

CCXI.—*The Influence of Certain Salts on the Dynamic Isomerism of Ammonium Thiocyanate and Thiocarbamide.*

By WILLIAM RINGROSE GELSTON ATKINS and
EMIL ALPHONSE WERNER.

THE experiments described in the present paper were carried out with two main objects in view: first, in the hope of obtaining some evidence likely to throw further light on the reversible isomerism of the above two compounds, and secondly, to ascertain if it is possible by the introduction of a new condition to disturb the normal equilibrium, and thus bring about a more complete conversion of ammonium thiocyanate into thiocarbamide than has hitherto been effected. Investigations of the change so far have proved that under the best conditions equilibrium is established when 25 per cent. of thiocarbamide, the less stable isomeride, has been produced. It is obvious from the study of the action of heat on thiocarbamide that any hope for success in this direction must lie in attempts to increase the stability of the compound at about 170° (the melting point of thiocarbamide when determined in the usual manner), a temperature at which thiocarbamide, under ordinary conditions, reverts with great rapidity until the equilibrium mixture is attained.

The comparatively high melting points of the compounds $(\text{CSN}_2\text{H}_4)_4, \text{KI}$ (189° : Werner, Proc., 1906, **22**, 245) and $(\text{CSN}_2\text{H}_4)_4, \text{RbI}$ (202° : Atkins and Werner, this vol., p. 1174) and other additive compounds seem to imply greater stability of the thiocarbamide in these substances, hence experiments have been made on the influence of different haloid salts of the alkali metals on the transformation of ammonium thiocyanate and thiocarbamide. Before describing the results which we have obtained, it may be stated at once that so far all attempts to increase the amount of thiocarbamide have been unsuccessful, and although the failure in this direction has been complete the results are nevertheless not without interest.

EXPERIMENTAL.*Action of Heat on Trithiocarbamide Potassium Thiocyanate.*

The preparation of the compound $(\text{CSN}_2\text{H}_4)_3, \text{KSCN}$ (m. p. 143°) has already been described (Atkins and Werner, *loc. cit.*). It is analogous to the compound $(\text{CSN}_2\text{H}_4)_3, \text{NH}_4\text{SCN}$ (*loc. cit.*, m. p. 144°), which is produced in the equilibrium mixture already men-

tioned. This substance, however, changes during liquefaction, as the thiocarbamide reverts to ammonium thiocyanate. The following experiments were carried out to ascertain what effect was occasioned by the replacement of ammonium by potassium. The results in the subjoined table were obtained by heating at 174°, the thiocarbamide, estimated by Reynolds and Werner's method in portions withdrawn at intervals, being calculated as a percentage of that originally present in the compound, not on the total weight of the latter.

$$t = 174^\circ.$$

| Time, in minutes. | Thiocarbamide, per cent. | $k = 1/t \log a/a - x.$ * |
|-------------------|--------------------------|---------------------------|
| 2 | 93.9 | 0.0157 |
| 7 | 77.0 | 0.0162 |
| 13 | 57.8 | 0.0183 |
| 23 | 40.6 | 0.0170 |
| 33 | 34.3 | 0.0140 |
| 43 | 26.7 | 0.0133 |
| 53 | 27.4 | 0.0106 |
| 90 | 25.5 | — |
| | Mean of first five | 0.0162 |

* There is a misprint in this formula in our previous paper.

It is clear that the reaction follows the unimolecular formula, although owing to the very great increase in velocity occasioned by small rises in temperature in this region the values of k are not in good agreement. The equilibrium percentage appears to be reached in about forty-five minutes, the value 27.4 per cent. lying slightly off the curve when the results are plotted; thus it may be seen that both in the time required to attain equilibrium and in the percentage composition of the resulting fusion (Reynolds and Werner, *Trans.*, 1903, **83**, 3) the behaviour of this compound closely resembles that of pure thiocarbamide. The potassium thiocyanate present has practically no effect, for as soon as ammonium thiocyanate is formed, the compound $(\text{CSN}_2\text{H}_4)_3 \cdot \text{NH}_4\text{SCN}$ must be present in the fusion, although largely dissociated; the thiocarbamide in this then reverts further.

