when heated with aqueous solutions of ammonium carbonate; good yields of the corresponding benzyl anilines when treated, similarly, with aniline, methyl aniline, toluidine, etc.

(5) Benzyl cyanide is obtainable in 50 to 60% yields from benzyl chloride and sodium cyanide in aqueous instead of alcoholic solution.

(6) It has been shown what conditions of procedure are likely to prove most serviceable in the hydrolysis of benzyl chloride to benzyl alcohol.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY.]

THE INTERACTION OF CARBON DISULFIDE WITH AMMONIUM CARBONATE.

BY FRANCOIS A. GILFILLAN.

Received July 2, 1920.

The work described in this paper represents one phase of an extensive investigation now in progress in the Sheffield Laboratory, dealing with the chemistry of carbon disulfide, and was undertaken by the writer at the suggestion of Professor Treat B. Johnson.[1]

In the development of the researches on pyrimidines and hydantoins which have been conducted in the above laboratory for several years, a wide use has been made of thio-urea for the synthesis of a great number of new combinations in these 2 cyclic series of organic compounds. The reagent has been used in large quantities for this work, and the largest proportion of it has been prepared by co-workers in the laboratory by molecular rearrangement of ammonium thiocyanate. The yield so obtained is not satisfactory, the best result that one can expect to obtain being about 25%.[2] Evidence has been obtained, however, which indicates that the velocity constant of the reversion of these 2 isomers is a varible factor, and that the equilibrium percentage of thio-urea is influenced, not only by the presence of other salts, but is also concerned with other important experimental factors or conditions which are not well understood.[3]

Inghilleri[4] has recently described in a paper entitled, "A New Process for the Preparation of Ammonium Sulphocyanate and Thio-urea," a method for synthesizing thio-urea, which gives, according to him, prac-

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[1] In our future work, we will take up the study of high temperature reactions with carbon disulfide, the influence of catalysts on well known reactions of this reagent which proceed with slow velocity, and also an investigation of photochemical influences at low and high temperatures. (T. B. J.)

[2] Reynolds and Werner, *J. Chem. Soc.*, **83**, I (1903).

[3] Atkins and Werner, *ibid.*, **101**, 1982 (1912); Johnson, Hill and Bailey, THIS JOURNAL, **37**, 2406 (1915); Claus, *Ann.*, **179**, 128 (1875); Waddell, *J. Phys. Chem.*, **2**, 525 (1898).

[4] Inghilleri, *Gazz. chim. ital.*, **39**, 634 (1909).

tically quantitative yields of this reagent. The method is based on the reactions which take place when carbon disulfide is heated with ammonium carbonate. According to Inghilleri the complete transformation proceeds in 3 stages, as follows, first, carbon disulfide adds ammonia with formation of ammonium dithiocarbamate (I); second, this salt then loses hydrogen sulfide with formation of ammonium thiocyanate (II); and third, the thiocyanate undergoes quantitative conversion into thio-urea (III).

$$\underset{\text{(I).}}{NH_2CS.S.NH_4} \longrightarrow \underset{\text{(II).}}{NH_4SCN} \longrightarrow \underset{\text{(III).}}{CS(NH_2)_2}$$

The first change is brought about by heating at 100° to 110°, the second from 120° to 130°, and the third by heating at 160°. By heating at 160°, he states that *sym*-diethyl-thio-urea melting at 77° is formed instead of thio-urea, if alcohol is present in the mixture.

The quantitative formation of thio-urea by application of Inghilleri's method of synthesis incited an interest in its practical application, not only because it offered an easy method of obtaining this reagent in quantity, but because it revealed for the first time experimental conditions which not only are productive of a pronounced increase in the velocity of change, but also lead to the maximum equilibrium percentage of thio-urea thus far obtained.[1]

In order to determine whether the products of reaction formed by heating carbon disulfide with ammonium carbonate, according to the conditions of Inghilleri's experiments, contribute to the success of this transformation into thio-urea by increasing the stability of this compound at 160°, it was decided to repeat his work and determine quantitatively the amount of ammonium thiocyanate and thio-urea formed, and also study the influence of different factors concerned in the production of the reaction-equilibrium. This study necessitated first the working out of reliable methods for determining quantitatively ammonium thiocyanate and thio-urea in the presence of each other. The thio-urea was determined successfully by application of the method devised by Reynolds and Werner,[2] namely, titration of aqueous solution with a standard solution of iodine. For the determination of ammonium thiocyanate in presence of thio-urea, we tried different methods which have been recommended for this purpose,[3] but found all of them unsatisfactory. A suitable method was finally developed after many trials on standardized solutions of the 2 reagents, which enabled us to determine with accuracy the amount of thiocyanate present. It is efficient, however, only when less than 40% of thio-urea is present in the mixture. Larger proportions of this reagent

[1] See Atkins and Werner, *J. Chem. Soc.*, 101, 1171 (1912).

