Some New Compounds of Urea with Acids and Salts.

DISSERTATION.

Addressed to the Academic Faculty of the
University of Virginia as part of the
Required Work for the Degree
of Doctor of Philosophy.

BY

JACK PERCIVAL MONTGOMERY, A.B.

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PREFACE.

An examination of the table of contents of almost any journal devoted to Chemistry will show that urea has been the subject of many investigations. In the light of this activity it might be supposed that a dissertation of this character is quite uncalled for, but the subject was not exhausted and hence there was ground for further research.

Very early in the history of urea it was found that it combines with acids, acting as a weak base. A number of these compounds were described prior to 1860, but since that time contributions to the list have been rare, notwithstanding the fact that a number of acids had not been combined with urea. In this paper are described some compounds not previously presented.

This investigation was undertaken at the suggestion or Dr. J. W. Mallet, and the greater portion of the work was executed in the laboratory of the University of Virginia. I am sincerely grateful to Dr. Mallet for his thorough instruction and helpful inspiration, and to Professor Dunnington for his kind interest in my work. I am indebted to Dr. C. J. Moore, my fellow student, for many helpful suggestions.

April, 1903. J. P. M.

Some New Compounds of Urea with Acids and Salts.

Urea was discovered by H. M. Rouelle in 1773. In 1799 Fourcroy and Vauquelin made a more careful investigation of it, this being the first exact examination of this interesting body. Urea has been prominent ever since Wöhler's classic experiment, showing that it can be made from mineral substances and without the aid of the life process, this being the first instance of the preparation of an organic substance by a method analogous to the usual methods for the formation of inorganic substances. Berzelius was the first to show that the same laws applied to complex organic bodies as were known to hold good for the simpler inorganic compounds. But there still remained much doubt as to the identity of the laws governing the formation of organic and inorganic compounds. Confusion arose from the fact that most mineral compounds could be formed by bringing the constituents together under the proper conditions, while no such simple way was known by which organic compounds could be prepared, the phenomena of life being apparently necessary in every case. Therefore it was a discovery of far-reaching importance when, in 1828, Wöhler prepared urea artificially by evaporating the aqueous solution of ammonium cyanate, thus showing that the life process was not essential to the formation of organic compounds. This great discovery did more for the solidarity of chemical science than any other single discovery has done, for it effectually removed all barriers between organic and inorganic chemistry. Because of this discovery alone, urea would have a very important place among chemical compounds, but it also has properties which make it noteworthy and interesting. That it holds a prominent place is shown by the fact that it has so often been the subject of research, not only among chemists but among physiologists as well.

Urea occurs in the urine of man and the flesh-eating animals, in small amount in the urine of herbivorous mammals, snakes and birds. It is the chief product of excretion from the oxidation of nitrogenous food and proteid tissues of the body. Its amount is determined by the amount and character of the food, and, to a small extent only, by the intensity of muscular exertion. The average man excretes about 33 grams of urea daily. Urea has been found in the vitreous humor of the eye, and in very small quantities in milk, blood, perspiration and pus.

Urea may be prepared from human urine as follows:[1] The urine is evaporated to small bulk and nitric acid is added, precipitating urea nitrate. This is filtered and washed, after which it is decomposed by barium carbonate, the urea being dissolved out by alcohol.

The best means to prepare urea is by evaporating a solution of ammonium cyanate. The process is as follows:[2] Cyanide of potassium is converted into the cyanate by fusion with litharge. The cyanate, without purification, is dissolved in water, and a solution of ammonium sulphate is added. The mixture of ammonium cyanate and potassium sulphate is evaporated over the water-bath, and freed as far as possible from crusts of potassium sulphate which are formed. The dried residue thus obtained is boiled with 80 per cent. alcohol. The solution, filtered from the rest of the potassium sulphate, gives by cooling, and further evaporation of the mother-liquor, colorless crystals of urea amounting to one-fourth the cyanide of potassium used.

Urea is a colorless, crystalline substance, readily soluble in water and alcohol, almost insoluble in ether. Its specific gravity is 1.35. It has a sharp, cooling taste; no odor. Fuses at 132° and decomposes at a slightly higher temperature, yielding ammonia and cyanuric acid. If gradually heated with water a sublimate of ammonium carbonate is produced.

Alkaline hypobromites decompose urea into carbon dioxide, water and nitrogen, though the decomposition is not complete, only about 90 per cent. of expected amount of nitrogen being evolved This fact is made use of in the determination of the amount of urea in urine, it being accepted that the urine contains other nitrogenous matter sufficient to make good the deficient amount of nitrogen from the urea. In this method the volume of nitrogen

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[1] Gmelin's "Handbook of Chemistry," VII, 361.

[2] Gmelin's "Handbook of Chemistry," VII, 365.

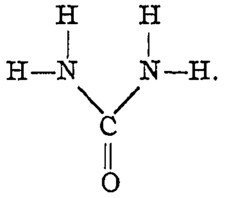
evolved from a given quantity of urine is measured, thus giving a rapid method of estimation.

Nitrous acid decomposes urea at ordinary temperatures into water, carbon dioxide and nitrogen, but at lower temperatures the action is slower in proportion to the lowering of the temperature.

