Hydrolysis of Carbohydrates in the Presence of Hydrochloric Acid or Acidic Ion-exchange Resins

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There have been several reports concerning the effect of the size of ion-exchange resin catalyst on the rate of organic reactions; e. g., esterification of oleic acid[1], hydrolyses of sucrose[2] and lower esters[3], and iodine-acetone reaction[4]. None of these investigators, however, has given any general quantitative conclusion theoretically supported. The present study is concerned with the development of this subject. First, the result of the hydrolysis of potato amylose and sucrose is shown in this paper. The amylose was chosen because of its high molecular weight and sucrose because of its low molecular weight.

Experimental

Preparation of Amylose.—A modified procedure[5] of K. H. Meyer's method was employed. That is, the amylose in potato starch was extracted into hot water (70°C), precipitated with *n*-butanol, dissolved once more into hot water (60°C), reprecipitated with ethanol and then dried at 70°C to a constant weight. The yield from 250 g. starch was 15 g.

Molecular Weight and Purity of Amylose.—The number average degree of polymerization of the amylose was measured by K. H. Meyer's method[6] (3, 5-dinitrosalicylic acid method) and found to be 175±10. Hence the number average molecular weight was $(3.2\pm0.2)\times10^4$. The absorption maximum of the amylose-iodine complex, prepared according to R. M. Mc Cready's method[7], was 625 mμ, which agreed well with R. E. Rundle's[8] result (626 mμ, for potato amylose). Hence the purity of the amylose was high enough to carry out this work.

Sucrose.—Twenty % aqueous solution of commercial crystalline sugar, demineralized by means of ion-exchanger, was used.

Ion-Exchange Resins. — Strongly acidic ion-exchange resin Amberlite IR-120, conditioned and washed, was fractionated into ten portions according to the grain size. The six larger fractions were prepared by a combined process of sieving and sedimentation of the original spherical resins. The four smaller fractions were

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[1] C. L. Levesque and A. M. Craig, *Ind. Eng. Chem.*. **40**, 96 (1948).

[2] G. Bodamer and R. Kunin, ibid., **43**, 1082 (1951).

[3] L. P. Hammett, et al., *J. Am. Chem. Soc.*, **71**, 1284 (1949), ibid., **75**, 1788, 5834 (1953).

[4] S. L. Bafna, *J. Phys. Chem.*, **59**, 1199 (1955).

[5] E. Husemann und R. Resz, *J. Polymer Sci.*, **19**, 397 (1956).

[6] K. H. Meyer, *J. Phys. Colloid Chem.*, **53**, 319 (1949); J. Nikuni, *Starch Chemistry* (*in Japanese*), Asakura-shoten Ltd., Tokyo, Japan (1951), p. 359.

[7] R. M. McCready and W. Z. Hassid, *J. Am. Chem. Soc.*, **65**, 1154 (1943).

[8] R. E. Rundle, ibid., **66**, 111 (1944).

prepared by sedimentation of pulverized resins. The average radius (R) of each fraction was determined microscopically according to the formula (1),

$$R=\bar{d}/2=\sum nd^3/2\sum nd^2 \qquad (1)$$

where d is the horizontal diameter of each particle, n is the number of particles, and $\bar{d}$ is the average diameter. The values of R were found to be 482, 418, 332, 300, 219, 191, 56.9, 37.2, 26.8 and 17.5 μ respectively.

Hydrolysis of Amylose (hydrochloric acid catalyst).—Two % amylose solution in N-sodium hydroxide was acidified with hydrochloric acid and stirred in a sealed vessel at 65±0.1°C. After every five minutes, a portion of the reaction mixture was taken out and neutralized with alkali to stop the reaction. This neutral solution was used for both preparation of the starch-iodine complex and determination of the number average degree of polymerization (P_n). The starch-iodine complex was prepared by the Mc Cready's method[7]. P_n was determined according to the Meyer's method[6], using glucose as a standard.

Hydrolysis of Amylose (pulverized resin catalyst) — Two % amylose solution in N-sodium hydroxide was demineralized with ion-exchange resins, added to a known volume of resin suspension containing a known weight of pulverized resin, and then stirred at 65±0.1°C. After a given period, the reaction mixture was quickly filtered to remove the resin. The filtrate was used for both preparation of starch-iodine complex and determination of P_n.

