A FURTHER INVESTIGATION OF THE VELOCITY OF SUGAR HYDROLYSIS.

BY R. H. CLARK.

The hydrolysis of cane sugar has been found by most investigators to be monomolecular with respect to sugar. If the amount of water is relatively large the velocity coefficient should be independent of the initial concentration of the sugar, according to the equation of mass action. Ostwald,[1] however, found that the velocity coefficient increased rapidly with the concentration of the sugar. For example, using a $0.5\ N$ hydrochloric acid solution as catalyzer he found the inversion coefficient to be 20.63 for a 10% sugar solution, 22.87 for 20% and 29.16 for a 40% solution.

E. Cohen[2] attributed the phenomenon to the fact that the volume of the reaction is reduced the greater the concentration of the sugar and hence the number of collisions between the molecules of sugar and the hydrogen ions is increased, causing an increase in the velocity of the reaction.

That this latter view was correct was experimentally demonstrated by Rosanoff, Clark and Sibley,[3] by preparing three pairs of solutions, in which the acid and water had exactly the same concentration in each pair, but the sugar in one solution of each pair was replaced, in part, by glucose. Preliminary experiments were carried out to find how much glucose must be added in place of part of the cane sugar in order to keep the volumes equal. For example, in one of the pairs containing (a) 50.500 g. of cane sugar, 195.73 g. of water and 28.750 g. of formic acid in 250 cc., and (b) 14.250 g. of cane sugar, 35.00 g. of glucose, 195.73 g. of water and 28.750 g. of formic acid in 250 cc., the velocity constants of the monomolecular mass-law equation were identical, although the initial concentrations of cane sugar were in the ratio of 3.54 to 1. More recently the present writer has confirmed this result using a strong acid, hydrochloric, as catalyzer. The velocity of cane sugar hydrolysis therefore is independent of the initial concentration of the sugar when the concentrations of both acid and water are constant. Consequently the following measurements were made, to find whether in a similar manner, adding an inert substance, glucose, to keep the concentration of the water and cane sugar constant while varying the concentration of the acid, would have an appreciable effect in yielding a numerical proportionality between the quantity of hydrogen ions present and the inversion velocity.

[1] Ostwald, *J. prakt. Chem.*, **31**, 316 (1885).

[2] E. Cohen, *Z. physik. Chem.*, **23**, 442 (1897).

[3] Rosanoff, Clark and Sibley, THIS JOURNAL, **33**, 1911 (1911).

It has long been known that there is only an approximate proportionality between the quantity of hydrogen ions and the inversion velocity of cane sugar. For example, in the case of hydrochloric acid, Ostwald found that a 0.5 N solution inverts 6.14 times more quickly than a 0.1 N solution and 64.66 times more quickly than a 0.01 N, although the 0.5 N solution contains only 4.65 times as many hydrogen ions as the 0.1 N and 44.73 times as many as the 0.01 N, as measured by the conductivity method.[4]

A theory to account for this variation was advanced by Arrhenius, namely, that the catalytic activity of hydrogen ions is greatly stimulated by the presence of other ions. More recently Bredig,[5] Acree,[6] Snethlage,[7] McBain and Coleman[8] and others, have advanced much evidence to show that the catalytic effect of the acid in this and other similar catalytic reactions is produced partly by the ions and partly by the undissociated acid.

In the experiments summarized below, the extent of hydrolysis was measured with a half-shade quartz-wedge compensation saccharimeter. The reaction mixtures were maintained at a temperature of $25° \pm 0.02°$. The rotations were observed at the same temperature as nearly as possible, the saccharimeter being enclosed in a wooden box for this purpose. Merck's glucose, after having been recrystallized three times from 95% alcohol, was used.

The measuring flasks were calibrated at $25°$ and the amount of glucose to be employed as space filler was obtained by preliminary experiments at this same temperature. All reaction mixtures containing glucose were allowed to stand until its rotation became constant before mixing. The cane sugar, glucose and exact weight of water needed for each experiment were put in a measuring flask and the acid in a glass-stoppered bottle; they were kept in the thermostat, and finally thoroughly and quickly mixed.

The inversion velocities of the following reaction mixtures were measured to find the effect of keeping the concentration of the water and sugar constant while varying the concentration of the respective acids employed as catalyzer. This was done by adding glucose to the weaker acid solutions to fill up the volume occupied by the acid removed.

In the tables, t denotes the time in hours, α the observed rotation, and k the velocity constant calculated from the monomolecular equation $k = \frac{1}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}$, α_0 and α_∞ denoting the initial and final rotations, respectively. The initial rotations ($t = 0$) were not observed but calculated by plotting on a large scale, the available values of $\log (\alpha - \alpha_\infty)$ and extrapolating to $t = 0$, to find $\log (\alpha_0 - \alpha_\infty)$ and hence α_0.

[4] From equivalent conductances, Whetham's "Theory of Solution." 1902, Cambridge University Press.

[5] Bredig, *Ann. Reports Chem. Soc.*, **1914**, p. 16.

[6] Acree, *Am. Chem. J.*, **49**, 353 (1913).

[7] Snethlage, *Z. physik. Chem.*, **85**, 255 (1913).

