

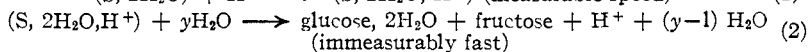
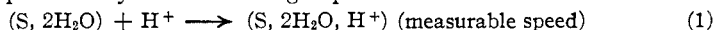
[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF LIVERPOOL]

THE ENERGETICS OF SUCROSE INVERSION

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In a recent paper,¹ Moran and Lewis, from an analysis of the kinetics of the process, have suggested a probable mechanism of the inversion of sucrose by hydrogen ion. It was concluded that the actual reactants are sucrose dihydrate and hydrogen ion, the sucrose dihydrate possessing the 2 molecules of water attached to the glucose portion, while the fructose portion is anhydrous. The sucrose dihydrate and hydrogen ion combine at measurable speed to give a complex which immediately reacts with water to produce invert sugar. Stoichiometrically, the inversion process may be expressed by the following equations.



where S stands for an unhydrated sucrose molecule. Reaction 1, being the slow one, was alone considered and it was shown that the velocity constant k_{bi} characteristic of this reaction is given by the equation

$$k_{bi} = \frac{k_a + a_{H_2O}^2 \times \eta^\alpha \times K}{a_{H^+}}$$

where k_a is the unimolecular velocity constant of inversion of sucrose (in terms of activity); a_{H_2O} is the activity of the water; a_{H^+} is the activity of the hydrogen ion; η is the viscosity of the solution; α is a constant at a given temperature; and K is the equilibrium constant between sucrose dihydrate and sucrose tetrahydrate. Furthermore, knowing the value of k_{bi} at two temperatures (25° and 35°) the sum of the critical increments of sucrose dihydrate and unhydrated hydrogen ion was calculated and found to be 40,000- Q calories, where Q is the heat of hydration of sucrose dihydrate. Assigning to Q a probable value of about 5,000 calories we thus conclude that the sum of the critical increments of the two reactants is 35,000 calories approximately.

If the mechanism outlined above is correct, it is essential that it should be substantiated by a detailed examination of the energy changes involved. The present paper deals with this point and bears out the validity of the mechanism already suggested.

The Energy Changes in the Inversion of Sucrose

In the calculation of the quantity 40,000- Q calories, the only doubtful factor involved is the effect of temperature on the potential difference (E_0) of the normal hydrogen electrode. In the work already referred to, this was assumed to be directly proportional to the absolute temperature,

¹ Moran and Lewis, *J. Chem. Soc.*, 121, 1613 (1922).

thus making the quantity C (which is constant at constant temperature) in the expression, $(RT/F)\log c_{\text{H}}/C$, independent of the temperature.

Miss D. E. Merriman, (working in this laboratory) has determined by the ordinary potentiometer method the e.m.f. (E) at 25° and 35° of the cell: N calomel electrode | sat. KCl | $0.1 N$ acetic acid | H_2 , and finds E_{25° equal to 0.4515 volts and E_{35° equal to 0.4546 volts. Assuming that the potential difference of the normal calomel electrode is 0.5600 volt at 18° , and giving to it the temperature coefficient of 0.00068 volt per degree,² we obtain the values for the potential difference ($\pi_{\text{H}+}$) of the hydrogen electrode in the above cell: $\pi_{\text{H}+(25^\circ)} = 0.1133$ volts; $\pi_{\text{H}+(35^\circ)} = 0.1171$ volts. H. C. Jones³ gives the following values for the degree of ionization of acetic acid.

Dilution v in liters	Percentage ionization	
	$t=25^\circ$	$t=35^\circ$
2	0.58	0.57
8	1.20	1.20
32	2.41	2.41
128	4.74	4.72

From this table we should conclude that the degree of ionization (γ) of $0.1 N$ acetic acid is practically the same at 25° and 35° , and by graphical interpolation from the above values we find 1.34 for 100 γ , corresponding to a concentration of hydrogen ion equal to 0.00134. It might also be pointed out that from the data of Kendall,⁴ who worked only at 25° , the value of c_{H} in $0.1 N$ acetic acid is 0.00135. If now, since the solutions are dilute and the electrolyte is weak, we identify the value 0.00134 with the values given by the hydrogen electrode, that is, the activity at both temperatures we can calculate the value of the normal hydrogen electrode at 25° and 35° by making use of the equations, $0.1133 = E_{0(25^\circ)} + 0.059 \log 0.00134$; and $0.1171 = E_{0(35^\circ)} + 0.061 \log 0.00134$. The values so determined are $E_{0(25^\circ)} = 0.2828$ volt and $E_{0(35^\circ)} = 0.2924$ volt. It is found that the ratio (0.2924/0.2828) is identical with the ratio (308/298), thus indicating that E_0 is very nearly proportional to the absolute temperature. The accuracy of the quantity 35,000 calories for the sum of the critical increments of sucrose dihydrate and unhydrated hydrogen ion, in so far as it is affected by the value of E_0 , is therefore justified.

