CCXI.—*The Action of Mercaptans on Acid Chlorides. Part I. Oxalyl Chloride; the Mono- and Di-thio-oxalates.**

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THE alkyl mercaptans and their derivatives react in general with acid acid chlorides to form esters of the corresponding thio-acids; thus, for instance:

$$3RSH + PCl_3 = P(SR)_3 + 3HCl.$$

The final products of the reaction depend on the stability or instability of the ester formed, and if it is unstable, on its manner of decomposition. From the stable esters it is possible to obtain potassium salts by the action on them of alcoholic potassium hydrosulphide, and these potassium salts have in some cases properties of special interest.

The simplest method of decomposition of phenyl thio-esters is by the elimination of phenyl disulphide, and this gives rise to the possibility of obtaining new oxides of common elements. Those salts, however, which are of this nature appear to avoid decomposition in the simple and normal manner.

Oxalyl chloride was prepared at first by a modification of the method used by Fauconnier (*Compt. rend.*, 1892, **114**, 122). Two gram-molecules of phosphorus pentachloride and one gram-molecule of ethyl oxalate were heated to 150—160° in sealed tubes and the product was distilled. The fraction boiling at 70—75° contained the largest percentage of oxalyl chloride, but contained also phosphorus trichloride and phosphoryl chloride, as well as *as*-dichloroethane. Further purification, however, by distillation or precipitation of the oxalyl chloride with dry pyridine was found to be impracticable.

The action of sodium phenylmercaptide on oxalyl chloride was at first investigated in the hope of obtaining a new oxide of carbon, C_2O_2. No definite gaseous product, however, was obtained from the reaction, and the only solid products, apart from sodium chloride, were phenyl disulphide, triphenyl trithiophosphite, and triphenyl trithiophosphate.

Later, oxalyl chloride was obtained pure by Staudinger's method (*Ber.*, 1908, **41**, 3558), and these experiments were repeated. A

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* Preliminary notes on portions of this work have already appeared (*Proc. Camb. Phil. Soc.*, 1909, **15**, 94; *Proc.*, 1908, **24**, 271).

small quantity of carbon monoxide was produced together with sodium chloride, phenyl disulphide in small quantity, and a substance which crystallised from alcohol in small, yellow needles.

If lead phenylmercaptide in ether suspension was used instead of the sodium salt, the reaction was less vigorous, and there was no production of gas or of phenyl disulphide, the only products being lead chloride and the yellow compound; this was presumed to be phenyl-dithio-oxalate, the reaction taking place thus:

$$(COCl)_2 + Pb(S\cdot C_6H_5)_2 = (CO\cdot S\cdot C_6H_5)_2 + PbCl_2.$$

Phenyl dithio-oxalate is best prepared by the action of one gram-molecule of oxalyl chloride on two of phenyl mercaptan. The reaction starts in the cold, and a brisk evolution of hydrogen chloride takes place. A yellow colour is produced on mixing the liquids, which eventually solidify to a crystalline, yellow mass.

On crystallisation from alcohol, sulphur-yellow, prismatic needles, melting at 119—120°, are obtained, which are readily soluble in ether or light petroleum:

0·2857 gave 0·6402 CO_2 and 0·0951 H_2O. C = 61·1; H = 3·7.
$C_{14}H_{10}O_2S_2$ requires C = 61·31; H = 3·65 per cent.

Treatment with hot potassium hydroxide solution converts the ester into potassium phenylmercaptide and potassium oxalate.

The ester distils unchanged under the atmospheric pressure, but is decomposed by concentrated sulphuric acid, giving carbon monoxide and a brownish-purple colour, which is a characteristic test for phenyl disulphide.

On being heated with sodium to a temperature of 200—300°, the substance chars and yields carbon monoxide.

The yellow colour of phenyl dithio-oxalate persists after repeated recrystallisation and treatment in solution with animal charcoal.

Ethyl dithio-oxalate is prepared by mixing one gram-molecule of oxalyl chloride with two of ethyl mercaptan in the cold. The liquid becomes yellow, and hydrogen chloride is evolved. The mixture is heated gently to expel any excess of either of the reacting substances, and, on cooling, sets to a yellow, crystalline mass with a characteristic and, to some, a nauseating odour. On crystallisation from ether, yellow needles are obtained, which melt at 27—27·5°, and distil unchanged at 235°; the spontaneous solidification of the crude mass thus evidences the remarkable purity of the substance. Its colour, although its existence is undeniable, is not so intense as that of the phenyl ester:

0·1826 gave 0·2694 CO_2 and 0·0883 H_2O. C = 40·3; H = 5·3.
$(CO\cdot S\cdot C_2H_5)_2$ requires C = 40·45; H = 5·6 per cent.

