CLXXVII.—*The Action of Nitrogen Sulphide on Organic Substances. Part IV.*

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NITROGEN sulphide acts slowly on the acids of the paraffin series, and Ruff and Giesel (*Ber.*, 1904, **37**, 1573), noticed that in the case of boiling acetic acid, sulphur dioxide was evolved and sulphur and some sulphuric acid formed; but small quantities of free nitrogen are also liberated and considerable amounts of acetamide and diacetamide are formed. Moreover, the sulphuric acid is present in the form of ammonium sulphate. The amount of the two amides obtained from 3 grams of nitrogen sulphide, namely, 2·5 grams of acetamide and about 0·6 gram of diacetamide, corresponds to about 22 per cent. of nitrogen, the theoretical amount present in the sulphide being 30·4 per cent.; with propionic acid, an exactly similar reaction takes place, but with greater velocity. Sulphur dioxide, nitrogen, and a small quantity of carbon monoxide are evolved, and the amounts of propionamide and dipropionamide formed only correspond to between 12 and 13 per cent. of nitrogen, showing that at the temperature of boiling propionic acid the direct decomposition of nitrogen sulphide into its constituents is greater than in the case of acetic acid. In one determination, an amount of free nitrogen was obtained corresponding to between 6 and 7 per cent., and the ammonium sulphate represented 7 per cent. of nitrogen, so that with 13 per cent. as the mixed amides, a total of about 26—27 per cent. of nitrogen is accounted for out of the theoretical amount, namely, 30·4 per cent.

Even with acetic anhydride, a similar decomposition took place with considerable charring, but the amount of amides obtained was much smaller, and that of ammonium sulphate larger than in either of the above cases; it is quite clear that a deep-seated decomposition of the molecule must have taken place. Although the formation of ammonium sulphate in these reactions indicates a process of oxidation, similar, in all probability, to that previously noticed with the aldehydes, no satisfactory explanation for this has yet been found.

As the formation of the amides is but of little value in elucidating the constitution of nitrogen sulphide, further work on the interaction of this substance and the paraffin acids was abandoned.

With the halogen-substitution products of acetic acid, the reaction was again very similar to that already described, but the formation of carbon monoxide in addition to sulphur dioxide and free nitrogen, and, further, of the corresponding ammonium haloid salt as well as ammonium sulphate, shows still more clearly that in these reactions a complete disruption of the molecule of the acid takes place.

Chloroacetic acid gave a mixture of chloroacetamide and chlorodiacetamide, the yield of the second substance predominating. With bromoacetic acid, the reaction is much more violent, as evidenced in the formation of a considerable quantity of ammonium bromide, a very much smaller amount of bromodiacetamide, and mere traces of bromoacetamide. With di- and tri-chloroacetic acids, only the corresponding amides were obtained, and in neither case was the formation of diamides observed.

An interesting feature in these reactions with the chlorine-substitution derivatives of acetic acid is that in each case approximately the same percentage of nitrogen present in the sulphide is converted into the mixed or simple amides, thus chloroacetic acid gives 6 per cent. of nitrogen as chloroacetamide and 6 per cent. as chlorodiacetamide. With dichloroacetic acid, 13·5 per cent. of nitrogen appears as dichloroacetamide, and with trichloroacetic acid 12 per cent. is found to be present as trichloroacetamide.

For reasons similar to those previously mentioned, no further investigations were carried out with the halogen-substituted acids.

EXPERIMENTAL.

1. *The Action of Nitrogen Sulphide on Acetic Acid, Acetic Anhydride, and Propionic Acid.*

When excess of acetic acid is heated for about ten hours with 3 grams of nitrogen sulphide, complete decomposition of the latter substance was effected, and on distilling off the excess of acid the temperature rose and a mixture of acetamide and diacetamide passed over. The substance had all the characteristic properties of acetamide and amounted to about 3·1 grams. The separation of the diamide was carried out by dissolving the mixed amides in ether and passing in hydrogen chloride, when acetamide hydrochloride crystallised out and was filtered off; this operation was repeated and finally about 0·6 gram of diacetamide was obtained from the filtrate.

The reaction with acetic anhydride was carried out in a similar manner and the separation of the amides effected as previously mentioned, but the amounts of these two substances obtained from 3 grams of nitrogen sulphide did not amount to more than 1 gram, and much larger quantities of ammonium sulphate were formed than in the case of acetic acid.

With propionic acid, the reaction was allowed to take place at the boiling point and the gases evolved were investigated; they were found to consist chiefly of sulphur dioxide and smaller quantities of free nitrogen and traces of carbon monoxide; in one experiment, 3 grams of the sulphide gave 0·2 gram of nitrogen, or 6·6 per cent. The reaction with this quantity of nitrogen sulphide is complete in about three hours, and on distilling off the excess of acid, the mixed amides pass over between 200° and 220°. The impure substance was dissolved in a small quantity of boiling alcohol, and, on cooling, 1·5 grams of dipropionamide melting at 154—155° crystallised out, the filtrate was evaporated to dryness, and the impure residue, after draining on a porous tile and recrystallisation from chloroform and light petroleum, gave about 1 gram of propionamide melting at 79°.

