## DIXON: THE ACTION OF PHOSPHORUS

## XVII.—The Action of Phosphorus Trithiocyanate on Alcohol.

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In a preliminary note (J. pr. Chem., 1872, [ii], 7, 474), Lössner records that he has obtained (1) by the action of phosphorus trichloride on potassium thiocyanate in alcoholic solution, a substance crystallising in fine needles, whose analysis leads to the empirical formula  $C_8H_{18}ON_4S_4$ ; and (2) from benzoyl chloride and alcoholic potassium thiocyanate, a compound,  $C_8H_9ONS$ . No analytical results are given in this note, which is very brief; but the interaction in which benzoyl chloride takes part is dealt with by Lössner at considerable length in a paper published a couple of years later (*ibid.*, 1874, [ii], 10, 237); the compound  $C_8H_9ONS$  now appears as  $C_{10}H_{11}O_2NS$ , that is, benzoyl thiocyanate *plus* a mol. of ethyl alcohol, and is regarded by him as 'benzoylethyloxysulphocarbamic acid,' PhCO·NEt·CO·SH; a paper dealing with the constitution of this substance and of certain of its derivatives has lately been published (Dixon, Trans., 1899, 75, 375).

No reference is made in Lössner's second communication to the compound  $C_8H_{18}ON_4S_4$ ; nor, in fact, so far as the author can ascertain, is any description of it to be found in chemical literature. It is not easy to understand how a substance of this composition could be formed out of the materials used, unless through the occurrence of some profound decomposition; with the view of ascertaining whether such a change really took place, and more particularly since the interaction to be expected of these substances appeared to belong to the class of interactions recently studied by the writer, in which phosphorus and phosphoryl 'thiocyanates' take part (Trans., 1901, 79, 541), it was decided to reexamine Lössner's reaction.

Before doing so, and incidentally to the incipient study just mentioned, some experiments were carried out in order to learn whether "phosphorus thiocyanate,"  $P(SCN)_3$  or  $P(NCS)_3$ , would unite directly with ethyl alcohol so as to afford a phosphoretted thiourethane, thus:

$$P(NCS)_3 + 3C_2H_5 \cdot OH = P(NH \cdot CS \cdot OC_2H_5)_3;$$

although, in view of the great ease with which both this and the corresponding phosphoryl derivative undergo hydrolysis, it scarcely seemed probable.

The phosphorus compound was prepared as already described (*loc. cit.*, p. 545), about 13 grams of phosphorus trichloride being used in each preparation: on treating the benzene solution with absolute

alcohol, there was marked evidence of chemical interaction, the temperature rising in three successive experiments in which it was measured, by  $47^{\circ}$ ,  $46^{\circ}$ , and  $59^{\circ}$  respectively, whilst free thiocyanic acid was evolved. On concentrating the mixture at the ordinary temperature, a yellow, crystalline solid was deposited; the mother liquor formed a clear brown syrup, intensely acid, reacting freely for thiocyanic acid and phosphorus, and soon beginning to decompose with evolution of mercaptan.

The solid product occurred in limited quantity, not more than a gram, at most, being obtained for every 13 grams of trichloride used; it was insoluble in benzene, sparingly soluble in boiling water, and moderately so in hot alcohol, but did not crystallise well from the latter solvent. When recrystallised from much boiling water, it was obtained in yellow, flexible, hair-like needles (on one occasion several inches long and closely resembling *Spirogyra* in outward appearance): they began to darken and change at about 230°, but were not melted at  $250^{\circ}$ .

The substance contains no phosphorus, and hence is not the desired phosphorus trithiotriurethane. It is desulphurised by heating in alcoholic solution with ammoniacal silver nitrate, or with alkaline lead tartrate; its aqueous solution is somewhat acid to litmus and gives with lead acetate a bright yellow precipitate. Ferric chloride yields practically no colour reaction, either when added to the aqueous solution or to the mixture produced by first dissolving the solid in warm alkali hydroxide and then acidifying the solution with hydrochloric acid. The substance dissolves readily in potassium cyanide solution, and the resultant liquid, if acidified and treated with ferric chloride, now gives the intense blood-red thiocyanic reaction.