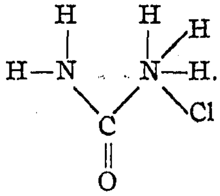
In the presence of a certain organized ferment a solution of urea undergoes alkaline fermentation, ammonium carbonate being formed.

Urea boiled with a fixed caustic alkali produces ammonia and an alkaline carbonate.

Urea is commonly regarded as the diamide of carbonic acid and is frequently called carbamide. It may be represented by the formula



It is feebly basic and forms distinct compounds with acids and salts. It enters into such compounds without change of composition, and, with few exceptions, the compounds so formed are not stable. Although a diamide, urea does not combine with more than one equivalent of acid, thus acting as a univalent radicle. When urea combines with acids it is probably the case that one of the nitrogen atoms becomes pentivalent, one of the extra bonds being satisfied by the acid radicle, the other by the hydrogen of the acid. In the case of salts the metal of the salt is combined in a manner analogous to the linkage of the hydrogen of the acid. For example, the formula of the compound formed by the union of urea and hydrochloric acid may be written



Walker and Hambly[1] have recently made an exhaustive study of the transformation of ammonium cyanate into urea, and some of their observations may be of interest. The transformation is reversible. Urea readily undergoes transformation into ammonium cyanate, though the tendency to do so is not strong. But when ammonium cyanate is converted to urea the whole mass does not seem to undergo the change, about 5 per cent. of the amount of ammonium cyanate remaining. In other words the end-point of the reaction is reached when 95 per cent. of the ammonium cyanate is transformed into urea. The temperature influences the end-point but little, the only difference being that the end-point is reached in a shorter time when the temperature is near 100°. The transformation of ammonium cyanate into urea is a bimolecular change. This may be accounted for on three different assumptions: two molecules of ammonium cyanate form one molecule of urea, or the cyanate is dissociated into ammonia and cyanic acid, or the cyanate is electrolytically dissociated into ammonium and cyanic ions. When sodium sulphate was added to the solution of the cyanate no change was noticed, but on the addition of ammonium sulphate the change was much more rapid. The explanation of this acceleration is that the quantity of one or more of the active substances has been increased by the addition of ammonium sulphate, though no such acceleration was noticed in the case of the addition of sodium sulphate. Since ammonium sulphate hastens the reaction, the assumption that the two molecules which react are molecules of ammonium cyanate is untenable. Unless we grant that ammonium sulphate is capable of dissociation into ammonia and sulphuric acid, we cannot hold that the second assumption is true. For in case it was correct, in order for acceleration to occur either ammonia or cyanic acid must be added. As it is a well-accepted fact that ammonium sulphate is dissociated into ammonium and sulphuric ions, the third assumption is evidently the correct one, that the ammonium cyanate is electrolytically dissociated into ammonium and cyanic ions. Potassium cyanate and ammonium hydroxide have, separately, the same hastening action, thus confirming the evidence in the previous case.

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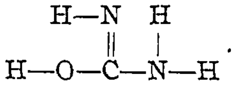
[1] Journal of the Chemical Society, 67, 746 (1895).

As there is a reverse change, it would follow that when urea is dissociated it breaks up into ammonium and cyanic ions, though urea is not easy to dissociate. This would indicate that in urea the nitrogen of the cyanic ion is more strongly united to the carbon than is the nitrogen formerly of the ammonium ion. But in carbamide the two nitrogens have the same linkage, and if this is true it would appear that urea is not identical with carbamide. That is, if the two atoms of nitrogen in urea are unequally linked, urea cannot be identical with its isomer carbamide.

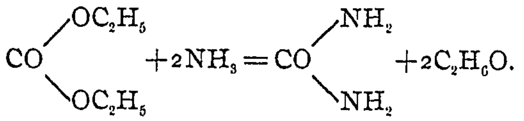
In fact the belief that urea and carbamide are identical has not passed unchallenged, it having been held that urea is a hydroxy-carbimidamide[1] represented by the formula



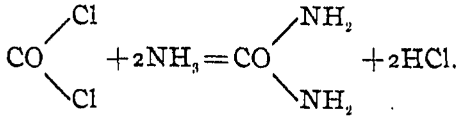
$$\begin{array}{ccccccccc} & & \mathrm{H} & — & \mathrm{N} & & \mathrm{H} & & \\ & & & & \| & & | & & \\ \mathrm{H} & — & \mathrm{O} & — & \mathrm{C} & — & \mathrm{N} & — & \mathrm{H} \end{array}$$

One of the reasons for the view that urea is not the same as carbamide was given in the preceding paragraph. The chief reason is found in the fact that urea acts as a univalent base when it might be expected to act as a bivalent one. The argument is that if the two nitrogen atoms are similarly linked they should in some cases act alike. That is, urea should under some conditions unite molecule for molecule with a dibasic acid, instead of always uniting molecule for molecule with the monobasic acids.

But there are stronger arguments on the other side of the question. A reaction generally used for making acid amides consists in treating the ethereal salt of the acid with ammonia. Urea may be made by treating ethyl carbonate with ammona :



Another reaction of common application consists in treating the acid chlorides with ammonia. Urea may be made by treating carbonyl chloride with ammonia.:



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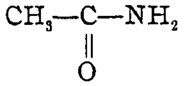
[1] Berichte der deutschen chemischen Gesellschaft, 15, 453.

