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The Structure of Urea–Formaldehyde Resins[1]

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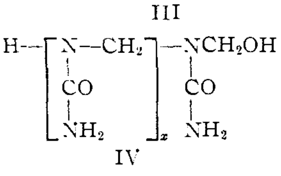
The conversion of urea and formaldehyde to an infusible and insoluble resin is well known but the exact reactions involved in the formation of the polymer are not completely understood. That formaldehyde converts urea to methylol urea (I) and dimethylol urea (II)[4] is well established. It has generally been assumed that these

$NH_2CONHCH_2OH$ I $HOCH_2NHCONHCH_2OH$ II

two intermediates are involved in the polymer formation and that water and formaldehyde are the simple products eliminated during the condensation. Two principal linear structural units (III and IV) have been supported for the main portion of the polymer and each of these linear units may react with formaldehyde in several possible manners to produce the cross-linking which would account for the properties of the final polymer.

$NH_2[CONHCH_2NH]_xCONHCH_2OH$ III



$$H-\left[\begin{array}{l}N-CH_2\\ |\\ CO\\ |\\ NH_2\end{array}\right]_x-\begin{array}{l}NCH_2OH\\ |\\ CO\\ |\\ NH_2\end{array}$$

IV

If the principal polymerization reaction leads to a polymer such as that shown in formula III, it might be expected that a symmetrically substituted dialkylurea RNHCONHR would react with formaldehyde to yield a linear polymer. If the principal polymerization reaction leads to a polymer such as that shown in formula IV it might be expected that an unsymmetrically substituted dialkylurea R_2NCONH_2 would react with formaldehyde to yield a linear polymer.

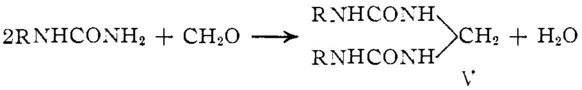
Actually no polymer has been reported from either of these reactions. Monosubstituted ureas react with formaldehyde to yield monomethylol ureas[4] and dimeric methylene bis-ureas, V.[5] This reaction is characteristic of amides. A secondary reaction between the methylene bis-urea and formaldehyde may give a methylol derivative (VI) which is easily reconverted to the original component.

$$RCONH_2 + CH_2O \longrightarrow RCONHCH_2OH$$

$$2RCONH_2 + CH_2O \longrightarrow RCONHCH_2NHCOR + H_2O$$

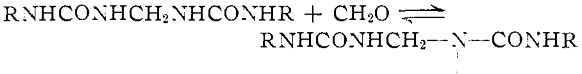
$$RNHCONH_2 + CH_2O \longrightarrow RNHCONHCH_2OH$$

IV



$$2RNHCONH_2 + CH_2O \longrightarrow \begin{array}{l}RNHCONH\diagdown\\ \qquad\qquad\quad CH_2\\ RNHCONH\diagup\end{array} + H_2O$$

V



$$RNHCONHCH_2NHCONHR + CH_2O \rightleftharpoons RNHCONHCH_2-\underset{\underset{CH_2OH}{|}}{N}-CONHR$$

VI

Primary amine groups may react with formaldehyde to yield methylol and methylene bis-amines[6] but the more common reaction is the formation of a methylene-imine (VIII) which tends to trimerize spontaneously to yield a cyclic N-substituted trimethylene triamine ring (VIII).[7]

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[1] This paper was presented in part at the Pittsburgh meeting of the American Chemical Society in September, 1943.

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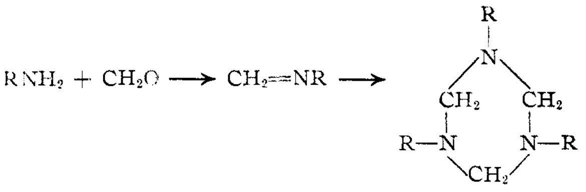
[4] Einhorn, *Ann.*, **343**, 207 (1905).

[5] Einhorn, *Ann.*, **361**, 113 (1908); Scheifler, Trostler and Salerlz, *Z. angew. Chem.*, **41**, 1305 (1928).

[6] Henry, *Bull. acad. roy. Belg.* [3] **29**, 35 (1895).

