

LIX.—*A Form of Tautomerism occurring amongst the Thiocyanates of Electronegative Radicles.*

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It is well known that the isomerism subsisting between the normal thiocyanates of fatty or benzenoid hydrocarbon radicles on the one hand, and the *isothiocyanates* (thiocarbimides) on the other, differs markedly from that which obtains between the corresponding derivatives of certain unsaturated hydrocarbon groups.

In the former case, a thiocarbimide,  $R\cdot NCS$ , once produced, continues to act as such under all ordinary chemical treatment; it is

quantitatively desulphurised by silver, or alkaline lead, salts, yields molecular additive compounds with nitrogenous bases, and when treated with ferric salts gives no reaction whatever for thiocyanic acid. In like manner, a thiocyanate,  $R \cdot SCN$ , once formed, exhibits great stability, and is for all practical purposes incapable of behaving as, or being converted into, a thiocarbimide.

In the latter case, this does not exactly hold; allyl thiocyanate, for instance, changes gradually on standing, or at once on heating, into the isomeric thiocarbimide, but once accomplished, this change is permanent, in the sense that it cannot by any known means be directly reversed.

The above remarks apply solely to combinations of the  $\cdot SCN$  or  $NCS$  group with distinctly electropositive radicles; amongst compounds of electronegative organic radicles with the groups in question, marked variations from the characters just indicated are observable, of which the most prominent is a tendency towards a kind of tautomerism. This phenomenon is manifested in respect of the  $CSN$  atomic complex, which may act either as  $\cdot SCN$  or  $\cdot NCS$ , or sometimes as both simultaneously, so that, as a rule, it cannot be asserted that a given compound behaves rather as a thiocyanate or a thiocarbimide until the conditions are defined under which it is observed to act.

Accounts have been given in previous communications of a number of such substances and their derivatives; the compounds themselves are prepared by acting with certain metallic thiocyanates upon acid chlorides, usually in presence of a solvent; in the main, and so far as they have been examined, their properties are akin to those of the alkyl thiocarbimides, and consequently they have all appeared under the name of "thiocarbimides" (compare *Trans.*, 1892, 61, 529; 1895, 67, 565, 1040; 1896, 69, 855, 1593; 1897, 71, 617; 1899, 77, 385, 388).

In relation to water, however, these substances commonly exhibit the characters of thiocyanates, undergoing hydrolysis more or less readily, with formation of thiocyanic acid:



and for this reason they cannot be separated from mixtures by the method of distillation in a current of steam, which is generally employed for their congeners of the purely hydrocarbon class.

As a rule, they unite equally readily with ammonia or nitrogenous organic bases, yielding thioureas or thiocarbamides, but it happens not unfrequently that a given compound of this class will behave almost quantitatively as a thiocarbimide towards an organic base, whilst if treated with ammonia, even although the latter be cautiously added and care taken to avoid excess, no thiourea, or practically none,

is formed, but ammonium or other thiocyanate instead; acetyl and stearyl thiocarbimides may be cited as cases in point.

Occasionally this tautomerism, if it may be so called, becomes still more limited, and, ceasing to depend on the varying nature of the bases presented, resolves itself almost entirely into a question of temperature. The author's assistant, Mr. R. E. Doran, has recently observed that, according to the temperature at which the operation is carried out, acetyl thiocarbimide is capable of yielding, with aniline, either acetylphenylthiocarbamide or aniline thiocyanate as main product, and hopes shortly to make a communication on the subject.

Certain non-metallic mineral chlorides are also known to exchange their halogen for the organic residue of lead and other metallic thiocyanates; the products thus obtained decompose readily on contact with water, thereby yielding thiocyanic acid, and consequently have always been regarded as thiocyanates pure and simple. They are: phosphorus thiocyanate,  $\text{P}(\text{SCN})_3$ ; arsenic thiocyanate,  $\text{As}(\text{SCN})_3$ ; silicon thiocyanate,  $\text{Si}(\text{SCN})_4$ , all prepared by Miquel (*Ann. Chim. Phys.*, 1877, [v], 11, 343, &c.). In addition to these, a substance having the empirical composition of thionyl thiocyanate has been described by McMurtry (*Trans.*, 1889, 55, 48) as resulting from the interaction of thionyl chloride and mercuric thiocyanate; it appears not to be strictly analogous to the preceding, and will be referred to presently.

