The table also gives the temperature coefficients for hydrochloric and sulfuric acids for this range using the values of Hantzsch and Weissberger for 25°.

TABLE V

Normality	HBr velocity constant *k*	HBr 25/20	HCl 25/20	H_2SO_4 25/20
1	0.00278	2.46	2.39	2.5
2	.00995	2.38	2.3	2.53
4	.06680	2.46	2.4	2.61
5	.1540			

The author wishes to express his thanks and appreciation to Professor T. M. Lowry for putting at his disposal the facilities of the Cambridge laboratory to carry out this research.

Summary

1. Velocity constants have been determined for sucrose hydrolysis in a 0.146 molal solution using hydrochloric acid from 1 to 9.96 molal, sulfuric acid from 0.525 to 6.52 molal and hydrobromic acid from 1 to 5 normal as catalysts.

2. The velocity constants are not directly proportional to either the concentration of the acid or the hydrogen-ion activity for hydrochloric or sulfuric acid.

3. The velocity constants can be calculated fairly accurately from the activities and therefore from e. m. f. measurements from a 3 molal to a 10 molal hydrochloric acid solution.

4. The hypothesis is put forward that sucrose hydrolysis with hydrochloric acid is catalyzed partly by the hydrogen ion and partly by the molecule or both ions. In a 1 molal solution, 99% is hydrolyzed by the hydrogen ion while in a 10 molal solution it hydrolyzes only 45%.

5. No simple relationship was observed between activities and velocity constants for sulfuric acid.

6. The ratios between the velocity constants for 20 and 25° have been calculated for hydrochloric, sulfuric and hydrobromic acids using the velocity constants obtained by Hantzsch and Weissberger for 25°.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

The Electromotive Force Measurements of Hydrochloric Acid Solutions with and without Sucrose and their Relation to the Rate of Sucrose Hydrolysis[1]

BY VERNON K. KRIEBLE AND FRED M. REINHART

In the previous paper evidence was submitted which seemed to indicate that the rate of hydrolysis of sucrose could be correlated with the electromotive force of the solution. The electromotive force measurements used, however, were those for pure hydrochloric acid solutions made at 25° instead of acid solutions containing sugar at 20°, at which temperature the hydrolysis was measured. It seemed worth while, therefore, to measure the electromotive force of such solutions to make certain that there was a real correlation between these two factors.

Experimental

Part I. Electromotive Force Measurements

Apparatus.—The null method was used for the electromotive force measurements, using a Leeds and Northrup Type K potentiometer, a type 2500-a galvanometer, an Eppley standard cell and a calomel and a bubbling hydrogen electrode. The apparatus was suspended in a thermostatic bath maintained at 20 ± 0.02°.

Experimental Procedure

Sucrose.—Bureau of Standards, Standard Sample 17 of sucrose was used for these measurements because it was found that the sucrose purified in this Laboratory and other grades were not of sufficient purity to give reproducible results as shown in the table; *T* is time in hours and *E* is volts.

TABLE I

Purified sucrose		Commercial sucrose		Crystal sucrose		Sample 17 sucrose	
T	*E*	*T*	*E*	*T*	*E*	*T*	*E*
2.00	0.22810	2.00	0.22855	2.00	0.22760	0.10	0.22675
2.50	.22183	3.00	.22904	3.00	.22842	0.50	.22843
3.00	.22822	4.00	.22942	4.00	.22865	1.00	.22833
3.50	.22825	5.00	.22940	5.00	.22884	1.25	.22829
4.00	.22837	6.00	.22955	6.00	.22902	1.50	.22824
5.00	.22862	7.00	.22966	7.00	.22917	1.75	.22821
6.00	.22925	8.00	.22974	8.00	.22927	2.00	.22822
6.50	.22956	9.00	.22980	9.00	.22931	2.50	.22825
9.50	.22984	10.00	.22984	10.00	.22942		
15.00	.22996	15.00	.22995	15.00	.22954		
24.25	.22986	25.50	.22994	25.50	.22956		

Mercury.—This was triply distilled and further purified by the electrolytic method.

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(1) From a master's thesis submitted by F. M. Reinhart in partial fulfilment of the requirements for a Master's degree at Trinity College, 1933.

Calomel.—This was prepared from the purified mercury, redistilled nitric acid, and constant boiling hydrochloric acid.

Hydrogen.—Commercial electrolytic hydrogen purified by passing it over a platinum coil heated to 550° was employed.