[2] Reynolds and Werner, *ibid.*, 83, 1 (1903).

[3] See Experimental Part of this paper.

mask the silver by formation of stable double combinations, rendering accurate titration with silver nitrate impossible. Whether a method of titrating accurately with silver salts for thiocyanate in the presence of large proportions of thio-urea can be developed, must be decided by further study of various factors influencing the reactions involved.

We now find that carbon disulfide and ammonium carbonate interact with formation of ammonium thiocyanate and finally thio-urea, but the yield of thio-urea is much lower than theory demands. In fact, the best yield that we were able to obtain was about 11%, which is 14% less than that which can be obtained by direct heating of ammonium thiocyanate as originally recommended by Reynolds.[1] In some experiments, the yield of this product was as low as 1.2%. It is apparent from our results that reversion to ammonium thiocyanate is favored by the hydrogen sulfide formed during the reaction. In other words, the results obtained in a quantitative study of this reaction do not recommend the method as a practical one for the synthesis of thio-urea. A description of the analytical procedure and other details of this research is recorded in the Experimental Part of this paper.

Experimental Part.

The thio-urea used in the analytical work discussed below was a very pure imported product, which gave no color with ferric alum. The ammonium thiocyanate employed was first recrystallized from alcohol, carefully dried, and its purity confirmed by titration against a standard silver nitrate solution. Seven mixtures of thio-urea and ammonium thiocyanate in definite ratios were prepared for experimental work. Each mixture, weighing 6 g., was dissolved in water, the solution diluted to a volume of 250 cc. and aliquot parts of these solutions then taken for the various titrations.

Determination of Ammonium Thiocyanate.—The method first employed for the determination of thiocyanate was that recommended by Krall.[2] This method of analysis did not give satisfactory results (Curve A; Fig. 1), especially with mixtures containing more than 15% of thio-urea, and when the percentage of thio-urea reached 60% of the mixture, the 40% of thiocyanate titrated as 60.4% or 151% of that actually present.

The second method employed for the determination of the thiocyanate was direct titration with silver nitrate. Analyses were made on the same mixtures as used above, and the procedure was as follows. A 10 cc. aliquot part of the solution was used, to which were added 20 cc. of water and 5 cc. of dil. nitric acid of the same concentration as stated above. Two drops of ferric alum indicator were added, and the titration made directly with standard silver nitrate solution, which was run in very slowly

[1] Reynolds and Werner, *loc. cit.*

[2] Krall, *J. Chem. Soc.*, **103**, 1385 (1913).

and with constant shaking to avoid the presence of an excess of silver nitrate in the solution at any time. The point at which the pink color disappears is best determined by comparison with an over-titrated standar . The results of the direct titration of the 7 mixtures used above, supplemented by results from several other determinations made by the same method, are shown in Curve B, Fig. 1. The values obtained show that direct titration against silver nitrate gives concordant results for mixtures containing not more than 40% of thio-urea. But between 40% and 50%, the curve turns sharply upward, and values obtained for thiocyanate in the presence of larger proportions of thio-urea are far too great. Results of analyses made by each of the 2 methods described above, are recorded in Table I.

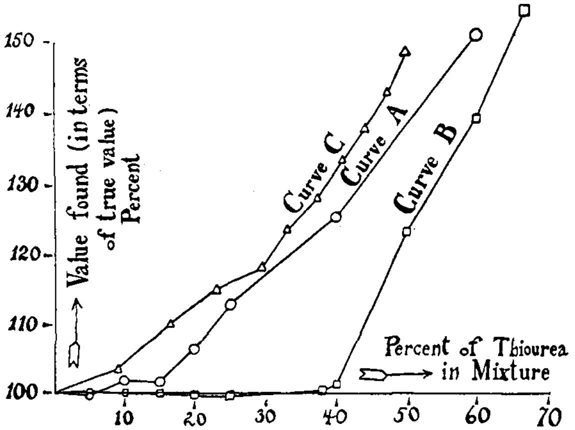

Fig. 1.

TABLE I.—ANALYSES.

