Polymerization in Liquid Ammonia

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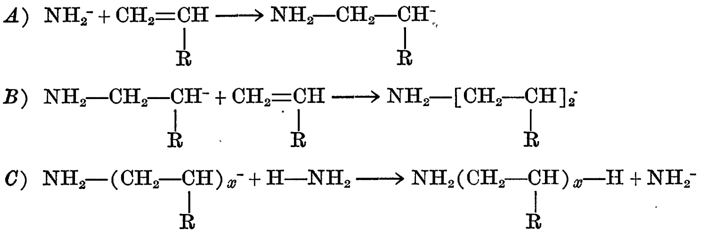
It has been reported (*1*) that glycollic acid amide and rhodizonic acid are formed when sodium is allowed to react with carbon monoxide in liquid ammonia and ammonium chloride is added to the reacting mixture prior to evaporation of the ammonia. Glycollic acid amide is obtained in best yield (15–20%) when the sodium is added in small quantities and care is taken to exclude oxygen from the reaction ingredients. Essentially the same technique is used in this laboratory for the polymerization of acrylic acid esters to low molecular weight polymers. In this instance the method of Beaman (*2*) is used, whereby the acrylic acid ester is added drop by drop to a solution of sodium in liquid ammonia and ammonium chloride is added to the reaction mixture prior to evaporation of the ammonia.

It occurred to the authors that an interesting parallelism exists between both reactions, and perhaps the same underlying mechanism may explain the formation of glycollic acid amide and rhodizonic acid, on the one hand, and the acrylic acid ester polymer, on the other. In regard to the polymerization of vinyl monomers in liquid ammonia, Beaman (*2*) and Evans *et al.* (*3*) have postulated that the reaction occurs by an anionic mechanism, and is initiated by the amide ion according to the following formulation:



A) $NH_2^- + CH_2{=}\underset{\mathrm{R}}{CH} \longrightarrow NH_2\text{—}CH_2\text{—}\underset{\mathrm{R}}{CH^-}$ (Initiation)

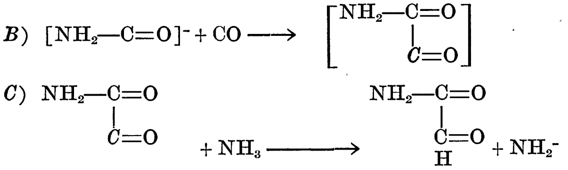
B) $NH_2\text{—}CH_2\text{—}\underset{\mathrm{R}}{CH^-} + CH_2{=}\underset{\mathrm{R}}{CH} \longrightarrow NH_2\text{—}[CH_2\text{—}\underset{\mathrm{R}}{CH}]_2^-$ (Propagation)

C) $NH_2\text{—}(CH_2\text{—}\underset{\mathrm{R}}{CH})_x^- + H\text{—}NH_2 \longrightarrow NH_2(CH_2\text{—}\underset{\mathrm{R}}{CH})_x\text{—}H + NH_2^-$ (Termination and chain transfer)

Termination of the growing chain is postulated to occur by proton transfer from the liquid ammonia.

The mechanism cited dictates the presence of nitrogen in the polymer in the form of an amine, and evidence obtained at this laboratory indicates that nitrogen is present in a polymer of ethyl acrylate made according to this reaction, and the infrared absorption spectrum (*4*) gives further evidence of the probable presence of an NH_2 group.