Methyl Dithio-oxalate.—Methyl mercaptan was passed into oxalyl chloride, when a yellow colour was produced and hydrogen chloride was evolved. On shaking the liquid with water, pale yellow crystals of methyl dithio-oxalate, melting at 81—82°, separated. In a later preparation, crystals were actually deposited from the reaction liquid, and, when crystallised from light petroleum, separated in small rhombs, melting at 82·5—83·5°. The odour of this ester is very objectionable.

Treatment with aqueous potassium hydroxide gave potassium oxalate and methyl mercaptan:

0·3211 gave 0·3755 CO_2 and 0·1179 H_2O. C = 31·9; H = 4·08.

$(CO{\cdot}S{\cdot}CH_3)_2$ requires C = 32·0; H = 4·00 per cent.

Propyl Dithio-oxalate.—This substance was prepared from oxalyl chloride and propyl mercaptan precisely in the same manner as the ethyl ester. At the ordinary temperature it is a yellow liquid boiling at 158°/15 mm.:

0·2121 gave 0·4755 $BaSO_4$. S = 30·8.

$(CO{\cdot}S{\cdot}C_3H_7)_2$ requires S = 31·6 per cent.

iso*Amyl dithio-oxalate* was prepared similarly from oxalyl chloride and *iso*amyl mercaptan. It is a yellow liquid, boiling at 206°/19 mm.:

0·2565 gave 0·4510 $BaSO_4$. S = 24·15.

$(CO{\cdot}S{\cdot}C_5H_{11})_2$ requires S = 24·4 per cent.

Potassium Dithio-oxalate.—By the action of an equivalent quantity of alcoholic potassium hydrosulphide on phenyl or ethyl dithio-oxalate, also in alcoholic solution, the alkyl mercaptan is formed, and a white, crystalline precipitate of potassium dithio-oxalate is obtained, which may be collected and washed free of potassium hydrosulphide with alcohol:

0·2195 gave 0·0950 CO_2. C = 11·8.
0·1185 ,, 0·2833 $BaSO_4$. S = 32·7.
0·2063 ,, 0·1795 K_2SO_4. K = 39·01.

$C_2O_2S_2K_2$ requires C = 12·1; S = 32·3; K = 39·4 per cent.

This salt is very soluble in water to a yellow solution, which on evaporation on a water-bath deposits large, colourless prisms. After recrystallisation, the salt appears to become less stable, and, on keeping, turns brown with, however, no formation of sulphide.

If dilute sulphuric acid is added to a solution of potassium dithio-oxalate, hydrogen sulphide is evolved, and a yellow, amorphous solid is precipitated, which is not sulphur. The identity and properties of this substance are now under investigation.

The solution also gives the following characteristic reactions with various metallic salts:

Silver nitrate	Orange precipitate, quickly turning black.
Lead acetate	Orange precipitate, turning black on standing.
Mercurous nitrate	Black precipitate.
Mercuric chloride	Pale yellow precipitate, stable on boiling.
Bismuth nitrate	Light yellow precipitate, turning dark brown on boiling.
Cadmium chloride	Pale yellow precipitate.
Copper sulphate	Dark brown precipitate, soluble in excess of the reagent to a dark green solution. This deposits a black precipitate on boiling.
Antimony chloride	Yellow precipitate, turning brick-red on boiling.
Stannic ,,	Light yellow colour in the cold. On boiling, a precipitate, which turns from white to dark brown.
Stannous ,,	Reddish-brown colour, giving a dark brown precipitate on boiling.
Ferrous sulphate	A brownish-pink coloration, giving on long standing a brown precipitate.
Ferric chloride	
Zinc sulphate	Pale yellow coloration.
Nickel ,,	Deep magenta coloration which is stable on boiling. This most characteristic reaction is dealt with more fully below.
Cobalt nitrate	Deep reddish-brown coloration.
Manganese sulphate	Yellowish-brown coloration.
Calcium chloride	No precipitate in neutral solution. On addition of ammonia there is precipitation of calcium oxalate, sulphide remaining in solution.
Palladium chloride	Deep brown coloration. Brown precipitate on standing.
Platinous ,,	Reddish-brown coloration.
Platinic chloride and sodium carbonate	Reddish-brown coloration, deepening on standing.

It is probable that the sulphide of the heavy metal is produced in all cases where decomposition occurs on boiling.

Potassium Nickelodithio-oxalate.—Equal weights of potassium dithio-oxalate and nickel sulphate crystals were mixed in concentrated solutions. There was a copious separation of small, almost black needles, which exhibited an iridescence like that of potassium permanganate crystals. On recrystallisation from water, another form is at times obtained in dark red octahedra, the composition of which has been proved to be identical with that of the needles. The conditions necessary to the formation of the octahedra have not, however, been thoroughly determined.