[8] McBain and Coleman, *J. Chem. Soc. Trans.*, [II] **105**, 1517 (1914).

REACTION MIXTURES.

In each case 57 g. of cane sugar was used.   The total volume was 250 cc.

Solution.	Water, g.	Acid, g.	N.	Glucose, g.
I	212.89	4.5562	HCl(0.5)	....
II	212.89	0.9112	(0.1)	2.40
III	212.89	0.0911	(0.01)	2.95
IV	211.35	7.875	HNO_3(0.5)	....
V	211.35	1.575	(0.1)	4.40
VI	211.35	0.1575	(0.01)	5.40
VII	211.99	10.125	HBr(0.5)	....
VIII	211.99	2.025	(0.1)	3.63
IX	211.99	0.2025	(0.01)	4.44
X	212.77	6.125	H_2SO_4(0.5)	....
XI	212.77	1.225	(0.1)	2.595
XII	212.77	0.1225	(0.01)	3.18

The results for the hydrochloric acid solutions only are tabulated in full, in Tables I–III; the inversion velocity constants for the other reaction mixtures are given in Table IV.

	TABLE I.			TABLE II.			TABLE III.	
t.	α.	k.	t.	α.	k.	t.	α.	k.
0.0	89.3°	......	0.0	(91.7°)	......	0.0	(91.8°)	......
0.25	79.3	0.1556	0.25	89.9	0.0276	0.25	91.6	0.0028
0.50	70.3	0.1544	0.7	86.7	0.0255	1.	91.1	0.0026
0.83	59.5	0.1537	1.5	81.9	0.0255	5.	88.8	0.0023
1.	54.2	0.1554	3.	73.0	0.0253	11.	85.0	0.0024
1.25	47.4	0.1545	5.	62.1	0.0255	29.	74.4	0.0024
1.5	41.2	0.1539	8.	48.2	0.0254	53.	61.8	0.0025
2.	29.4	0.1564	11.	36.3	0.0255	99.	41.9	0.0025
2.5	19.8	0.1572	14.	26.7	0.0253	∞	−24.0	......
3.	11.9	0.1575	∞	−24.9	......			Av. 0.0025
4.	−0.3	0.1585			Av. 0.0255			
5.	−8.4	0.1576						
6.5	−16.3	0.1571						
∞	−27.4	......						
	Av. 0.156							

TABLE IV.

Solution.	N, Acid.	Inversion coefficient.
IV	0.5 HN_2O_3	0.154
V	0.1	0.0252
VI	0.01	0.0024
VII	0.5 HBr	0.169
VIII	0.1	0.0260
IX	0.01	0.00245
X	0.5 H_2SO_4	0.0797
XI	0.1	0.0157
XII	0.01	0.0020

The results show, for example, that the 0.5 N hydrochloric acid solution

inverts the cane sugar with a velocity 6.11 times as great as the 0.1 N and 62.36 times as great as does the 0.01 N solution. The results with the other acids are similar; in no case, does the expedient of adding an inert substance, glucose, in order to keep the concentration of the water and cane sugar constant while varying the concentration of the acid, produce any appreciable effect in yielding a numerical proportionality between the quantity of hydrogen ions employed as catalyzer and the inversion velocities.

Fairly wide differences for the degree of dissociation of the various acids have been used by various investigators, in calculating the catalytic effect of the hydrogen ions and the undissociated part of the acid. For purposes of comparison with the results obtained by Marshall[9] from Ostwald's sugar inversion measurements, the degrees of dissociation of hydrochloric, nitric and hydrobromic acids employed by him, have been used in calculating from the above measurements, the values of K_m and K_i and the ratio K_m / K_i, which is the ratio between the catalytic effect of undissociated acid and that of an equal concentration of hydrogen ions. From the values of K_m and K_i obtained, K_m the molecular inversion velocity for the different concentrations has been calculated for comparison with that experimentally found.

HYDROCHLORIC ACID AND SUGAR.

$K_m = 0.632 \quad K_i = 0.236.$

Conc. of acid, N.	α.	K_m / K_i.	K_n found.	K_n calc.
0.5	0.809	2.67	0.312	0.312
0.1	0.953	....	0.255	0.255
0.01	1.000	....	0.250	0.236

NITRIC ACID AND SUGAR.

$K_m = 0.626 \quad K_i = 0.233.$

0.5	0.811	2.68	0.308	0.308
0.1	0.953	....	0.252	0.252
0.01	1.000	....	0.240	0.234

HYDROBROMIC ACID AND SUGAR.

$K_m = 0.768 \quad K_i = 0.234.$

0.5	0.805	3.28	0.338	0.338
0.1	0.951	....	0.260	0.260
0.01	1.000	....	0.245	0.235

SULFURIC ACID AND SUGAR.