The formulas given for ethyl carbonate and for carbonyl chloride represent the only possible arrangement in the structure of these bodies, and as the change in each case to urea is one of substitution it follows that the two ammonia residues are properly represented as equally linked to the carbon. If this is a correct assumption urea is identical with carbamide. That it is correct can hardly be disputed.

But the fact remains that urea is a univalent base, and those who contend that urea is not identical with carbamide may in justice ask for an explanation of this apparent anomaly. It is a well-known fact that the basic properties of an ammonia residue are destroyed when the residue is combined with carbon which is in combination with oxygen. Because of this the amides as a class are neutral substances, the acid properties being destroyed by the removal of the hydrogen of the acid, and the basic properties being overcome by means of the acid residue. But in urea, or carbamide, we have two ammonia residues to one acid residue. It would follow then that the acid residue would destroy the basic properties of one ammonia residue, while the other ammonia residue, not being completely satisfied, would be capable of further combination. Considered from this standpoint it is no longer remarkable that only one of the nitrogen atoms is capable of changing its valence and uniting with other substances. It would rather indeed be strange if urea should ever act as a bivalent base.

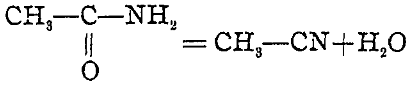
Those who have sought to disprove the identity of urea and carbamide have made much of another point, the fact that urea is converted into cyanamide by the removal of one molecule of water. Urea treated with sulphurous chloride loses the constituents of one molecule of water, the residue being cyanamide. The argument is that in carbamide the oxygen is carbonyl oxygen and is therefore not so easily removed as hydroxyl oxygen would be. Since the oxygen is not hard to remove in the reaction mentioned, the oxygen of urea must be hydroxyl oxygen and therefore urea cannot be carbamide. In advancing such an argument a very important analogous case has been overlooked, that of the conversion of acetamide into methyl cyanide by the removal of water through the agency of anhydrous phosphorus pentoxide.

No one doubts that the structure of acetamide is represented by the following formula:

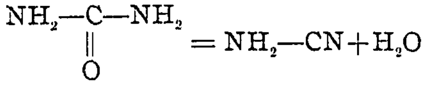


$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2$$

That is, acetamide contains carbonyl oxygen which can be readily removed. A comparison of the reactions may be instructive.



$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 = CH_3-CN+H_2O$$



$$NH_2-\underset{\underset{O}{\|}}{C}-NH_2 = NH_2-CN+H_2O$$

It will be noticed that the reactions in each case represent the removal of carbonyl oxygen, and that they differ only in that one has the group CH_3 where the other has NH_2. It is no harder to remove the carbonyl oxygen from one than it is from the other. It follows that the reaction in question is a proof rather than a denial that urea and carbamide are identical.

From a consideration of both sides of the question it may be safely concluded that urea is carbamide.

Since 1860 very few compounds of urea with acids and salts have been described. This is a peculiar fact, since there remained a number of acids and salts with which urea had not been combined, and because prior to that time a great deal of activity had been shown. The favorite method with those who have worked along this line was to cause interaction between urea oxalate and the calcium salt of the acid to which urea was to be united. Calcium oxalate was precipitated and filtered off, the filtrate on evaporation yielding the compound of urea and the acid. In very few instances was the compound produced by the direct union of urea and the acid. Nitric and oxalic acids were exceptions since their urea salts are not easily soluble in water, and so could hardly have escaped the notice of the early investigators of urea. It is a rule, with very few exceptions, that the compounds of urea are not stable and that they are easily decomposed in unexpected ways. In many of the compounds the urea may be more soluble in a certain solvent than the acid with which it is combined, or the reverse may be the case. Under these circumstances it frequently happens that the solvent decomposes the substance by dissolving out part of it, so weak is the combination. Another reason for the instability of these compounds lies in the fact that the urea is so easily decomposed.

The compounds of urea, with acids and salts, hitherto described are as follows:

Urea sulphate.[1,3,4,]
Urea nitrate.[1]
Urea hydrochlorate.[1]
Urea phosphate.[3,4]
Urea trichloracetate.[4,5]
Urea fumarate.[4]
Urea maleate.[4]
Urea malate.[4]
Urea gallate.[2,4]
Urea succinate.[2,4]
Urea parabanate.[4]
Urea tartrate.[2,4]
Urea acid tartrate.[4]
Urea citrate.[4]
Urea acid citrate.[4]
Urea cyanurate.[4,3]
Urea picrate.[4]
Urea benzoate.[2]
Urea styphnate.[2]
Urea hippurate.[2]
Urea meconate.[2]
Urea oxalate.[2,3,4]
Urea acetate.[5]
Urea glycollate.[5]
Urea with silver oxide.[3,4,]
Urea with mercuric oxide.[3,4]
Urea with silver nitrate.[3]
Urea with palladium chloride.[4]

[1] Gmelin's "Handbook of Chemistry," VII, 369-370.

[2] Gmelin's "Handbook of Chemistry," XIII, 405-406.

[3] Dictionnaire de Chemie (Wurtz), III, 565.

[4] Watts' "Dictionary of Chemistry," IV, 832.

[5] Bulletin de la Société Chimique de Paris, Series 3, Vols XI-XII, No. 12.

