

NOTES

Complex Formation between Starch and Organic Molecules

BY RICHARD S. BEAR

In a previous study¹ it was suggested that in the complexes with starch formed by a variety of reagents (iodine, methanol, ethanol, *n*-propanol, *n*-butanol, the tertiary butyl and amyl alcohols, acetone and glycerol) is to be sought evidence for the helical starch configuration of Freudenberg, *et al.*² Recently Rundle and his students³ have furnished detailed pictures for the helical structures of the iodine and *n*-butanol complexes.

From the diffraction standpoint the solids which resulted from precipitation of starch by normal alcohols in the early investigation¹ appeared to be identical, but another pattern was obtained by using the tertiary alcohols. At that time the diffraction patterns were relatively poor, since proper procedures for washing and drying the precipitates were not known. Subsequently, with improved methods and an enlarged series of alcohols, these experiments have been repeated.

It can now be said, to considerable detail regarding positions and relative intensities of the diffractions, that starch solids obtained with linear alcohols (normal propyl, butyl and amyl alcohols) are identical. The solids yielded by branched-chain alcohols (iso-, secondary, and tertiary butyl and tertiary amyl alcohols) are distinctly different from the former materials, but among themselves cannot be distinguished. The dried precipitates of the second class have diffractions extending to lower angles (larger spacings) than the first group.

In addition may be mentioned a few exploratory experiments designed to indicate the variety of organic substances which can form complexes with amylose. The complex precipitates were recognized microscopically in these instances by the presence of the iodine-staining, two- to six-lobed roset spherocrystals described by Schoch,⁴ though in some cases large tufted spherocrystals of less regular shape were formed. The following list of complex-forming agents as thus determined is not exhaustive, but added to the previously mentioned substances it indicates that the ability to associate with amylose to form crystalline precipitates is a fairly common property of organic molecules: secondary amyl, normal hexyl, benzyl

and diacetone alcohols; 4-methyl-2-pentanol; methyl ethyl and methyl *n*-propyl ketones; *n*-valeric, *n*-butyric and α -bromopropionic acids; benzaldehyde, aniline, and phenol; *o*-, *m*- and *p*-cresol.

Experimental.—Preliminary X-ray examination indicated that the results of butanol precipitation of corn and potato starch dispersions were the same, for diffraction purposes, as those obtained from the more convenient soluble (Baker's Lintner) starch, hence the latter was employed as follows: to hot (70°) 4% solutions of soluble starch excess higher alcohol was added and the precipitated complex allowed to settle on cooling. The collected precipitate was washed with the same hot alcohol present in the complex, and then dried in air and finally in an oven at 60°. Powder diffraction patterns were obtained with filtered Cu K α radiation at a 5 cm. specimen-to-film distance. Normal alcohols yielded substances whose patterns were essentially identical with that of the dry *n*-butanol precipitate of Rundle and Edwards.³ The dry branched-chain alcohol precipitates all possessed the following pattern: 0.0015 m, 0.0036 s, 0.0059 ms, 0.0073 ms, 0.0092 w, 0.0123 m, 0.0176 w, 0.0211 m, 0.0245 s, 0.0276 mw, 0.0300 mw, 0.0390 w, 0.0471 w, where to facilitate comparison with the data of Rundle and Edwards $\sin^2\theta$ values are given, intensity relations being denoted by s = strong, m = medium, w = weak.

The crystalline precipitates for microscopic examination were obtained using amylose solutions prepared by leaching 2% suspensions of cornstarch at 80°, followed by centrifugation to remove the undispersed granules. Excess of the precipitating agent was added, with agitation, at 70° and the hot solution or mixture transferred to a Dewar flask. After slowly cooling to room or refrigerator temperatures the solids were examined microscopically, immersed in the supernatant liquor.

Discussion.—The facts presented herein must be considered in any general theory of complex formation between starch and simpler substances. The wide variety of small molecules listed above as being capable of association with starch have but one readily apparent similarity: possession of a permanent electric moment or of a tendency to assume an induced moment (iodine). Rundle, Foster and Baldwin³ have described how the interaction of the electric moments of the amylose chain and the iodine molecules can result in formation of an amylose helix, within which the smaller molecules are absorbed.

A helix loop made of six consecutive glucose residues, as postulated by Rundle, *et al.*,³ is able to encompass iodine or normal alcohol molecules provided these absorbed molecules are aligned with their long axes paralleling the helix axis, in which case the amylose is required to wrap itself about only their thinner dimensions. Consideration of available space shows that this structure is not possible for the branched-chain alcohol complexes *unless* one supposes that the amylose coil can be enlarged in internal diameter by increasing the number of residues per turn. With Rundle's conception and this added assumption of variable helix size it becomes clear why the

(1) R. S. Bear, *THIS JOURNAL*, **64**, 1388 (1942).(2) K. Freudenberg, E. Schaaf, G. Dumpert and T. Ploetz, *Naturwissenschaften*, **27**, 850 (1939).(3) R. E. Rundle and R. R. Baldwin, *THIS JOURNAL*, **65**, 554 (1943); Rundle and D. French, *ibid.*, **65**, 558, 1707 (1943); Rundle and F. C. Edwards, *ibid.*, **65**, 2200 (1943); Rundle, J. F. Foster and Baldwin, *ibid.*, **66**, 2116 (1944).(4) T. J. Schoch, *THIS JOURNAL*, **64**, 2957 (1942).

alcohol complexes investigated with X-rays in this study have structures depending more on the number of hydrocarbon chain branches of the alcohols than on the branch lengths. Apparently the starch helix enlarges to accommodate the more bushy branched-chain alcohols. Correspondingly the unit cell becomes larger, as is evidenced by the general displacement of the diffractions to lower diffraction angles. Unfortunately, the pattern of the branched-chain alcohol precipitates becomes definitely non-hexagonal, which makes it impossible to determine the changes in helix dimensions quantitatively from powder patterns alone. It can be shown, however, that with the spacings observed (up to 20 Å.) it is possible to construct helix models which are able to include the branched-chain alcohols.