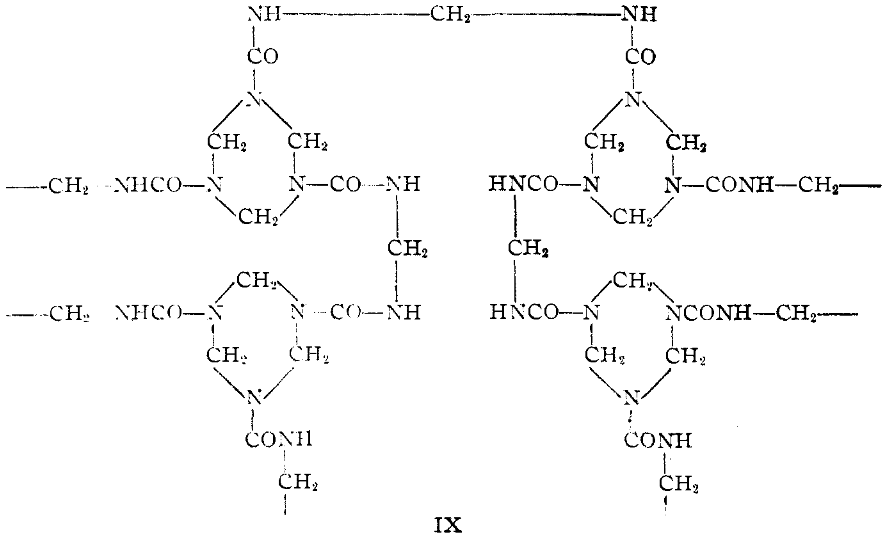
[7] Cambier and Brocket, *Bull. soc. chim.*, [3] **13**, 404 (1895); Einhorn and Prettner, *Ann.*, **334**, 217 (1904); Henry, *Bull. acad. roy. Belg.*, [3] **26**, 206 (1893); **28**, 359 (1894); **29**, 26 (1895); Franchimont and Van Erp, *Rec. trav. chim.*, **15**, 169 (1896).



VII VIII

Thurston[8] has suggested that urea and formaldehyde may react in a similar fashion, both —NH_2 groups of the urea going to methylene imine groups which then trimerize to give cyclic triamides. This would result in a complex cross-linked type of polymer such as the well-known urea–formaldehyde polymer.

However, neither the assumption that urea reacts with formaldehyde as a diamide nor that it reacts as a diamine seems to fit the facts which have been determined by various investigators who have studied this problem. We propose that urea reacts with formaldehyde as an amino acid amide. In such a molecule the amine —NH_2 would react with formaldehyde to yield methylene-imine derivative which would trimerize to a cyclic trimethylenetriamine compound, and the amide —NH_2 would react with formaldehyde to yield methylene bis amide links between the rings. The resulting polymer would be a highly cross-linked structure such as shown in formula IX.



IX

The view that urea acts as an amino acid amide is in harmony with the fact that urea forms a rather stable salt with nitric acid. Further evidence for this postulate is found in the reaction of substituted ureas and formaldehyde. As stated before no polymers have been obtained from the reaction of mono alkyl or aryl substituted ureas and formaldehyde, but rather simple dimeric methylene-bis compounds which are characteristic of the reaction of amides and formaldehyde have been isolated.[1,2] The substitution of an R group for one of the hydrogens of an —NH_2 group would increase that group's basicity, render it the amine group and thus prevent the cyclization phase of the reaction. The remaining —NH_2 group would be the amide group under such conditions and thus would be expected to form only the simple dimeric reaction product which is obtained. No polymer would result from such a reaction and no polymers are formed when alkyl ureas and formaldehyde react under mild conditions.

The substitution of an acyl or aryl group for one of the hydrogens of an —NH_2 group of urea should tend to make that nitrogen an amidic nitrogen. Since imide groups are known to react readily with formaldehyde to form methylol compounds (1), an acyl urea such as acetyl urea might be expected to form a polymer. Polymers were obtained from the reaction of acetyl urea and formaldehyde, but analysis of the polymer indicated that hydrolysis of the acetyl groups had occurred during the process and a urea formaldehyde polymer had been formed.

Formaldehyde is known to be lost when dimethylol urea polymerizes. Walter determined the methylene and methylol groups in resins prepared by him and they were present to the extent of about 1.7 group per urea residue.[9] The theoretical methylene group content of the resin shown in formula IX is 1.5 per urea residue. Walter's resins were soluble and of low molecular weight. On the basis of the structure proposed in our theory such resins would be composed of trimethylenetriamine rings in which all the methylol groups on the amide nitrogens had not yet reacted to form methylene-bis-amide links between rings.

The theoretical nitrogen content of a resin containing 1.5 methylene groups per urea residue [Formula IX] is 36.0%. Dixon[10] prepared resins in which the nitrogen content is 32.8% and Hodgins and Hovey[11] have obtained these with 35.2% nitrogen. The variation in nitrogen content can easily be accounted for by assuming varying degrees of cross-linking. If the idea that urea reacts with formaldehyde as an amino amide is

(8) Thurston, "Chemistry of Melamine Resins," Gibson Island Conference on Polymeric Materials, 1941.