Urea with sodium chloride.[1]
Urea with sodium nitrate.[1]
Urea with ammonium chloride.[1]
Urea with magnesium nitrate.[1]
Urea with calcium nitrate.[2]
Urea with zinc chloride.[1]
Urea with cadmium chloride.[1]
Urea with mercuric chloride.[1]

The compounds described in this paper are as follows:

Urea hydrobromate.
Urea with urea hydrobromate.
Urea with sodium bromide.
Urea with ammonium bromide.
Urea with calcium bromide.
Urea with platinum tetrabromide.
Double bromide of platinum and urea.
Urea hydriodate.
Urea with ammonium iodide.
Urea with sodium iodide.
Urea hydrofluorate.
Urea with urea hydrofluorate.
Urea hydrofluorate with mercuric fluoride.
Urea hydrofluorate with aluminum fluoride.
Urea sulphate (new method).
Urea with copper sulphate.
Urea with zinc sulphate.
Urea selenate.
Urea chlorate.
Urea nitrite (?)
Urea with sodium nitrite.
Urea salicylate.
Urea with ammonium salicylate.
Urea with sodium salicylate.
Urea monochloracetate.
Urea trichloracetate.
Urea butyrate.
Urea with urea butyrate.

[1] Watts' "Dictionary of Chemistry," IV, 832.
[2] Dictionnaire de Chemie (Wurtz), III, 565.

Urea with zinc butyrate.
Urea with copper butyrate.
Urea phthalate.
Negative results.

METHODS OF ANALYSIS.

Nitrogen was determined by the Kjeldahl method, modified to the extent that nothing but sulphuric acid was used in the digestion, since this is sufficient to decompose the urea.

Since silver chloride is soluble to a certain extent in an aqueous solution of urea, it was necessary to determine silver as follows: An excess of sodium hydroxide was added to the compound; the mixture was evaporated and ignited to destroy the urea present, leaving sodium chloride in the residue; the chlorine was then determined in the usual way by precipitation as silver chloride.

Sulphuric acid was determined as barium sulphate.

Selenic acid was determined as barium selenate.

Bromine and iodine were determined in a manner similar to the determination of chlorine.

Fluorine was determined as follows: Sodium carbonate was added in excess to a weighed quantity of the salt. To the boiling solution of sodium fluoride, so formed, calcium chloride was added until no further precipitate was formed. The precipitate of calcium fluoride and carbonate was filtered, washed, dried, and ignited. Acetic acid was then added in excess and the mixture was evaporated and kept hot on the water-bath until there were no odors of acetic acid. The calcium fluoride was filtered, dried and ignited. It was weighed as such.

Nitrous acid was determined by titration with potassium permanganate. Salicylic acid was determined colorimetrically, a standard solution of sodium salicylate being used for comparison, and ferric chloride as an indicator.

Sodium was determined as the chloride by adding hydrochloric acid to a weighed portion of the salt to be analyzed and destroying the organic matter by ignition.

Calcium was determined by precipitation as the carbonate.

Mercury was determined as the sulphide.

The platinum compounds were of such character that they could be ignited with the loss of everything except the platinum, and it was so determined.

Aluminum was precipitated as the hydroxide, by ammonia, and ignited to the oxide.

Copper was precipitated as the carbonate which was ignited to the oxide.

UREA HYDROBROMATE.

Prepared by passing dry hydrobromic acid over dry urea. The hydrobromic acid used was made by the action of strong phosphoric acid on potassium bromide. It was dried by passing over calcium bromide, and further dried by passing over anhydrous phosphorus pentoxide. From the drying tubes the acid was passed directly over the urea which was spread out over the bottom of a small flask.

Urea absorbs the acid with evolution of heat. If the current of acid be at all rapid, enough heat will be produced to melt the mass, and in the melted condition only half the calculated amount of acid was absorbed. If the heat is kept down by surrounding the flask with cold water no liquefaction occurs until the urea is almost saturated with the acid. At this point the mass becomes an oily liquid of lemon-yellow color which gives off fumes in the air and is very corrosive. The oily liquid thus obtained shows a variable behavior, sometimes resisting all efforts to crystalize it, and at other times readily forming radiated masses of white sectile needles. The crystals are very deliquescent and, when moist, give off fumes of hydrobromic acid. Water decomposes the compound, about half the acid being set free. Freely soluble in alcohol. Melts at 38°. Decomposition takes place at 130°, but is more rapid at high temperatures.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.HBr.$ Per cent.	Found. I. Per cent.	II. Per cent.
Br................	56.74	56.56	56.40

UREA WITH UREA HYDROBROMATE.

In preparing the preceding salt it was noticed that when hydrobromic acid was passed over urea, if the temperature was not kept down, the expected amount of acid was not absorbed. It was found that if the mass was gently heated just half the expected amount of acid was absorbed, resulting in a compound made up of two molecules of urea and one molecule of hydrobromic acid. When urea unites with acids it has the power to combine molecule for molecule with monobasic acids. But here we have a seeming contradiction, two molecules of urea to one of a monobasic acid. But an explanation may be found in the fact that urea forms compounds with salts, molecule for molecule, *e. g.*, urea with sodium bromide, and we may take this as an analogous case, that is, urea with urea hydrobromate.

This compound resembles urea hydrobromate, forming white, sectile, deliquescent crystals. Not entirely decomposed by water, but if left in moist condition the urea slowly decomposes. Soluble in water and alcohol. Melts at 47°. Slowly decomposed at 130°.

