CCXII.—The Action of Mercaptans on Acid Chlorides. Part II. The Acid Chlorides of Phosphorus, Sulphur, and Nitrogen.

By HUBERT SANDERSON TASKER and HUMPHREY OWEN JONES.

THE presence of phosphorus trichloride and phosphoryl chloride in crude oxalyl chloride resulted, as has been shown in the preceding paper, in the formation of triphenyl trithiophosphite and triphenyl trithiophosphate when the liquid was allowed to react with sodium phenylmercaptide.

Schwarze (J. pr. Chem., 1874, [ii], 10, 222) claimed that he obtained triphenyl trithiophosphate by the action of phosphoryl chloride on phenyl mercaptan, ascribing to it the melting point 72°.

Michaelis (*Ber.*, 1907, **40**, 3419) has investigated the properties of triphenyl trithiophosphite and triphenyl trithiophosphate, and finds that their melting points are 77° and 115° respectively. He suggests that Schwarze's product was merely phenyl disulphide. If this be so, as is improbable, for the melting point of phenyl disulphide is 61°, it becomes likely that the reaction may give an interesting reduction product of phosphoryl chloride, thus:

 $POCl_3 + 2C_6H_5 \cdot SH = POCl + (C_6H_5 \cdot S)_2 + 2HCl.$

This point has been investigated, and results seem to show that Michaelis's surmise was incorrect, although his general results were confirmed. Incidentally, it was found that triphenyl trithiophosphite can be oxidised to triphenyl trithiophosphate by potassium dichromate and sulphuric acid, or by nitric acid. \mathbf{It} forms noadditive product with methyl iodide or hydrogen chloride. \mathbf{The} interaction of phenyl mercaptan and phosphoryl chloride in molecular proportions at 100° resulted in the production of a mixture of triphenyl trithiophosphate and phenyl disulphide. The two products could be completely separated by crystallisation from All attempts to isolate the hypothetical compound POCl alcohol. failed, and it is probable that phenyl disulphide is formed in the reduction of phosphoryl chloride to phosphorus trichloride, thus:

 $\mathbf{POCl}_3 + 2\mathbf{C}_6\mathbf{H}_5 \cdot \mathbf{SH} = \mathbf{H}_2\mathbf{O} + \mathbf{PCl}_3 + (\mathbf{C}_6\mathbf{H}_5 \cdot \mathbf{S})_2.$

The water would then form phosphoric acid with the excess of phosphoryl chloride, and the phosphorus trichloride would probably be carried off at the temperature of the reaction in the streams of hydrogen chloride which are evolved.

It thus seems probable that Schwarze's compound was triphenyl trithiophosphate, as his analyses go to prove, the low melting point being accounted for by the contamination with phenyl disulphide.

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The Acid Chlorides of Sulphur.

Holmberg (Annalen, 1908, **359**, 81) has stated that sulphuryl chloride reacts with alkyl mercaptans to give the corresponding alkyl disulphide, sulphur dioxide, and hydrogen chloride, thus:

$$2\mathbf{RSH} + \mathbf{SO}_2\mathbf{Cl}_2 = \mathbf{R}_2\mathbf{S}_2 + \mathbf{SO}_2 + 2\mathbf{HCl}.$$

This result has been confirmed for phenyl mercaptan. By using lead phenylmercaptide, however, or phenyl mercaptan in ethereal solution, evidence was obtained for the transitory existence of an unstable phenyl dithiosulphate.

Sulphuryl chloride in ethereal solution was added to lead phenylmercaptide at the ordinary temperature. Sulphur dioxide was evolved at once, and the residue was found to consist of lead chloride and phenyl disulphide.

When, however, the reaction was carried out in a freezing mixture, the formation of lead chloride was detected by the change in colour of the lead phenylmercaptide, but the solution became reddish-yellow, and no gas was evolved. On warming the solution, however, or allowing it to evaporate, the colour disappeared, sulphur dioxide and phenyl disulphide being obtained.