(9) Walter, *Trans. Faraday Soc.*, **32**, 377, 396 (1936).

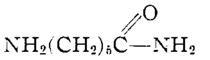
(10) Dixon, *J. Chem. Soc.*, **113**, 238 (1918).

(11) Hodgins and Hovey, *Ind. Eng. Chem.*, **30**, 1021 (1938); **31**, 673 (1939).

sound, then other amino amides should react in a similar fashion to yield polymeric materials. This idea has been tested by using glycinamide (X) and ε-aminocaproamide (XI) in place of urea.

$NH_2CH_2CONH_2$

X



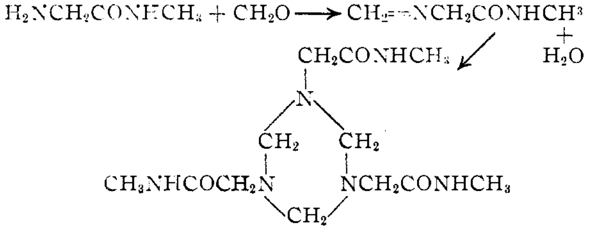
XI

$$NH_2(CH_2)_5C(=O)-NH_2$$

At room temperature and *p*H 4.2 an aqueous solution of one mole of glycinamide and two moles of formaldehyde react to form a white, opaque gel within a few hours. After drying this resin is a brittle solid whose composition corresponds closely to that of 1.5 methylene groups per glycinamide residue. ε-Aminocaproamide also reacts with aqueous formaldehyde solution. In this case there is an immediate reaction, as shown by the evolution of heat when the two compounds are mixed. A semi-solid gel is formed in about an hour and after four days the gel resembles "art gum." The composition of this resin corresponds closely to 1.5 methylene groups per amino acid amide.

These resins are insoluble in water and the common organic solvents such as acetone, ethyl acetate and alcohol. On heating the hard brittle resin from glycinamide and formaldehyde decomposes at about 200°. The resin from ε-aminocaproamide and formaldehyde softened at 100° and decomposed at 185°.

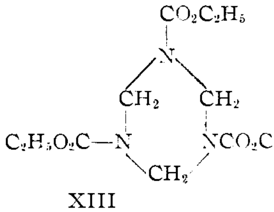
Amino acid amides which are substituted on the amide nitrogen would be expected to yield trimers when they react with formaldehyde since the basic amine nitrogen atom would be converted to the methylene amine, which would then trimerize. Glycine methylamide $NH_2CH_2CONHCH_3$ does react with formaldehyde to form such a trimeric molecule (XII) as shown by analysis and molecular weight of the product.



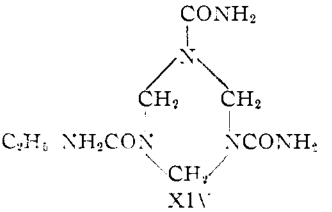
XII

This compound could conceivably react further with formaldehyde since there is a hydrogen on each of the amide groups. This further reaction, however, is unlikely since under such mild conditions substituted amides have never been observed to react with formaldehyde to form methylene-bis-amides, but attempts to obtain such reactions have proved futile.[4]

An attempt was made to synthesize the trimeric intermediate which has been postulated in the urea–formaldehyde reaction. Bischoff and Reinfeld[12] and Conrad and Hock[13] have condensed urethan with formaldehyde to yield a product which melts at 101–102° for which they proposed a dimeric structure. Later Giva and Raccin[14] described the compound as a trimer (XIII). We



XIII



XIV

have repeated the preparation and confirm the view that the product is a trimer. We have attempted to convert this urethan to the urea derivative (XIV) but all conditions which we used were unsatisfactory and the cyclic urethan was recovered unchanged.

Mono substitution on the amine nitrogen of an amino acid amide should prevent entirely the formation of a cross-linked polymer in the reaction with formaldehyde. The reaction of sarcosinamide $CH_3NHCH_2CONH_2$ with formaldehyde might be expected to give a linear polymer since secondary amines have been shown[6,15] to react with formaldehyde to form methylene-bis-amines and amides give a similar reaction. When sarcosinamide is treated with formaldehyde a very viscous, water soluble oil is formed. This reacts with hydrogen chloride to give an oily salt. Molecular weight studies and analysis indicate that this oily salt is a low molecular weight linear polymer having approximately one methylene group per amino acid amide residue.