The Reversion of Thiocarbamide in the Tetrathiocarbamide Alkali Halogen Compounds.

The following experiments were carried out chiefly with the potassium iodide member of the series, $(\text{CSN}_2\text{H}_4)_4 \cdot \text{KI}$ (m. p. 189°). In dilute aqueous solution it is practically completely dissociated, as shown by the molecular-weight determinations here recorded, giving four thiocarbamide molecules and two ions of the salt.

| Compound, per cent. | M. W. |
|---------------------|-------|
| 2.12 | 77 |
| 5.73 | 78 |

Theory requires 78.3 for complete dissociation. Determinations in boiling ethyl alcohol give the following values:

| Compound, per cent. | M.W. |
|---------------------|------|
| 2.19 | 81 |
| 4.39 | 96 |

Theory requires 94 for dissociation into thiocarbamide and potassium iodide, five molecules in all. Since this is so, it is to be expected that the reversion will be complete in aqueous solution, so it was not studied. It may here be remarked that thiocarbamide itself consists of simple molecules when in aqueous solution.

The high melting point of the compound $(\text{CSN}_2\text{H}_4)_4, \text{KI}$, namely, 189° , determined in the usual manner, as against 169° for thiocarbamide under similar conditions (we have already shown that the true melting point of the latter is about 200°), leads one to expect that its stability is greater than that of free thiocarbamide. The action of heat on the potassium compound gave results as follows:

SERIES I.

| Temperature. | Time, in minutes. | Thiocarbamide, per cent. |
|--------------|-------------------|--------------------------|
| 142° | 72 | 100.0 |
| 178 | 72 | 15.8 |
| 182 | 72 | 14.8 |
| 188 | 90 | 13.5 |
| 188 | 315 | 13.9 |

In the last two experiments the percentages recorded are corrected for loss by volatilisation. At the lower temperatures and shorter times this loss did not amount to 0.2 per cent., usually much less. It may be seen that, whilst at 142° the potassium compound is perfectly stable, whereas free thiocarbamide at this temperature reverts fairly rapidly, yet at the higher temperatures the reversion proceeds even further than with thiocarbamide alone, a state of equilibrium being reached at about 14 per cent. of the latter.

To determine this point more accurately, the compound $(\text{CSN}_2\text{H}_4)_4, \text{KI}$ was heated at 189° and at 184° for various lengths

SERIES II.— $t = 189^\circ$.

| $(\text{CSN}_2\text{H}_4)_4, \text{KI}$. | | |
|---|----------------------|--------------------------------------|
| Thio- carbamide, per cent. | Time, in minutes. | $k = \frac{1}{t} \log \frac{a}{a-x}$ |
| 43.4 | 10 | |
| 15.5 | 20 | 0.0447, between |
| 15.0 | 30 | $t = 10$ and $t = 20$ |
| 14.3 | 41 | |
| 14.4 | 50 | |
| 14.0 | 60 | |
| 14.4 | 70 | |
| 14.5 | 80 | |
| 13.7 | 100 | |

SERIES III.— $t = 184^\circ$.

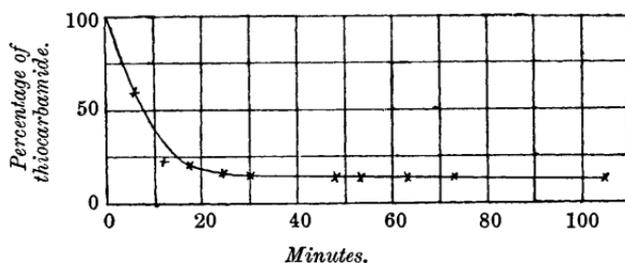
| $(\text{CSN}_2\text{H}_4)_4, \text{KI}$. | | |
|---|----------------------|--------|
| Thio- carbamide, per cent. | Time, in minutes. | k . |
| 59.7 | 6 | 0.0373 |
| 20.8 | 18 | 0.0378 |
| 15.6 | 24 | 0.0336 |
| 14.1 | 30 | — |
| 13.7 | 48 | — |
| 13.3 | 53 | — |
| 13.6 | 63 | — |
| 13.6 | 73 | — |
| 12.1 | 105 | — |

of time, and the results are shown in Fig. 1; the data are given in Series II and III.