The essential mode of preparation and the characters of the substances just mentioned (with the exception of McMurtry's compound), so far as they have been recorded, are somewhat similar to those of the acidic organic thiocarbimides; consequently, in view of the "tautomeric" phenomena presented by the latter, it seemed desirable to investigate more closely the action of thiocyanates on the chlorides of some electronegative mineral elements, or groups, in order to learn whether the products might not equally be capable, when placed under suitable conditions, of acting as thiocarbimides. This inquiry had, moreover, a special interest, for hitherto no isomerism (or tautomerism) has been established amongst mineral derivatives analogous to that subsisting between the normal and isothiocyanates of organic radicles.

In attempting to obtain a satisfactory answer to the question here raised, a good deal of experimental difficulty has been encountered; qualitative evidence that isomerism or tautomerism exists may easily be secured but the isolation, in a pure state, of such compounds as are suitable for definitely establishing it is greatly hindered by various causes; for instance, the readiness with which many of them undergo hydrolysis, and the fact that the mineral thiocyanates cannot, as a rule, be distilled, even in a vacuum, without decomposition.

It was the intention of the author to refrain from publishing any

account of the work done in the direction indicated until more decisive results should be forthcoming, but recently the study of acid thiocarbimide derivatives has begun to engage the attention of a number of chemists, and it therefore seemed best, with a view to avoid collision with the work of others, to give a brief description of the principal results hitherto attained. Notwithstanding that upwards of fifty distinct experiments have now been conducted on the interaction of thiocyanates with the mineral chlorides named below, and with certain others (for instance, chromyl chloride, stannic chloride, and the chlorides of phenylsulphonic and ethylsulphuric acids), it must be admitted that the precise mechanism of the chemical changes is still far from clear, and the present paper is therefore put forward merely as an instalment. As the study is not yet completed, it has been considered unnecessary to give details of the experiments, save those requisite to explain the general line of work, and to support such conclusions as may be drawn provisionally.

Generally speaking, the method of operating was as follows. The chloride, dissolved in a suitable anhydrous solvent, was added to a considerable excess of dry, finely-powdered thiocyanate (the lead, mercury, copper, ammonium, potassium, and silver salts were all tried), and the mixture either heated or allowed to stand for a month or two at the ordinary temperature; the solid residue was then removed by means of the pump. The filtrate, when shaken with water or mixed with dilute spirit, was tested for thiocyanic acid with ferric chloride, and for thiocarbimide product by ammoniacal silver nitrate, and by boiling with an alkaline solution of lead. In making the experiments, the following, amongst other chlorides, were used: carbonyl chloride, thionyl chloride, sulphuryl chloride, phosphorus trichloride, phosphorus oxychloride, phosphorus pentachloride; as solvents, carbon disulphide, light petroleum, chloroform, benzene, toluene, xylene, cumene, all carefully dried. In time-experiments, a flask with drying tube was employed; where heat was applied, the mixture was boiled under a reflux condenser, or else heated in a sealed tube. Every product, when examined as described above, proved to contain much thiocarbimide; on the other hand, not one was perfectly free from thiocyanic acid, the amount of which was often considerable, although in a few cases only trifling.

To each product an equivalent quantity of organic base was next added, usually pure aniline; if this caused a precipitate, it was filtered off and examined, otherwise the solution was concentrated by evaporation. In every case, such precipitate, or solid product obtained by concentration, was found to answer to the silver and lead tests for a thiocarbamide.