That helix cross section and packing does not change greatly on removing the alcohol was shown by Rundle and Edwards³ for the *n*-butanol complex. Similar effects can be inferred for the present cases, in which the linear or branched alcohols leave their imprints behind after being driven off by heat. The simplest hypothesis to account for these facts is one postulating an internal absorption of the alcohol molecules, since otherwise the structures might be expected to collapse to the same condition in every case on removing the alcohol and/or to show some relation to the hydrocarbon chain lengths.

That the seven alcohols considered in these experiments yield only two different dry solids from starch is preliminary evidence that the amylose chain can coil only in a limited number of ways. The realizable configurations, possibly possessing various numbers of residues per turn, plus other variations, can be discovered by X-ray examination of the many complexes formed by association of organic substances with amyloses.

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Vapor Phase Hydrogenation of Naphthalene and Tetralin over Nickel Catalyst

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Sabatier and Senderens¹ reported in 1901 that tetralin was the only product when naphthalene was hydrogenated in vapor phase over nickel. Lush² confirmed this work in 1927, reporting that neither naphthalene nor tetralin could be hydrogenated to decalin in vapor phase, and presenting an explanation why vapor phase hydrogenation gave only tetralin whereas liquid phase hydro-

genation gave decalin. However, in 1904, Leroux³ reported that he repeated the experiments of Sabatier and Senderens and found that tetralin was easily hydrogenated to decalin. In 1938, Smith, Rall, and Grandone⁴ also concluded that decalin could be produced in vapor phase from naphthalene.

Because of these contradictions and because we considered this alleged selectivity unlikely, we studied the vapor phase hydrogenation of naphthalene and tetralin over nickel and found that decalin was readily obtained.

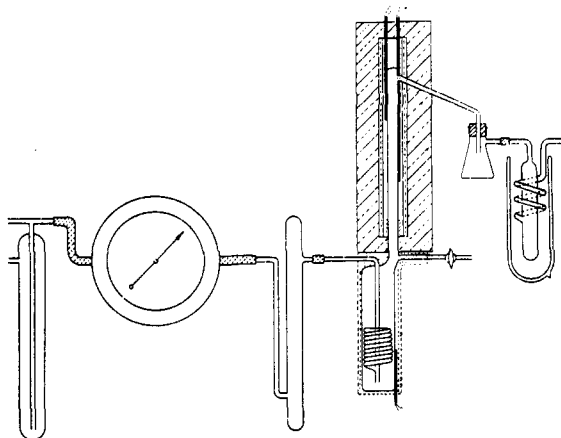


Fig. 1.—Apparatus for vapor phase hydrogenation.

The apparatus (Fig. 1) was constructed of glass and consisted of a vaporizer⁵ sealed to a vertical (14 mm. i. d.) catalyst tube. A known volume of dry hydrogen was passed through the heated vaporizer ($\approx 110^\circ$ for naphthalene, $\approx 114^\circ$ for tetralin) whence the gas mixture passed upward through a 6-inch section of catalyst tube packed with 3 inches of glass wool followed by 3 inches of glass pearls, and finally through a 2.5-inch catalyst bed and out the exit arm. The entire length of the catalyst tube was at a uniform temperature which was always higher than the temperature of the entering gas. The low partial pressure of the hydrocarbon in the gas mixture and the operation of the catalytic unit guaranteed true vapor phase conditions during hydrogenation. The catalyst was in the form of $1/8" \times 1/8"$ pills containing about 65% of nickel and 35% of diatomaceous earth;⁶ the catalyst was reduced by hydrogen at 425° before use. After the naphthalene runs had been made, the apparatus was dismantled and cleaned, and a new catalyst bed was charged for the tetralin runs. Hydrogenation was run for two hours at each set of conditions to attain steady state before collecting product.

The naphthalene feed (Koppers Company, Chemical Grade) was desulfurized by sodium;⁷ the desulfurized product froze at 80.2° (cooling curve) and contained 0.001% of sulfur. The tetralin feed was twice distilled at 50 mm. through a 3-foot Fenske column with 15/1 reflux at the start and 7/1 on the plateau, the middle 75% of the plateau being taken; f. p. -35.9° (cooling curve), b. p. 207.2° (760 mm.), n_{20}^D 1.5412, d_{20}^{20} 0.971, sulfur 0.001%. According to Rossini and Mair⁸ the constants

(3) Leroux, *Compt. rend.*, **139**, 872 (1904).

(4) Smith, Rall and Grandone, U. S. Bureau of Mines, Tech. Paper No. 587 (1938).

(5) Corson, *Ind. Eng. Chem., Anal. Ed.*, **10**, 646 (1938).

(6) Ipatieff and Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

(7) Schroeter, U. S. Patent 1,763,410 (1930).

(8) Rossini and Mair, *Refiner Natural Gasoline Mfr.*, **20**, 494 (1941).

(1) Sabatier and Senderens, *Compt. rend.*, **132**, 1254 (1901).

(2) Lush, *J. Soc. Chem. Ind.*, **46**, 454T (1927); British Patent, 304,403, Jan. 24, 1929.