At 189° equilibrium was reached in about thirty minutes; the amount of thiocarbamide which remained was found to be 14.3 per cent. of that originally present, taking the mean value of Series II. It may be pointed out that the isomerides were then present in the ratio of one molecule of thiocarbamide to six of ammonium thiocyanate, and that there was 1 molecule of thiocarbamide to 2.03 molecules of potassium iodide, assuming that double decomposition had not occurred. Since, however, the reversion proceeds further in the case of the compound $(\text{CSN}_2\text{H}_4)_4\text{KI}$ than in that of thiocarbamide, it seemed probable that this was due to double decomposition with the production of ammonium iodide and potassium thiocyanate. Experiments with the compound $(\text{CSN}_2\text{H}_4)_3\text{KSCN}$,

FIG. 1.

Temperature 184°.

Decomposition of thiocarbamide in $(\text{CSN}_2\text{H}_4)_4\text{KI}$.

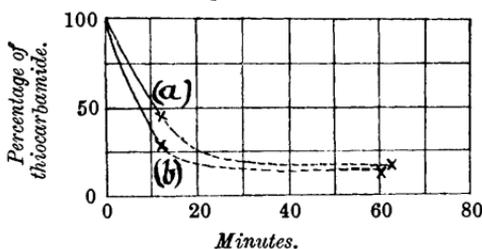
however, showed that in the latter case equilibrium was established when the normal 25 per cent. was present; thus it would appear that the further transformation was due to the amount of ammonium thiocyanate having diminished. Considering molecular proportions, however, it is seen that, assuming double decomposition to be complete, this explanation will not explain the results quantitatively, as out of every gram-molecule of the compound $(\text{CSN}_2\text{H}_4)_4\text{KI}$ there remains more than 54 grams of ammonium thiocyanate above that accounted for both by the above assumption, and by the formation of the 25 per cent. equilibrium. So even allowing that the double decomposition has been complete, the equilibrium percentage of thiocarbamide is 18.9.

In order to ascertain whether the potassium iodide compound alters the equilibrium percentage of thiocarbamide when the two are heated together, a mixture containing free thiocarbamide and the compound in the proportion of 3 grams of the former to one

of the latter was maintained at 184° until equilibrium was reached. Calculating on the basis that the compound $(\text{CSN}_2\text{H}_4)_4, \text{KI}$ leaves only 14.3 per cent. of its thiocarbamide unchanged after heating, it was found that of the added thiocarbamide only 20.2 per cent. remained instead of 25 per cent. This result was confirmed in another experiment. The addition of potassium iodide to the compound $(\text{CSN}_2\text{H}_4)_4, \text{KI}$ so that the total salt was slightly in excess of the thiocarbamide only lowered the equilibrium position to 12.3 per cent. The temperature maintained in the previous experiments was 184° , as in Series III.

The results of the action of heat on the reversion of thiocarbamide in the compounds $(\text{CSN}_2\text{H}_4)_4, \text{RbI}$ and $(\text{CSN}_2\text{H}_4)_4, \text{CsI}$ are shown in Fig. 2. The details are given in Series IV. They furnish almost identical equilibrium percentages, namely, 16.9 and 16.6

FIG. 2.

Temperature 184° .