There seems little doubt that phenyl dithiosulphate is formed in solution, but it was found impossible to isolate it. The reaction could then be represented thus:

$$\begin{split} & \mathrm{SO}_2\mathrm{Cl}_2 + \mathrm{Pb}(\mathrm{S}\text{\cdot}\mathrm{C}_6\mathrm{H}_5)_2 = \mathrm{Pb}\mathrm{Cl}_2 + \mathrm{SO}_2(\mathrm{S}\text{\cdot}\mathrm{C}_6\mathrm{H}_5)_2, \\ & \mathrm{SO}_2(\mathrm{S}\text{\cdot}\mathrm{C}_6\mathrm{H}_5)_2 = \mathrm{SO}_2 + (\mathrm{S}\text{\cdot}\mathrm{C}_6\mathrm{H}_5)_2. \end{split}$$

The behaviour was similar when an ethereal solution of phenyl mercaptan reacted with sulphuryl chloride at low temperatures.

These considerations made the study of the behaviour of thionyl chloride with phenyl mercaptan and its derivatives one of especial interest, for an analogous reaction might be expected to give rise to a new oxide of sulphur, SO, thus:

$$\begin{aligned} \operatorname{SOCl}_2 + 2\operatorname{C}_6\operatorname{H}_5 \cdot \operatorname{SH} &= \operatorname{SO}(\operatorname{S} \cdot \operatorname{C}_6\operatorname{H}_5)_2 + 2\operatorname{HCl}.\\ \operatorname{SO}(\operatorname{S} \cdot \operatorname{C}_6\operatorname{H}_5)_2 &= \operatorname{SO} + (\operatorname{S} \cdot \operatorname{C}_6\operatorname{H}_5)_2. \end{aligned}$$

The expectation, too, was strengthened by the fact that a similar but paler transient colour was noticed when phenyl mercaptan or lead phenylmercaptide was allowed to react with thionyl chloride in ethereal solution at a low temperature.

The gaseous products of the reaction were therefore subjected to examination.

One gram-molecule of thionyl chloride was allowed to react with two of phenyl mercaptan at 0° or at other temperatures down to -70° , and the gases evolved were swept by means of a stream of

Downloaded by Stanford University on 27/03/2013 14:33:41. Published on 01 January 1909 on http://pubs.rsc.org | doi:10.1039/CT9099501910 dry hydrogen through U-tubes cooled to -70° , so that the gases might be liquefied.

Hydrogen chloride was obtained, and sulphur dioxide was detected in large quantity, both by its odour and by its boiling point. This indicated that the decomposition of thionyl chloride involves the participation of more than one molecule, and the simplest hypotheses for the reaction become:

and

(2) $6C_6H_5 \cdot SH + 3SOCl_2 = 6HCl + 3(C_6H_5 \cdot S)_2 + SO_2 + S_2O.$

(1) $4C_6H_5 \cdot SH + 2SOCl_2 = 4HCl + 2(C_6H_5 \cdot S)_2 + SO_2 + SO$

The latter hypothesis would involve the formation of another new oxide of sulphur, S_2O .

The reduction of thionyl chloride by nickel carbonyl was found to throw light on the problem by analogy. These substances interact vigorously in the cold; sulphur dioxide and carbon monoxide are evolved, and a brown mass remains which consists of nickel chloride and sulphur—it being possible to extract the latter by solution in carbon disulphide. The reaction, although so vigorous, lowered the temperature of the reaction mixture.

It was found impossible, however, in the case of the reaction with phenyl mercaptan to extract sulphur from the residue.

It was therefore decided to collect the gases evolved, and to determine their total acidity, and also the extent to which they could reduce iodine.

4.1 Grams of thionyl chloride were allowed to react with 7.3 grams of phenyl mercaptan in a distilling flask at a low temperature. The gases evolved were swept by means of a stream of dry hydrogen through an empty wash-bottle and two U-tubes into 200 c.c. of N-sodium hydroxide solution.

It was possible, by surrounding the U-tubes with freezing mixtures, to estimate approximately the boiling points of the gases evolved.

When violent reaction had ceased, the temperature of the reaction flask was raised until the residue melted and ceased to evolve gas. The residue at 60° was a clear, yellow liquid, which deposited phenyl disulphide on cooling. This could be collected, and the viscous liquid so obtained continued for some time to deposit small quantities of phenyl disulphide.

In addition to this yellow oil and phenyl disulphide, there appeared drops of a less dense and more mobile liquid, which was identified as water by the coloration of anhydrous copper sulphate and by its action on sodium. It seemed to be a product of the reaction, for it invariably appeared in spite of special precautions which were taken to dry the hydrogen used. Its amount could not be estimated, owing to the small quantity formed, and the large excess of the other residual products.