Experimental

Reaction of Glycinamide with Formaldehyde.—Glycinamide hydrochloride and glycinamide were prepared by the method of Bergell and v. Wulfing.[16] Commercial formalin solution which contained 39.5 g. of formaldehyde per 100 ml. of solution was used in all the following experiments.

The reaction with formaldehyde was carried out with either glycinamide or glycinamide hydrochloride as the starting material and a white opaque gel was produced. In the latter case, glycinamide was prepared *in situ* by neutralizing the hydrochloric acid with a strong base such as sodium or potassium hydroxide. The reaction with formaldehyde to form an insoluble polymer was dependent on the mole ration of formaldehyde to glycinamide, the *p*H of the solution, and the temperature.

Gelation of the reaction mixture occurred only when 1.5 or 2 moles of formaldehyde per mole of glycinamide (or glycinamide hydrochloride) was present. Gelation did not occur when 1 mole or 4 moles of formaldehyde per mole of glycinamide was present. The reaction was about twice as fast as measured by the time required to form a gel when 1.5 moles of formaldehyde per mole of glycinamide was used as when 2 moles of formaldehyde was used.

The *p*H of the reaction mixture had to be within rather narrow limits for gelation of the solution to occur. Solutions containing two moles of formaldehyde per mole of glycinamide hydrochloride and a trace of monosodium phosphate as buffer were neutralized with sodium hydroxide to give solutions which varied in *p*H in steps of about

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[12] Bischoff and Reinfeld, *Ber.*, **36**, 39 (1903).

[13] Conrad and Hock, *ibid.*, **36**, 2206 (1903).

[14] Giva and Raccin, *Atti accad. sci. trans.*, **64**, 300 (1929).

[15] Kolotov, *Bull. soc. chim.*, (2) **43**, 112 (1885).

[16] Bergell and v. Wulfing, *Z. physiol. Chem.*, **64**, 354 (1910).

one from *p*H 3.2 to 9.8. The *p*H of the solutions was measured by means of a glass electrode and calomel half-cell. At room temperature gelation of the solution of *p*H 4.2 occurred within a few hours. Gelation did not occur in solutions of *p*H less than 3.2 or of 5.0 or higher.

Gelation was also dependent on the temperature of the reaction. The gelation of the solutions described in the above paragraph was studied at temperatures of 0°, room temperature and 60°. At 0° the solution of *p*H 4.2 gelled over a period of several weeks to yield a very soft, opaque material. At room temperature the solution of *p*H 4.2 formed a strong, opaque gel within a few hours. None of the other solutions showed evidence of gelation. At 60° no gelation was observed in any of the solutions. Solutions of *p*H lower than 6.5 yellowed on heating to 60°; those of *p*H 6.5 or higher remained water-white on heating at 60° for twenty-four hours and then deposited a small amount of amorphous material and became somewhat viscous on standing for a week at room temperature.

The polymer was prepared by treating one mole of glycinamide hydrochloride with 2 moles of formaldehyde at room temperature in an aqueous solution which was adjusted to *p*H 4.2 with sodium hydroxide. The water was removed by drying in a vacuum desiccator over phosphorus pentoxide. The dried cake was powdered and washed thoroughly with distilled water to remove dissolved salts. The residue was dried in a vacuum desiccator over phosphorus pentoxide for a day. The polymer was a white, brittle material.

Anal. Calcd. for the unit $C_{21}H_{36}N_{12}O_6$: C, 45.6; H, 6.58; N, 30.4. Found: C, 43.34; H, 6.44; N, 28.43.

Another polymer was prepared by allowing 2 moles of formaldehyde per mole of glycinamide to react at room temperature in the presence of very dilute hydrochloric acid. The *p*H of the solution was not measured. The resultant gel was dried in a vacuum desiccator over phosphorous pentoxide, powdered and washed with distilled water. The residue was dried for six hours under reduced pressure over phosphorus pentoxide at 100°.

Anal. Found: C, 46.59; H, 6.84; N, 27.48.

Preparation of Ethyl ε-Aminocaproate Hydrochloride.—To 100 g. (0.77 mole) of ε-aminocaproic acid dissolved in 370 cc. of absolute alcohol in a 1-liter, three-necked flask equipped with a stirrer, condenser bearing a hydrogen chloride gas trap, and a hydrogen chloride gas inlet tube reaching nearly to the surface of the liquid, hydrogen chloride was added until the solution was saturated at room temperature. The contents of the flask were then refluxed for two hours. The reaction mixture was filtered and the filtrate concentrated by vacuum distillation at 50° until crystals began to separate. Enough water was added to dissolve the crystals, the solution treated with decolorized carbon for ten minutes at room temperature, filtered, and the filtrate treated with 10 volumes of absolute alcohol. The solution was placed in a refrigerator to cause crystallization. The yield of ethyl ε-aminocaproate hydrochloride, m. p. 54–58°, was 84 g. or 56%.