Hydrolysis of Sucrose.—The demineralized 20% sucrose solution was mixed with catalyst (conc. hydrochloric acid, pulverized resin suspension, or swollen spherical resin filtered to remove the extra water) and stirred in a sealed vessel at 50±0.1°C. The stirring velocity was kept within a range of 500—550 r. p. m. and did not affect the reaction rate. After a given period, a portion of the reaction mixture was taken out to measure the optical rotation (α) by a saccharimeter. The α value at complete hydrolysis was also measured (α_∞). When $\ln(\alpha-\alpha_\infty)$ were plotted against t (reaction time), straight lines were obtained, the slopes indicating the rate constants k according to the formula (2).

$$kt=\ln(\alpha-\alpha_\infty)+const. \qquad (2)$$

Results and Discussions

Hydrolysis of Amylose

i. N-Hydrochloric acid catalyst—Amylose was easily hydrolysed at 65°C. Both P_n of the hydrolyzate (Table I) and the absorption spectrum of the hydrolyzate-iodine complex (Fig. 1) changed with time. The relation between the wave length of the absorption maximum and P_n was nearly in harmony with that in the case of synthetic dextrins worked by Swanson[9] (Table II), showing that the mechanism of hydrolysis was just the inverse of synthesis. The mean rate constants through time 0~t (k in Table II) were computed, applying Ekenstam's[10] equation (3) of random degradation.

$$\ln[1-P_n(t)^{-1}]=\ln[1-P_n(0)^{-1}]-kt \qquad (3)$$

k increased as the reaction proceeded, resembling Freudenberg's[11] result of hydrolysis of soluble starch in 50% sulfuric acid.

TABLE I

HYDROLYSIS OF AMYLOSE (HCl CAT.)

Time (min.)	$-\log T$[a]	P_n	$k\times10^4$ (min.$^{-1}$)
0	0.010	175±10	—
5	0.062	95± 3	4.3±0.5
10	0.144	55± 1	5.5±0.3
15	0.170	49± 1	4.3±0.2
20	0.303	31.2±0.3	5.9±0.2
25	0.355	27.0±0.2	6.0±0.1
30	0.450	21.9±0.1	6.0±0.1
35	0.575	17.5±0.1	6.6±0.1

a) T is the transmission coeff. of sample soln. treated with 3, 5-dinitrosalicylic acid, at the wave length of 525 mμ. Sugar concentration was 1.67 % concerning the original amylose.

TABLE II

ABSORPTION MAXIMA OF STARCH-IODINE COMPLEXES

P_n	Wave length (mμ)	
	D[a]	A[a]
7.4	500	
12.9	520	
17.5±0.1		550
18.3	540	
20.2	560	
27.0±0.2		560
29.3	580	
34.7	580	
49±1		585
55.6	600	
95±3		600
97.4	600	
146.5	600	
175±10		625

a) D: Synthetic dextrins by Swanson[9].
A: Hydrolyzed amyloses by the author.

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[9] M. A. Swanson, *J. Biol. Chem.*, **172**, 825 (1948); J. Nikuni, *Starch Cecmistry*, Asakura-shoten Ltd., Tokyo, Japan (1951), p. 57.

[10] A. af Ekenstam, *Ber.*, **69**, 540, 553 (1936).

[11] K. Freudenberg, et al., *Ber.*, **63**, 1519 (1930).

TABLE III

HYDROLYSIS OF AMYLOSE (RESIN CAT.)

Resin	Time (min.)	Ppt.[c]	$-\log T$
$R=17.5\mu$[a]	0	−	0.002
	30	−	0.004
	60	−	0.003
	94	−	0.005
	124	+	—
original[b], unfractionated	0	−	0.004
	10	−	0.004
	30	−	0.004
	40	+	—

a), b): Sugar concentrations of the sample solutions were 1.33% and 2.00%, respectively.

c) Ppt. of retrograded amylose.

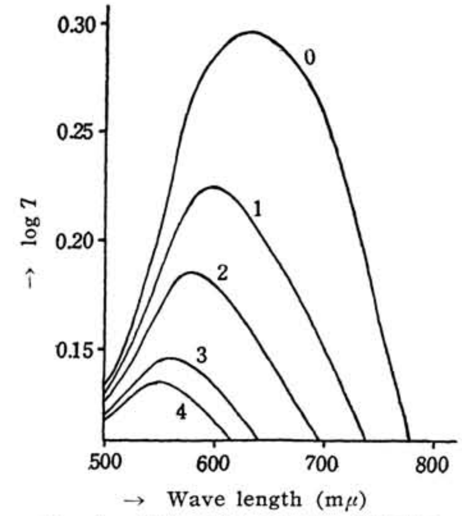

Fig. 1. Absorption spectra of iodine-hydrolyzed amylose complexes.