Applying the same mechanism to the formation of glycollic acid amide, the following steps may be noted:

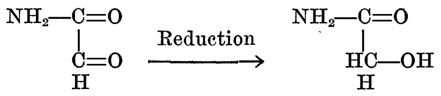


A) $NH_2^- + CO \longrightarrow [NH_2\text{—}CO]^-$ (Initiation)

B) $[NH_2\text{—}C{=}O]^- + CO \longrightarrow \left[\begin{array}{c} NH_2\text{—}C{=}O \\ | \\ C{=}O \end{array}\right]$ (Propagation)

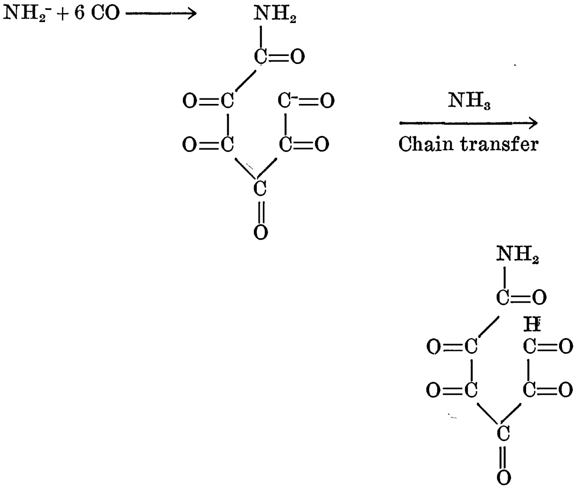
C) $\begin{array}{c} NH_2\text{—}C{=}O \\ | \\ C{=}O \end{array} + NH_3 \longrightarrow \begin{array}{c} NH_2\text{—}C{=}O \\ | \\ C{=}O \\ H \end{array} + NH_2^-$ (Termination and chain transfer)

In the absence of oxygen, and in a reducing atmosphere, the glyoxalic acid amide formed as the result of the proton transfer could easily be reduced to the glycollic acid amide, namely:



$$\begin{array}{c} NH_2\text{—}C{=}O \\ | \\ C{=}O \\ H \end{array} \xrightarrow{\text{Reduction}} \begin{array}{c} NH_2\text{—}C{=}O \\ | \\ HC\text{—}OH \\ H \end{array}$$

The initial step in the formation of rhodizonic acid is explainable by the same ionic mechanism:



The acid amide thus formed could possibly be converted to rhodizonic acid via an acyloin-type or benzoin-type condensation.

The ionic chain mechanism presented accounts for the polymerization of the vinyl monomer, on the one hand, and for the "polymerization" of carbon monoxide to glycollic acid amide, on the other. It also accounts for the initial formation of a hexamer of carbon monoxide which may be cyclized to rhodizonic acid through an acyloin- or benzoin-type condensation. It is conceivable that under favorable conditions—e.g., low concentration of ammonia and high concentration of carbon monoxide—higher polymers of carbon monoxide may be formed.

References

1. Scott, A. F. *Science*, **115**, 118 (1952).
2. Beaman, R. G. *J. Am. Chem. Soc.*, **70**, 3115 (1948).
3. Evans, M. G., Higginson, C. C., and Wooding, N. S. *Proc. Intern. Colloquium on Macromolecules, Amsterdam (1949)*. Amsterdam: D. B. Centen's Uitgevers-Maatschappij NV, 60 (1950).
4. Counts, J. B. Private communication.

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Dental Caries in Rats Fed a Diet Containing Processed Cereal Foods and a Low Content of Refined Sugar

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There has been slow progress in formulating dietary regimens on which laboratory animals develop dental caries, which may be regarded in all respects as a satisfactory analog of human dental caries. The coarse particle diets of Shibata (*1*) and Hoppert, Weber, and Canniff (*2*) and the refined diets containing an excessive amount of sugar (*3–5*) produce carious lesions which occur almost exclusively on occlusal surfaces and originate, with very few exceptions, only in the deep fissures. The identity of this type of caries with human dental caries has been questioned for numerous reasons (*6, 7*). One of the most disconcerting facts of such experimental caries is the general failure of caries to develop on buccal, lingual, or proximal surfaces, whereas these surfaces in human dentition are highly susceptible to caries. During the course of our present studies, however, Stephan (*8*) reported that low-fat, high-sugar diets, consisting chiefly of skimmed milk powder and cane sugar supplemented with cod liver oil, induced buccal and lingual surface caries as well as proximal and occlusal surface caries in white rats. It has been observed also that the Syrian hamster may develop a cervical type of surface caries in addition to buccal caries, on a finely powdered diet consisting chiefly of powdered corn meal and whole milk powder (*9*) and also on a diet of whole wheat flour, cornstarch, confectionary sugar, whole powdered milk, and alfalfa (*10*). In one other species (the cotton rat), caries is produced under a number of dietary regimens but presumably occurs only "deep in the occlusal fissures of the molars" (*11*).