From these qualitative results, one inference, at least, is clear,

namely, that the  $\cdot\text{SCN}$  residue of metallic thiocyanates, when transferred under the above conditions to an inorganic electronegative radicle, no longer retains its purely thiocyanic character in the new product. Nevertheless, it is not entirely lost, since, as indicated above, if treated with boiling water, these compounds, or mixtures, give a more or less intense red coloration with ferric chloride.

In order to establish the thiocarbimide nature of the products obtainable from metallic thiocyanates and electronegative mineral chlorides, or their capacity to act entirely or in part as such, it was obviously desirable to secure more decisive evidence than that attaching solely to the desulphurisation of their solutions by lead and silver salts. One of the most characteristic and general properties of all true thiocarbamides is their power of uniting directly with primary bases to form thiocarbamides, and consequently attention has been mainly directed towards obtaining such additive products.

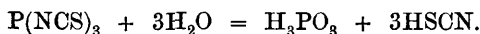
It is in this connection that the experimental difficulties before mentioned have been especially prominent. For the thiocarbimides, produced in solution as described above, are usually far from pure: sometimes they contain unaltered chloride, occasionally decomposition products; they invariably give, more or less, the reaction for thiocyanate; and they cannot, any more than their organic congeners, be distilled in a current of steam. Consequently, when treated with a base, the solid product is apt to be a mixture, and hitherto no trustworthy method has been found suitable for extracting the thiocarbamide alone. Moreover, in many cases, the thiocarbamide itself is readily hydrolysed, so that until some better method of working is devised, it is necessary either to identify the latter by its products of hydrolysis, or by analytical figures which are only approximate.

#### *Experiments with Phosphorus Trichloride.*

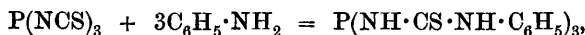
This substance, dissolved in dry benzene, was heated with  $1\frac{1}{2}$  to 2 equivalents of lead, or ammonium, thiocyanate, until a fragment of copper oxide, moistened with a drop of the solution ceased to give a green flame coloration.\* In one case, where potassium thiocyanate was employed, practically no thiocarbimide was obtained; in ten other experiments, the filtrate, when shaken up with water, was intensely acid, gave a strong red coloration with ferric chloride, and was copiously desulphurised by ammoniacal silver nitrate, or by warming with alkaline

\* Miquel states (*loc. cit.*, p. 348) that "en diluant le chlorure de phosphore dans l'éther anhydre, ou dans tout autre liquide inerte, il perd la propriété d'attaquer les sulfocyanates métalliques." The present writer's experience is different, for he finds that a quantity of dissolved product, sufficient to give marked desulphurisation with lead and silver salts, can be obtained after two or three minutes' boiling of a solution of phosphorus trichloride in pure ether with dry lead thiocyanate.

lead tartrate. From the two latter results, the presence of thiocarbimide product is inferred; it is uncertain whether the former (thiocyanic) reaction is due to the hydrolysis of phosphorus thiocyanate, or of the corresponding thiocarbimide:



To the filtrate, aniline, dissolved in benzene, was slowly added, sometimes in deficiency, sometimes in slight excess, of the amount required by the equation,

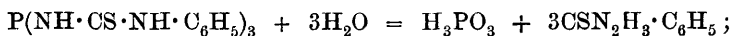


supposing the chloride to have been quantitatively converted into  $\text{P(NCS)}_3$ . No very considerable difference was noticed in the results, which may be approximately described as follows:

Slight heat is developed, and a yellowish-white, amorphous precipitate falls; this is sticky at first, but presently hardens; a further small quantity is deposited as the mixture cools down. The solid dissolves to some extent in chloroform, but the solution, if moisture be excluded, does not crystallise; it is very sparingly soluble in benzene, but very freely so in acetone, and in alcohol, by which it is decomposed; when heated with dilute nitric acid, it is oxidised vigorously, with formation of sulphuric and phosphoric acids.

If boiled with water, it melts and gradually dissolves; the resulting solution is intensely acid, gives more or less the reactions for aniline thiocyanate, and on cooling deposits crystals of phenylthiourea; the mother liquor, after treatment with dilute nitric acid, responds to the ammonium molybdate and magnesia tests for phosphoric acid.