By cooling the U-tubes, hydrogen chloride and sulphur dioxide were identified by their boiling points, but there was no evidence of any other volatile product boiling above -70° .

The sodium hydroxide solution was titrated first with N/10-sulphuric acid, and then with N/10-silver nitrate, to determine the amount of hydrogen chloride evolved. Sulphur dioxide was estimated by titration of the neutral solution with standard iodine solution.

Two experiments were made, and the quantity of hydrogen chloride estimated differed by only 2 per cent., showing that the gases were thoroughly swept out of the apparatus. As a mean of the two experiments, 2.55 grams of hydrogen chloride and 0.777 gram of sulphur dioxide were produced by the interaction of 4.1grams of thionyl chloride and 7.3 grams of phenyl mercaptan.

The first hypothetical equation demands 2.45 grams of hydrogen chloride and 1.06 grams of sulphur dioxide, whilst the second requires 2.45 grams of hydrogen chloride and 0.71 gram of sulphur dioxide.

Low, rather than high, readings would be expected, and the fact that the sulphur dioxide results are relatively high tends to discountenance the validity of the second equation.

In these equations, too, the possible presence and volatility of the compound S_2O has been ignored. Its presence would be expected at least to double the power of the products to reduce iodine, so that the observed reading would fall very far short of that required.

Nor did the solution on qualitative examination show any evidence for the existence in it of a salt corresponding with a new oxide of sulphur.

Examination of the residual mass gave further evidence in support of the first equation.

The liquid obtained after collecting the phenyl disulphide which separated was distilled under diminished pressure. Between 180° and 220°/10 mm. phenyl disulphide distilled over, and an amorphous, sticky, brown mass remained behind. Phenyl disulphide, when distilled alone, does not decompose, and leaves no residue.

Analyses of two specimens of the liquid gave the following results:

It seemed probable that the liquid is either view Article Online sulphide which still holds a little phenyl disulphide in solution, or else a difficultly crystallisable solution of sulphur in phenyl disulphide.

Phenyl tetrasulphide is described as a viscid, yellow oil, which decomposes on distillation into sulphur and phenyl disulphide. The properties of the oil obtained closely correspond with these.

A solution of sulphur in phenyl disulphide in the proportions corresponding with $(C_6H_5)_2S_4$ was prepared. It solidified, on cooling, to a hard, cream-coloured mass, the appearance of which had nothing in common with that of the liquid obtained from the reaction.

Thus an equation can be written to include the phenyl tetrasulphide which seems to be formed:

 $8C_{6}H_{5} \cdot SH + 4SOCl_{2} = 8HCl + 2SO_{2} + 3(C_{6}H_{5} \cdot S)_{2} + (C_{6}H_{5})_{2}S_{4}.$

In support of this, it was found that 14.6 grams of phenyl mercaptan and 8 grams of thionyl chloride produced 10.65 grams of phenyl disulphide, whilst the above equation requires 11.27 grams.

Thus the equation represents the reaction fairly well, except for the water, a small quantity of which is invariably formed.

At this point our attention was drawn to a statement by Holmberg (*loc. cit.*), to the effect that alkyl mercaptans react with thionyl chloride in accordance with the general equation:

 $4RSH + SOCl_2 = R_2S_2 + R_2S_3 + H_2O + 2HCl.$

This hypothesis accounts for the formation of water, but takes no account of the evolution of sulphur dioxide, and since phenyl trisulphide is a solid, it would demand that the residual mass should become completely solid at the ordinary temperature. Reference to the experiments already quoted suggested that the two reactions might proceed simultaneously, for sulphur dioxide was always produced in quantity smaller than that required by the equation proposed.

Further experiments were devised to ascertain whether either of the two hypotheses correctly represents the reaction under any special conditions.

It will be convenient if the two equations be henceforth referred to as A and B, thus:

(A) $8C_6H_5 \cdot SH + 4SOCl_2 = 8HCl + 2SO_2 + 3(C_6H_5 \cdot S)_2 + (C_6H_5)_2S_4$.