A solution of these crystals does not give at once the usual tests for nickel in solution. Sodium hydroxide solution changes the colour to a greyish-brown, and nickel hydroxide precipitates only after some time. Nickel sulphide also is precipitated very slowly on addition of potassium hydrosulphide. Mercuric chloride gives a yellow precipitate, which appears to be mercuric dithio-oxalate, leaving nickel in solution.

These facts suggest that the substance is potassium nickelodithio-oxalate, and the structural formula $\mathrm{KS{\cdot}CO{\cdot}CO{\cdot}S{\cdot}Ni{\cdot}S{\cdot}CO{\cdot}CO{\cdot}SK}$ is suggested :

0·2097 gave 0·0979 CO_2. C = 12·78.
0·1974 ,, 0·4960 $BaSO_4$. S = 34·4.
$C_4O_4S_4K_2Ni$ requires C = 12·74; S = 34·0 per cent.

It is probable that those metals (iron and cobalt) which give similar colorations with potassium dithio-oxalate form compounds of the same type. These, however, are very soluble, and do not crystallise so well as does the nickel compound.

The sensitiveness of these colours as tests for the presence in solution of iron, nickel, cobalt, or dithio-oxalate was determined.

The colour effect can be used to detect nickel at a dilution of one part of nickel in 40,000,000 of water if sufficient of the solution is used to fill a large beaker, and one part in 8,000,000 can be detected readily in a test-tube. The colour is about three times as intense as that of potassium permanganate, and half as intense as that of rosaniline, if the concentrations are calculated weight for weight.

The cobalt coloration is just as intense as that of nickel, and at a dilution of one part of cobalt in 4,000,000 is about identical with the colour produced by the addition of potassium thiocyanate to a solution of ferric chloride containing one part of iron in 400,000. It will therefore be seen that the formation of these colorations constitutes a test remarkably delicate in consideration of the fact that they depend on the formation of a complex ion in dilute solution.

The iron coloration was just perceptible at a strength of 1 in 100,000 of iron.

The nickel coloration could be detected in a solution of potassium dithio-oxalate of the strength of 1 in 100,000.

The cobalt salt is much more stable than that of nickel. It decomposes on standing in solution much more slowly, and the coloration is comparatively little destroyed by the addition of hydrochloric acid or potassium cyanide. The nickel coloration, on the other hand, is destroyed slowly by dilute hydrochloric acid, but at once by excess of concentrated acid. Potassium cyanide also quickly discharges it.

This fact makes it possible to detect cobalt in a mixture containing 10 per cent. of cobalt and 90 per cent. of nickel. On adding potassium dithio-oxalate to the solution, a deep purple coloration is obtained, but on addition of excess of potassium cyanide the purple coloration disappears and the solution remains brown.

It will be seen from statements made above that the presence of iron does not interfere with the detection of nickel and cobalt in dilute solutions.

Ammonium dithio-oxalate is prepared by the action of alcoholic ammonium hydrosulphide on phenyl dithio-oxalate. It is a crystalline solid, which gives the characteristic tests for dithio-oxalates, but is decomposed by heating its solution on the water-bath.

It may be conveniently mentioned here that, with the preparation of the compound C_2O_2 as object, the action of nickel carbonyl on oxalyl chloride was examined. When the substances react in the liquid state, the evolution of gas is very rapid, and the reaction mixture falls in temperature.

The gas evolved appears to be carbon monoxide, and nickel chloride is deposited. This was confirmed by allowing the substances to react in the gaseous state. Two bulbs of equal volume, each surrounded by a bath and each connected with a mercury manometer, were respectively filled with the vapours of nickel carbonyl and oxalyl chloride. The bulbs were connected by a tube fitted with a tap, which was closed before the bulbs were filled. The pressure in each bulb having been noted, the tap was opened, and the gases thus allowed to mix. The pressure was read from time to time, until it ceased to increase.*

If the reaction takes place in accordance with the equation

$$Ni(CO)_4 + (COCl)_2 = NiCl_2 + 6CO,$$

the final pressure will be three times as great as the initial pressure.

Two experiments, in which the following results were obtained, may be quoted as typical:

Pressure of vapour of $Ni(CO)_4$.	Pressure of vapour of $(COCl)_2$.	Final pressure.
34 mm.	39 mm.	109 mm.
52 ,,	59 ,,	158 ,,

Thus it seems that the above equation represents the course of the reaction, and hence it may be concluded that the C_2O_2 formed momentarily is so unstable that it at once decomposes to give two molecules of carbon monoxide in the cold.

The colour and other optical properties of the compounds here described and of other sulphur compounds are being investigated.

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* This apparatus is convenient for the investigation of reactions between vapours, and will be described more fully in another communication.