An alternate method which gave an even better yield is the following[17]: To a solution which contained 450 g. (3.97 moles) of ε-aminocaprolactam (commercial grade) in 1350 ml. of water was added 412 cc. of concentrated hydrochloric acid. This solution was refluxed for about one hour to ensure complete hydrolysis. The hydrolyzed solution was then distilled to dryness under reduced pressure (water pump), benzene was then added and removed by distillation to remove the last traces of moisture. The crude salt was then recrystallized from a mixture of absolute alcohol and dry ether. Six hundred and thirty-nine grams (96% of theoretical) of ε-aminocaproic acid hydrochloride, m. p. 124–125°, were obtained. Two hundred and fifty-three grams of the above ε-aminocaproic acid hydrochloride was dissolved in the smallest possible amount of water. This solution was added to 800 ml. of absolute alcohol and 600 ml. of benzene and refluxed through a Barrett modified Stark and Dean trap for 48 hours. The resulting solution was then distilled to dryness under reduced pressure. The residue was dissolved in a small amount of alcohol, diluted with 700 cc. of absolute ether and cooled in an ice–salt-bath; 356 g. (84% of theoretical) of ethyl-ε-aminocaproate hydrochloride melting at 54–58° was obtained.

Preparation of Ethyl ε-Aminocaproate.—One hundred ninety-five grams (1 mole) of ethyl ε-aminocaproate hydrochloride was dissolved in 126 cc. of water, cooled to 0° in an ice–salt-bath, and 158.4 g. (1 mole) of cold 33% sodium hydroxide solution was added slowly with stirring and external cooling. The solution was transferred to a separatory funnel and extracted consecutively with four 200-cc. portions of ether. The ether extracts were combined and dried over anhydrous sodium sulfate. The ether was removed by distillation; the ester distilled under reduced pressure, b. p. 122° at 28 mm. (90–92° at 4 mm.). The yield was 82 g. (52%). A large amount of residue which solidified on cooling was left after the distillation of the ester. The yield probably would be increased by distilling the ester at a lower pressure.

Preparation of ε-Aminocaproamide.—Twenty-five grams (0.157 mole) of ethyl ε-aminocaproate was shaken on a mechanical shaker with 275 cc. of concentrated aqueous ammonia for sixty hours. The solution was then filtered and the water and excess ammonia removed by vacuum distillation at 40–45°. Benzene was added to the residue and the mixture again vacuum distilled at 40° to remove traces of moisture. The residue was dissolved in chloroform and 2 volumes of absolute ether added. On standing overnight in a refrigerator 12 g. of the amino acid amide separated. The filtrate yielded another gram of material on being diluted to twice its original volume with absolute ether and standing in a refrigerator for two days. The total yield was 13 g. (63%).

The amide is very hygroscopic and absorbs carbon dioxide from the air. The melting point is 50–51°.

Anal. Calcd. for $C_6H_{14}N_2O$: C, 55.35; H, 10.84; N, 21.52. Found: C, 55.50; H, 10.61; N, 20.20.

Reaction of ε-Aminocaproamide with Formaldehyde.—A solution composed of two moles of formaldehyde and one mole of ε-aminocaproamide was thoroughly stirred and then allowed to stand at room temperature. A considerable amount of heat was given off on mixing the reactants and on standing for an hour a semi-solid gel formed. This gel was allowed to stand at room temperature for one week, after this time it resembled "art gum." This material was crushed and dried at 100° in a vacuum of 2 mm. over phosphorus pentoxide for four days. The yield of the polymer, based on 1.5 methylene units per amino acid amide unit, was 97.5%.

Anal. Calcd. for $C_{15}H_{28}N_4O_2$: C, 60.77; H, 9.52; N, 18.91. Found: C, 59.22; H, 9.23; N, 14.83.

