ON THE HYDROLYSIS OF CANESUGAR IN PRESENCE OF ACID SOL

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The study of the influence of acid sols on the velocity of hydrolysis of canesugar has revealed that we are here dealing with a simultaneous reaction, (a) the inversion of canesugar in the homogeneous liquid phase by H^+ ions present in that phase, and (b) the inversion taking place on the surface of the acid sols. The velocity of this second reaction is proportional to the concentration of the acid sol.

This investigation has been undertaken to study the influence of acid sols on hydrolysis of canesugar.

Experimental

The course of inversion of sucrose whether by hydrochloric acid alone, or in presence of colloidal acids, has been followed by means of a polarimeter of Schmidt and Haensch type. The observation tube was surrounded water-tight by a metallic box, covered all over with asbestos board. Since the tungstic acid sol was found to be reduced when it came in contact with any metal, specially copper, zinc, tin, nickel, antimony, the observation tube was made of glass with circular plane parallel plates of glass, pressed water-tight against the polished ends of the tube by means of screw-caps. The length of the tube used is 1 dcm. The temperature of the box surrounding the observation tube was kept constant within $0.1°$ throughout the experiment by circulating water by means of a pump from an electrically heated thermostat. The source of light used is a sodium lamp supplied by Zeiss which is made spectroscopically homogeneous by passing it through a potassium dichromate filter.

All the chemicals used in the present investigation were of high grade of purity, either Merck's or Kahlbaum's reagents.

A mixture of x c.c. of sodium tungstate of definite strength (say 0.1 M) and x c.c. of HCl of definite strength (say 0.2N), kept for sometime to ensure the formation of sol, was mixed with $2x$ c.c. of sucrose solution of definite strength (say 20% solution). The p_n of this mixture was then determined by using a quinhydrone electrode; the hydrogen electrode could not be used, as it has been found that the tungstic acid sol is reduced by hydrogen gas. The solution of hydrochloric acid ($2x$ c.c.), which together with $2x$ c.c. of the same sugar solution will give exactly the same p_n as the above mixture (of HCl, sucrose and colloidal acid), was prepared by repeated trial.

The observation tube (rather the box surrounding it) was kept in place and the box was raised to the desired temperature by passing water from the thermostat, the circulation of water having been so satisfactorily regulated that the temperature remained constant within $0.1°$. The circulation was stopped for a minute and the observation tube was quickly filled with the reaction mixture. The temperature of the reaction mixture was raised to that of the bath before it was introduced into the observation tube. The water was circulated again and when the temperature became constant, polarimetric readings were taken at intervals. The final reading was taken after passing water at a still higher temperature for some hours to ensure complete reaction and then maintaining the system at the temperature at which the reaction had been studied until they became constant.

The unimolecular velocity constant was calculated according to the equation :

$$k = 2.3/t_n \cdot \log_{10}(A_0 - A) - \log_{10}(A_n - A) \qquad \dots \ (1)$$

where　　$A_0 =$ the initial angle of rotation,

$A_n =$ the angle of rotation at the time n,

$A =$ the final angle of rotation, and

$t_n =$ time which has elapsed since the reaction started.

The hydrolysis experiments had to be carried out at 60° and 70° as otherwise for the p_a of the system used (between 2 and 3), the velocity becomes too small to be measured within reasonable time intervals.

TABLE I

Influence of p_a on hydrolysis of 10% sucrose solution.

		(a) with HCl at 70°.			(b) with HCl+0.25M tungstic acid at 70°.		
p_a at 30	...	2.05	2.42	2.99	2.05	2.42	2.99
k_1 at 70°	...	0.0172	.00635	0.00164	0.02022	0.00837	0.00245

TABLE II

Influence NaCl on hydrolysis of 5% sucrose solution.

				Conc. of NaCl	
				0	0.43 M
p_a at 30°	...	...	...	2.42 M	2.42
k_1 at 70°	...	...	...	0.00632	0.00635

The salt effect due to the presence of sodium chloride when tungstic acid sol is formed by the addition of hydrochloric acid to the sodium tungstate has been found to be negligible for a salt concentration of 0.038M (the amount formed from 0.025M sodium tungstate, according to the equation $4Na_2WO_4 + 6HCl \rightleftharpoons 2Na_2O, 4WO_3 + 6NaCl + 3H_2O$) as will be seen from the table.

TABLE III

Influence of tungstic acid sol upon hydrolysis of 10% sucrose solution at 70°.

p_a at 30°.	k_1 with HCl (comp. as in Table Ia).	k_1 with tungstic acid (comp. as in Table Ib)	% Diff.
2.05	0.01720	0.02022	14.9
2.42	0.00635	0.00837	24.1
2.99	0.00164	0.00245	33.0

It is obvious from Table III that the presence of tungstic acid sol appreciably enhances the velocity of hydrolysis and the relative enhancement becomes greater, the greater the p_a of the system, other factors remaining the same.