(B) $4C_6H_5 \cdot SH + SOCl_2 = (C_6H_5 \cdot S)_2 + (C_6H_5)_2S_3 + H_2O + 2HCl.$

A weighed quantity of thionyl chloride was allowed to react with an excess of lead phenylmercaptide in a U-tube. A continual stream of dry air, freed from carbon dioxide, swept the gases evolved into a measured volume of standard sodium hydroxide solution. After sweeping with air for eight hours, it was found that no more gas was absorbed by the alkali. The sodium hydroxide solution was neutralised and titrated with standard iodine to estimate the sulphur dioxide, when it was found that 1.955 grams of thionyl chloride gave 0.473 gram of sulphur dioxide. If thionyl chloride is decomposed in accordance with equation A, 0.526 gram of sulphur dioxide should be evolved. In this case, by the use of a metallic derivative of phenyl mercaptan, the formation of water as demanded by equation B was prevented. The satisfactory agreement obtained (considering the nature of the experiment) indicates that in this case a modification of equation A would adequately represent the reaction.

Unfortunately, an experiment of similar nature with phenyl mercaptan itself, in place of the lead derivative, was found to be impracticable, for the stream of air carries over into the sodium hydroxide considerable quantities of that one of the reactive liquids which happens to be present in excess. Another method was therefore devised.

The hydrogen chloride and sulphur dioxide produced were estimated by heating the total products of the reaction with a measured excess of standard alkali and by titration of the solution obtained. The two liquids were weighed, and the effect of an excess of either on the titrations was allowed for.

The suitability of the method for discrimination between equations A and B depends on the proportions of the reacting substances used. The proportion of 8 gram-molecules of phenyl mercaptan to 4 gram-molecules of thionyl chloride demands, according to A, 12 equivalents of alkali and 4 equivalents of iodine, and exactly the same quantities are required according to B. Thus, if the substances are used in this proportion, no discriminative result will be obtained. A more decisive result can be obtained by using 16 gram-molecules of phenyl mercaptan to 4 of thionyl chloride. Equation A will then require 20 equivalents of alkali and 12 of iodine (one gram-molecule of phenyl mercaptan neutralises one gram-molecule of sodium hydroxide, and reduces one gram-atom of iodine), whilst B will require 8 equivalents of alkali and no iodine.

This was the proportion used in the experiments. Standard solutions of phenyl mercaptan and of thionyl chloride in dry ether were made. The required volume of each was measured into a stoppered bottle, and the bottle was shaken from time to time. A measured excess of N-sodium hydroxide solution was then added, and, after further shaking, the whole was titrated, first with acid, and then

with iodine. Preliminary experiments proved that the titrations were sufficiently accurate under these conditions. Two experiments may be quoted to illustrate the results obtained.

	Thionyl chloride, gram.	Phenyl mercaptan, gram.	Readings.	$\begin{array}{c} {\rm Equation} \ {\it A} \\ {\rm requires} \end{array}$	Equation <i>B</i> requires
1.	0.128	0.664	7·1 c.c. N-alkali 0·477 gram iodine	7 •5 c.c. 0 •573 gram	3·0 e.c.
2.	0.171	0.632	5 [.] 8 e.c. <i>N</i> -alkali 0 [.] 395 gram iodine	7·15 c.c. 0·545 gram	2·85 c.e.

These results seem to indicate that both reactions, represented by equations A and B, take place simultaneously.

In order to carry out the same type of experiment, using the pure substances instead of the ethereal solutions, a special device was adopted.

One of the substances was weighed into a large flask fitted with two tap funnels, one small and the other large. The small funnel, containing about the right amount of the other substance, was weighed before the reaction, and weighed again when the reaction was over and the liquid had been allowed to enter the flask. The large funnel contained 100 c.c. of N-sodium hydroxide solution. The liquid in the small funnel was allowed to run by small instalments into the flask, the evolved gases being allowed to escape through the alkali in the large funnel so as to absorb all the hydrogen chloride and sulphur dioxide.

The pressure in the flask was easily regulated by heating and cooling. The reaction being quite finished, the sodium hydroxide solution was allowed to run into the flask, and the contents were shaken. The solution was then filtered through glass wool, made up to 200 or 250 c.c., and titrated with acid and iodine.

