 33.02 per cent.

From this it follows that the compound $C_5H_{11}N_3S, 2AgNO_3$, which would require 44.49 per cent. of silver, has not been produced; but the compound (which could not be obtained quite pure) is identical with the preceding.

Action of Water upon the Silver Compound.—The nature of this action was next investigated. When placed in contact with cold water, the silver compound soon begins to darken, and in a short time the mixture becomes black. If warmed with water, the decom-

position sets in at once; aldehyde—easily recognised by its odour—is evolved, and a brilliant speculum of silver sulphide is formed on the sides of the tube.

Since the molecule contains but one atom of silver to one of sulphur, the decomposition by water can only* involve elimination of half the sulphur in combination with the metal. The filtrate from the sulphide, after previous boiling until aldehyde ceases to be evolved, does, in fact, contain sulphur in solution; thus, it gives a black precipitate with ammoniacal silver nitrate, and is readily desulphurised by warming with alkaline solution of lead. These reactions suggest the presence of thiourea, as a product of the partial desulphurisation: the latter was recognised in another portion of the filtrate by Claus' method (*Annalen*, **179**, 129), namely, after treating with ethylic nitrite, ferric chloride produces an intense blood-red coloration, due (according to Claus) to the conversion of the thiourea into ammonium thiocyanate. These facts may be represented by the following equation:—

Action of Acetic Anhydride.—It has been shown by R. Schiff (*Ber.*, **9**, 570) that warm acetic anhydride readily acts upon the compound of phenylthiocarbamide with aldehyde-ammonia, thereby producing acetylphenylthiourea. Further on, it will be shown that a similar reaction holds in the case of the tolylthiocarbimide aldehyde-ammonia compound. The question therefore arose, whether, under like conditions, the aldehyde groups would be split off from Nencki's thiourea derivative, or whether, on the other hand, it would simply undergo acetylation.

To ascertain this, 10 grams (1 mol.) of the substance, dried by standing over sulphuric acid, were added to acetic anhydride (rather more than 2 mols.) contained in a flask provided with a bent delivery tube; the pasty mixture, on warming, began to turn red in spots, and, on further raising the temperature, a vigorous action commenced, which the heat evolved was sufficient to complete. Gas came off freely with effervescence, and the solid rapidly dissolved forming a deep brownish-red solution.

By means of the bent delivery tube, the gas was led into water; the aqueous solution thus obtained, when treated with a few drops of ammonia and boiled with ammoniacal silver nitrate, freely reduced the latter, thus showing the presence of aldehyde, and therefore indicating disruption of the molecule.

* Unless hydrogen sulphide be liberated. In this case, as also in that of the homologue next to be described, not a trace of hydrogen sulphide was evolved.

The contents of the flask were now mixed with water; a quantity of blackish-brown, sticky oil separated, which was removed by filtration, and the brown-red filtrate twice treated with animal charcoal. A golden-yellow solution was thus obtained, which was evaporated to dryness and extracted with boiling ether. The residue left after the evaporation of the latter was dissolved in hot water, and the solution filtered; on cooling, well-formed, almost white, rhombic prisms separated, melting at about 163° . In appearance and melting point, this compound resembled acetylthiourea (m. p. 165° , Nencki and Leppert, *Ber.*, **6**, 905), and this was confirmed by the result of a nitrogen determination.

0.2126 gram of substance, burnt with copper oxide, gave 43.7 c.c. nitrogen, measured at 16.5° and 758.8 mm.

	Calculated for $\text{CSN}_2\text{H}_3\cdot\text{CO}\cdot\text{CH}_3$.	Experiment.
N	23.77 per cent.	23.86 per cent.

Under the action of acetic anhydride, therefore, Nencki's compound behaves like thiocarbimide derivatives of aldehyde-ammonia, the aldehyde groups being split off as such, together with one of the three nitrogen atoms, whilst an acetylated thiourea is left. The action may be thus represented—

but it is by no means quantitative; much decomposition occurs, and tarry-looking substances are produced, the separation of which is accompanied by heavy loss of the acetylated thiourea.

Acetylthiourea very readily parts with its sulphur; cold silver nitrate produces a white precipitate, which blackens gradually on standing, or instantly on the addition of ammonia. It is also easily desulphurised by warming with alkaline lead solution, with production of a brilliant galena speculum.

Thiourea and Isovaleraldehyde-ammonia.

The generality of the interaction between the thiocarbimides and aldehyde-ammonias having been established within the limits stated above, it remained now to be learned whether the thiourea reaction could be extended.

Isovaleraldehyde-ammonia was selected for experiment.

Thiourea (1 mol.), dissolved in boiling concentrated alcohol, was added to an alcoholic solution of the aldehyde-ammonia obtained from isovaleraldehyde (2 mols.). On heating the mixture to near its

514 DIXON: CHEMISTRY OF THE COMPOUNDS OF THIOUREA

boiling point, ammonia was freely evolved; the solution was now let cool, and the solvent allowed to evaporate at the ordinary temperature. The residue, when collected and recrystallised from alcohol, yielded fine, large, glass-clear, rhombic plates which were practically pure (about 52 per cent. of the theoretical). The mother liquors, when poured into water, gave a further crop of the crude substance.

A portion of the first crop was further purified by precipitating the alcoholic solution with water, washing the precipitate well with ether, and recrystallising from alcoholic ether. The product, a brilliant, white powder, consisting of minute, flattened, rhombic crystals, was perfectly free from the odour of valeraldehyde, and melted at 120—121°. It was dried over sulphuric acid and analysed.

- I. 0.1935 gram of substance, burnt with copper oxide, gave 30.3 c.c. nitrogen, measured at 16° and 758.4 mm.
 II. 0.2890 gram of substance gave 0.2810 gram BaSO₄.
 III. 0.3171 ,, ,, 0.3138 gram BaSO₄.

	Calculated for CSN ₃ H ₃ (C ₅ H ₁₀) ₂ .	Experiment.		
		I.	II.	III.
N	18.38 p. c.	18.31	—	— p. c.
S	13.98 „	—	13.36	13.60 „

The product is, accordingly, a homologue of Nencki's compound; its formation is thus represented:—

The substance is moderately soluble in cold alcohol, but only very sparingly in ether, which precipitates it from the alcoholic solution. In cold water it is insoluble, but on boiling gradually dissolves with decomposition, evolving valeraldehyde and ammonia. The residual solution, after cooling, gives a black precipitate with ammoniacal silver nitrate. Since the original substance, when dissolved in dilute alcohol, gives with this reagent a curdy, *white* precipitate, the presumption was that thiourea was a product of the decomposition: on applying Claus' test, it was found to be present. The substance breaks down, therefore, under the influence of water, similarly to Nencki's compound:—

Action of Silver Nitrate.—Alcoholic solutions of the constituents were mixed. On the addition of water, the silver derivative separated as a curdy, white precipitate, which was washed, first with much

water, then with a little alcohol, and finally with more water. It was free from odour.