ANALYSIS.

	Calculated for $(NH_2.CO.NH_2)_2HBr$. Per cent.	Found. I. Per cent.	Found. II. Per cent.
Br	39.80	39.62	39.55
N	27.86	27.76	27.61

UREA WITH SODIUM BROMIDE.

Prepared by mixing the concentrated solutions of urea and sodium bromide, in equal numbers of molecules, and evaporating at atmospheric temperature in sulphuric acid desiccator.

Transparent, shining, deliquescent plates, containing two molecules of water. Soluble in water and alcohol. Crystals melt at 52°, and decompose at 140°. The compound was recrystallized several times and the most perfect crystals were chosen for analysis.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.NaBr.2H_2O$. Per cent.	Found. I. Per cent.	Found. II. Per cent.
Br	40.16	40.36	40.40
Na	11.58	11.62	11.70

UREA WITH AMMONIUM BROMIDE.

Prepared by mixing the concentrated solutions of urea and ammonium bromide, in equal numbers of molecules, and evaporating in sulphuric acid desiccator. The crystallization was repeated several times, and the best formed crystals were chosen for examination.

White, octahedral crystals, slightly deliquescent. Soluble in water. Decomposed by alcohol, which removes the urea from the compound. Crystals melt at 85°, decompose at 135°.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.NH_4Br$. Per cent.	Found.	
		I. Per cent.	II. Per cent.
Br	50.58	50.70	50.90
N	26.57	26.41	26.35

UREA WITH CALCIUM BROMIDE.

Prepared by mixing the concentrated solutions of urea and calcium bromide, in molecular proportion 2 : 1, and evaporating in sulphuric acid desiccator. The compound was recrystallized and the most perfect crystals were separated.

Large plates with pearly luster, containing four molecules of water; very deliquescent, soluble in water, partially decomposed by alcohol.

ANALYSIS.

	Calculated for $(NH_2.CO.NH_2)_2CaBr_2.4H_2O$. Per cent.	Found.	
		I. Per cent.	II. Per cent.
Br	40.77	40.70	40.63
Ca	10.26	10.31	10.35

UREA WITH PLATINUM TETRABROMIDE.

Prepared by mixing urea and platinum tetrabromide, molecular proportion 2 : 1, in concentrated solution, and evaporating in sulphuric acid desiccator. Yellow octahedral crystals. Soluble in 25 parts of water. Decomposed at 140°.

ANALYSIS.

	Calculated for $(NH_2.CO.NH_2)_2PtBr_4$. Per cent.	Found.	
		I. Per cent.	II. Per cent.
Pt	30.70	30.65	30.86
N	8.81	8.71	8.75

UREA HYDROBROMATE WITH PLATINUM TETRABROMIDE.

Prepared by passing dry hydrobromic acid over a mixture of urea and platinum tetrabromide, in molecular proportion 2 : 1. Urea hydrobromate was thus formed in contact with the platinum tetrabromide with which it united. To insure the thorough contact of the two substances, the containing flask was shaken from time to time. Crystals formed in the flask when the proper concentration of the acid was reached. These were dissolved in alcohol and recrystallized under diminished pressure.

Red needles, slightly deliquescent. Soluble in alcohol. Decomposed by water.

ANALYSIS.

	Calculated for $(NH_2.CO.NH_2)_2H_2PtBr_6$. Per cent.	Found. I. Per cent.	Found. II. Per cent.
Pt	27.97	27.90	27.88
Br	68.86	68.80	68.74
N	8.03	8.00	7.98

UREA HYDRIODATE.

Prepared by passing dry hydriodic acid over dry urea. The acid was made by gently heating red phosphorus and iodine with a small quantity of water, just enough to dampen the mixture thoroughly. The action is similar to that described in the case of the hydrobromate, and the same precautions were observed.

Urea hydriodate crystallizes in needles, white when pure, closely resembling urea hydrobromate. It is deliquescent but not to such an extent as the hydrobromate. The compound is not stable, iodine being easily liberated, causing the crystals to become discolored. Soluble in alcohol. Decomposed by water.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.HI$. Per cent.	Found. I. Per cent.	Found. II. Per cent.
I	67.55	67.55	67.63

UREA WITH AMMONIUM IODIDE.

Prepared by mixing the concentrated solutions of urea and ammonium iodide, molecular proportion 1 : 1, and crystallizing in sulphuric acid desiccator. The crystals so formed were recrystallized and the more perfect ones examined.

White, shining, deliquescent needles, easily decomposed, turning brown. Soluble in water and alcohol.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.NH_4I$. Per cent.	Found. I. Per cent.	Found. II. Per cent.
I	61.90	62.02	62.07
N	13.65	13.50	13.57

UREA WITH SODIUM IODIDE.

Prepared by mixing the concentrated solutions of urea and sodium iodide, in molecular proportion 1 : 1, and crystallizing in sulphuric acid desiccator. The compound was recrystallized, and only the clean, well-formed crystals were examined.

White, shining, deliquescent needles, decomposing easily. Soluble in ten parts of water. Decomposed by alcohol, which dissolves out the urea.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.NaI$. Per cent.	Found. I. Per cent.	II. Per cent.
I	60.47	60.52	60.55
Na	10.95	10.90	10.88

UREA HYDROFLUORATE.