Preparation of Glycine Methylamide Hydrochloride.—To 280 cc. of a 35% aqueous solution of monomethylamine in a pressure bottle was added 21 g. (0.24 mole) of ethyl glycinate, b. p. 70–72° at 36 mm. The bottle was stoppered and placed on a mechanical shaker for sixty hours. The reaction mixture was removed from the shaker and the water and excess methylamine removed by vacuum distillation at 40°. The residue was mixed with 75 cc. of benzene and the benzene vacuum distilled at 30° to remove the water. The residue was dissolved in 20 cc. of water, and 25 cc. of concentrated hydrochloric acid was added while the reaction mixture was cooled in an ice-bath. The solution was treated with decolorizing carbon for ten minutes at room temperature, filtered and 400 cc. of absolute alcohol added. The solution was placed in a refrigerator to crystallize. Only a slight opalescence developed overnight. The volatile portion of the solution was removed by vacuum distillation and the residue dissolved in boiling 95% alcohol, treated with decolorizing carbon for fifteen minutes, filtered and the filtrate placed in a refrigerator. The yield of white crystals, m. p. 153.5–156°, was 15.5 g. (60%).

Anal. Calcd. for $C_3H_9ClN_2O$: C, 28.9; N, 7.23. Found: C, 29.00; H, 7.00.

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[17] Eck, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 28.

Reaction of Glycine Methylamide with Formaldehyde.—A solution of 2 moles of aqueous formaldehyde and one mole of glycine methylamide hydrochloride was adjusted to *p*H 4.2 by the addition of sodium hydroxide. No gelation occurred when this solution stood at room temperature for three weeks, nor when it was heated to 60° for twenty-four hours.

A solution of 1.25 g. (0.01 mole) of glycine methylamide hydrochloride and 0.77 cc. (0.01 mole) of formalin solution was made slightly alkaline to litmus by means of sodium hydroxide. The solution was heated to 60° for four hours. The water was removed by vacuum distillation at 60°. The last traces of moisture were removed by adding dry benzene to the residue and distilling at atmospheric pressure and finally at reduced pressure. The residue was extracted twice with *t*-butyl alcohol, the extracts combined and the alcohol removed by evaporation on a steam cone. A pale yellow oil remained which tended to crystallize on continued heating on a steam cone. The oil was dissolved by heating in benzene containing a little *t*-butyl alcohol. High petroleum ether was added to the hot solution and the solution evaporated slowly on a steam cone. Long, white needles gradually formed in the solution. All attempts to crystallize at lower temperatures led to the formation of oils or gummy solids. The yield of crystals, m. p. 167.5–169°, was 0.150 g. (12%). No attempt was made to obtain the maximum yield of crystalline material.

Anal. Calcd. for $(C_4H_8N_2O)_3$: C, 48.0; H, 8.0; mol. wt., 300. Found: C, 48.33; H, 8.16; mol. wt. (ebullioscopic in chloroform), 310.

Preparation of Sarcosinamide Hydrochloride.[18]—In a 1-l., 3-necked flask equipped with an efficient stirrer, reflux condenser, and thermometer was placed 266 cc. of 35% aqueous methylamine solution (3 moles). The solution was cooled to 0° by an ice–salt-bath and 72 g. of α-chloroacetamide (0.27 mole) was added. The temperature of the reaction was maintained below 5° and the contents of flask stirred until the chloroacetamide had gone into solution. Eight hours were required for the reaction. The reaction mixture was filtered from a small amount of unreacted material and the water and excess methylamine removed by vacuum distillation. The residue was dissolved in 40 ml. of water and 400 cc. of absolute ethanol was added to precipitate the sarcosinamide hydrochloride. The crystals were separated by filtration, dissolved in 95% ethanol, treated with decolorizing carbon and the solution filtered. On standing overnight in a refrigerator, 64 g., 67% of the theoretical amount, of a fluffy mass of needle crystals separated. On heating the material shrinks at 151° and the final melting occurs sharply at 161°.

Anal. Calcd. for $C_3H_9ClN_2O$: Cl, 28.5; N, 22.6. Found: Cl, 28.4; N, 22.41.

Reaction of Sarcosinamide and Formaldehyde.—A aqueous solution composed of two moles of formaldehyde and one mole of sarcosinamide hydrochloride was adjusted to *p*H 4.2 by means of sodium hydroxide. No gelation was observed when this solution stood at room temperature for several weeks, nor when the solution was heated at 60° for twenty-four hours.

A solution of 1.24 g. (0.01 mole) of sarcosinamide hydrochloride was shaken with 2.24 g. (0.01 mole) of lead oxide, litharge, for one-half hour. The mixture was cooled in an ice-bath and filtered. The filtrate was mixed with 0.77 ml. (0.01 mole) of formalin and solution acidified with two drops of concentrated hydrochloric acid. The solution was heated to 60° for four hours and the excess water then removed by vacuum distillation at 60°. The residue was a very viscous oil, soluble in water and insoluble in absolute ethanol, chloroform, acetone, ethyl acetate and ether. All attempts to isolate a crystalline material from the reaction mixture either in form of the free amine or as its hydrochloride gave only an oil.