When heated in a narrow tube, it begins to darken at about 151°, and appears to melt at 152—153°. A little gas is given off, and the residue instantly changes to a coal-black, solid mass.

A portion was dried over sulphuric acid, and the silver estimated.

0.3749 gram of substance, oxidised by nitric acid, gave 0.1374 gram AgCl.

	Calculated for $C_{11}H_{23}N_3S, AgNO_3$.	Experiment.
Ag	27.03 per cent.	27.04 per cent.

As in the case of the lower homologue, a monomolecular addition compound alone could be obtained. It is much more stable than the corresponding one previously described.

Action of Water upon the Silver Compound.—When boiled with water alone, the (dried) silver compound is very slowly attacked, as it floats, almost unwetted, on the liquid; but on the addition of a little alcohol, which facilitates admixture, decomposition rapidly commences, silver sulphide is produced, and valeraldehyde evolved, whilst thiourea and a nitrate are found in solution.

The decomposition by water may be thus represented :—

Action of Acetic Anhydride.—The valeraldehyde compound dissolves readily in hot acetic anhydride; decomposition occurs, and valeraldehyde is freely evolved. The action is thus presumably similar to that with Nencki's compound, but owing to want of material it was not investigated in detail.

Picrate.—Molecular proportions of the valeraldehyde compound and picric acid were mixed in warm alcoholic solution; on cooling, yellow needles separated, and the mixture was exposed freely to the air in order to concentrate further. Next day the needles had given place to a quantity of hexagonal crystals, and the odour of valeraldehyde was distinctly perceptible. The crystals, when recrystallised from water, yielded on analysis 22.15 per cent. of nitrogen; whilst theory would require for the picrate 18.38 per cent. On repeating the experiment, substantially the same phenomena were observed, and the resultant solid contained approximately the same amount of nitrogen as before, namely, 21.80 per cent.

As more or less valeraldehyde was evidently split off, it seemed probable that the picrate had decomposed under the continued standing in contact with alcohol and water; the preparation was therefore

516 DIXON: CHEMISTRY OF THE COMPOUNDS OF THIOUREA

again attempted, but on this occasion the yellow needles were filtered off as soon as the solution had become cold, and after being well washed with cold water, were dried over sulphuric acid. This time the odour of valeraldehyde was but faintly noticeable.

A nitrogen determination gave the following result:—

0·2251 gram of substance, burnt with copper oxide, gave 36·5 c.c. measured at 16° and 756 mm., or N = 18·79 per cent.

Calculated for $C_{11}H_{23}N_3S, C_6H_2(NO_2)_3 \cdot OH$, N = 18·38 per cent.

When heated in a narrow tube, the picrate begins to redden and shrink at 119°; but no further sign of fusion appears below 165°. From this temperature on, the substance gradually softens, but is not completely melted below 192°, when it forms a reddish-black liquid which soon evolves gas.

The nature of the foregoing decomposition was investigated. A preliminary qualitative experiment showed that the substance, when heated in aqueous solution, readily evolves valeraldehyde; whilst a new picrate separates, as the liquid cools, in long, canary-yellow prisms; the latter undergo no change when heated to 200°.

At first the idea suggested itself that this might possibly be the hitherto unknown thiourea picrate,* produced thus:—

The crystals, however, proved, on examination, to contain no sulphur; the latter was found in the mother liquor in the form of thiourea. They were purified by recrystallisation from water, dried over sulphuric acid, and completely analysed.

I. 0·2976 gram of substance gave 0·3183 gram CO_2 , and 0·0835 gram H_2O , or C = 29·16 per cent.; H = 3·11 per cent.

II. 0·2245 gram of substance gave 44·8 c.c. nitrogen, measured at 18° and 758 mm., or N = 23·12 per cent.

These results indicate that the substance is ammonium picrate.

	Calculated for $C_6H_2(NO_2)_3 \cdot ONH_4$.	Experiment.
C.....	29·24 per cent.	29·16 per cent.
H.....	2·44 ,,	3·11 ,,
N.....	22·82 ,,	23·12 ,,
O.....	45·50 ,,	—

The decomposition occurs as follows:—

* Thiourea and picric acid do not directly unite (at least under the conditions realised by me) when brought together in either aqueous or alcoholic solution.

Urea and Aldehyde-ammonia.

Numerous attempts were made, under various conditions, to cause ordinary urea to interact with acetaldehyde-ammonia, but without success, so far as the production of an oxygen analogue of the thio-urea compound is concerned.

Methylthiocarbimide and Aldehyde-ammonia.

Methylthiocarbimide and aldehyde-ammonia, both in warm alcoholic solution, were mixed in the proportions required by the equation

On cooling, the mixture set to a crystalline mass, which was drained on the filter-pump, pressed between folds of bibulous paper, and recrystallised from boiling alcohol. Rosettes of long, snowy-white needles separated, which, after being well washed with cold spirit, and dried over sulphuric acid, amounted to over 70 per cent. of the theoretical.

The formula was checked by a sulphur determination:—

0·3865 gram of substance gave 0·5711 gram BaSO₄.

	Calculated for C ₆ H ₁₃ N ₃ S.	Experiment.
S	20·13 per cent.	20·32 per cent.

When heated in a narrow tube, the substance melts at 142—143° (uncorr.) to a rich, golden-yellow liquid, which soon changes, with evolution of gas, to a deep mahogany-red.

Boiling alcohol dissolves the compound tolerably freely; but it is somewhat sparingly soluble in the cold. It dissolves readily in cold water, but the aqueous solution, on boiling, at once begins to decompose, ammonia and aldehyde are evolved, and the residual liquid, when concentrated by evaporation, deposits large, well-formed prisms, melting between 117° and 118°. This agrees with the melting point given by Andreasch (*Monats. f. Chem.*, **2**, 277) for methylthiourea, namely, 118°; a sulphur determination established its identity.

I. 0·2909 gram of substance gave 0·7432 gram BaSO₄.

	Calculated for CSN ₂ H ₃ (CH ₃).	Experiment.
S	35·55 per cent.	35·12 per cent.