Actual thio-urea. %.	Actual NH$_4$CNS. %.	Thiocyanate found.		NH$_4$SCN found (in terms of true value).	
		Krall's method. %.	Direct titration. %.	Krall's method. %.	Direct titration. %.
0	100	100.0	100.0	100.0	100.0
5	95	94.6	95.2	99.6	100.2
10	90	91.7	90.0	101.9	100.0
15	85	86.4	85.0	101.6	100.0
20	80	85.0	79.8	106.3	99.8
25	75	84.5	74.8	112.7	99.7
38	62	...	62.2	...	100.3
40	60	75.1	60.8	125.2	101.3
50	50	...	61.5	...	123.0
60	40	60.4	55.6	151.0	139.0
67	33	...	51.3	...	155.5
80	20	...	54.6	...	273.0

The data in Table I were used in constructing the 2 Curves, A and B, shown in Fig. 1. The per cent. of thio-urea in the mixture is plotted along the horizontal axis, and the value found (in terms of true value) on the vertical axis. From these 2 curves it is evident that Krall's method[1] is not reliable for mixtures containing more than 15% of thio-urea, while direct titration will give accurate results for those containing up to 40%

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[1] *Loc. cit.*

of thio-urea. No method was devised for the correct estimation of thiocyanate in mixtures where more than 40% of thio-urea was present.

A third procedure was tried for determining quantitatively the influence of thio-urea on the reaction of thiocyanate with silver nitrate. Aqueous solutions of pure thio-urea and ammonium thiocyanate were prepared of equal strength and an aliquot part of the standard thiocyanate solution titrated with silver nitrate to a colorless end-point. The addition of thio-urea solution to this colorless solution was found to restore at once the pink color, which could again be discharged by further titration with silver nitrate. Following this procedure, successive additions of thio-urea solution were made, titrating with silver nitrate after each addition. The results of these titrations are given in Table II.

TABLE II.—INDIRECT TITRATIONS METHOD.

Actual thio-urea. %.	Actual NH_4CNS. %.	NH_4CNS found. %.	Value found (in terms of true value). %.
0	100.0	100.0	100.0
9.1	90.9	94.1	103.5
16.7	83.3	91.6	110.0
23.1	76.9	88.4	115.0
28.6	71.4	84.3	118.0
33.3	66.7	82.3	123.5
37.5	62.5	80.0	128.0
41.2	58.8	78.4	133.3
44.4	55.6	76.6	137.8
47.4	52.6	75.2	142.9
50.0	50.0	74.2	148.4
54.5	45.5	72.2	158.7
60.0	40.0	69.4	173.5
66.7	33.3	65.5	196.4
71.4	28.6	63.0	220.2
75.0	25.0	60.8	243.1
77.7	22.3	60.7	272.4
80.0	20.0	59.4	297.2

The above results are plotted as Curve C in Fig. 1, in which they are compared with results of the direct titration method, and Krall's excess silver nitrate methods, respectively. Curve C is comparable with Curve A (Krall's method), and gives incorrect values for thiocyanate, even with very low concentrations of thio-urea.

In all the 3 analytical methods outlined above, it was observed that the amount of precipitated silver thiocyanate decreased rapidly with increasing concentration of thio-urea, and finally when the thio-urea was increased to about 55%, the precipitate did not appear, but oily drops gathered on the side of the titration flask. These could be made to solidify to a white crystalline solid by rubbing with a stirring rod. Their composition was not determined, but they undoubtedly consist of silver thiocyanate combined with thio-urea.

The action of silver nitrate on a solution of pure thio-urea was also investigated. When equal molecular proportions of thio-urea and silver nitrate in aqueous solution were mixed, and the silver nitrate titrated for in the usual way with standard potassium thiocyanate solution, it was found that only about 50% of the original silver could be accounted for. The other half mole was masked by the one mole of thio-urea present. When 2 moles of thio-urea were added to one mole of silver nitrate solution, the silver was then entirely masked by the thio-urea. Direct titration gave the same results as were obtained in the indirect titration. In each case one mole of silver was masked by 2 moles of thio-urea.

Determination of Thio-urea.—The method of Reynolds and Werner[1] was employed for the determination of thio-urea by titration with iodine. According to Werner,[2] this method gives low results if the concentration of the thio-urea exceeds 0.02 g. per 100 cc. of the titration mixture. Several titrations were made of solutions containing mixtures of thio-urea and ammonium thiocyanate, the results of which are recorded in Table III.

TABLE III.—DETERMINATION OF THIO-UREA.