The acids and alkalies were of the best grades obtainable.

Calomel Electrode.—The calomel was washed with hydrochloric acid of the concentration to be measured, the bottle filled with that acid and the contents shaken from time to time for ten days before the cell was assembled. The stopcock was lubricated with a film of the acid in the cell as this gave sufficient contact for conduction.[2] The stopcock was kept closed at all times after the cell was assembled. It was found that if the electrodes were carefully made they checked each other within 0.00002 volt. A series of experiments was conducted using an acid solution of sucrose in the calomel electrode and identical results were obtained as with pure hydrochloric acid of the same concentration. Therefore only pure acid was used in the calomel electrodes throughout this investigation.

Hydrogen Electrode.—The hydrogen electrode was prepared according to the method of Harned.[3] The hydrogen electrode and the bubbler tubes were filled with pure hydrochloric acid of the same concentration as that in the electrode. By using the bubbling tubes the pressure and the concentration of the acid in the cell were kept constant during the course of the experiment. The levels of the liquid in all parts of the cell were kept the same to maintain the pressure within the cell the same as the atmospheric pressure, as changes in the pressure affect the electromotive force of the cell.[4]

When the experiment was to be started the cell was put into the bath and hydrogen bubbled through it for half an hour before readings were recorded. The readings were recorded every fifteen minutes until they were constant for one hour; values were considered constant when they agreed within one-tenth of a millivolt. A cell usually reached equilibrium within two hours after being immersed in the bath. After equilibrium was reached enough sucrose was added to the cell to make the concentration of the sucrose 0.292 mole per liter of solution, equilibrium was again established and the values recorded. Above four molal acid it was impossible to measure the electromotive force of the sucrose solutions due to the fact that, above this concentration, the hydrochloric acid started to decompose the fructose molecule before equilibrium could be established. The measurements are given in Table II where m is the molality of the acid; P, the atmospheric pressure; E_m, the measured electromotive force; E_c, the electromotive force corrected to 760 mm. pressure.

Calculations.—The formula $0.1183 \log \gamma = E^0 - (E - 0.1183 \log m)$, developed by Lewis and Randall, was used to calculate the activity coefficients of the solutions, where γ is the activity coefficient, E^0 was taken as 0.2234 volt as determined by Linhart.[5]

TABLE II

HYDROCHLORIC ACID

m	P	E_m	E_c	E	γ
0.533	764.7	0.31587	0.31579	0.26919	0.770
1.068	758.6	.27593	.27593	.22935	.837
2.188	769.4	.22597	.22581	.17921	1.08
4.110	768.4	.16413	.16398	.11738	1.92
HYDROCHLORIC ACID + 0.292 MOLE OF SUCROSE					
0.533	764.7	0.31372	0.31364	0.26704	0.803
1.068	758.6	.27196	.27188	.22528	.903
2.188	769.4	.22190	.22174	.17514	1.17
4.110	768.4	.16020	.16005	.11345	2.07

Fales and Morrell[6] show that for very dilute hydrochloric acid solutions the electromotive force is the same whether sucrose is present or not, so E^0 was taken as 0.2234 volt for the sucrose solutions as well; E is the measured electromotive force, and m is the molality of the acid. The activity coefficients, γ, are given in Table II, column 6.

Discussion

In order to compare these results with those of Lewis and Randall,[7] it was necessary to change the electromotive force values from the calomel electrode standard to the silver–silver chloride electrode standard. Lewis and Randall found that these two electrodes differed from each other at all concentrations by 0.04660 volt. These values, E, column 5, Table II, were used to calculate the activity coefficients of the solutions. When the logarithms of these activity coefficients were plotted against the molalities of the acid the curves were found to be parallel to the Lewis and Randall curve for values measured at 25°. The electromotive force measurements of this work and those of Lewis and Randall were plotted against the molalities of the acid on a large scale and were found to differ by a constant amount, 0.0004 volt. When this electromotive force was subtracted from the Lewis and Randall electromotive force measurements, the activities calculated and plotted as before, the Lewis and Randall and the experimental curves were identical, and parallel to the experimental curve for acid plus sucrose. Since our experimental curve for the activity of acid plus sucrose paralleled the Lewis and Randall curve for the activities up to 4 molal acid, it was assumed permissible to extend the experimental curve for acid plus sucrose to ten molal acid and to use the Lewis and Randall curve for pure acid, in order to get the activities of these solutions for

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[2] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

[3] Harned, *ibid.*, **48**, 326 (1926).