- (a). Decomposition of thiocarbamide in $(\text{CSN}_2\text{H}_4)_4, \text{RbI}$.
 (b). " " " " $(\text{CSN}_2\text{H}_4)_4, \text{CsI}$.

respectively. The velocity-constant of the caesium compound is slightly higher than that of the potassium member of the series at the same temperature, whilst that of the rubidium member is much lower. This may probably be taken as due to delay at the start owing to the much higher melting point of the latter substance.

SERIES IV.— $t = 184^\circ$.

| $(\text{CSN}_2\text{H}_4)_4, \text{RbI}$ (m. p. 202°). | | | $(\text{CSN}_2\text{H}_4)_4, \text{CsI}$ (m. p. 191°). | | |
|--|----------------------|--------|--|----------------------|--------|
| Thio- carbamide, per cent. | Time, in minutes. | k . | Thio- carbamide, per cent. | Time, in minutes. | k . |
| 47.5 | 12 | 0.0269 | 29.3 | 12 | 0.0444 |
| 16.9 | 62 | — | 16.6 | 60 | — |

*The Reversion of Thiocarbamide in the Presence of Alkali
Halogen Salts.*

Since potassium iodide alters the equilibrium percentage of thiocarbamide, it became advisable to study the influence of this salt

on the velocity-constant of the reversion of the two isomerides. Accordingly, thiocarbamide and ammonium thiocyanate were heated alone and with the addition of one molecular proportion of iodide to form molecular proportions of each isomeride. The subjoined figures show that the rate of reversion of the non-saline isomeride was increased, whilst that of the saline isomeride was diminished. The temperature was maintained at 168°.

| | | | |
|--|------------|-------------------------------|------------|
| Composition. | <i>k</i> . | Composition. | <i>k</i> . |
| CSN ₂ H ₄ | 0·0056 | NH ₄ SCN | 0·0037 |
| 4CSN ₂ H ₄ +KI | 0·0074 | 4NH ₄ SCN+KI | 0·0034 |

These increases and decreases were more marked when approximately the same molecular proportions of sodium iodide, NaI, 2H₂O, were employed instead of potassium iodide. It was, moreover, found that all the thiocarbamide reverted when heated with a large excess of this sodium salt. As the reversion is known to be complete in aqueous solution, it was thought that the above behaviour might be due to the presence of water. Further experiments were therefore made with the anhydrous salt, and to include the entire series thiocarbamide was intimately mixed and heated with from seven to eleven times its weight of the chlorides, bromides, and iodides of potassium, sodium, and ammonium, until equilibrium had been attained with certainty at a temperature of 170°. The excess of salt being great in each case, the fluctuations in the proportions are not appreciable, for no correlation could be found between the percentages of thiocarbamide remaining and the excess taken. The table below shows the equilibrium percentages of thiocarbamide obtained in the presence of excess of the several salts.

Thiocarbamide per cent.—t=170°.

| | Cl. | Br. | I. |
|-----------------------|-------|-------|-------|
| K | 12·89 | 12·24 | 9·04 |
| Na | 14·64 | 17·26 | 0·58 |
| NH ₄ | 19·57 | 21·70 | 12·43 |

When a small quantity of water was added to a mixture of potassium iodide and thiocarbamide similar to the one taken above, only 3·27 per cent. of the latter remained after heating.

A peculiar feature of the above table is the great difference between the effect produced by sodium iodide as compared with that of the other salts; thus, whilst reversion proceeds furthest in the presence of iodides, it is almost complete with the sodium salt. A larger percentage of thiocarbamide appears to persist with the bromides than with the chlorides, except for potassium, where the small difference is in favour of the chloride, and may be due to experimental error. It will also be noticed that, except in the

case of sodium iodide, reversion to ammonium thiocyanate diminishes in the order: potassium, sodium, ammonium.