The decomposition, under the influence of water,* accordingly runs a course similar to that of the thiourea compound; it may be thus formulated:—

On account of this decomposition, the substance is, of course, desulphurised by boiling with alkaline solution of lead.

Picrate.—Like the compounds above described, the methyl derivative also readily unites with picric acid. If warm alcoholic solutions be mixed, golden-yellow, hexagonal plates separate on standing; these are readily soluble in warm water, and, on cooling, come down in beautiful, yellow, iridescent prisms, which can easily, even when working on the small scale, be obtained several inches in length.

After drying over sulphuric acid, the picrate was burnt for nitrogen with the following result:—

0.2027 of substance gave 38.1 c.c. nitrogen, measured at 16° and 759 mm.

	Calculated for $\text{C}_6\text{H}_{13}\text{N}_3\text{S}_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}.$	Experiment.
N	21.69 per cent.	21.87 per cent.

This salt does not melt at 200°. When heated more strongly, it melts quietly, with decomposition, to a reddish-brown liquid.

A silver nitrate compound could not be obtained pure. On the addition of silver nitrate, and working either in aqueous or alcoholic solution, a sticky, clotted precipitate forms, which is very unstable, beginning to darken almost as soon as produced, and becoming in a few minutes black and tarry. As it was desirable, however, if possible, to investigate the silver nitrate derivatives of the compounds of aldehyde-ammonia with thiocarbimides, in order to compare them with the silver derivatives already described, the action was tried on some other compounds of the class in question.

Action of Silver Nitrate on the Compound of Phenylthiocarbimide with Aldehyde-ammonia.—To 1 mol. proportion of the latter compound,† carefully purified by recrystallisation, and dissolved in

* Further investigation with other compounds of this class showed that the behaviour is general; thus the compound of phenylthiocarbimide and aldehyde-ammonia, when boiled with water, gave ammonia, aldehyde, and phenylthiourea; whilst that of benzylthiocarbimide with valeraldehyde-ammonia yielded in like manner benzylthiourea, ammonia, and valeraldehyde. In the latter case, prolonged boiling is necessary to complete the decomposition, as the compound is not only lighter than, and insoluble in, water, but is also wetted by this liquid with some difficulty.

† The constituents of this compound readily unite to form it when fused together in the absence of any solvent.

strong alcohol cooled by a freezing mixture, 2 mol. proportions of silver nitrate in alcoholic solution were added, also well cooled. A white precipitate was produced which was rapidly filtered off by means of the vacuum-pump, and well washed with ether; neither water nor alcohol is admissible for this purpose, as these liquids both dissolve and decompose the silver compound. The product was dried over sulphuric acid in a vacuum, and the silver estimated.

0·2447 gram of substance, oxidised with nitric acid, yielded 0·1225 gram AgCl.

	Calculated for $C_{11}H_{15}N_3S_2AgNO_3$.	Experiment.
Ag.....	38·46 per cent.	38·60 per cent.

As already mentioned, the silver salt is somewhat soluble in water; the solution soon begins to decompose, even at the ordinary temperature, and in a short time becomes black. If warmed with water, the substance blackens immediately; aldehyde is evolved, and silver sulphide deposited as a speculum on the sides of the containing tube. The residual liquid, when cleared by filtration, gives the reaction for a nitrate.

Containing, as it does, 2 mols. of silver nitrate to 1 of base, the silver derivative in question undergoes under the influence of water a change slightly different from those previously described. Thus, when boiled until the smell of aldehyde is no longer perceptible, and filtered from the silver sulphide, the following observations were made:—

1. The liquid is strongly acid to test-paper.
2. Ammoniacal nitrate of silver produces a *white* precipitate, even in the warm solution.
3. No desulphurisation occurs on boiling with alkaline solution of lead.

The latter reactions indicate that the whole of the sulphur has been removed in combination with the silver. Moreover the filtrate is free from silver.

These various facts may be summed up by the equation:—

A similar derivative was obtained in the case following.

Silver Nitrate and Orthotolylthiocarbimide-aldehyde-ammonia Compound.—Molecular proportions of the orthotolyl compound and silver nitrate were mixed, in cold concentrated alcoholic solution. The liquid darkened somewhat, but scarcely any solid matter sepa-

520 DIXON: CHEMISTRY OF THE COMPOUNDS OF THIOUREA

rated. On adding excess of the nitrate, a copious, finely-divided precipitate formed, which was quickly filtered off, and well washed with cold, nearly anhydrous, alcohol.

The silver derivative, like the preceding, is very unstable, soon decomposing even in contact with cold alcohol. If water be added to the alcoholic mixture, the solid dissolves, and the solution blackens forthwith.

The substance, when dried over sulphuric acid in a vacuum, gave the following data on analysis:—

0.4148 gram of substance, oxidised with concentrated nitric acid, yielded 0.2055 gram AgCl.

The filtrate from the above yielded 0.1694 gram BaSO₄.

	Calculated for CSN ₃ H ₂ (C ₇ H ₇)(C ₂ H ₄) ₂ , 2AgNO ₃ .	Experiment.
Ag.....	37.52 per cent.	37.29 per cent.
S	5.57 „	5.61 „

When heated in a narrow tube, the salt darkens at about 85° and by 90° is quite black; if heated quickly on platinum foil, it burns with an explosive puff. On keeping, it gradually darkens, even when quite dry.

The action of water is substantially the same as in the case of the corresponding phenyl compound. The solid is decomposed, gradually by cold water, or at once on warming; aldehyde is evolved, and the tube brilliantly coated with a mirror of silver sulphide. The filtrate gives the reaction for nitric acid, and is strongly acid to test-paper. It gives no perceptible black coloration with ammoniacal silver nitrate, but is nevertheless not absolutely free from sulphur; for, on boiling with alkaline lead solution, a trifling desulphurisation occurs. Further examination showed the reason of this; the substance on treatment with water—even on washing—loses a trace of silver, which passes into solution, and can be detected in the filtrate by the addition of dilute hydrochloric acid. The substance having thus become somewhat poorer in silver, is not perfectly desulphurised on boiling with water. The action may be substantially represented as follows:—

Thus it appears that the silver nitrate derivatives of the thio-carbimide compounds selected as representatives of their class agree in composition and in the mode of their interaction with water.

