L.—*Interaction of Phenylthiocarbimide with Acetic and Propionic Acids respectively.*

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THE interaction of phenylthiocarbimide with acetic acid was originally made the subject of an experiment by A. W. von Hofmann (*Ber.*, **3**, 770) and later on by Claus and Völtkow (*Ber.*, **14**, 445). According to the former, the substances interact at 130—140° with production of *diacetanilide*, in accordance with the equation

Claus and Völtkow* heated the mixture at 160°, and showed that under these conditions the product is *acetanilide*, while CO_2 , H_2S , and COS are the bye-products of the decomposition.

* These chemists appear to have overlooked Hofmann's experiment, as their paper contains no reference to it.

In neither case were the experiments exhaustive, analytical data being absent from both papers.

In order to finally establish the exact nature of the action, I have, in connection with the previous paper (this vol., p. 396), made a careful reinvestigation of the subject; in the meantime, I have been, to a certain extent, anticipated in my work by the recent publication of a paper by Messrs. Cain and Cohen dealing with the same change (this vol., p. 327).

While I agree with these gentlemen that diacetanilide is not formed under any conditions of interaction between phenylthiocarbimide and glacial acetic acid, my results, on the other hand, compel me to differ entirely from their conclusions with respect to the exact course of the change.

Since the thiocarbimides are readily decomposed by water at moderately high temperatures, a careful exclusion of water in studying these actions is of paramount importance; the neglect of this precaution has, I believe, caused Messrs. Cain and Cohen to be misled by their results.

The details of my experiments are as follows:—

I. *Phenylthiocarbimide and Anhydrous Acetic Acid.*

In all the experiments recorded in my previous paper (this vol., p. 396), the conditions were such that water was obviously absent from the materials. In preparing, therefore, a specimen of pure acetic acid for the present work, the following method was adopted. The fraction distilling at 118–121° from a specimen of commercial pure acetic acid was subjected to a second distillation, and a fraction collected which distilled over at 119°.

A careful titration of the acid in this fraction showed it to contain 98·4 per cent. of real acetic acid. The necessary amount of pure acetic anhydride to yield a 100 per cent. acid was now added to a weighed quantity of this fraction, and the product heated on the water-bath in a sealed tube for several hours.

The results of my experiments prove conclusively that my specimen of acid was absolutely anhydrous.

Exp. 1.—Since I have already stated in the previous paper that the action takes place according to the equation

equal molecular proportions were accordingly used in the first experiments.

The quantities employed were:—

$$\begin{cases} 6\cdot8 \text{ grams } \text{C}_6\text{H}_5\cdot\text{NCS} & \dots & 1 \text{ mol. prop.} \\ 3\cdot0 \quad \text{,,} \quad \text{CH}_3\cdot\text{COOH} & \dots & 1 \quad \text{,,} \end{cases}$$

Phenylthiocarbimide and pure acetic acid are freely miscible in these proportions. The mixture was heated in a sealed tube of stout glass at 135—140° for three hours. On cooling, the contents had become a solid, crystalline mass of a pale yellow tint. There was a considerable rush of gas on opening the tube. The following observations on this gas prove that it was, practically, pure COS. With a *neutral* solution of lead nitrate, it produced no precipitate, and hence *sulphuretted hydrogen was absent*. With an *alkaline* lead solution and with ammoniacal silver nitrate, it produced an immediate *black* precipitate of sulphide of the metal. The gas burnt with a lavender-blue flame, producing CO₂ and SO₂, but *no water*, as shown by the absence of a deposit of "dew" on the sides of a funnel held over the flame. The odour, while characteristic of COS, was perfectly free from the smell of H₂S.

The weight of the solid product, after gentle warming to expel every trace of occluded gas, was 6.9 grams.

Hence loss due to gas evolved was $9.8 - 6.9 = 2.9$ grams, or 29.59 per cent. of the materials used. Theory for the above equation, 30.76 per cent.

The solid product was *completely* dissolved in sufficient boiling distilled water, from which it separated on cooling in thin, glistening prisms melting at 112—113°, and possessing all the properties of acetanilide. From the mother liquor, two further crops of crystals were obtained; the melting point was in each case, after a single recrystallisation, 112—113°.

The following analytical data prove conclusively that acetanilide is the sole constituent of the solid product of the interaction:—

1st crop of crystals:—0.2098 gram gave 19.1 c.c. nitrogen at 18° and 766 mm.

2nd crop of crystals:—0.1928 gram gave 17.9 c.c. nitrogen at 15° and 757 mm.

3rd crop of crystals:—0.1725 gram gave 16.0 c.c. nitrogen at 14° and 751 mm.