The phenylthiourea appears to be produced by hydrolysis:



it is also left when the alcoholic solution is allowed to evaporate; moreover, the original solid, even if left exposed to the moist air of the laboratory (but not if kept in a desiccator), very slowly changes to a crystalline mass consisting largely of this substance. That the phosphorus does not exist as a salt of phosphorus anilide,  $\text{P(NH}\cdot\text{C}_6\text{H}_5)_3$ , may be inferred from the fact that the solid, if freshly ground up with cold water, yields a filtrate containing mere traces of phosphorus; if the residue be washed repeatedly with water, this element is continuously, but slowly, withdrawn, apparently by hydrolysis, as explained above.

There was considerable variation in the melting points observed for the crude products; one specimen melted at  $65^\circ$ , another at  $77^\circ$  another at a somewhat higher temperature, and in no case was the melting point sharp. As might have been expected, the analytical

results from different preparations were very discordant, a number of sulphur determinations yielding from 17·8 to 21·4 per cent., whilst the phosphorus varied from 2·5 to 5·4 per cent. No method hitherto tried for isolating the constituents of these mixtures, either by extraction, crystallisation, or precipitation of a solution, has proved successful.

As the dissolved products obtained from lead thiocyanate and phosphorus trichloride were obviously impure, an attempt was made to get a pure specimen of phosphorus trithiocyanate by distilling the solution (in dry commercial benzene) under reduced pressure. The solvents came over below 50° under 30 mm. pressure, leaving a reddish-yellow, clear, dense oil, which gave the reactions for thiocyanate, thiocarbimide, and phosphorus. When this was further heated under the same pressure, it darkened somewhat up to 105°, when there were signs of boiling, although nothing distilled over. The thermometer now rose quickly to 170°, at which temperature the contents of the flask suddenly changed, without evolution of gas, to a sticky, black solid, which presently became hard and brittle. This was insoluble in water, and only very sparingly soluble in alcohol, but easily so in warm alkali, yielding a dark red solution, which contained little thiocyanate, but was desulphurised by boiling with ammonia and silver nitrate; it was oxidised vigorously by nitric acid, with production of sulphuric and phosphoric acids. Possibly it is a polymeric form of  $P(NCS)_3$ , analogous to the "metabenzoylthiocarbimide" of Miquel,  $[C_6H_5 \cdot CO(CNS)]_n$  (*loc. cit.*, p. 304); but the experiment, so far as the isolation of phosphorus thiocyanate is concerned, was a failure.

The evidence for the existence of  $P(NCS)_3$ , or a compound capable of behaving as such, and of the corresponding  $P(NH \cdot CS \cdot NH \cdot C_6H_5)_3$ , is therefore so far imperfect that neither compound has actually been obtained in a state of purity. On the other hand, the benzene solution gives abundantly those metallic reactions whereby the presence of a thiocarbimide, or some immediate derivative, is commonly ascertained, and the dissolved constituent unites spontaneously with a primary base, to afford a product out of which, by mere dissolution in water, a typical thiourea originates.

*Action of o-Toluidine.*—Pure *o*-toluidine, diluted with dry benzene, was added to a cumene solution of "phosphorus trithiocyanate"; the precipitated amorphous solid, after several washings, first with benzene and then with light petroleum, was dried at a gentle heat in a current of dry air; it formed a yellowish, granular powder, beginning to shrink at 79–80°, and melting slowly between 81° and 83°, to a clear brown liquid.

When treated in alcoholic solution with silver, or alkaline lead, salts, it was very easily and copiously desulphurised, its properties in this and all other respects generally resembling those of the corresponding phenylic derivative. As was to be anticipated from the want of sharpness in the melting point, it proved to be somewhat impure, containing a very perceptible amount of toluidine thiocyanate. The latter could not be extracted by water, even in the cold, without decomposing the main product; an attempt to remove it by boiling the powder with dry benzene also failed, the melted residue forming a stiff, glue-like, brown mass which was still impure.