G. of thio-urea per 100 cc. of titration mixture.	Apparent per cent. of actual thio-urea present.
0.0450	84.7
0.0290	88.6
0.0190	90.7
0.0120	94.3
0.0096	94.8
0.0072	96.8
0.0048	100.8
0.0024	102.0

From these results it is apparent that concentrations of more than 5 mg. of thio-urea per 100 cc. of titration mixture cannot be correctly estimated. Ammonium thiocyanate did not interfere in the determination of thio-urea by this method. According to Reynolds and Werner[3] the proportion must be greater than 16 parts of thiocyanate to one of thio-urea before it seriously influences the titration.

The Action of Ammonia on Carbon Disulfide.—Inghilleri found that carbon disulfide and ammonium carbonate interact when heated in sealed tubes, and yield thio-urea, ammonium thiocyanate, hydrogen sulfide, and carbon dioxide. His method of operating was to heat at 100° to 110° for 6 hours, and for the same period at 125° to 130° for 2 hours at 160°, releasing the pressure in the tube after each operation. At the end of the 100° period, he identified carbon dioxide but no hydrogen sulfide. After the 130° period, hydrogen sulfide and ammonium thiocyanate were identified, and after heating at 160°, thio-urea was obtained as a final product

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[1] Reynolds and Werner, *J. Chem. Soc.*, **83**, 6 (1903).

[2] Werner, *ibid.*, **101**, 2166 (1912).

[3] *Loc. cit.*

melting at 169°. No quantitative analysis was made for the determination either of the thio-urea or of the thiocyanate produced in the reaction.

Inghilleri used 6 g. of carbon disulfide and 8 g. of unanalyzed ammonium carbonate, and reported his yield of 1.1 g. of thio-urea as almost quantitative. Basing calculations on the weight of the carbon disulfide a quantitative yield of thio-urea would be 6 g., thus Inghilleri's calculations are at fault, and his yields much lower than theory demands.

In our work the carbon disulfide was purified by allowing to stand for 12 hours over anhydrous copper sulfate, shaking with mercury, drying over anhydrous sodium sulfate, and finally distilling. A product distilling uniformly at 46.3°, uncorr., was obtained. The ammonium carbonate used was analyzed and found to contain 25.08% of ammonia.

TABLE IV.

				Heated.					Composition of final product.		Yield of total HN_4-CNS and thio-urea based.		
Expt.	CS_2. G.	Ammo. carb. G.	Calc. NH_3. G	Hrs.	At °C.	H_4CNS titrat. G.	Thio-urea titrat. G.	Total NH_4CNS and thio-urea. G.	NHC_3NS. %.	Thio-urea. %.	On CS_2. %.	On NH_3 %.	Time left standing in closed tube under pressure before opening.
1.....	5.05	9.50	2.38	6 7½ 2	100 135 160	4.26	0.281	4.54	93.8	6.2	90.0	...	4 hrs.
2.....	5.10	9.54	2.39	6 6 2	100 135 160	4.35	0.133	4.48	97.0	3.0	87.8	...	15 hrs.
3.....	3.80	7.16	1.79	6 6 2	100 135 160	2.96	0.036	3.00	98.8	1.2	78.9	...	5 days[b]
4.....	3.80	7.16	1.79	6 6 2	100 135 160	2.90	0.037	2.94	98.7	1.3	77.4	...	5 days[b]
5.....	3.80	7.16	1.79	6 6 2	100 135 160	3.04	0.110	3.15	96.5	3.5	82.9	...	..
6.....	6.00	8.00	2.00	..	..	4.11	0.355	4.47	92.1	7.9	..	100.0	..
7.....	6.44	8.67	2.17	6 2½ 3½	100 130 160	..	...	..	93.2	6.8	..	...	..
8.....	6.41	8.01	2.00	6 6	100 160	3.80	0.465	4.27	89.1	10.9	..	95.5[a]	4 hrs.
9.....	6.42	8.00	2.00	6 6	100 160	4.32	0.524	4.85	89.2	10.8	..	108.0	4 hrs.

The tubes in Expts. 1, 2, 3, 4 and 5 above were charged with ammonium carbonate equivalent to an excess of 5% of ammonia, while those in Expts. 6, 7, 8 and 9 contained 33%, 33%, 43% and 43%, respectively, of an excess of ammonia.

[a] This value is too low on account of loss of material when tube was opened.

[b] There was very little internal pressure in these tubes when opened.