This oil was very hygroscopic. On strong drying over phosphorus pentoxide it had the appearance of amber glass, which soon turned to a viscous liquid when in contact with the air.

Anal. Calcd. for $C_4H_9ON_2Cl$: Cl, 25.96; N, 20.51. Found: Cl, 22.58; N, 18.80.

The observed values show approximately the same ratio of chlorine to nitrogen as do the calculated values. Since this resin is so very hygroscopic and hard to handle, these values, although low, may be taken as evidence that a low molecular weight linear polymer had been produced.

Reaction of Acetylurea and Formaldehyde.—Two grams (0.0196 mole) of acetylurea was added to a solution of 1.5 cc. (0.0196 mole) of formalin in 25 ml. of water. The mixture was acidified with two drops of concentrated hydrochloric acid and allowed to stand on a steam-bath at 70° for four hours. Then the solution was cooled to room temperature and allowed to stand overnight. The product which formed was removed by filtration, washed with water and dried in the air. The yield of resinous material m. p. 245–246°, was 1.7 g.

Anal. Calcd. for acetylurea, $C_3H_6N_2O_2$: C, 35.6; H, 5.88; N, 27.5. Found: C, 34.98; H, 5.77; N, 34.45.

The above experiment was repeated using 3 cc. (0.0392 mole) of formalin solution. The yield of resinous product, m. p. 275–285° dec. was 2.0 g.

Anal. Found: C, 38.39; H, 5.80; N, 28.74.

In order to yield condensation products containing a higher percentage of nitrogen than the acetylurea, hydrolysis of the acetyl group must take place. The condensation products are then probably urea-formaldehyde resins.

Acetylurea was recovered unchanged from any attempted condensation with formaldehyde in neutral or basic solution.

Reaction of Urethan with Formaldehyde. Preparation of Tri-N-carbethoxytrimethylenetriamine.—Eighty-nine grams (1 mole) of urethan was placed in a 500-ml. round-bottomed flask equipped with a reflux condenser and thermometer, and 93 cc. (1.1 mole) of formalin solution and 25 ml. of concentrated hydrochloric acid were added. An exothermic reaction began to take place immediately and the temperature rose to 45°. As soon as the reaction had subsided the contents of the flask were heated at reflux temperature for five hours. A heavy oil separated during the heating period. The contents of the flask were cooled to room temperature and extracted with ether. The ether was dried over anhydrous sodium sulfate and evaporated leaving a nearly colorless oil. The yield was 95 to 100 g. or 95 to 100% of the theoretical amount. This oil was then heated at reduced pressure to remove the last traces of ether and cooled in a Dry Ice–acetone-bath in which it solidified to a brittle glass. This glass was allowed to come to room temperature. The resulting grainy oil was dissolved in acetone and absolute alcohol was added until the acetone solution just became cloudy. This solution was then cooled in a Dry Ice–alcohol-bath where the material began to crystallize. The crude crystalline product was filtered off and recrystallized from a benzene–ligroin mixture. The product is a white crystalline material, m. p. 101–102°. The molecular weight, determined cryoscopically in benzene, was 275. The theoretical molecular weight of tri-N-carbethoxytrimethylenetriamine is 303.

Anal. Calcd. for $C_{12}H_{21}O_6N_3$: N, 13.86. Found: N, 13.89.

Attempted Preparation of Tri-N-carbamyl-trimethylenetriamine.—Several methods of replacing the ethoxy groups of tri-N-carbethoxytrimethylenetriamine with amide groups were tried. (1) Tri-N-carbethoxytrimethylenetriamine was shaken at room temperature with a solution of alcohol saturated with ammonia. (2) The crystalline trimer was treated with liquid ammonia in a bomb at 100° for twenty-four hours. (3) An alcoholic solution of the trimer was treated with liquid ammonia and ammonium chloride in a bomb at 105°. (4) The trimer was treated with liquid ammonia and ammonium chloride at 125–130° for seventy-two hours. In each case the starting material was recovered, as shown by melting points and mixed melting points, and no evidence of replacement was observed.

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(18) Schiff, *Ann.*, **319**, 301 (1901).

Summary

1. A mechanism for the polymerization of urea–formaldehyde resins, based on the view that urea is an amino acid amide has been suggested. The polymerization is postulated as proceeding in two stages: first, the formation of trimethylenetriamine rings from methylene urea or the monomeric methylene methylol urea, and then the formation of methylene-bis-amide links to tie the rings together to form a cross-linked molecule.