The Absorption of Sucrose in the Short Infra-red Region

It may be assumed that hydrogen ion itself, being the best catalyzing agent known, requires no sensible energy of activation. On this basis the quantity 35,000 calories would represent the critical increment, in respect of inversion, of sucrose dihydrate itself, and applying the theory

² Chroustchhoff and Sitnikoff, *Compt. rend.*, **108**, 2118 (1920).

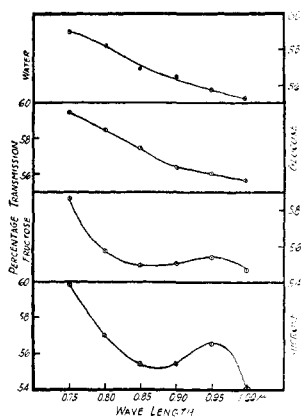
³ Jones, *Carnegie Inst. Pub.*, **170** (1912).

⁴ Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

of W. C. M. Lewis⁵ connecting the critical increment and the frequency, characteristic of the substance, which brings about the reaction, we should expect it to exhibit a marked band at the wave length 0.815μ . Accordingly, this conclusion was submitted to the test of experiment.

Experimental

The measurements consisted of a series of determinations of the optical absorptive capacities of aqueous solutions of glucose, fructose, sucrose and pure water in the very short infra-red region. The method of observation was identical with that used previously by one of us.⁶ Each solution was examined over a range 0.75μ to 1.00μ , and the transmission curves were plotted. The solutions used were 20%, the cells being 0.0731 and 0.0064 cm. in thickness, giving a net layer of 0.0667 cm. Since the solutions of glucose, fructose and sucrose were of the same strength and the layers examined were of the same thickness, comparison of the transmission curves of the solutions was direct. On the other hand, in order to compare these curves with that found for water, the thickness of the water layer



to be examined must be less than 0.0667 cm. (namely, that for the solution) since the effective thickness of the water itself in the solutions is less than 0.0667 cm. In 20% sucrose solution there are 46.11 out of 55.55 g.-moles per liter of free water, and hence the thickness of the water layer examined should be $(0.0667 \times 46.11) / 55.55$, or 0.0554 cm. The cells made up to measure the absorption of the water when actually measured were found to give a layer 0.0548 cm. thick. Under these conditions direct comparison could be made between the transmission curves found for water and the 3 solutions. The graph appended shows these results.

It will be observed that the sucrose solution exhibits a marked band at 0.875μ which does not appear in the water spectrum. Further, fructose solution shows a tendency towards a band in the same position, while in glucose solution there is a complete absence of any band in the region examined, the curve for glucose closely resembling that found for water alone.

The fact of a band in the fructose solution at the same position as that found in the sucrose solution, coupled with the fact that glucose exhibits no absorption in this region, appears to be in good agreement with the mechanism of the inversion of sucrose which regards the fructose portion of

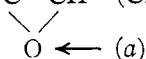
⁵ W. C. M. Lewis, *J. Chem. Soc.*, 113, 471 (1918).

⁶ Taylor and Lewis, *ibid.*, 121, 665 (1922).

the sucrose molecule as being the reactive part (compare succeeding section).

Discussion of the Mechanism of Inversion

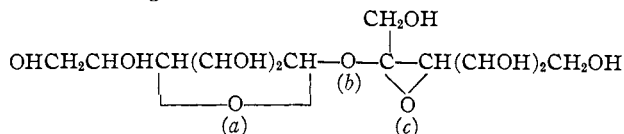
The critical increment corresponding to a band 0.875μ would be 32,600 calories. The discrepancy of 2,400 calories between the observed and calculated values may be due to one or more of three causes: (1) the heat of hydration of sucrose dihydrate may be more than 5,000 calories; (2) hydrogen ion itself may possess a critical increment; (3) if we consider sucrose dihydrate, the portion of the molecule which gives rise to the calculated band at 0.815μ is the anhydrous fructose portion, as shown thus, HOH₂C—C—CH—(CH.OH)₂.CH₂OH, 35,000 calories probably being



a measure of the stability of the oxygen ring. If now we consider sucrose tetrahydrate with the extra 2 molecules of water attaching themselves to the oxygen atom (a), it is evident that such attachment will tend to decrease the strength of the oxygen ring and, therefore, the tetrahydrate should show a band corresponding to a smaller critical increment. This agrees with the experimental facts, as 0.875μ corresponds to a critical increment of 32,600 calories.