[4] Ellis, *ibid.*, **38**, 737 (1916).

[5] Linhart, *ibid.*, **39**, 2601 (1917); **41**, 1175 (1919).

[6] H. A. Fales and J. C. Morrell, *ibid.*, **44**, 2081 (1922).

[7] Lewis and Randall, "Thermodynamics," p. 336.

the second part of this work. From these curves the activities of the hydrogen ion and the undissociated acid molecule were obtained and are given in Table III, where $a_{\pm}$ is the activity of the hydrogen ion and a_2 the activity of the undissociated acid molecule.

TABLE III

HCl + 0.292 mole sucrose				HCl		
m	γ	$a_{\pm}$	a_2	γ	$a_{\pm}$	a_2
0.929	0.873	0.811	0.657	0.815	0.751	0.576
1.908	1.09	2.08	4.34	1.01	1.93	3.72
2.904	1.43	4.15	17.2	1.32	3.84	14.73
3.666	1.79	6.57	43.1	1.67	6.11	37.4
4.025	2.01	8.08	65.3	1.86	7.50	56.2
5.349	3.03	16.2	262.0	2.82	15.1	227.0
6.095	3.82	23.3	543.0	3.53	21.5	463.0
7.730	6.34	49.0	2400.0	5.98	45.2	2038.0
8.468	7.81	66.1	4371.0	7.24	61.3	3755.0
9.846	10.97	108.0	11655.0	10.3	101.0	10316.0

Fales and Morrell[8] have shown that when sucrose is added to a hydrochloric acid solution electromotive force measurements indicate that the activity of the hydrogen ion is not decreased but increased. Their experiments show that a 0.2988 molar sucrose solution in a one normal hydrochloric acid solution has a hydrogen ion activity 37.6% greater than a hydrochloric acid solution of the same concentration. The above experiments also show that the presence of sucrose increases the hydrogen-ion activity of the solution but at 0.929 molal acid 0.292 mole of sucrose causes an increase in the hydrogen-ion activity of only 7.9%. This difference of nearly 30% between our experimental results and those of Fales and Morrell is attributed to some impurity in the sucrose used by Fales and Morrell in their electromotive force measurements. As they have stated, they purified their own sugar, while the sucrose of this investigation was a carefully purified sample of the Bureau of Standards. Sucrose purified in this Laboratory by a method which was essentially the same as that of Fales and Morrell gave much greater differences in the activity of the hydrogen ion between the pure acid and the acid sucrose solutions of equivalent concentration but reproducible results could not be obtained. Therefore, it seems more probable that Fales and Morrell failed to extract some impurity which caused their activities to differ by such large percentages. The results of this investigation, however, show that the activities of the hydrogen ion in a sucrose hydrochloric acid solution parallel those of pure hydrochloric acid from one to four molal while the results of Fales and Morrell show a divergence in hydrogen ion activities to one molar solution.

Part II. Velocity Constant Measurements

Since various samples of sugar gave markedly different electromotive force measurements it was necessary to measure the rates of hydrolysis of these samples if a correlation between the two is to be established.

The method of carrying out these experiments was the same as that described in the previous paper except that a C. P. Goerz half-shadow instrument was used instead of a Schmidt-Haensch polarimeter. It has already been pointed out that only sucrose of the highest purity can be used for electromotive force measurements. These infinitesimally small amounts of impurities, however, have no effect whatever on the rates of hydrolysis. The average velocity constant for the Bureau of Standards sample, (α) +78.342, with 2.9041 molal hydrochloric acid was 0.01467, while our purified sample, (α) +78.42, gave 0.01467 and the Eimer and Amend sample, (α) +78.366, gave 0.01477. Table IV gives the velocity constants for acid concentrations from 0.9285 to 9.8460, column 2.