The results of our experiments are recorded in Table IV. The method of operating was, in general, that used by Inghilleri, but contrary to his statement, heating at 100° was always productive of large quantities of hydrogen sulfide, which was determined by passing the mixed gases into a solution of copper sulfate when the tube was opened, and precipitating as copper sulfide. The precipitated cupric sulfide was filtered, dried, ignited in hydrogen, and weighed as Cu_2S. According to this method of determination, heating at 100° produced in Expt. 1 a volume of 750 cc. of hydrogen sulfide and 1275 cc. of carbon dioxide, the gases being measured at 20°.

The yield of total thiocyanate and thio-urea, based on carbon disulfide in the presence of a 5% excess of ammonia, varied between 77.4% and 90.9%. Based on ammonia in the presence of 33% excess disulfide, the yield was about quantitative. The difficulty of accurately estimating yields based on ammonia content is apparent from Expt. 9 where the ammonia carbonate used was obviously richer in ammonia than that used in the analysis upon which yields were calculated.

In no case did the percentage of thio-urea in the equilibrium mixture approach the value found by Reynolds and Werner to be about 25%. The highest value found was 10.9%, and other values ranged as low as 1.2%. The lowest percentages of thio-urea were found in those tubes which had been permitted to stand for some time at room temperature after heating at 160°, in the presence of the hydrogen sulfide and carbon dioxide generated at that temperature. In these tubes also the yield of total thio-urea and thiocyanate was lower than in those which were opened immediately after cooling. These results seem to indicate that hydrogen sulfide influences the equilibrium, reverting thio-urea to ammonium thiocyanate. It apparently affects also the formation of the ammonium salt. The action of hydrogen sulfide on these 2 isomeric substances will receive further attention at a later date.

Summary.

1. Quantitative determinations of ammonium thiocyanate in the presence of thio-urea cannot be carried out accurately by indirect titration with excess of silver nitrate if the thio-urea exceeds 15% of the mixture.

2. Direct titration for ammonium thiocyanate with silver nitrate can be applied successfully in mixtures containing as high as 40% thio-urea. This interference in titration is apparently due to the solubility of silver thiocyanate in thio-urea solutions with formation of a complex ion.

3. Thio-urea can be determined by titration with iodine if the concentration of thio-urea does not exceed 5 mg. per 100 cc. of the titration mixture.

4. Carbon disulfide and ammonium carbonate interact at 160° giving a mixture of ammonium thiocyanate and thio-urea; the equilibrium de-

pending upon the concentration of reagents used, temperature, time of heating and finally upon the concentration of hydrogen sulfide formed in the reaction. The reaction is not productive of a quantitative yield of thio-urea.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LELAND STANFORD JUNIOR UNIVERSITY.]

THE ALKYL AMINES AS SOLVENTS.

BY HOWARD MCKEE ELSEY.

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That primary amines are ionizing solvents has been shown by the work of Gibbs[1] and others, and by analogy we would expect that a salt soluble in ammonia would be less soluble in methylamine, still less soluble in ethylamine and dimethylamine, and perhaps insoluble in propylamine and trimethylamine. Indeed Shinn[2] found potassium iodide, a salt very soluble in liquid ammonia and fairly soluble in methylamine, to be entirely insoluble in ethylamine, the next higher ammono alcohol. From this, it would seem that the higher amines would be very poor solvents for inorganic substances.

The salts used in the present solubility determinations were of the ordinary commercial variety, dried as thoroughly as was possible without danger of decomposition. Excepting in a very few cases those compounds only were taken from which all the water was known to have been removed.

The ethyl-, methyl-, propyl- and isopropylamines used as solvents were water-free imported samples. To ensure their remaining dry, they were stored over metallic sodium. The dimethyl and trimethylamines were purchased as the water solutions. They were recovered as the water-free substances by distilling from a flask through an inverted condenser and then a soda-lime tube and finally condensing in a glass container cooled by a liquid ammonia bath. Several pieces of freshly cut sodium were added to the container to remove the last traces of moisture present and to absorb any that might later be introduced. Some difficulty was encountered in preventing loss of the amine by leakage through the stopcock of the container. The value of the amines as organic solvents is shown by the ease with which they dissolved any lubricant which was placed on the stopcock; and it was finally found necessary to keep the tube, holding the stock of amine, in an ice-bath while working, and to seal the stopcock off at night.

Since the lower amines are gases under operating conditions the solubility determinations were made in hermetically sealed glass tubes. For

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[1] Gibbs, THIS JOURNAL, 28, 1395 (1906).

[2] Shinn, *J. Phys. Chem.*, 11, 537 (1907).