$K_m = 0.179 \quad K_i = 0.144.$

0.5	0.550	1.244	0.1598	0.1594
0.1	0.620	....	0.1574	0.1570
0.01	0.850	....	0.1522	0.1600

The value of α for 0.5 N sulfuric acid was calculated from the equivalent conductances as given by Kohlrausch[4] for a temperature of 18° after

[9] Marshall, *Am. Chem. J.*, **49**, 353 (1913).

being corrected to $25°$ by Jones'[10] temperature coefficient. The values for the other two concentrations are the average given by Noyes.[11]

The agreement between the calculated and found values of K_n is of the same order as that calculated by Marshall from Ostwald's measurements. The values of K_i, for the hydrogen ion, from the first three acids are the same, $(K_i = 0.234)$ but for sulfuric acid has fallen to $K_i = 0.144$. Likewise the activity of the nonionized acid, which is from 2.6 to 3.3 times that of the hydrogen ions for the three acids, hydrochloric, nitric and hydrobromic, is in the case of sulfuric only 1.24 times as great.

The Effect of Neutral Salts.

Analogous experiments were carried out to find the comparative effect produced on the rate of inversion by a strong acid (Solution XIII), a strong acid together with a neutral salt containing a common ion (Solution XIV), and a strong acid together with an inert substance, glucose (Solution XV), the glucose occupying the same volume as the neutral salt in the preceding series. In this series also 57 g. of cane sugar was used, and the volume was 250 cc. In each solution the weight of nitric acid was 0.7875 g.

Solution.	Water.	KNO₃.	Glucose.
XIII	214.36	. . . .	. . . .
XIV	198.46	10.1100	. . . .
XV	198.46	. . . .	6.89

Solution XIII.			Solution XIV.			Solution XV.		
t.	α.	k.	t.	α.	k.	t.	α.	k.
0.0	(88.6°)		0.0	(88.2°)		0.0	(95.8°)	
0.25	87.0	0.0212?	0.75	85.4	0.0141	0.25	94.9	0.0136?
3.	78.7	0.0128	1.5	82.6	0.0144	0.75	93.3	0.0127
6.	70.4	0.0123	3.	77.3	0.0143	1.5	90.9	0.0125
11.	57.7	0.0122	8.	61.4	0.0142	3.	86.2	0.0125
19.	40.7	0.0124	16.	40.0	0.0141	6.	77.4	0.0126
29.	23.9	0.0122	25.	23.1	0.0143	10.	67.0	0.0125
37.	13.5	0.0122	33.	11.2	0.0143	13.	60.0	0.0124
47.	3.1	0.0123	43.	0.6	0.0142	23.	40.1	0.0124
55.	−3.2	0.0123	51.	−6.0	0.0142	30.0	28.5	0.0125
75.	−14.1	0.0124	∞	−27.7		46.	10.5	0.0126
∞	−27.8	. . . . . .				∞	−20.2	. . . . . .
	Av. 0.0123			Av. 0.0142			Av. 0.0125	

The effect produced on the inversion velocity by an amount of glucose occupying the same volume as the potassium nitrate is seen to be very slight. The increase in velocity produced by the neutral salt can to a very

[10] Jones, "Electrical Conductance," etc. *Carnegie Inst. Pub.*, **1912**, p. 170.

[11] Noyes, "The Electrical Conductance of Aqueous Solutions," A. A. Noyes, *ibid.*, **63**, 268 (1907).

little extent therefore be attributed to the fact that the volume of reaction mixture is reduced by the presence of the neutral salt. This in in agree-ment with the conclusions arrived at by McBain and Coleman,[12] who have shown in a number of cases that if the catalytic effect of the un-dissociated acid formed in the presence of neutral salts be taken into ac-count the velocities of inversion are within 4% of the predicted rates.

Summary.

The addition of an inert substance, to keep the concentration of water and cane sugar constant while varying the concentration of the acid, has no appreciable effect in producing a numerical proportionality between the quantity of hydrogen ions present and the inversion velocity of cane sugar.

The increase in velocity of cane sugar hydrolysis produced by a strong acid in the presence of a neutral salt of that acid, over the velocity pro-duced by that acid alone, can to very little extent be attributed to the fact that the volume of the reaction is reduced by the presence of the salt.

On the assumption that both the undissociated and dissociated forms of an acid are catalytically active in cane sugar inversion, the values of K_i for the hydrogen ion from hydrochloric, hydrobromic and nitric acids have the same value $(K_i=0.234)$; the corresponding value for sulfuric acid is considerably lower $(K_i=0.144)$.

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THE VISCOSITY OF GELATIN SOLS.

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Introduction.

A mathematical expression for the viscosity of two-phase systems was developed by A. Einstein[2] in 1906 and generalized by E. Hatschek[3] in 1910–1913. According to the latter investigator, the viscosity of all two-phase systems may fall in one of two possible conditions. So long as the particles of dispersed phase occupy so small a proportion of the total volume of the system that they do not touch each other, the increase of vis-cosity should be a linear function of the concentration only and indepen-dent of the size of the particles. In the derivation of his formula, the particles of dispersed phase are assumed to be spherical, undeformable, and

[12] McBain and Coleman, J. Chem. Soc., [II] 105, 1523 (1914).

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[2] A. Einstein, Ann. Physik., 19, 289 (1906).

[3] E. Hatschek, Kolloid, Z., 7, 301 (1910); 8, 34 (1911); Trans. Faraday Soc., 9, 80 (1913).