Action of Acetic Anhydride on the Orthotolylthiocarbimide-aldehyde-ammonia Compound.—A quantity of this substance, purified by

repeated recrystallisation,* was added, little by little, to excess of acetic anhydride, the latter being warmed on the water-bath; aldehyde was freely evolved, and the solid dissolved, forming a deep-red solution. When the odour of aldehyde ceased to be perceptible, the mixture was thrown into water; a brown, curdy mass separated, which, on washing with alcohol, became white. After two recrystallisations from boiling alcohol (in which it is only moderately soluble), the substance was obtained in beautiful, white, glittering prisms, insoluble in water, and melting at 184° (uncorr.). From its appearance, melting point, &c., it was evidently identical with the acetylorthotolylthiourea which I previously described (Trans., 1889, 304) as prepared from acetylthiocarbimide and orthotoluidine.

A sulphur estimation gave the following result :—

0.2017 gram of substance gave 0.2402 gram BaSO_4 .

	Calculated for $\text{CSN}_2\text{H}_2(\text{C}_7\text{H}_7)\cdot\text{CO}\cdot\text{CH}_3$.	Experiment.
S	16.68 per cent.	16.37 per cent.

The product is accordingly acetylorthotolylthiourea, and the interaction runs the same course as in the case of the corresponding phenyl compound. It may be noted that the melting point of the ortho- is higher than that of the para-tolylthiourea; the latter, according to Miquel (*Bull. Soc. Chim.*, **28**, 103), melts at 175 — 176° .

Phenylcarbimide and Aldehyde-ammonia.

If a mixture of these substances be gently warmed on the water-bath, a violent action occurs, the isocyanate disappears, and a brittle, white solid is formed, from which the new compound can be easily isolated. It was found better, however, to operate as follows :—

Aldehyde-ammonia, dissolved in as little absolute alcohol as possible, was well diluted with anhydrous ether, and added to an equal weight of phenylcarbimide, also freely diluted with ether. Most of the latter was distilled off on the water-bath, and the solid residue (which was quite free from the odour of isocyanate) collected and purified by recrystallisation from much boiling alcohol. The substance was thus obtained as a felted mass of very delicate, white needles, having a beautiful satiny lustre, and melting, with decomposition, at 199 — 200° (uncorr.) to a mahogany-red liquid.

It is insoluble in water and in benzene; very sparingly soluble in boiling alcohol or carbon bisulphide, almost insoluble in the cold.

It was dried at 100° and analysed, with the following results :—

* If this purification be omitted, the product is a black, tarry oil, from which scarcely any solid matter can be extracted.

522 DIXON: CHEMISTRY OF THE COMPOUNDS OF THIOUREA

- I. 0.2222 gram of substance gave 0.5229 gram CO_2 and 0.1458 gram H_2O .
 II. 0.2312 gram of substance gave 40.7 c.c. nitrogen, measured at 19° and 755 mm.

These figures lead to the formula $\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}$.

	Theory.	Experiment.
C	64.30 per cent.	64.18 per cent.
H	7.32 „	7.30 „
N	20.53 „	20.23 „
O	7.85 „	—

This substance is therefore the oxygen analogue of that resulting from the interaction of phenylthiocarbamide with aldehyde-ammonia; its formation occurs thus:—

It is more stable than the corresponding sulphur compound; when boiled with water alone, it is not sensibly attacked, but on the addition of dilute hydrochloric acid it dissolves readily, and with evolution of aldehyde. From the residual liquid, on cooling, colourless needles separate, sparingly soluble in cold water, melting at 143 — 144° , and further characterised as carbanilamide by the following reactions:—

1. When heated in a dry tube, ammonia is evolved, and a crystalline sublimate forms.

2. The latter, on further heating, emits the pungent odour of phenylcarbimide.

Thus, in its decomposition by (acidified) water, this substance behaves like its sulphur analogue:—

A number of experiments was made with the view of acquiring some further information regarding the chemistry of the thiocarbimide derivatives; a few of these may be mentioned.

1. *Action of Nascent Hydrogen upon the Phenyl Compound.*—This experiment was undertaken in order to ascertain whether the two aldehyde groups would be split off along with one of the nitrogen atoms, so as to yield diethylamine, thus:—

Owing to the instability of the compound, neither strongly acid nor alkaline reducing media could be employed; it was therefore treated with sodium amalgam, dilute hydrochloric acid being added from time to time, so as to keep the mixture faintly acid. Under these conditions, decomposition took place, but not in the sense hoped for; the escaping hydrogen smelt of aldehyde, and in the residue were found sodium and ammonium chlorides, together with a substance melting at 150° , and easily recognised as monophenylthiourea:—

2. *Desulphurisation of the Phenyl Compound.*—Two experiments were made in this direction:—

In the first, the compound was desulphurised by freshly-precipitated yellow oxide of mercury, in presence of aniline. As before, the molecule broke down, with evolution of aldehyde; the desulphurisation product was a deep brownish-red, tenacious, basic oil.

In the second, the substance was treated alone, the conditions being otherwise the same as when aniline was present. A solid was thus obtained, which, on recrystallisation, came down in woolly masses of fine needles. These melted at 199 – 200° , were freely soluble in alcohol and hot water, sparingly in the cold, and, on heating with dilute hydrochloric acid, *evolved no aldehyde*. The amount of material obtained was too small to admit of a complete examination, but I did not consider it necessary to pursue this subject further, my immediate object being merely to ascertain whether the phenyl compound would yield, on desulphurisation, a substance identical with the phenyl isocyanate-aldehyde-ammonia product. That this was not the case followed as well from the negative result on hydrochloric acid treatment, as from the ready solubility of the compound in alcohol and hot water.

3. *Action of Nitrous Acid on the Phenyl Compound.*—A quantity of the latter substance was mixed with alcohol, a slight excess of dilute hydrochloric acid added, and then, little by little, a concentrated aqueous solution containing excess of sodium nitrite. At first the mixture cleared and assumed a green colour, but as the addition of the nitrite was continued, it began to become turbid; and, after a short time, a lemon-yellow, crystalline solid separated, which, in the crude state, smelt of phenylthiocarbimide. This, when collected, washed well with spirit, and recrystallised from much boiling alcohol, was obtained in delicate, canary-yellow, odourless needles, which at 183 – 184° (uncorr.) decomposed with an explosive puff. When dissolved in phenol and treated with a few drops of sulphuric acid, a deep purple-red coloration is produced, which, on the addition of water and excess of caustic alkali, changes to a beautiful, azure-blue (Liebermann's nitroso-reaction).