The cariogenic properties of the following basal diet (586) are being studied:

Ingredients	Percentage
Cerelose (commercial glucose)	18.0
Enriched rye bread (dry)	25.0
Enriched white bread (dry)	25.0
Cooked rolled oats (dry)	15.0
Cooked yellow corn grits (dry)	15.0
Sodium chloride	2.0

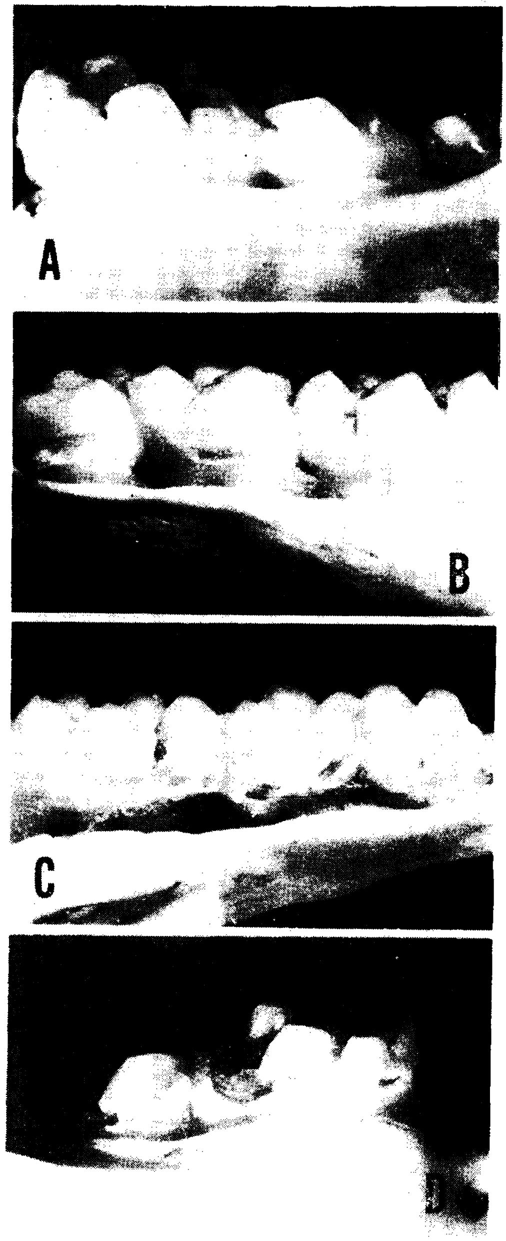

Fig. 1. *A*, lower buccal surfaces showing "orange peel" appearance of extensive white opaque area. At this stage, enamel will crumble easily on probing. Initial white areas may be smaller and more sharply defined. *B*, enamel is destroyed, exposing areas of dentin. *C*, further destruction on interproximal and distal areas. *D*, caries below gingival line and extensive destruction of occlusal areas.

The rolled oats and corn grits were cooked about 1 hr, dried at 100° C, and ground to a fine powder. The bread was dried at 100° C for a period of approximately 8 hr to a golden-brown color and ground fine. Vitamin B concentrates were added to provide thiamine 2.0 ppm, riboflavin 3.0 ppm, pyridoxine 2.5 ppm, calcium pantothenate 20.0 ppm, choline hydrochloride 1000 ppm, and inositol 25.0 ppm. Vitamin A and D concentrate (Natola) was given in separate feed cups