In order to learn whether the original product had approximately the composition required for the formula  $P(NH \cdot CS \cdot NH \cdot C_7H_7)_3$ , it was analysed with the following results:

Found, N = 16.47; S = 18.31, 18.03; P = 5.67 per cent.

$C_{24}H_{27}N_6S_3P$  requires N = 16.00; S = 18.27; P = 5.89 per cent.

Notwithstanding that the analytical figures obtained differ but little from those calculated, it cannot thence be inferred that the compound is really pure, for not only was toluidine thiocyanate detected in it, but the percentages of the four elements in the latter substance lie rather close to those in the phosphoretted compound, the phosphorus present in this causing but a small increase in the molecular weight as compared with that due to  $3CSN_2H_2 \cdot C_7H_7$ . Nevertheless the conditions under which the parent substance is formed, its thiocarbimidic reactions, its direct union with the base, and the ready conversion by water of the product thus obtained into tolylthiourea and an acid of phosphorus, all point clearly to the existence of a phosphorus compound of this thiourea, although its definite isolation as a chemical individual still remains to be accomplished.

#### *Experiments with Phosphorus Oxychloride.*

When a solution of phosphorus oxychloride in dry benzene was boiled with lead thiocyanate, little change occurred. Using toluene as solvent, marked interaction took place, but as this proved to be still incomplete, cumene was substituted with satisfactory results. After a few minutes' boiling, the filtrate no longer contained chlorine, but freely gave the reactions for dissolved thiocarbimide.

To the clear filtrate, aniline, diluted with benzene, was added in equivalent proportion to the oxychloride used, whereupon a yellow solid was deposited. Immediately after precipitation, this tends somewhat to choke the filter, but it granulates on standing, and may then be filtered without difficulty. A specimen thus prepared, well washed



with benzene and dried as far as possible over shredded wax in a vacuum, formed a mobile, pale-yellow powder, whose weight amounted to more than 90 per cent. of that theoretically obtainable from the oxy-chloride employed, supposing the latter to have been converted, first into phosphoryl trithiocarbimide, and thence into the corresponding phenylated thiourea.

In order to remove the last traces of solvent, the powder was gently warmed in a flask through which dry air was caused to stream for several hours. When heated in a narrow tube, it began to shrink at about  $108-109^{\circ}$ , and melted at  $111-112^{\circ}$  to an amber-coloured liquid. Other preparations melted at temperatures approximating to that given; for instance, at about  $114-115^{\circ}$  and  $113-114^{\circ}$  in two different experiments, with preliminary softening at two or three degrees below the actual melting point.

Thus obtained, the substance is practically insoluble in cold water. The latter, if poured off from it, is very faintly acid, gives almost no red coloration with ferric chloride, and does not give the reactions for aniline. When boiled with water, however, it gradually dissolves, all save a trace of yellowish, oily matter. The solution is intensely acid, gives a faint reaction for aniline, and a marked one for thiocyanic acid. On cooling and allowing to stand, it deposits phenylthiourea in prisms.

It is insoluble, or nearly so, in ether, chloroform, carbon disulphide, cold benzene, or light petroleum; easily soluble in ethyl acetate, acetone, glacial acetic acid, or nitrobenzene, and very freely so in alcohol. It dissolves also in sulphuric acid and in caustic potash; if hydrochloric acid be added to the latter solution, a precipitate is formed and hydrogen sulphide escapes. The solution in potash is desulphurised with remarkable ease by lead salts; if alkaline lead tartrate be added to it, a white precipitate falls, which gradually changes in the cold through yellow, orange, deep crimson, and brown to full black; the last change occurs at once if the mixture be gently warmed. In like manner, the sulphides of mercury and cadmium are precipitated when these metals, in alkaline solution, are warmed with the solution of the phosphorus compound.