Prepared by dissolving urea in a 40 per cent. solution of hydrofluoric acid and evaporating until the mass became syrupy, when excess of acid was removed by a brisk current of air. The liquid slowly crystallized, forming white needles. Very soluble in water, the solution slowly attacking glass. Melts at 70° and decomposes at 98°.

ANALYSIS.

	Calculated for $NH_2CO.NH_2.HF$. Per cent.	Found. I. Per cent.	II. Per cent.
F	23.75	23.85	23.88

UREA WITH UREA HYDROFLUORATE.

Prepared by mixing the concentrated solutions of urea and urea hydrofluorate, in molecular proportion 1 : 1, and crystallizing.

White needles, more stable than the hydrofluorate. Melts at 82°. Decomposes at 105°. The compound is not deliquescent and is not readily decomposed by moist air.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2HF$. Per cent.	Found. I. Per cent.	II. Per cent.
F	13.57	13.40	13.45

UREA HYDROFLUORATE WITH MERCURIC FLUORIDE.

Prepared by mixing urea hydrofluorate and mercuric fluoride, in molecular proportion 1 : 1, in dilute hydrofluoric acid, and crystallizing. Light yellow, imperfectly formed octahedrons. Very slightly soluble in water. Soluble in dilute hydrofluoric acid. The compound is not deliquescent and is very stable.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.HF.HgF$. Per cent.	Found. I. Per cent.	II. Per cent.
Hg	62.89	62.53	62.60
F	17.92	17.80	17.83

UREA HYDROFLUORATE WITH ALUMINUM FLUORIDE.

Prepared by dissolving urea and aluminum oxide, molecular proportion 1 : 1, in 40 per cent. solution of hydrofluoric acid. On evaporating, the compound separates as a scum, which, on drying, shows a slight tendency to crystallize.

White mass, slightly deliquescent. Decomposes, if moist for any length of time, hydrofluoric acid being given off. Soluble in sixteen parts of water, the solution slowly attacking glass. Decomposes at 110°.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.HF.AlF_3$. Per cent.	Found. I. Per cent.	Found. II. Per cent.
Al	16.46	16.65	16.69
F	46.46	46.26	46.30

UREA SULPHATE.

In Gmelin's "Handbook of Chemistry," Vol. 7, page 369, the following directions are given: "A mixture of 100 parts of oxalate of urea, 125 parts of crystallized gypsum, and a small quantity of water is slightly warmed. The mixture is exhausted with four times its weight of alcohol and the filtrate evaporated."

A more simple way was found to be as follows: To a known amount of urea, normal sulphuric acid was added, molecular proportion 2 : 1. The solution was evaporated and crystallized.

White needles and plates, slightly deliquescent, of sour taste, soluble in small quantity of water. If the compound remains long in the moist condition, the urea is decomposed and ammonium sulphate is produced. Melts at 82° to an oily liquid. Decomposes at 110°.

ANALYSIS.

	Calculated for $(NH_2.CO.NH_2)_2H_2SO_4$. Per cent.	Found. I. Per cent.	Found. II. Per cent.
SO_4	44.04	44.16	44.24
N	25.68	25.51	25.53

UREA WITH COPPER SULPHATE.

Prepared by mixing the aqueous solutions of urea and copper sulphate, molecular proportion 1 : 1, and crystallizing in sulphuric acid desiccator.

Light blue, shining plates containing 5 molecules of water. Very easily undergoes partial decomposition, ammonium carbonate being formed, causing precipitation of the copper as the carbonate. Oxide of copper is precipitated from a boiling solution of the salt.

In this compound, and in others analogous to it, the urea readily undergoes decomposition and the products of the decomposition cause a precipitation of the metal. The effect is the same as when ammonium carbonate reacts upon the sulphate of the metal.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.CuSO_4.5H_2O$.	Found.	
	Per cent.	I. Per cent.	II. Per cent.
Cu	20.39	20.19	20.23
SO_4	31.07	30.91	30.93

UREA WITH ZINC SULPHATE.

Prepared by mixing the solution of urea and zinc sulphate, molecular proportion 1 : 1, and crystallizing.

Shining, transparent plates, containing seven molecules of water. The compound is slightly deliquescent, and in the moist state easily undergoes partial decomposition, zinc carbonate being formed. Not permanent even in the dry condition.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.ZnSO_4.7H_2O$	Found.	
	Per cent.	I. Per cent.	II. Per cent.
Zn	18.73	18.54	18.61
SO_4	27.69	27.58	27.73

UREA WITH CADMIUM SULPHATE.

Prepared by mixing the solutions of urea and cadmium sulphate, in molecular proportion 1 : 1, and crystallizing.

White opaque needles, poorly crystallized, containing four molecules of water. Easily undergoes partial decomposition, cadmium carbonate being formed.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.CdSO_4.4H_2O$.	Found.	
	Per cent.	I. Per cent.	II. Per cent.
Cd	32.94	32.77	32.83
SO_4	28.24	28.02	28.09

UREA SELENATE.

Prepared by mixing solution of urea and dilute selenic acid, in molecular proportion 2 : 1, and crystallizing.