Though a nitroso-substance, it is *not* a derivative of the aldehyde-ammonia compound; here, as in many other cases, decomposition occurs, and the product is a derivative of the resultant monophenylthiourea.

This compound does not volatilise in a current of steam; is practically insoluble in water, ether, chloroform, benzene, and hydrochloric acid, very sparingly in boiling alcohol, still less so in the cold; slightly in boiling glacial acetic acid, by which, however, it is to some extent decomposed. Cold, concentrated sulphuric acid readily dissolves the substance, producing a beautiful scarlet liquid, which changes to purple on warming. It is insoluble in cold aqueous potassium hydroxide, but dissolves easily in alcoholic, giving a bright, scarlet solution resembling the preceding; this liquid is decolourised by warming alone, or desulphurised by heating with alkaline solution of lead.

On treating phenylthiourea with nitrous acid in like manner, a yellow solid was obtained, which, in the crude state, smelt faintly of phenylthiocarbimide. By recrystallisation from much boiling alcohol, delicate, canary-yellow needles were obtained; these deflagrated at 184°, gave Liebermann's reaction, yielded with sulphuric acid the scarlet and purple colorations, and, in short, were identical with the nitroso-compound previously described.

Nitrous acid, according to Hector (*Ber.*, **22**, 1177), acts upon phenylthiourea to form a basic substance dianilido-oiazothiole, $\begin{matrix} \text{N}:\text{C}(\text{NPh}) \\ | \\ \text{N}:\text{C}(\text{NPh}) \end{matrix} > \text{S}$. No details are given regarding its preparation from these materials, but from a description of its properties, it was evidently different from the compound in question. Amongst its derivatives, however, a substance is briefly referred to as nitrosodianilido-oiazothiole, $\begin{matrix} \text{N}:\text{C}(\text{NPh}\cdot\text{NO}) \\ | \\ \text{N}=\text{C}(\text{NPh}) \end{matrix} > \text{S}$, obtained by the action of nitrous acid on the base. This is described as a yellow powder, insoluble in water and alcohol; it puffs at 179°. There could be little doubt that the substance which I obtained by the direct action of excess of nitrous acid on the aldehyde-ammonia compound, and on phenylthiourea, was Hector's nitroso-compound, but in a pure condition. A nitrogen determination (made with the aldehyde-ammonia product) showed this to be the case:—

0.1635 gram of substance gave 34 c.c. nitrogen, measured at 20° and 748 mm.

Calculated for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{SO}$.	Experiment.
N 23.62 per cent.	23.57 per cent.

From orthotolylthiourea,* by similar treatment, a corresponding nitroso-derivative was obtained, together with a yellow, sticky, semi-solid material. The former (not recrystallised) occurs in long, yellow needles, insoluble in water, moderately soluble in alcohol, and melting, with copious effervescence, at 150—151°, to a mahogany-brown liquid. It gives Liebermann's reaction, and yields with cold alcoholic potash a bright, scarlet solution, but dissolves in sulphuric acid without colour-change.

Ethylthiourea and Nitrous Acid.

Interaction occurred with much effervescence, a disgusting isocyanide-like odour was produced, and soon drops of a yellow oil separated. The latter, when extracted with ether, and the ether distilled off, was miscible with alcohol, freely desulphurised on treatment with alkaline lead solution, gave no colour with alcoholic potash, and smelt pungently of ethylthiocarbimide. The equation representing the production of this substance may be written thus:—

but it by no means expresses the whole action, for amongst the products sulphuric acid was identified, recognised both by barium nitrate and by its charring effect on paper.

In another experiment where a considerable excess of nitrite was employed, no ethylthiocarbimide was detected, but the resultant solution contained much free sulphuric acid.

Allylthiourea was treated in like manner with a similar result; the mixture smelt, first of isocyanide, then pungently of mustard oil, and sulphuric acid was found in the solution.†

Thiourea and Nitrous Acid.

Earlier in the present paper (p. 512), Claus' test for thiourea is mentioned. According to this chemist (see also *Ber.*, 4, 140; and 6, 726), the production of a blood-red coloration with ferric chloride,

* The melting point given by Staats (*Ber.*, 13, 136) for this compound, namely, 155°, is somewhat low; a preparation made from orthotolylthiocarbimide and ammonia, and purified by recrystallisation from water, melted at 160—161° (uncorr.). A specimen of pure di-orthotolylthiourea was found to melt at 159° (uncorr.); the melting points recorded by Girard (*Ber.*, 4, 935) and Berger (*ibid.*, 12, 1854) are 165° and 156° respectively.

† This action appears to be very complicated. Not only were the above phenomena observed, and some evidence of the presence of Hector's diallyldithiotetrahydrotriazole (Abstr., 1892, 292) obtained, but also of at least one other product, to which he does not appear to refer. At present, I have not access to his original paper.

after previous treatment of thiourea with ethyl nitrite, is due to the conversion of the urea into the metameric ammonium thiocyanate. No explanation is offered regarding the mechanism of the production of the latter substance, which, moreover, was not isolated; and, indeed, no further experimental evidence of its presence is adduced than the ferric chloride reaction, and the fact that a yellow substance was obtained resembling in the main pseudosulphocyanogen (though the analytical data diverged considerably from those required by theory), which yellow substance resulted also on treatment of ammonium thiocyanate with nitrous acid under similar conditions.

But as more or less thiocarbimide was produced by the action of this acid upon the monosubstituted thioureas above mentioned, it seemed worth while to try whether thiourea really underwent conversion into an ammonium compound. For if the action proceeded upon the same lines as where the substitution derivatives are concerned, free thiocyanic acid, rather than ammonium thiocyanate, might be expected.

An experimental investigation of the action was therefore commenced, the detailed study of which, as well as that of nitrous acid upon the substituted thioureas generally, was interrupted when I learned that Hector desired to reserve it. But the following qualitative data, which bear chiefly on the first stage of the decomposition, may be here recorded.

On mixing a solution of thiourea* in dilute spirit with ethyl nitrite, the mixture became first deep red, then yellow, and a gas containing free nitrogen and its oxides was evolved with effervescence. A portion of the resultant clear solution was freely diluted with water and divided into two parts; to one of these, ferric chloride was added, and to the other, Nessler's reagent. In the former, the rich blood-red thiocyanate coloration appeared; whilst the latter gave no indication of the presence of ammonia, but a pale, primrose-yellow, finely-divided precipitate formed. For the purpose of comparison, a solution of ammonium thiocyanate was prepared, giving with ferric chloride a colour of the same depth as that previously obtained; a portion of this solution, when treated with Nessler's reagent, gave the deep, orange-brown coloration and turbidity characteristic of ammonium salts.