The results obtained are expressed, as before, in grams of iodine required to oxidise the sulphur dioxide and phenyl mercaptan and in c.c. of *N*-acid required to neutralise the sulphur dioxide, phenyl mercaptan, and hydrogen chloride produced. The theoretical amounts are calculated by finding the amount of alkali

1.	Thionyl chloride, grams. 1·984	Phenyl mercaptan, grams. 1·742	Readings. 54°8 c.c. <i>N</i> -alkali 2°51 grams iodine	Equation A requires 59.0 c.c. 3.652 grams	Equation B requires 58°8 c.c. 3°23 grams
2.	0.828	3.408	22.4 e.e. <i>N</i> -alkali 1.13 grams iodine	38·4 c.c. 2·99 grams	16·3 c.c. 0·205 gram
3.	2.186	5.477	59°5 c.c. N-alkali 2°75 grams iodine	68.2 c.e. 3.6 grams	48.6 c.c. 1.5 grams
4.	1.0102	3.63	25°0 c.c. <i>N</i> -alkali 0°85 gram iodine	41 5 c.c. 3 11 grams	17.1 c.c. 0.04 gram

or iodine required by the reaction products (the reaction is assumed to use up the substance not present in excess), and by adding to these values the amounts required by the excess of the other reacting substance.

The first experiment serves to show the limited accuracy of the method, the calculated results being about the same for each equation.

In the other cases, the observed value is always intermediate between the two calculated values, and if a rough correction be made for the losses as observed in experiment 1, the experimental values are found to give the balance of evidence in favour of equation A.

In experiments 2 and 4, the proportions taken are about those demanded for equation B_2 and in these cases the reaction seems to follow this equation to a greater extent than in 3, where there is a larger proportional amount of thionyl chloride.

It is unfortunate that the addition of a further amount of thionyl chloride renders the method no longer discriminative.

It must be concluded that the two different reactions take place simultaneously. The proportions in which the reacting substances are present may be one of the factors which determine the ratio of the extents to which the two reactions proceed.

Nitrosyl Chloride.

The behaviour of nitrosyl chloride with mercaptans is apparently analogous to that of sulphuryl chloride.

When nitrosyl chloride is passed into phenyl mercaptan, the liquid turns port-wine red, and hydrogen chloride is evolved. The nitrosyl chloride is completely absorbed by the mercaptan, but the coloured liquid rapidly evolves nitric oxide. If the introduction of nitrosyl chloride is stopped, the colour gradually disappears with slower and slower evolution of nitric oxide, and phenyl disulphide finally separates out.

It would thus appear that the coloured and unstable phenyl thionitrite is formed in solution, and that this decomposes to give the final products of the reaction, thus:

 $C_{6}H_{5} \cdot SH + NOCl = HCl + C_{6}H_{5} \cdot SNO \quad (unstable).$ $2C_{6}H_{5} \cdot SNO = (C_{6}H_{5} \cdot S)_{2} + 2NO.$

It is, however, possible that the colour may be due to a direct additive product of phenyl mercaptan and nitrosyl chloride. To test this, nitrosyl chloride was allowed to react with an ethereal suspension of lead phenylmercaptide. The red colour was again produced, and lead chloride was left in suspension. Thus, a compound such as

H C₆H₅·S·N:O Cl

cannot be responsible for the colour of the solution.

The unstable, intermediate product may be preserved some time if the solution is kept at a low temperature, but all attempts to isolate it failed.

The corresponding ethyl and methyl compounds were obtained in solution.

On passing nitrosyl chloride into an ethereal suspension of mercury methylmercaptide, $Hg(S \cdot CH_3)_2$, the liquid became brownish-pink, and mercuric chloride was formed. The colour rapidly disappeared on standing and nitric oxide was evolved.

This behaviour is quite analogous to that observed in the case of lead phenylmercaptide.

The action of ethyl mercaptan on nitrosyl chloride at a low temperature resulted at first quite normally in the formation of a magnificent cherry-red colour, and in the evolution of hydrogen chloride. The red colour eventually disappeared with evolution of nitric oxide. In a freezing mixture of solid carbon dioxide dissolved in ether, however, a white, crystalline solid was deposited in small quantity. This was separated from the solution and recrystallised from alcohol. It was eventually identified as hydroxylamine hydrochloride, and must be the product of a side-reaction involving the reduction of the nitrosyl chloride.

The unstable, coloured thionitrites show two absorption bands, one sharply defined and broad in the yellowish-green, and the other narrower and diffuse in the green portion of the spectrum. The substitution of an alkyl group of high molecular weight for one of low molecular weight shifts the bands towards the red end of the spectrum.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.