Crystals resemble those of urea sulphate. Decomposed by hydrochloric acid. Easily undergoes decomposition if damp, and, as it is very deliquescent, is not at all stable if exposed. The salt is readily soluble in water but is partially decomposed by alcohol, which seems to dissolve the urea away from the acid.

ANALYSIS.

	Calculated for $(NH_2CO.NH_2)_2H_2SeO_4$.	Found.	
	Per cent.	I. Per cent.	II. Per cent.
N................	21.13	20.90	20.96
SeO_4..............	53.96	53.72	53.80

UREA CHLORATE.

Prepared by adding urea to an excess of chloric acid and crystallizing.

Transparent right prisms, with hopper-shaped ends. Soluble in water and alcohol. Deflagrates when heated on charcoal. Decomposes with violence when acted upon by sulphuric acid.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.HClO_3$.	Found.	
	Per cent.	I. Per cent.	II. Per cent.
N................	19.39	19.13	19.19
Cl	25.20	25.28	25.35

UREA NITRITE(?).

The fact that nitrous acid does not decompose urea very rapidly at even moderately low temperatures led to the hope that at quite low temperatures urea nitrite might be produced. With that end in view, urea hydrochlorate was made to act upon silver nitrite. The silver nitrite was partly dissolved, partly suspended, in about 25 parts of water and poured upon dry urea hydrochlorate, in molecular proportion 1 : 1. Silver chloride was precipitated, and nitrogen and carbon dioxide were given off with slight raising of the temperature. The precipitated silver chloride was filtered off as quickly as possible, the filtrate being received in an evaporating dish surrounded by a freezing-mixture. The evolution of gas continued until the liquid came in contact with the cold dish, when bubbles ceased to appear. As the liquid cooled, a white flocculent precipitate was formed. It was quickly dried on filter-paper but as it became warm it decomposed very rapidly, giving off nitrogen and carbon dioxide. The substance contained urea and nitrous acid, but, as decomposition was fast enough to prevent quick weighing, it was impossible to secure a satisfactory analysis or to assign a formula to the substance. But as the substance decomposes entirely at ordinary temperatures and as it contains nothing but urea and nitrous acid, it follows that it is probably urea nitrite. It is certainly true that the temperature has great influence upon the rate of decomposition of urea when it is acted upon by nitrous acid, and at moderately low temperatures the action ceases altogether.

UREA WITH SODIUM NITRITE.

On mixing urea and sodium nitrite, in equal numbers of molecules, there was slow decomposition of the urea. But if the solution is strong there separates a crystalline mass, needles and arborescent forms. These crystals were rapidly dried on filter paper and in a sulpuric acid desiccator.

Moderately stable in dry state. Slowly decomposes in cold water, rapidly when heated. Soluble in water and alcohol. Insoluble in ether.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.NaNO_2$. Per cent.	Found. I. Per cent.	II. Per cent.
Na	17.83	18.05	18.12
NO_2	35.66	35.46	35.39

UREA SALICYLATE.

Equal numbers of molecules of calcium salicylate and urea oxalate were brought together in alcoholic solution. Calcium oxalate was precipitated and filtered, leaving a solution which, on evaporation, yielded crystals of urea salicylate.

White, shining needles and prisms showing a tendency to form twin crystals. Soluble in 80 parts of water. Freely soluble in alcohol and ether, though the ether decomposes the salt slowly by dissolving the acid and leaving the urea undissolved. Remains unchanged in the air if dry, but if moist the crystals become brown.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.HC_7H_5O_3$. Per cent.	Found. I. Per cent.	II. Per cent.
N	14.14	14.00	13.93
$HC_7H_5O_3$	69.69	69.80	69.80

UREA WITH AMMONIUM SALICYLATE.

Prepared by mixing equal numbers of molecules of urea and ammonium salicylate, and crystallizing from aqueous solution. The substance was recrystallized and the more perfect crystals were examined.

Large, white, shining needles. Slightly deliquescent. Unchanged in dry air, but turns brown if exposed to moist air. Soluble in water but not as abundantly as in alcohol and ether.

ANALYSIS.

	Calculated for $NH_2CONH_2.NH_4C_7H_5O_3$. Per cent.	Found. I. Per cent.	Found. II. Per cent.
N	19.53	19.39	19.35
$HC_7H_5O_3$	63.95	63.77	63.82

UREA WITH SODIUM SALICYLATE.

Prepared by mixing sodium salicylate and urea, molecular proportion 1 : 1, in aqueous solution and crystallizing in a sulphuric acid desiccator. The compound was recrystallized and the more perfect crystals were chosen for examination.

Large plates showing a tendency towards twinning. Slightly deliquescent. Unchanged in dry air, but becomes brown if exposed to moist air. Soluble in water and alcohol. Decomposed by ether.

ANALYSIS.

	Calculated for $NH_2.CO.NH_2.NaC_7H_5O_3$ Per cent.	Found. I. Per cent.	Found. II. Per cent.
N	12.73	12.51	12.43
Na	10.45	10.30	10.33
$HC_7H_5O_3$	62.73	62.65	62.70

UREA MONOCHLORACETATE.

Prepared by mixing equal numbers of molecules of urea and monochloracetic acid in concentrated solution and crystallizing. The substance was recrystallized and the more perfect crystals were chosen for examination.