The remainder of the former solution contained in a dish was placed in a desiccator over oil of vitriol, the dish being surrounded by pieces of filter-paper moistened with solution of ferric chloride. The air was exhausted, and in a short time the pieces of paper became intense blood-red, indicating the presence of the volatile thiocyanic

* Similar results were obtained when (as in Claus' experiments) the solid substance was employed.

Published on 01 January 1892. Downloaded by University of Victoria on 27/10/2014 08:21:53.

Published on 01 January 1892. Downloaded by University of Victoria on 27/10/2014 08:21:53.

Published on 01 January 1892. Downloaded by University of Victoria on 27/10/2014 08:21:53.

Published on 01 January 1892. Downloaded by University of Victoria on 27/10/2014 08:21:53.

Published on 01 January 1892. Downloaded by University of Victoria on 27/10/2014 08:21:53.

In attempting to realise these latter interactions, the following compounds were used, together with acetaldehyde-ammonia:—

Numerous experiments were made, the conditions being varied as regards (1) the nature of the solvent employed; (2) the degree of concentration of the solutions; (3) the time (this was varied from a few minutes to months); (4) the temperature; and (5) the presence or absence of acid. Under none of the conditions attained was the desired combination effected.

It now remains to describe some instances in which the interaction between certain thiocarbimides and aldehyde-ammonias proceeds upon lines differing from those hitherto recorded.

Phenylthiocarbimide and Chloral-ammonia.

These, in the proportions of 1 mol. of the former to 2 of the latter, were mixed in concentrated alcoholic solution, and the mixture warmed to just below its boiling point. The now somewhat red liquid was decanted from a trace of white, amorphous precipitate, and the clear liquid set aside. On standing for a short time, colourless, well-formed prisms began to separate; these contained no chlorine; melted at 153° ; were moderately soluble in hot water, nearly insoluble in cold, and tasted extremely bitter; on warming with alkaline solution of lead, they gave the galena reaction readily. Analysis was unnecessary, as the substance was obviously phenylthiourea. Therefore the expected chlorinated derivative,

is not the product of this action; but the elements of NH_3 , having been removed from the chloral-ammonia, combine with the thiocarbimide to form phenylthiourea.

It was thought that the heating to which the mixture had been subjected might possibly have facilitated the decomposition of the chloral-ammonia into its constituents; but on employing cold solutions interaction took place, with precisely similar results.

This rather unexpected behaviour of chloral-ammonia with phenylthiocarbimide led to an experiment to ascertain whether the former would combine with thiourea to yield a chlorinated derivative of Nencki's acetaldehyde compound.

Theoretical quantities of the constituents were heated together in alcoholic solution, whereby some decomposition occurred, and the mixture became reddish, but, on evaporating the solvent, the residue was found to be thiourea. It is worthy of remark that the latter separated in large, thin, six-sided plates; on recrystallisation from water, these were obtained in the ordinary rhombic form.

Some experiments were carried out with thiocarbimides containing acid radicles; these (sometimes termed thiocyanates) are obtained by the action of the corresponding acid chloride upon lead thiocyanate (Miguel, *Ann. Chim. Phys.* [5], 11, 295). In this connection, it is interesting to note that the acetyl compound was evidently originally obtained by Nencki, who records (*Ber.*, 6, 599) that "on heating acetylthiourea with phosphoric anhydride, a pungently-smelling oil distilled over, which sank in water." The considerable carbonisation which occurred, and consequent small yield, prevented his further examining the product. But the latter was doubtless identical with the so-called "acetyl thiocyanate," which, four years later, Miguel (*loc. cit.*) obtained as an excessively pungent smelling liquid, of sp. gr. 1.151.

Acetylthiocarbimide reacts with extreme readiness. The following observations were made in a case where alcohol had been employed to dilute the liquid.

15 grams of acetylthiocarbimide were added to about the same bulk of cold, nearly anhydrous alcohol. After the lapse of some minutes, a violent action took place, by which a considerable portion of the contents was projected out of the containing tube. Ethyl acetate was readily recognised, by its odour, as one of the products:—

but the decomposition had gone far beyond this; on pouring away the remaining liquid, which still smelt pungently of the thiocarbimide, yellow pellets were found, varying in size from duck shot downwards. These were hard and brittle, burned with a blue flame,

evolving sulphurous anhydride, and consisted of fused sulphur. The principal residue was a deep-yellow powder, insoluble in water, but soluble in concentrated sulphuric acid and in caustic alkalis; the latter solution, when boiled for some time and subsequently acidified with hydrochloric acid, gave a blood-red coloration with ferric chloride. Further, the soda solution, when boiled and treated with excess of acetic acid, gave a yellow precipitate with lead acetate. These reactions, as well as the appearance of the substance, characterised it as pseudosulphocyanogen.

Acetylthiocarbimide and Aldehyde-ammonia.

These substances interact readily with evolution of much heat, but, unless careful attention be paid to conditions, the process tends to become complicated, and sticky or tarry matters are produced. After many trials, using different methods, the following was found to give the most satisfactory result.

12·2 grams of aldehyde-ammonia were dissolved in the least possible quantity of almost anhydrous alcohol, the solution largely diluted with anhydrous ether, and well cooled by a freezing mixture. To this was added, little by little, a solution of 20·2 grams of pure and freshly-distilled acetylthiocarbimide in about $2\frac{1}{2}$ times its volume of anhydrous ether, the latter solution being also strongly cooled. The mixture, greenish at first, became yellow during the addition of the second half of the thiocarbimide solution, and a slight precipitate gradually formed.

The product was now exposed freely to the air in an open dish; as the solvent evaporated, a white solid separated, which was removed by filtration, and the mother liquor set aside. This process was continued, and successive crops of solid substance collected, until the filtrates, now red in colour, began to become syrupy. The mixed residues were washed with ether and twice recrystallised from alcohol, then treated with a small quantity of hot water, and the mixture filtered. On cooling, this filtrate first deposited a trifling quantity of short, well-formed prisms, and then almost solidified from separation of woolly-looking masses of fine, slender needles; the former adhered to the surface of the containing vessel, so that the remaining crystals could be readily separated, by inverting the dish and allowing its free contents to fall out. The latter were well washed with cold water, and dried over sulphuric acid in a vacuum.