		Theory for acetanilide.	Theory for diacetanilide.
1st. N....	10.53 per cent.	10.37 p. c.	7.90 p. c.
2nd. N....	10.75 „		
3rd. N....	10.72 „		

These determinations of nitrogen were necessary for identification, since v. Hofmann states that diacetanilide melts at 111—112°, and resembles acetanilide in its properties.

The total weight of acetanilide crystals obtained was 6.78 grams, corresponding to 69.18 per cent. of the materials used.

Theory for the above equation, 69·23 per cent.

Exp. 2.—This was a repetition of the preceding experiment, as regards the molecular proportions and quantities used; the mixture, however, was heated for two hours at 160—170°, the same temperature as that adopted by Claus and Völtzkow in their experiment. The results are practically the same as at the lower temperature, namely:—

Gas evolved.....	2·95 grams.	Theory....	3·0 grams.
Acetanilide crystals.	6·69 ,,	,, 	6·75 ,,

Exp. 3.—In this case, *two* molecular proportions of acetic acid were used to one of the thiocarbimide, these being the ratios demanded by the equation given by v. Hofmann.

The quantities used were $\left\{ \begin{array}{l} 3\cdot4 \text{ grams } \text{C}_6\text{H}_5\cdot\text{NCS} \\ 3\cdot0 \quad \quad \quad \text{,,} \quad \text{CH}_3\cdot\text{COOH.} \end{array} \right.$

Heated for three hours at 135—140°.

The product of the action was a viscid liquid, until the gas had been expelled from the tube, when it almost completely solidified. It smelt strongly of acetic acid, and, in order to estimate the amount of the latter, the product was extracted with cold water, and the solution filtered from excess of acetanilide was directly titrated with standard soda; 1·41 grams of unaltered acetic acid was present, or practically half the quantity used.

The weight of acetanilide obtained was 3·2 grams. Theory, 3·37 grams. Therefore the interaction was simply between equal molecular proportions.

Exp. 4.—The reverse of the last; namely, two molecular proportions of phenylthiocarbimide to one of acetic acid.

Quantities used $\left\{ \begin{array}{l} 6\cdot8 \text{ grams } \text{C}_6\text{H}_5\cdot\text{NCS} \\ 1\cdot5 \quad \quad \quad \text{,,} \quad \text{CH}_3\cdot\text{COOH.} \end{array} \right.$

Heated for three hours at 135—140°.

The product of the action was a soft solid, about the consistency of suet. It smelt strongly of phenylthiocarbimide, and was therefore added to water and subjected to steam-distillation.

2·98 grams of $\text{C}_6\text{H}_5\cdot\text{NCS}$ were collected from the distillate; the almost unavoidable error in collecting a small quantity of the thiocarbimide is sufficient to account for the slight deficiency (0·42 gram) from the theoretical, for one molecular proportion.

Weight of acetanilide obtained, 3·17 grams. Theory, 3·37 grams. Therefore interaction was again restricted to equal molecular proportions.

Since the previous investigators* agree in mentioning sulphuretted hydrogen as one of the gaseous products of decomposition, the absence of which I proved in all the foregoing experiments, it seemed probable that the occurrence of this gas must be attributed to the presence of water in the materials. With the object of studying this point, and of further testing the possibility of the formation of diacetanilide under such conditions, the following experiments were conducted:—

II. *Phenylthiocarbimide and Acetic Acid containing 10 per cent. of Water.*

Exp. 5.—Quantities used $\left\{ \begin{array}{l} 3.4 \text{ grams } \text{C}_6\text{H}_5\text{NCS (1 mol. prop.)} \\ 1.5 \text{ ,, } \text{CH}_3\text{COOH (1 mol. prop.)} \\ 0.15 \text{ ,, } \text{H}_2\text{O.} \end{array} \right.$

The thiocarbimide is not completely miscible with acetic acid diluted to the above extent. The mixture was heated in a sealed tube at 135—140° for three hours. On opening the tube, there was abundant evolution of gas, *containing much sulphuretted hydrogen*, recognised by following tests:—

- a. The characteristic smell.
- b. With *neutral* lead nitrate solution, an immediate black precipitate of PbS.
- c. On combustion of the gas, *water was formed*, together with SO₂ and CO₂.

The gas evolved from the tube consisted of H₂S, CO₂, and COS.

The strong odour of acetic acid in the solid product of the action proved that a certain portion had escaped decomposition, which was not the case when the same molecular proportions were caused to act in the absence of water.

The solid product, after complete extraction with boiling water, left 0.68 gram of an insoluble substance which evidently resulted from secondary action due to the presence of water. The total weight of acetanilide obtained from the aqueous extract was 2.27 grams.

That this consisted solely of acetanilide was proved by a nitrogen determination in a mean sample taken from the whole product.