No.	0	1	2	3	4
Reaction time (min.)	0	5	15	25	35

ii. resin catalyst. — The resin of the smallest size ($R=17.5\,\mu$) was used at a concentration of nearly 0.02 equivalent per liter and caused no significant change in either the transmission coefficient of solution for measurement of P_n (Table III) or the absorption maximum of tho iodine complex. There seemed to be, therefore, no significant hydrolysis even at the end of 94 min. at 65°C. Several other experiments, using resins of a larger size at concentrations up to one equivalent per liter, also showed no proof of hydrolysis. One of these data is also shown in Table III.

iii. Comparison of hydrochloric acid and resin catalyst.—These experimental results show that the efficiency of resin catalyst is negligibly small as compared with hydrochloric acid in the case of hydrolysis of amylose. It is more desirable to compare their efficiencies numerically. But unfortunately it is impossible in this study.

Hydrolysis of Sucrose. — Sucrose was easily hydrolyzed by means of resin catalysts at 50°C and the first order rate constants (k) were obtained. The second order rate constants (k') were computed according to the formula (4),

$$k'=k/\rho H=kV/A \qquad (4)$$

where ρ is the volume ratio of swollen resin and the outer solution, H the exchange capacity per unit volume of the resin, V the total volume of the solution, and A the total exchange capacity of the resin catalyst.

The relationships $k'\sim R$ and $k'\sim 1/R$ are shown in Fig. 2. If the rate were proportional to the surface area of the catalyst, $k'\sim 1/R$ curve would be a straight line passing through the original point. Though the curve in Fig. 2 does not agree with this, it is inclined to approach a linear figure near the original point ($R\rightarrow\infty$). On the other hand, if the rate were proportional to the volume of resin phase, $k'\sim 1/R$ curve would be a straight line parallel to the $1/R$ axis. The curve in Fig. 2 does not agree with this, either. But it seems probable that the curve approaches a linear horizontal line as R approaches zero.

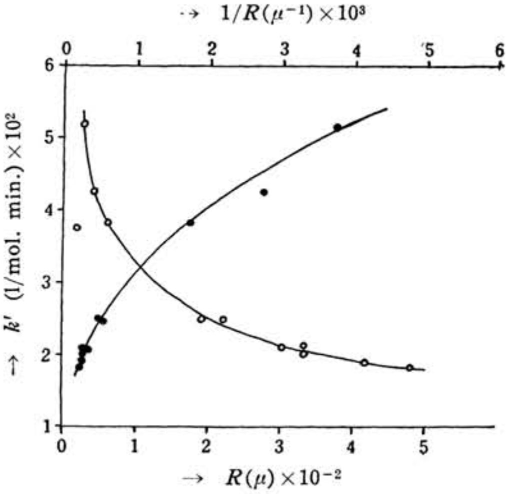

Fig. 2. $k'\sim R$, $k'\sim 1/R$ Curves.

At any rate, R and k' are related in a mediate way between the afore-mentioned two extremes. It is concluded that neither the surface only nor the whole resin phase uniformly acts as catalyst, but the real is a compromise. This is a proof that the overall rate is largely affected by the diffusion rate of sucrose in the resin. This knowledge will be valuable in studying the theoretical expression of the overall rate.

In the case of hydrochloric acid catalyst, k was directly proportional to the concentration of the acid. The proportionality constant (equals k', because $\rho=1$) was found to be 0.104 l/mol. min. at 50°C, which was greater than k' of any resin catalyst.

Summary

Potato amylose and sucrose were hydrolyzed in the presence of hydrochloric acid or acidic ion-exchange resin catalyst. In hydrolysis of amylose at 65°C, the efficiency of resin catalysts was negligibly small as compared with that of hydrochloric acid. In hydrolysis of sucrose at 50°C, the efficiency of resin catalysts was less than that of hydrochloric acid and different according to their sizes. The relation between the average radius and the rate constant was obtained in a broader range than ever.

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