On analysis, the following data were obtained:—

0·2032 gram of substance gave 0·3043 gram CO_2 and 0·1375 gram H_2O .

0.2033 gram of substance gave 36.6 c.c. nitrogen, measured at 16° and 757.5 mm.

0.2072 gram of substance gave 36.8 c.c. nitrogen, measured at 17° and 763 mm.

0.1994 gram of substance gave 0.2305 gram BaSO₄.

From which results the formula C₇H₁₅N₃SO₂ is deduced.

	Calculated.	Experiment.	
C.....	40.93 per cent.	40.83 per cent.	
H.....	7.32 „	7.58 „	
N.....	20.53 „	20.91 „	20.68
S.....	15.62 „	15.89 „	
O.....	15.60 „	—	

The interaction may be thus represented :—

On comparing this with the equation representing the action between acetaldehyde-ammonia and the thiocarbamides containing hydrocarbon radicles, it is noticeable that, whilst in both cases union occurs in the proportion of 1 mol. of thiocarbamide to 2 mols. of aldehyde-ammonia, in the present instance only a single molecule of water is eliminated. The idea that the interaction might have run the ordinary course, but that the product was a hydrate, was negatived, for a quantity of the substance, dried in the cold over sulphuric acid, underwent no perceptible alteration in weight after being heated for an hour at 100°. This acetyl derivative, therefore, holds in distinct chemical combination the elements of a molecule of water more than its congeners.

The substance gives no colour-reaction on the addition of ferric chloride. With ammoniacal silver nitrate, a yellow coloration is produced, which rapidly gives place to a copious black precipitate; and the sulphur is also very readily removed by warming with alkaline solution of lead. It is scarcely attacked by boiling water alone, but is at once decomposed on heating with dilute hydrochloric acid, with evolution of aldehyde.

It is readily soluble in boiling water, sparingly in cold; very freely in hot alcohol, moderately in cold; slightly soluble in hot benzene, practically insoluble in ether. When purified by repeated crystallisation from aqueous alcohol, the substance melts at 187° (uncorr.) with effervescence to a brown liquid, which rapidly acquires a deep bromine-red colour. The melting point is, however, extremely sensitive to impurities, and traces of the latter, which chemical analysis fails to detect, will lower it by nearly 10°.

Benzoylthiocarbimide and Aldehyde-ammonia.

Since the former substance, according to Miguel, is a true thiocarbimide, it was anticipated that the interaction between these would run a course parallel to that of the alkylthiocarbimides. Experiment has failed to verify this expectation.

The two constituents were mixed in concentrated alcoholic solution, with cooling by water. In about an hour crystals began to form in the brownish liquid, and after 12 hours the separation was complete; the solid product was drained on the filter pump, washed with spirit, and recrystallised twice from alcohol. As thus obtained, the substance forms vitreous, oblique prisms, perfectly colourless, and melting at 170—171° (uncorr.).

On the addition of ammoniacal silver nitrate to the alcoholic solution, a black precipitate falls; and on treatment with alkaline lead solution, a very brilliant galena speculum is produced. But on boiling with dilute hydrochloric acid not a trace of aldehyde was evolved; it was, therefore, improbable that the compound

was in hand; this suspicion was confirmed by the results of analysis.

0.2302 gram of substance gave 30.2 c.c. nitrogen, measured at 11° and 749 mm.

0.2275 gram of substance gave 0.2974 gram BaSO₄.

These data lead to the conclusion that the substance is benzoylthiourea.

	Calculated for $\text{CSN}_2\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_5$.	Experiment.
N	15.59 per cent.	15.37 per cent.
S	17.79 ,,	17.97 ,,

The melting point of this compound is given by Pike (*Ber.*, 6, 755) as 169—170°; and by Miguel (*Ann. Chim. phys.* [5], 11, 313) as 171°; as already stated, the melting point observed lies between 170° and 171°. The substance, moreover, is sparingly soluble in cold water, and has an extremely bitter taste.

In the interaction, therefore, between benzoylthiocarbimide and aldehyde-ammonia, only the elements of NH₃ in the latter compound have taken part—

The experiment was several times repeated, and the conditions varied, but without affecting the result.

It may here be added, that benzoylthiourea dissolves in benzene and

in chloroform, crystallising from either in brilliant, silvery prisms. It is soluble also, without decomposition, in concentrated sulphuric acid, from which it separates on dilution with water in fine, silvery needles.

The information now acquired regarding the acetaldehyde- and valeraldehyde-ammonia compounds of thiourea on the one hand, and the alkylthiocarbimide derivatives of aldehyde-ammonia, may be generally stated as follows:—

- a. They combine with picric acid, forming equimolecular additive compounds.
- b. They are decomposed by hot acetic anhydride, with elimination of both aldehyde groups, together with one of the three nitrogen atoms, and production of the corresponding acetylated thiourea.
- c. Boiling with water effects an analogous decomposition, save that the resultant thiourea is not acetylated.
- d. They combine with silver nitrate, yielding sparingly soluble additive products, which are more or less unstable in presence of water.

From the striking resemblance in the behaviour of these compounds, the conclusion may, I think, be fairly drawn that they are all members of the same class. Their decompositions, so far as they have been studied, all proceed upon the same lines, and the only point of distinction observed between the thiocarbimide and the thiourea compounds lies in the power which the molecules of the former possess, of uniting with 2 mols. of silver nitrate, whilst those of the latter, under the same conditions, can hold but one. But even amongst these metallic derivatives, the resemblance otherwise still holds; all readily break down on mere contact with hot water, and the resultant decompositions run essentially the same course. In each case, the two aldehyde groups, as such, are split off, and one-third of the nitrogen leaves the compound in the form of ammonia; the residual nitrogen is found either as a urea or a urea *plus* a thiourea, according to the amount of metal present. From the nature and uniformity of these changes, it may be inferred: first, that the two aldehyde groups, existing as such, together with a nitrogen atom, occupy a constant position in the molecule; and, secondly, that the remainder of the molecule is a thiourea residue.

What the structure of the former portion may be is still rather obscure; for, though the uniformity in decomposition is highly suggestive of similarity in structure, it does not throw much light upon the atomic arrangement.

But whilst the constitution of this aldehydic fraction of the mole-

cule still requires further examination, the present investigation has brought to light some interesting observations bearing upon that of the residual portion, which observations tend to corroborate the conclusions drawn by Professor Emerson Reynolds (Trans., 1891, 394) from an experimental study of the thiocarbamidammonium compounds.