The dipropionamide gave the following data on analysis: found N = 10·76; $C_5H_{11}O_2N$ requires N = 10·85 per cent.

2. *The Action of Nitrogen Sulphide on the Halogen-substituted Acetic Acids.*

A. Chloroacetic acid. Fifty grams of this acid were heated for thirty-six hours on a water-bath with 15 grams of nitrogen sulphide, and at the end of that time the contents of the flask had solidified. The gases evolved consisted chiefly of sulphur dioxide with smaller quantities of nitrogen and carbon monoxide. The semi-solid mass was drained at the pump and afterwards on a porous tile, when 21 grams of solid were obtained. This product was freed from small amounts of ammonium sulphate and chloride by washing with cold water, and the residual mixture of chloroacetamide and chlorodiacetamide partially separated by warm water, in which the former is much more soluble than the latter, further purification being effected by recrystallisation from alcohol. In this way, 6 grams of pure chloroacetamide melting at 125° were obtained, the melting point usually given being between 119° and 120°. The following data were obtained on analysis: found

N = 14·95 ; Cl = 37·42 ; C_2H_4ONCl requires N = 14·98 ; Cl = 37·90 per cent.

The substance of lesser solubility and higher melting point was contaminated with small quantities of free sulphur ; it was purified by recrystallisation from either boiling water or alcohol, in which it is less soluble than the chloro-acetamide. After several crystallisations, 12 grams of pure chlorodiacetamide were obtained. This substance gave the following results on analysis : found C = 28·64 ; H = 3·36 ; N = 8·12 ; Cl = 41·52 ; $C_4H_5O_2NCl$ requires C = 28·26 ; H = 2·94 ; N = 8·24 ; Cl = 41·69 per cent.

Chlorodiacetamide, which does not appear to have been previously described, shows an intensely acid reaction in aqueous solution, is easily decomposed by alkalis with evolution of ammonia, crystallises in well-formed needles from either benzene or toluene, and melts at 195—196°, subliming in snow-white needles at a temperature below, but not far removed from, its melting point.

B. Bromoacetic acid. Twelve grams of the acid were heated on the water-bath with 5 grams of nitrogen sulphide, an energetic reaction took place, and sulphur dioxide, nitrogen, and carbon monoxide were liberated. The solid, which slowly separated, was washed with a small quantity of ether ; the filtrate on evaporation left an oil which afterwards partially solidified ; the semi-solid mass was then drained on a porous tile, and after recrystallisation from benzene gave a small quantity of the well-crystalline bromoacetamide melting at 92—93°. The substance insoluble in ether consisted chiefly of ammonium bromide, with smaller quantities of ammonium sulphate ; these were washed out with cold water, and the residue on recrystallisation from alcohol gave about 1 gram of bromodiacetamide melting at 192° ; like the corresponding chloro-derivative, this compound shows acid properties in aqueous solution. The following data were obtained on analysis : found Br = 62·15 ; $C_4H_5O_2NBr$ requires Br = 61·7 per cent.

C. Dichloroacetic acid. Twenty-three grams of the acid were heated for forty-eight hours at 100°, with 13 grams of nitrogen sulphide. The gases evolved consisted of sulphur dioxide, carbon monoxide, and smaller quantities of free nitrogen. The solid which separated was washed with cold water, dried, and recrystallised from benzene, when 16 grams of dichloroacetamide melting at 98° were obtained, and no substance of higher melting point was formed in the reaction. The aqueous solution contained ammonium sulphate and chloride.

D. Trichloroacetic acid. The reaction between excess of this acid and 5 grams of nitrogen sulphide was carried out as in previous cases and the same gases were evolved, but the amount of carbon monoxide was very much less than in the case of dichloroacetic acid. The separation of ammonium sulphate and smaller quantities of the chloride was carried out by means of cold water, and the trichloroacetamide present was purified by recrystallisation from benzene; 7 grams melting at 144° were obtained (Zincke gives the melting point of this substance as 141°).

With the last two acids, experiments were carried out in a current of carbon dioxide, and the gases evolved passed through a tube surrounded by a freezing mixture and then into a large eudiometer filled with concentrated aqueous caustic potash. In each instance, the gases insoluble in this solution were found to consist of nitrogen and carbon monoxide, the former largely predominating in the case of the trichloro-acid, the latter in that of the dichloro-acid. In both cases, a very small amount of a fuming liquid collected in the cooled tube; its odour resembled that of sulphur chloride, mixed perhaps with acetyl chloride. The liquid generated heat on treatment with water and gave the chlorine reaction with silver nitrate, but the amount of liquid was quite insufficient for further examination.

When ethyl chloroacetate is used instead of the free acid, long-continued heating with nitrogen sulphide appears to result only in the slow decomposition of that substance into its constituents. Sulphur dioxide is not evolved, and by distillation the ester can be recovered unchanged.

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