2. As support for this theory, resins have been prepared from the reaction of glycinamide and ε-aminocaproamide with formaldehyde. The composition of these resins indicates that they are composed of trimethylenetriamine rings linked by methylene bridges between amide groups on different rings.

3. The trimers of the methylene-imine derivative of glycine methylamide and urethan have been prepared.

4. Sarcosinamide appears to react with formaldehyde to give a low molecular weight linear polymer.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Kinetics of Decomposition of Benzoyl Peroxide in Solvents. I

BY KENZIE NOZAKI[1] AND PAUL D. BARTLETT

Introduction.—Despite a considerable amount of able investigation of the thermal decomposition of acyl peroxides,[2] one encounters many unanswered questions in the attempt to deal kinetically with peroxide-induced polymerization. Perhaps the simplest of these questions concerns the kinetic order of the decomposition. This decomposition is so nearly unimolecular that it is usually treated as such,[2,3,4] but its rate definitely varies with concentration.[4,5] Brown[5] showed that this variation could be accounted for on the basis of concurrent first- and second-order decompositions, and he assigned velocity constants to these processes.

In view of our observation[6] that the decomposition of benzoyl peroxide can be strongly induced by free radicals, it seems likely that such decomposition is induced in part by the radicals normally present in a solution of decomposing benzoyl peroxide. The result of this would be a reaction of higher order accompanying the unimolecular decomposition. All the observed decomposition products of benzoyl peroxide can be fitted into this scheme, the following example showing how one of these products, phenyl benzoate, might be formed as a product of the chain reaction. Every other product of the decomposition can be formulated as arising in a more or less similar fashion.

$$C_6H_5COO{-}OOCC_6H_5 \longrightarrow 2C_6H_5COO{-} \qquad (1)$$

$$2C_6H_5COO{-} \longrightarrow CO_2 + C_6H_5COOC_6H_5 \qquad (2)$$

$$C_6H_5COO{-} + C_6H_5COO{-}OOCC_6H_5 \longrightarrow CO_2 + C_6H_5COOC_6H_5 + C_6H_5COO{-} \qquad (3)$$

In general the benzoate radicals will also attack the solvent, as they are known to do in the case of benzene.[7] If such attack (chain transfer to the solvent) results in new free radicals which are more stable and less reactive than the benzoate radicals, the effect of the solvent should be to suppress the chain decomposition shown in equation 3. If, on the other hand, chain transfer to the solvent yields new radicals comparable in activity to the old, this process will affect only the products and not the kinetics of the over-all reaction. The special case in which chain transfer to the solvent results in a change in the chain-terminating reaction will be dealt with in a forthcoming paper.

In order to test the reality of this picture of the decomposition of benzoyl peroxide, we have first established that a part of the decomposition of benzoyl peroxide in common solvents is of chain character (a) by showing that it responds to inhibitors, and (b) by inducing it with known free radicals. Next a survey has been made of the over-all rates of decomposition of benzoyl peroxide in a series of solvents. Finally, a kinetic equation derived from the chain mechanism has been rigorously tested in a number of solvents and velocity constants determined for the spontaneous and induced parts of the decomposition.

The Effect of Inhibitors on Benzoyl Peroxide Decomposition.—If the decomposition of benzoyl peroxide can be induced by free radicals, the addition of inhibitors for radical chain reactions to benzoyl peroxide solutions should result in a decreased rate of decomposition. It is evident from Table I that such is the case.

Oxygen, hydroquinone, *p-t*-butylcatechol, *m*-dinitrobenzene and picric acid are all inhibitors for the reaction. This evidence not only supports induced decomposition but also renders unlikely Price's suggestion[8b] that the recombination of two benzoate radicals to reform benzoyl peroxide is

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[2] For historical references see McClure, Robertson and Cuthbertson, *Can. J. Research*, **20B**, 103–113 (1942).

[3] Kamenskaya and Medvedev, *Acta Physicochim., U. R. S. S.*, **13**, 565 (1941).

[4] Bartlett and Altschul, THIS JOURNAL, **67**, 816 (1945).

[5] D. J. Brown, *ibid.*, **62**, 2657 (1940).

[6] Bartlett and Nozaki, *ibid.*, **68**, in press (1946).

[7] Gelissen and Hermans, *Ber.*, **59**, 662 (1926); Wieland, Popper and Seefried, *ibid.*, **55**, 1816 (1922); Hey, *J. Chem. Soc.*, 1966 (1934).

[8] (a) Price, *Ann. N. Y. Acad. Sci.*, **44**, 351 (1943); (b) *ibid.*, p. 365; (c) Matheson, *J. Chem. Phys.*, **13**, 584 (1945).