In the communication in question, it is pointed out that, whilst thiourea readily unites with ammonium chloride, bromide, and iodide, and (though less readily) with di-, tri-, and tetr-ethyl ammonium bromides, on the other hand, none of these compounds could be caused to combine with substituted thioureas. Adopting the view that union occurs by means of the nitrogen, the author reasons that "the loss of power of combination with ammonium bromide when but one atom of hydrogen in thiocarbamide is displaced by a more positive radicle, such as ethyl or phenyl, is inconsistent with the symmetrical constitution of thiocarbamide, which should still have an NH_2 group unaffected and available for union, but is quite consistent with its unsymmetrical structure." On this and other grounds he considers that the constitution is best expressed by the unsymmetrical formula $\text{HN}:\text{C} < \begin{smallmatrix} \text{NH}_2 \\ \text{SH} \end{smallmatrix}$. In the case of monosubstitution deriva-

tives the choice lies between $\text{RN}:\text{C} < \begin{smallmatrix} \text{NH}_2 \\ \text{SH} \end{smallmatrix}$ and $\text{HN}:\text{C} < \begin{smallmatrix} \text{NHR} \\ \text{SH} \end{smallmatrix}$, preference being given to the former, as according best with the genesis of these compounds from RNCS and ammonia; and he explains the failure of the monosubstituted thioureas to yield addition products with ammonium haloids, by suggesting that "the presence of the positive radicle in the imidic group paralyses the power of combination, which appears in consequence to be exclusively due to the NH of the substance we have been accustomed to term thiocarbamide."

The results obtained on treating aldehyde-ammonia with thiourea and its substitution derivatives respectively, not only afford evidence of the unsymmetrical nature of these molecules, but also, I think, support the view above quoted. For the fact that thiourea interacts quite as readily with valeraldehyde-ammonia as with its lower homologue indicates that combination is not specially dependent upon the nature of the aldehydic hydrocarbon residue. But, in sharp contrast to this, is the fact that even a single substitution in the thiourea suffices to completely destroy its power of interaction; just as in the cases cited by Professor Reynolds, it paralysed its power of forming addition compounds.

Whilst admitting the unsymmetrical structure of the mono-substitution derivatives,* it might, however, be argued that their genera-

* Moreover, evidence gained from a study of the melting points of these com-

tion from RNCS and ammonia, though evidence in favour of the formula $\text{RN:C} \begin{smallmatrix} \text{NH}_2 \\ \text{SH} \end{smallmatrix}$ does not necessarily exclude the other— $\text{HN:C} \begin{smallmatrix} \text{NHR} \\ \text{SH} \end{smallmatrix}$; that power of interaction or combination may be determined by the NH_2 , but lost when this becomes NHR .

It was hoped that a study of the action of nitrous acid on these compounds might serve to decide between the above formulæ. For, assuming the structure to be $\text{NH:C} \begin{smallmatrix} \text{NHR} \\ \text{SH} \end{smallmatrix}$, a nitroso-compound might be expected to result; but this, as already shown, is not the case. On the other hand, if the substances in question are of the form $\text{RN:C} \begin{smallmatrix} \text{NH}_2 \\ \text{SH} \end{smallmatrix}$, the non-formation of a nitroso-derivative is intelligible; here the attack on the amidic group might give rise to an unstable alkylimidothiocarbonic acid, $\text{RN:C} \begin{smallmatrix} \text{OH} \\ \text{SH} \end{smallmatrix}$, which, by loss of the elements of water, could yield the corresponding thiocarbimide—a compound which (though in small proportion) is actually formed. And in like manner the formation of thiocyanic acid from thiourea is explicable:—

But the action of nitrous acid, under the conditions stated, is unfortunately for this purpose, far from simple; and hence scarcely allows of any definite conclusion being drawn.

The bearing of the foregoing upon the constitution of Nencki's compound and its homologue, and the thiocarbimide derivatives of aldehyde-ammonias, remains to be considered. Assuming that, in the former, interaction occurs exclusively through the imidic group, their production may be thus represented:—

pounds points to the conclusion that they differ in structure from the disubstituted thiocarbamides. But as there is considerable reason for believing the latter to be symmetrical—at least in the solid state—it may be inferred that the former are not. I hope later on to make a communication on this subject.

But the close resemblance in general properties and decompositions between these and the thiocarbimide compounds affords, as already pointed out, strong evidence of similarity in structure; in which case the latter would have to be regarded as substitution derivatives of the form, $\text{HS}\cdot\text{C}\begin{smallmatrix} \text{NHR}' \\ \text{N}-\text{N} \end{smallmatrix} \begin{smallmatrix} \text{CHR} \\ \text{CHR} \end{smallmatrix}$.

Such a derivative, however, in breaking down so as to afford the corresponding substituted thiourea must either yield an isomeric compound of the form $\text{HS}\cdot\text{C}\begin{smallmatrix} \text{NHR}' \\ \text{NH} \end{smallmatrix}$, or the radicle must alter its position. There is no substantial ground for the latter assumption, but the observed phenomena may, I think, be explained as follows:—In the case of thionurea, both amidic and imidic groups simultaneously giving up hydrogen to the hydroxyl groups of the aldehyde-ammonia to form water, the residue can then unite, with elimination of ammonia, to form the compound $\text{HS}\cdot\text{C}\begin{smallmatrix} \text{NH} \\ \text{NH}\cdot\text{N}(\text{C}_2\text{H}_4)_2 \end{smallmatrix}$. But with substituted thioureas this simultaneous loss of 2H cannot occur, and hence no interaction takes place. The substitution derivatives obtained from the thiocarbimides may be formulated thus:— $\text{HS}\cdot\text{C}\begin{smallmatrix} \text{NR} \\ \text{NH}\cdot\text{N}(\text{C}_2\text{H}_4)_2 \end{smallmatrix}$, whereby the decomposition by water becomes intelligible; the molecule readily breaks down at the point of junction of the two directly linked nitrogen atoms; ammonia and 2 mols. of aldehyde result, and the residue is a monosubstituted thiourea $\text{HS}\cdot\text{C}\begin{smallmatrix} \text{NR} \\ \text{NH}_2 \end{smallmatrix}$. From Nencki's compound, or its homologue, by a precisely similar interaction, thiourea itself, $\text{HS}\cdot\text{C}\begin{smallmatrix} \text{NH} \\ \text{NH}_2 \end{smallmatrix}$, would result.

*Chemical Laboratory,
Queen's College, Cork.*