The p_a of the reaction mixture remained constant throughout the experiments, 8 hours being the maximum time taken. The p_a also did not change on heat treatment of the solution to a temperature of 70° and cooling again to 30°.

TABLE IV

p_x at 30°.	Temp.	(a) With HCl		(b) . With HCl and 0.025M tungstate.	
		k_1.	$\frac{k_{(t°+10°)}}{k_t}$.	k_1.	$\frac{k_{(t°+10°)}}{k_t}$
(a) 2.05	60°	0.00634	2.73	0.00742	2.73
2.05	70	0.01720		0.02023	
(b) 2.42	60	0.00238	2.65	0.00304	2.75
2.42	70	0.00635		0.00837	

It will be seen that the temperature coefficient of the velocity constant of hydrolysis is the same in hydrochloric acid solution or in tungstic acid sol andhydorchloric acid mixture.

TABLE V

Influence of tungstic acid conc.

Temp.—30. $p_x = 2.42$.   Conc. of sucrose = 5%.

| Tungstate conc. (M)	...	...	0.25	0.05	0.075
k_1 at 30°	...	...	0.00800	0.00951	0.01081

TABLE VI

Influence of silicic acid on hydrolysis.

Temp. = 70°.   Conc. of Na silicate = 0.1M.   Conc. of HCl = 0.165M,
p_n at 30° = 2.05.

Conc. of sucrose.			k_1 with HCl (alone).	k_1 with HCl & silicic acid mixture.	%Diff.
10M	...	...	... 0.00489	0.00611	19.9
20	...	...	... 0.00519	0.00643	19.3

As the sol concentration increases, the velocity constant of hydrolysis increases. Fig. 1 shows that if the value of k_1 is obtained by extrapolation for zero concentration of tungstic acid sol, we get the value 0.00640 which is practically the velocity constant observed (0.00635) with pure hydrochloric acid at p_n 2.42.

Fig. 1

Conc. of tungstate (M).
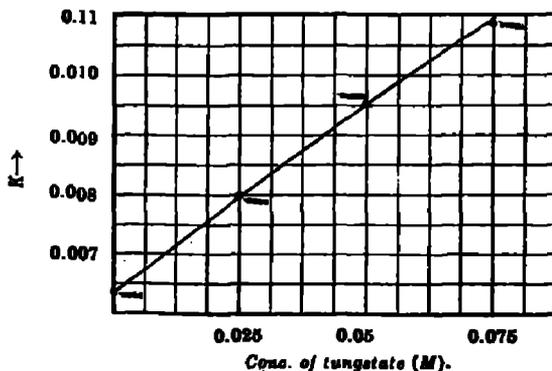
It is thus clear that we are dealing with two independent velocities, one due to hydrochloric acid in homogeneous solution of p_H 2.42 and the other due to the presence of tungstic acid sol particles in the medium. The surface area of the sol particle may be considered to be proportional to the concentration of the sol, if the particles are of uniform size and the increased velocity must be ascribed to the hydrolysis of canesugar on the surface of the sol. Thus we have,

$$dx/dt = dc_0/dt + dc_1/dt$$

where dx/dt is the observed change.

dc_0/dt is the change due to H^+ in the homogeneous solution and dc_1/dt is the change due to the reaction on the surface of tungstic acid sol.

Again

$$dc_1/dt = k_1 . Sp_H . C$$

or

$$-1/C . dc/dt = k_1 Sp_H$$

where S=surface of tungstic acid sol and C=conc. of sucrose.

The observed unimolecular velocity constant minus the velocity constant due to hydrolysis by HCl alone for the same p_H should therefore be proportional to the concentration of tungstic acid sol in the medium, which is actually found to be the case.

DISCUSSION

Weigner (*J. Soc. Chem. Ind.*, 1931, 50, 110r) has compared the concentrations of hydrogen ions in suspensions of acid clay, tungsten trioxide (aged), silica, etc. potentiometrically and inversometrically. With suspensions of tungsten oxide (aged) and silica, he reported the following data :—

	$\dfrac{C_H^+ \text{ inversometrically}}{C_H^+ \text{ potentiometrically}} \times 100.$
Uncoagulated suspensions	
Silica	115.5
Tungsten oxide (aged) coagulated suspension ..	114.8
Silica	1.47

He pointed out that the differences in the above ratio observed with uncoagulated suspension of tungsten oxide and silica were not great. Our experiments have shown that the difference observed by Weigner with suspensions of tungsten oxide and silica, though not great, was definite and have quantitatively corroborated the findings of Weigner.

It has also been shown that we are here dealing with a simultaneous chemical reaction, (a) the inversion of canesugar in the homogeneous liquid phase by the H^+ ions present in that phase, and (b) the inversion taking place on the surface of the sol particles due to the influence of the H^+ ions attached to that surface on the canesugar molecules which have diffused into that surface. The velocity of this second reaction is proportional to the concentration of tungstic acid sol.