It is evident, therefore, that the calculated critical increment for sucrose dihydrate, namely, 35,000 calories, is a very probable one, and the finding of a band, hitherto unknown, in so close proximity to the calculated position is further evidence in favor of the general correctness of the view outlined above.

The conclusions arrived at on the basis of the kinetics of the inversion process as summarized in Equations 1 and 2 would be in harmony with the following structural considerations. Haworth and Law⁷ consider that the glucose residue of sucrose contains a butylene oxide ring structure and the fructose portion is characterized by an ethylene oxide ring, according to the following scheme.

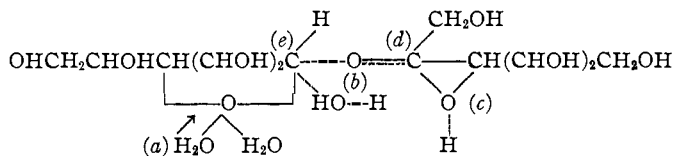


Moreover, in calculating the activity of sucrose,¹ it was demonstrated that this sugar is hydrated in solution to the extent of 4, that is to say, there are 4 molecules of water attached to a molecule of sucrose. By a similar series of calculations glucose was shown to exist mainly as a dihydrate. Combining these two conclusions, it was suggested that the sucrose molecule has 2 water molecules attached to each of the oxygen atoms (a) and (c) in the rings, that the hydrated form of sucrose was in fact an oxonium compound.

⁷ Haworth and Law, *J. Chem. Soc.*, 190, 1314 (1916).

From several points of view the inversion process would appear to have its origin in the fructose portion of the sucrose molecule. Armstrong⁸ compares the relative rates of inversion of the disaccharides sucrose and turanose by considering the proximity of the ethylene oxide ring in the fructose residue to the anhydride oxygen atom (*b*), where the break during inversion must eventually take place. He also emphasizes the fact that fructosides are hydrolyzed with remarkable ease. In other words it seems reasonable to relate the ease of hydrolysis of sucrose as compared say with turanose to the nearness of the fructose ring to the oxygen atom (*b*). Further, the ethylene oxide structure of the fructose ring renders it much less stable than the corresponding 5-membered ring in the glucose portion. On this basis, therefore, it was suggested by Moran and Lewis¹ that the primary reactant was sucrose dihydrate with the 2 molecules of water attached to the oxygen atom (*a*), leaving the oxygen atom (*c*) free, and not rendered inactive by the presence of attached water molecules.

The next point of importance is the fact that hydroxyl ion will not invert sucrose. The sugar forms sodium saccharate on the addition of caustic soda. This will be largely hydrolyzed in solution, owing to the very weak acidic portion; in other words a large amount of sucrose can exist in the presence of hydroxyl ion. In view of this it was concluded that the interaction of the hydrogen ion with sucrose is a specific one and, hence, it was suggested that a complex is formed between the two. From conductivity measurements it follows, however,⁹ that this complex has only a fugitive existence; nevertheless, its rate of formation appears to be the measurable term in the actual inversion process (compare Equation 1). Regarding the succeeding (rapid) series of changes involved in the reaction of the sucrose-hydrogen-ion complex with water to produce invert sugar, the following suggestions are due (in part) to Professor I. M. Heilbron. The various stages are regarded as being associated fundamentally with changes in valence linkings. In the initial formation of the sucrose-hydrogen-ion complex, a partial valence of the oxygen atom (*c*) is used up, in consequence of which the end carbon atom (*e*) of the glucose portion effectively gains a free positive valence. This immediately links up with the hydroxyl of a neighboring water molecule to give a system which may be represented thus,



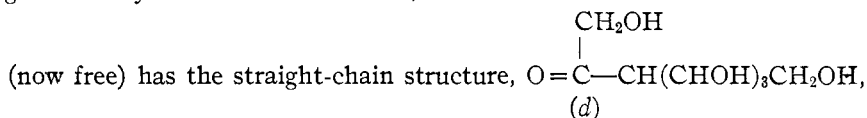
⁸ Armstrong, "The Simple Carbohydrates and The Glucosides," Longmans, Green and Co., 1919.

⁹ Kieran, *Trans. Faraday Soc.*, **18**, Part 1 (1922).

It will be observed that we have now an ethylene oxide ring, which normally is very unstable, with a weak linking at the oxygen atom (*c*). The ring therefore immediately breaks at the dotted line C----O leaving a free valence at the carbon atom (*d*). Thus, a new —CHOH— grouping is formed temporarily in the fructose residue. It is obvious that this could not occur had any ion other than hydrogen ion been attached to the sucrose in the first instance.