	Found.	Theory.
N	10.63 per cent.	10.37 per cent.

The main portion of the work in the present paper was completed in the autumn of last year.

Therefore, no diacetanilide ($N = 7.9$ per cent.) was present in the product.

A quantity of the insoluble product, accumulated from three experiments, was purified by crystallisation from hot alcohol, from which it separated almost completely, on cooling, in the form of fine, slender, colourless prisms having a beautiful, silky lustre. The crystals do not contain sulphur.

The analyses of a specimen, purified by two crystallisations from boiling alcohol, lead to the empirical formula $C_{13}H_{12}N_2O$ for the substance.

Data :—

- I. 0.2429 gram gave 0.124 gram H_2O (the carbon of this experiment was lost).
 II. 0.2035 gram gave 0.1108 gram H_2O and 0.546 gram CO_2 .
 III. 0.1865 gram gave 21.6 c.c. of nitrogen at 16° and 755 mm.

	Found.			Theory for $C_{13}H_{12}N_2O$.
	I.	II.	III.	
C	—	73.16	—	73.58 per cent.
H	5.66	6.04	—	5.66 „
N	—	—	13.35	13.20 „
O	—	7.45	—	7.55 „
		(by diff.)		

The crystals melt at $234-235^\circ$, and, when fused with phosphoric anhydride, evolve at once the irritating odour of phenyl isocyanate.

These results, verified by a direct comparison with a specimen of carbanilide melting at 235° , prove the identity of the substance.

The formation of diphenylurea, shown by this experiment to be due to the presence of water, is readily explained by the equation

the correct nature of which is proved by the quantitative results obtained. Thus, according to this equation, 0.15 gram water should give rise to the formation of

Diphenylurea .. 0.588 gram. Found .. 0.68 gram (crude).

whilst, under the circumstances, the weight of acetanilide produced should be—

Theory 2.52 grams. Found .. 2.27 grams.

A closer agreement with the theoretical numbers was not to be expected in an experiment of this nature, where great accuracy was not aimed at.

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I may add that three other experiments were carried out in presence of water, and in each case H_2S and diphenylurea were produced, the quantity of the latter varying directly with the amount of water present; it is unnecessary to give the details of these experiments, as the next point of interest in connection with the present investigation lies in the following:—

Exp. 6.—Quantities used $\begin{cases} 3.4 \text{ grams } \text{C}_6\text{H}_5\cdot\text{NCS}. \\ 1.5 \text{ ,, } \text{CH}_3\cdot\text{COOH}. \\ 0.15 \text{ ,, } \text{H}_2\text{O}. \end{cases}$

Heated in sealed tube for three hours at $160\text{--}170^\circ$, that is, at the temperature as adopted by Claus and Völtzkow. Under these conditions, the weight of carbanilide obtained was only

0.09 gram.

Theory .. 0.588 gram,

whilst the weight of acetanilide was increased to 2.95 grams. As before, the gas evolved consisted of CO_2 , H_2S , and COS .

Therefore, at the *higher* temperature, the diphenylurea undergoes decomposition, giving rise to acetanilide, in accordance with the equation

This decomposition is independent of the presence of water, as a direct experiment has shown that pure anhydrous acetic acid decomposes diphenylurea at $160\text{--}170^\circ$, though for complete decomposition a large excess of the acid and prolonged heating is required.

III. Phenylthiocarbimide and Propionic Acid.

Quantities used $\begin{cases} 6.8 \text{ grams } \text{C}_6\text{H}_5\cdot\text{NCS}. \\ 3.7 \text{ ,, } \text{C}_2\text{H}_5\cdot\text{COOH}. \end{cases}$

The specimen of propionic acid was obtained from Messrs. Harrington Bros., of Cork; a determination of its strength proved it to contain 99.56 per cent. of real acid. The mixture was heated at $130\text{--}140^\circ$ for two hours. A *trace* of sulphuretted hydrogen was evolved, due to the small quantity of water present. The weight of diphenylurea obtained was 0.11 gram. The weight of propionanilide (m. p. $99\text{--}100^\circ$)

6.85 grams.

Theory 7.45 grams.

The product from the action smelt slightly of phenylthiocarbimide, and contained a small amount of unaltered acid; complete action, therefore, had not taken place.

The results of this single experiment prove that with propionic

acid interaction takes place in exactly the same manner as with acetic acid.

In the case of a single experiment with phenylthiocarbimide and a sample of formic acid containing 99.1 per cent. of real acid, there was obtained, besides formanilide and diphenylurea, a small quantity of sulphocarbamilide.

Therefore, in this case a further secondary decomposition appears to take place, not noticed with either acetic or propionic acids.

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