From the properties just described, there could be little doubt that the substance was nothing more than *iso*persulphocyanic acid,  $C_2H_2N_2S_3$ , and the results of analysis showed this to be the case:

S found, 64.3; N found, 18.9;  $C_2H_2N_2S_3$  requires S = 64; N = 18.7 per cent.

The mechanism whereby this substance comes to be formed is probably as follows : the "phosphorus thiocyanate" is decomposed in part by the alcohol, yielding free thiocyanic acid :

 $P(SCN)_3 + 3C_2H_5 \cdot OH = P(O \cdot C_2H_5)_3 + 3HSCN ;$ 

whilst another portion, in like manner, yields phosphorous acid : under the influence of this mineral acid, the former could afford *iso*persulphocyanic acid, thus :

$$3\mathrm{HSCN} = \mathrm{C_2H_2N_2S_3} + \mathrm{HCN}.$$

Save the isopersulphocyanic acid, no other solid product was found;

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consequently, if the phosphorus trithiotriurethane is formed, or, at all events, continues to exist, under the above conditions, it must be as one of the constituents of the acid, syrupy mother liquor, but the foul smell of the latter rendered it so unpleasant to work with that it was not examined further. However, as phosphorus trithiotriurethane, if capable of existence under ordinary circumstances, would probably be a solid substance more or less easily decomposable by moisture, it is doubtful whether it could have been extracted from the liquor, even if present.

As regards the interaction between alcoholic potassium thiocyanate and phosphorus trichloride, there was scarcely any reason to anticipate that it would run a course materially different from that between phosphorus trithiocyanate and alcohol; however, the experiment was tried, with the following result.

On dropping phosphorus trichloride into a saturated solution of potassium thiocyanate in 99.5 per cent. alcohol, violent action occurred, and potassium chloride was precipitated; on filtering this off and concentrating the filtrate by slow evaporation, thiocyanic acid escaped, and yellow, crystalline material separated in an oily, very acid, liquid; the former, when recrystallised from boiling water, proved to be identical with the solid obtained from phosphorus thiocyanate and alcohol, namely, isopersulphocyanic acid. In this case, as the liberated thiocyanic acid is in contact with much free hydrochloric acid proceeding from the interaction between the phosphorus haloid and the alcohol, it is a simple matter to account for the production of isopersulphocyanic acid. As in the preceding case, the quantity of this acid bears but a small proportion to the amount of phosphorus chloride used. So far, the writer has failed to identify any other substance in the solid product, yet Lössner, strange to say, does not mention the occurrence of isopersulphocyanic acid at all.

It would seem, therefore, either that the interaction must have proceeded on different lines when conducted by this chemist, or else that, through some accident, he must have attributed to *iso*persulphocyanic acid,  $C_2H_2N_2S_3$ , the formula  $C_8H_{18}ON_4S_4$ . How this could happen it is not very easy to see, considering that the percentages of sulphur are 64 and 40.8, respectively. It is conceivable, however, that some unsuspected cause of error may have temporarily crept into his analytical practice, more especially bearing in mind that his benzoyl chloride product, above mentioned, which was stated in the preliminary note to have, according to the results of analysis, the formula  $C_8H_9ONS$ , turns out to be really  $C_{10}H_{11}O_2NS$ ; here the theoretical results are by no means so widely divergent as in the preceding case, but still the figures differ by nearly 4 per cent. for the sulphur, 3 per cent. for the nitrogen, and so on.

In the hope of possibly obtaining phosphorus tribenzyltrithiocarbamate, a cold, somewhat dilute solution of "phosphorus thiocyanate" in benzene was treated with benzyl alcohol. Interaction occurred at once, the temperature of the mixture rising by about 30°; but after driving off the solvent and allowing the residue to stand, a mere trace of white, solid matter was deposited, the amount being too small to permit of identification. It crystallised well in white prisms from boiling water, volatilised completely, on heating, without preliminary fusion, gave no ammonia when heated with alkali, contained no phosphorus, gave no colour reaction with potassium cyanide, hydrochloric acid, and ferric chloride, and consequently was neither isopersulphocyanic acid nor phosphorus tribenzyltrithiocarbamate. The mother liquor was almost completely volatile in a current of steam; the distillate, a yellowish oil, consisted partly of unchanged benzyl alcohol, and partly of an unpleasant smelling oil which contained sulphur but no phosphorus, the latter being wholly retained in the triffing residue of the steam distillation.

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