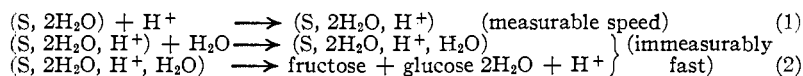
The next step concerns the free valence produced at the carbon atom (*d*). This can go to so strengthen the carbon-oxygen linking between (*d*) and (*b*) that the already weakened linking between (*e*) and (*b*) would be completely broken. The glucose and fructose portions of the sucrose molecule are now separated. As a result of the increase in free valence produced at the carbon atom (*e*), its union with the hydroxyl of the attached water molecule is now strengthened, with the result that hydrogen ion is split off from this water molecule, thereby yielding a molecule of glucose dihydrate and at the same time regenerating free hydrogen ion, the concentration of which is thus maintained constant in agreement with known experimental fact. If the above view is correct, it would follow that the free hydrogen ion generated in the process is not the actual individual which was introduced in the first place, the latter having permanently disappeared as such by entrance into the structure of the fructose molecule ultimately produced.

At the moment at which the hydrogen ion was regenerated and the glucose dihydrate molecule formed, it is obvious that the fructose residue



which immediately passes over into a mixture of the tautomeric forms.

In view of the above considerations it would appear that Equations 1 and 2 are really too simple in form. What occurs is more probably given by the following series.



Summary

1. The effect of temperature on the potential difference of the normal hydrogen electrode has been discussed. E.m.f. measurements with acetic acid indicate that it is (very approximately) proportional to the absolute temperature.

2. Measurements have been carried out on the very short infra-red absorption of aqueous solutions of sucrose, glucose and fructose in the

region 0.75 to 1.0μ . Sucrose and fructose exhibit a band at 0.875μ . This band is absent from glucose. The bearing of these results on the critical increment of sucrose dihydrate and on the mechanism of the inversion of sucrose has been discussed.

3. The series of structural changes most probably involved in the inversion process have been considered in some detail.

The above work was carried out at the suggestion of Professor W. C. M. Lewis, to whom the authors wish to express their thanks. In addition, they desire to acknowledge their indebtedness to the Department of Scientific and Industrial Research of the British Government for grants, which enabled them to carry out the investigation.

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NOTES

A New Vessel for Electrometric Titration.—Among the many vessels for electrometric titrations which have been described in chemical literature, I did not find one which was suitable for class work, especially for

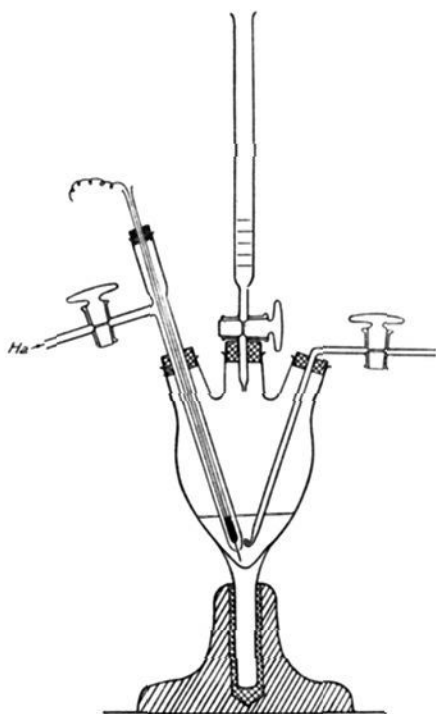


Fig. 1.

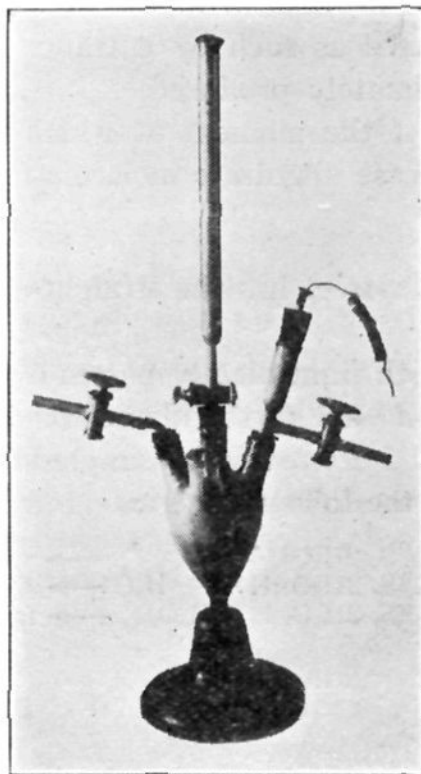


Fig. 2.

the titration of solutions the hydrogen-ion concentration of which is influenced by the partial pressure of carbon dioxide in the surrounding air. The Clark electrode with its many stopcocks is too complicated and