The aqueous solution contains phosphoric acid, as shown by the magnesia and molybdate tests. Since the original solid is nearly insoluble in cold water, and its solution in hot water gives only phenylthiourea on cooling, it would appear that the phosphoric acid is formed by hydrolysis.

Attempts to purify the substance by crystallisation led to no satisfactory result. It does not crystallise from any of the liquids named above as solvents, and though occasionally crystals were deposited, they proved to be only phenylthiourea. Failing any better material,

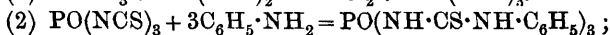
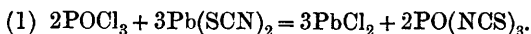
therefore, a thoroughly washed crude product was analysed, with the following results :

Found, C = 50.15 ; H = 4.46 ; N = 16.7 ; S = 20.07 and 20.62 ; P = 6.51.

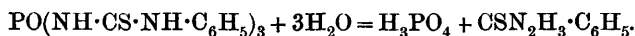
The above figures, save as regards the sulphur, are in fair agreement with those calculated for the formula  $C_{21}H_{21}ON_6S_3P$ , namely,

C = 50.35 ; H = 4.26 ; N = 16.38 ; S = 19.21 ; P = 6.20 per cent.

Accordingly, the production of this compound may be represented as follows :



and its decomposition by water into phenylthiourea,



The last equation does not, however, furnish a complete account of the interaction with water, inasmuch as thiocyanic acid is also produced ; it cannot at present be stated whether this originates through some decomposition of the phosphoryl trithiocarbamide, or from the presence of some other material in the crude substance. At all events, the hydrolysis formulated above does not occur quantitatively, for a rough experiment, made by boiling a known weight of material with water, and collecting the phenylthiourea thereby produced, afforded but 33 per cent. of the amount calculated from the equation, and the latter is only given provisionally, until further experiments shall have been carried out.

*o*-Toluidine gave a tenacious paste, dissolving somewhat in the hot mixture of cumene and benzene ; it separated on cooling as a clear, brownish oil, which presently hardened to a resin-like substance. The product was very easily soluble in spirit or acetone, the solutions being readily desulphurised by lead, silver, or cadmium salts. The finely powdered solid, if shaken up with cold water, gave up to it a mere trace of thiocyanic acid, but if boiled with water, it mostly dissolved, and the solution now gave a distinct, although not strong, red coloration with ferric chloride ; toluidine was not detected in the aqueous solution, which, as usual, was intensely acid.

As in the preceding case, all attempts to purify the product of the interaction were abortive ; a sample, treated as there described, was partially analysed, with the following results :

Found, N = 14.2 ; S = 16.3 ; P = 5.3.

$C_{24}H_{27}ON_6S_3P$  required N = 15.5 ; S = 17.7 ; P = 5.7 per cent.

*Action of Ammonia*.—According to Miquel (*loc. cit.*, p. 351), phosphorus trithiocyanate is decomposed by aqueous ammonia in the same

way as by water, alkalis, and acids, that is, into phosphorous and thiocyanic acids. In order to avoid the hydrolysing action of water, dry ammonia gas was led into a benzene-cumene solution of the corresponding phosphoryl derivative, whereupon a pale yellow, granular solid was precipitated. This, when washed with benzene followed by light petroleum, and dried in a desiccator, melted imperfectly below  $60^{\circ}$ . The substance was somewhat deliquescent on exposure to ordinary air, dissolved almost completely in water, yielding an intensely acid solution which contained a good deal of ammonium thiocyanate, but was also very freely desulphurised by warming with alkaline solutions of mercury, silver, lead, or cadmium. Phosphoric acid was present, as shown by the molybdic reaction, but apparently *not ready formed*, for when a freshly-made solution in cold water was divided into two parts and one of these treated with excess of ammonia, followed by magnesia mixture, it remained practically clear for a considerable time, whilst the other, if boiled for a few minutes, cooled, and then treated as described, gave an abundant precipitate consisting of ammonium magnesium phosphate. It seems probable, therefore, that the phosphorus exists mainly as  $\text{PO}(\text{NH}\cdot\text{CS}\cdot\text{NH}_2)_3$  (representing the thiourea residue as symmetrical), which affords the reaction for phosphoric acid only after hydrolysis. Attempts to remove the ammonium thiocyanate were unsuccessful, the phosphor-ettet compound dissolving easily in all the solvents of the former, and being readily decomposed. Incidentally, it became necessary to ascertain the solubility relations of ammonium thiocyanate, which, strange to say, do not appear to have been recorded, and may therefore here be mentioned. It is freely soluble in hot methyl or ethyl alcohol, acetone, ethyl acetate, or glacial acetic acid, and moderately so in boiling amyl alcohol and in nitrobenzene, but practically insoluble in chloroform, pure ether, carbon disulphide, benzene, toluene, or light petroleum.