In the production of these equilibria two and possibly three factors are obviously concerned. Since equilibrium between thiocarbamide and ammonium thiocyanate is one between the molecules, and not directly between thiocarbamide and ammonium and thiocyanate ions, as is shown by the complete reversion of the non-saline isomeride in dilute aqueous solution, and by the decrease in thiocarbamide when water as well as potassium iodide was added to the fusion, it is clear that any cause which increases the degree of ionisation of ammonium thiocyanate in the fusion must alter the equilibrium percentage in favour of the latter isomeride. The addition of any salt appears to increase the ionisation, as double decomposition has already been shown (in the case of the compound $(\text{CSN}_2\text{H}_4)_4\text{KI}$) to be by itself insufficient to explain the quantitative results obtained; thus, although double decomposition with the formation of partly undissociated chlorides, bromides, and iodides of ammonium and thiocyanates of sodium and potassium in the respective cases must lessen the amount of the saline isomeride and so disturb the normal 25 per cent. equilibrium, yet this in itself cannot explain the results; for when ammonium salts are added there can be no such exchange, since the only positive ion present is ammonium. Indeed, it is rather to be expected that the ionisation of ammonium thiocyanate would have been diminished by such an addition, but as the composition of the fusion has obviously changed, its properties as an ionising medium have probably changed also.

The third factor is the possibility of the occurrence of compounds such as $(\text{CSN}_2\text{H}_4)_4\text{MX}$ undissociated in the fusion, thus probably increasing the stability of thiocarbamide and checking its reversion. In the case of the alkali chlorides, however, the existence of such compounds is so far only represented by $(\text{CSN}_2\text{H}_4)_4\text{NH}_4\text{Cl}$ (m. p. 154° : Emerson Reynolds, *Trans.*, 1891, **59**, 385), and hence this is probably not a factor of importance.

Preparation of Additive Compounds of Thiocarbamide with Saline Iodides.

The general procedure adopted in the preparation of the following compounds consisted in mixing hot alcoholic solutions of thiocarbamide and the saline iodide; in many cases the additive compound was directly produced and separated on cooling, whilst in a few instances, more particularly with the complex tertiary and quaternary iodides, it was found necessary to heat the solutions to boiling under a reflux condenser for fifteen minutes to an hour. In

all cases the compounds were purified by recrystallisation from absolute alcohol before being analysed. The results obtained are as follows:

Thiocarbamide and Hydrazine Hydriodide.—The compound separated in a felted mass of long, slender needles, with satiny lustre, melting at 136° :

0.25 gave 0.068 I. $I=27.2$.

$C_4H_{16}N_8S_4, N_2H_4, HI$ requires $I=27.37$ per cent.

Thiocarbamide and Hydroxylamine Hydriodide.—This forms long, slender, silky needles, melting at 178° :

0.25 gave 0.0685 I. $I=27.4$.

$C_4H_{16}N_8S_4, NH_2 \cdot OH, HI$ requires $I=27.31$ per cent.

Thiocarbamide and Aminoguanidine Hydriodide.—This compound separates in long, slender, hair-like needles with satiny lustre, melting at 174° :

0.25 gave 0.0628 I. $I=25.12$.

$C_4H_{16}N_8S_4, CN_4H_6, HI$ requires $I=25.09$ per cent.

Guanidine hydriodide did not form a compound.

Thiocarbamide and Pyridine Hydriodide.—It was found necessary to boil the alcoholic solution for half an hour. The compound separates in slender, glistening needles, melting at 157° :

0.25 gave 0.08826 I. $I=35.3$.

$C_2H_8N_4S_2, C_5H_5N, HI$ requires $I=35.37$ per cent.

Thiocarbamide and Pyridine Methiodide.—The compound is readily formed. It separates from alcoholic solution in slender, flat, lustrous prisms, melting at 144° :

0.25 gave 0.08509 I. $I=34.036$.

$C_2H_8N_4S_2, C_5H_5N, MeI$ requires $I=34.04$ per cent.

Thiocarbamide and Quinoline Hydriodide.—The compound is readily formed, and separates in minute rosettes of silky, yellow needles, melting at 137° :

0.25 gave 0.07874 I. $I=31.49$.