Discussion

The velocity constants fall within experimental error on the same curve as those given in the previous paper. If the velocity constants are compared with the activities of the hydrogen ion as determined in part one it is found that the velocities increase faster than the activities. This suggests, as was pointed out in the previous paper, that there must be two reactions; one catalyzed by the hydrogen ion and the other by both the hydrogen ion and chloride ion or by the hydrochloric acid molecule. By again applying the equation $K = k_1a_{\pm} + k_2a_2$ and solving it for k_1 and k_2 from the experimental results one finds a value of 0.00367 for k_1 and 0.000025 for k_2, using the activities of the hydrogen ion in the acid plus sucrose solution. If the activities of the pure acid are used then k_1 becomes 0.004 and k_2, 0.000028. Using the first set of values for k_1 and k_2 which are based on the activities of acid plus sucrose the calculated velocity constants given in column 3, Table IV, are obtained. When the values for k_1 and k_2 which are based on the activities of pure acid are used the velocity constants become those given in column 4, Table IV. It is, evident, therefore, that the calculated velocity

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(8) Fales and Morrell, THIS JOURNAL, **44**. 2071 (1922).

constants based on the electromotive force measurements of pure acid are just as accurate as those based on the electromotive force measurements of acid plus sucrose solutions. The calculated velocity constants agree very well with those determined by experiment above 3 molal acid, for more dilute concentrations they are too high. This same discrepancy was noted in the previous paper, but it was hoped that when the activities of the sugar solutions were used for the theoretical calculations the discrepancy would disappear.

TABLE IV

m	K obs.	K calcd.	K calcd.
0.929	0.00215	0.00298	0.00302
1.908	.0066	.00775	.00784
2.904	.0147	.0156	.0160
3.666	.0251	.0252	.0255
4.025	.0316	.0312	.0316
5.349	.0667	.0660	.0667
6.095	.1030	.0991	.0992
7.730	.2260	.2400	.2380
8.468	.3540	.3530	.3510
9.846	.6880	.6880	.6930

Summary

1. The electromotive force measurements of hydrochloric acid and hydrochloric acid plus sucrose for 1 to 4 molal concentration have been measured at 20° and the activities calculated.

2. The velocity constants for (0.292 molal) sucrose hydrolysis with hydrochloric acid, varying in concentration from 1 to 9 molal, were determined.

3. A definite relationship between activities and velocity constants was noted using the electromotive force measurements of either the pure hydrochloric acid solutions or the hydrochloric acid containing sucrose, for calculating the activities.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Thermal Decomposition of Propylamine

BY DARRELL V. SICKMAN AND O. K. RICE

In the course of a study of a number of unimolecular reactions whose rate constants begin to decrease at pressures higher than would be expected from the size of the molecule involved, the decomposition of *n*-propylamine was carried to fairly low pressures in an attempt to discover whether the effect predicted by one of us[1] actually occurred. This reaction has been studied at moderate pressures by H. A. Taylor and Achilles,[2] who reported that it was homogeneous and apparently unimolecular, the rate falling off at pressures below 200 mm. Their results indicated extensive secondary reactions such as are met with in nearly all organic reactions that proceed at high temperatures. The effect of the inert gases hydrogen, helium and nitrogen was to decrease the rate markedly.

Experimental Method

The apparatus used was practically that described previously.[3] As stopcock grease is rapidly liquefied by propylamine vapor, mercury traps were used instead of stopcocks. The reaction vessel was a liter Pyrex flask placed in a fused salt thermostat whose temperature was regulated to ±0.2°. The reaction was followed manometrically, the lower pressures being read on a small multiple range McLeod gage. The results do not seem to warrant the small correction of 4–7% to the measured rates to correct for the external volume, but a correction for the material appearing slowly, apparently from the glass,[4] has been made for the runs at the lower pressures.

The propylamine used was purchased from the Eastman Kodak Co., and was purified by drying with fused potassium hydroxide and fractionating.

Results and Discussion

In view of the complexities of the reaction the rate constants calculated during the course of a run, which fall rapidly except in a narrow pressure range, are not useful. The rate constant reported has been calculated by graphical determination of the initial slope of the time–pressure curve of each run. The rate constant is then the ratio of this initial slope to the extrapolated initial pressure.[5] In order to minimize the rather large error possible in the determination of the initial slope, two separate calculations were made, and

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(1) O. K. Rice, *Z. physik. Chem.*, **7B**, 226 (1930).

(2) Taylor and Achilles, *J. Phys. Chem.*, **35**, 2658 (1931).

(3) O. K. Rice and D. V. Sickman, THIS JOURNAL, **56**, 1444 (1934), Apparatus I.

(4) Reference 3, page 1447.

(5) The exact expression for the rate constant is, of course, $dp/dt/(n - 1)p$, where n is the number of molecules of product. The adopted expression assumes $n = 2$.