Colorless prisms surmounted by sharp four-sided pyramids. Very deliquescent, easily absorbing enough water to completely dissolve in a very short time. Soluble in small amounts of water and in alcohol. Decomposed by ether. Small crystals gyrate actively when thrown upon the surface of water. Decompose at 130°.

ANALYSIS.

	Calculated for $NH_2CO.NH_2\ HC_2H_2ClO_2$. Per cent.	Found.	
		I. Per cent.	II. Per cent.
Cl	22.98	22.85	22.89
N	18.12	18.03	18.07

UREA TRICHLORACETATE.

This salt is mentioned in Watts' "Dictionary of Chemistry," IV, 832, but is not fully described.

Prepared by mixing the concentrated solutions of urea and trichloracetic acid, molecular proportion 1 : 1, and crystallizing. The compound was recrystallized and the more perfect crystals were chosen for examination.

Colorless prisms and plates. Slightly deliquescent. Soluble in water and alcohol. Insoluble in ether. Decomposes at 130°.

ANALYSIS.

	Calculated for $NH_2CO.NH_2.HC_2Cl_3O_2$. Per cent.	Found.	
		I. Per cent.	II. Per cent.
Cl	47.95	47.80	47.87
N	12.53	12.38	12.43

UREA BUTYRATE.

Calcium butyrate and urea oxalate, in molecular proportion 1 : 1, were ground together with a small amount of water, forming calcium oxalate and urea butyrate. The calcium oxalate was filtered off, urea butyrate remaining in solution. On evaporation in sulphuric acid desiccator the filtrate yielded long prisms capped by four-sided pyramids. These crystals were soluble in water in which they dissolve with active gyrations. Decomposed by ether. When dissolved in alcohol the salt is changed to a compound consisting of two molecules of urea to one of acid. This change is analogous to that which occurs when urea hydrobromate is dissolved in water.

If exposed to air, urea butyrate becomes rancid and acquires the unpleasant odor of free butyric acid. Before this takes place the odor is not unpleasant.

ANALYSIS.

	Calculated for $NH_2CO.NH_2.HC_4H_7O_2$. Per cent.	Found.	
		I. Per cent.	II. Per cent.
N	18.91	18.73	18.79

UREA WITH UREA BUTYRATE.

When an excess of urea is dissolved in an aqueous solution of butyric acid there is obtained, upon evaporation, a crop of crystals unlike those of urea butyrate. These contain two molecules of urea to one of acid. The same compound is formed when urea butyrate is dissolved in alcohol.

White, six-sided, double pyramids. Soluble in water and in alcohol.

ANALYSIS.

	Calculated for $(NH_2.CO.NH_2)_2HC_4H_7O_2$.	Found.	
	Per cent.	I. Per cent.	II. Per cent.
N	26.92	26.73	26.77

UREA WITH ZINC BUTYRATE.

Prepared by bringing together in aqueous solution zinc butyrate and urea, molecular proportion 2 : 1, and crystallizing.

Shining prisms, slightly deliquescent. Soluble in water and alcohol.

ANALYSIS.

	Calculated for $(NH_2.CO.NH_2)_2Zn(C_4H_7O_2)_2$.	Found.	
	Per cent.	I. Per cent.	II. Per cent.
N	15.68	15.47	15.51
Zn	18.20	18.50	18.42

UREA WITH COPPER BUTYRATE.

Prepared by mixing alcoholic solutions of urea and copper butyrate, molecular proportion 2 : 1, and crystallizing.

Olive-green, oblique prisms with shining faces. Soluble in alcohol, decomposed by water into urea and butyrate of copper.

ANALYSIS.

	Calculated for $(NH_2.CO.NH_2)_2Cu(C_4H_7O_2)_2$.	Found.	
	Per cent.	I. Per cent.	II. Per cent.
N	15.77	15.52	15.58
Cu	17.74	17.89	17.90

UREA PHTHALATE.

Prepared by adding urea to an alcoholic solution of phthalic acid, in molecular proportion 2 : 1, and evaporating spontaneously. Crystals so obtained were dodecahedrons. Soluble in alcohol. Only feebly soluble in water. Decomposed at 135°.

ANALYSIS.

	Calculated for $(NH_2.CO.NH_2)_2H_2C_8H_4O_4$. Per cent.	Found. I. Per cent.	Found. II. Per cent.
N................	19.58	19.32	19.44

NEGATIVE RESULTS.

An attempt to produce urea sulphite resulted in the oxidation of the acid and the formation of urea sulphate.

Boric acid was added to melted urea and the mass allowed to cool. A mass of crystals separated but they were not distinct and did not give a constant analysis for urea borate.

Urea and iodic acid failed to combine when left in contact.

Urea was dissolved in formic acid but in every case crystallized out unchanged.

Lactic acid dissolves urea abundantly but no crystals were formed. It is possible that urea lactate exists in liquid form and does not crystallize, but several analyses of the liquid were barren of results.

Urea with hydrazoic acid gave some crystals unlike urea, but the yield was small, most of the crystals obtained being urea. Not enough of the desired compound was produced for analysis.

Urea dissolved in a solution of tannic acid made the mass syrupy and no crystals were formed.

Urea was mixed with the alcoholic solutions of stearic and palmitic acids and on evaporation crystallized out separately.

An attempt to produce a compound of urea and dichloracetic acid resulted in the urea crystallizing out of solution.