$C_2H_8N_4S_2, C_9H_7N, HI$ requires $I=31.05$ per cent.

Thiocarbamide and Quinoline Methiodide.—This compound forms very slender, silky needles melting at 134° , and resembling in appearance the characteristic form of tetrathiocarbamide derivatives:

0.25 gave 0.0757 I. $I=30.28$.

$C_2H_8N_4S_2, C_9H_7N, MeI$ requires $I=30.02$ per cent.

Thiocarbamide and Quinoline Ethiodide.—This compound separates in bright, canary-yellow prisms, melting at 126° . After two recrystallisations:

0.25 gave 0.88 I. $I = 35.2$.

$C_2H_4N_2S_2, C_9H_7N, EtI$ requires $I = 35.18$ per cent.

Thiocarbamide and Trimethylethylammonium Iodide.—This compound separated in slender, glistening prisms, melting at 141° , after the alcoholic solution of the components had been boiled for half-an-hour:

0.25 gave 0.08763 I. $I = 35.05$.

$C_2H_8N_4S_2, NMe_3EtI$ requires $I = 34.6$ per cent.

Thiocarbamide and Tripropylamine Hydriodide.—This compound separates in microscopic, silky needles, melting at 166° :

0.25 gave 0.075 I. $I = 30.0$.

$C_2H_8N_4S_2, N(C_3H_7)_3HI$ requires $I = 30.02$ per cent.

Thiocarbamide and Methyltripropylammonium Iodide.—This compound separates in stout prisms or slender needles depending on the concentration. It melts at 128° :

0.25 gave 0.073 I. $I = 29.2$.

$C_2H_8N_4S_2, N(C_3H_7)_3MeI$ requires $I = 29.06$ per cent.

Thiocarbamide and Triethylpropylammonium Iodide.—This compound forms slender, brittle, needle-like crystals, melting at 165° :

0.25 gave 0.074 I. $I = 29.6$.

$C_2H_8N_4S_2, NEt_3(C_3H_7)I$ requires $I = 30.02$ per cent.

Thiocarbamide and Phenyldimethylethylammonium Iodide.—This compound separates in stout, truncated prisms, which melt at 112° , and at a higher temperature readily decompose, giving mercaptan:

0.25 gave 0.07366 I. $I = 29.46$.

$C_2H_8N_4S_2, NPhMe_2EtI$ requires $I = 29.60$ per cent.

Tetramethylammonium iodide and thiocarbamide were boiled together in alcoholic solution for two hours, but not a trace of a compound was formed. The iodine was estimated in all the above compounds by boiling with an excess of ferric sulphate in strong solution, and titration of the liberated iodine with $N/10$ -sodium thiosulphate.

The above series of compounds was prepared in order to obtain data regarding the ratio in which thiocarbamide unites directly with saline iodides of different constitution.

It is noteworthy that although aminoguanidine hydriodide unites readily with thiocarbamide, no compound was obtained with guanidine hydriodide. The compound $(CSN_2H_4)_2, NEt_4I$ (m. p. 135°) was prepared by Emerson Reynolds (Trans., 1891, 59, 388). We have not been able to obtain any compound with tetramethylammonium iodide, which thus behaves like sodium iodide, in

exhibiting no tendency to unite with thiocarbamide (Werner, Proc., 1906, **22**, 245); the displacement of one methyl group by ethyl, however, is sufficient to enable a compound to be formed.

Whilst the simple ammonium bases and primary amines (see Emerson Reynolds, *loc. cit.*) form tetrathiocarbamide derivatives, the tertiary amines and quaternary bases appear to always produce dithiocarbamide compounds.

We have obtained one exception to the latter rule, namely, the compound $\text{CsN}_2\text{H}_4, \text{C}_9\text{H}_7\text{N}, \text{C}_2\text{H}_5\text{I}$ (m. p. 126°).

UNIVERSITY CHEMICAL LABORATORY,
TRINITY COLLEGE, DUBLIN.