#### *Thionyl Thiocyanate.*

In McMurtry's experiment, referred to above, thionyl chloride dissolved in carbon disulphide is allowed to stand for a few days in contact with excess of lead thiocyanate; the solution is then poured off, evaporated in a vacuum, and the residue washed, first with hot benzene and afterwards with ether. The product forms an amorphous, orange powder having the empirical composition of thionyl thiocyanate,  $\text{SO}(\text{SCN})_2$ , nearly insoluble in most solvents, only slightly soluble in ammonia, and not affected by boiling with hydrochloric acid. Similar results are obtained with lead or silver thiocyanate.

This preparation has now been repeated under various conditions, using the thiocyanate of lead, mercury, or potassium; and as solvents, toluene, chloroform, benzene, or light petroleum. The tem-

perature has been varied from the boiling point of toluene (which causes decomposition and evolution of sulphur dioxide) down to that of the laboratory. At the latter temperature, the duration of the experiment has been extended to three months; also, a benzene mixture with potassium thiocyanate has been heated for two hours at 100° in a sealed tube. In no case was the chlorine completely eliminated as metallic chloride; on the other hand, the filtered liquid in every case gave abundantly the reaction for dissolved thiocarbimide. The amorphous, orange product, if thoroughly washed with water, dissolves more or less completely in warm dilute caustic alkali. The solution thus obtained, if acidified with hydrochloric acid and treated with ferric chloride, yields no red coloration or else only a very trifling one, hence it would seem that the compound is not a true thiocyanate. But the solution in alkali, if mixed with solution of lead or mercury and warmed, or if treated with ammoniacal silver nitrate, is copiously blackened, the material thus exhibiting the characteristics of a thiocarbimide. Probably, considering its stability (to which McMurtry calls attention), its indifference to ammonia and its physical state, it will prove to be a polymeric form  $[\text{SO}(\text{NCS})_2]_n$ .

If the clear solution in chloroform, benzene, or light petroleum obtained by digesting thionyl chloride in one of these solvents with a metallic thiocyanate be treated with aniline, a precipitate falls at once, consisting partly of aniline hydrochloride. If this precipitate be filtered off, well washed, and then digested with water in order to remove the aniline salt, a brownish-yellow residue is left, nearly insoluble in boiling alcohol. This substance, when dissolved in alkali, responds freely to the desulphurisation tests for a thiocarbimide.

From these results, it would appear that thionyl chloride, under the conditions stated, is converted, at least in part, into thionylthiocarbimide,  $\text{SO}(\text{NCS})_2$ , or else a polymeride, or probably both; but hitherto the products have been obtained in very limited quantity, and it is yet uncertain whether one or more forms are present. In a three months' experiment at atmospheric temperature, not more than about one-tenth of the chloride used had undergone conversion, and the experiments are being continued, allowing a longer period for interaction, and otherwise varying the conditions.

*Carbonyl chloride*, dissolved in toluene, gave, with lead thiocyanate, somewhat similar results. On treatment of the product with aniline, carbanilide was formed, together with small quantities of a thiocarbamide melting at about 174°, which has not yet been obtained in a pure state.

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