THE KEY ROLE PLAYED BY SUGAR IN EARLY EXPERIMENTS IN KINETICS AND EQUIILIBRIA*

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Enormous quantities of sucrose, the common chemical name for cane or beet sugar, are consumed not only in commercial and domestic food making; in fact, this cheap and biorenewable compound has other industrial uses, an example being in the production of polyurethane foam, where the original feedstock, petroleum or glycerol, has been replaced by sucrose (1). At the other extreme, small quantities of sucrose played an important role in the early development of chemical kinetics, and of concepts such as the relative strengths of acids and bases. This is the theme of the present account.

(Friedrich) Wilhelm Ostwald (1853-1932), Fig. 1, carried out his doctoral research at Dorpat, on "The Mass Action of Water," in particular the hydrolysis of $BiCl_3$, showing that the hydrolysis increased as more water was added to the solution. In his ten-year career at Dorpat, where he quickly became recognized as a promising scientist, Ostwald realized that the study of phenomena in solutions should employ effects that do not themselves alter the concentrations of the reacting substances. He became especially interested in the "affinities" (i.e., the relative strengths) of acids.

Julius Thomsen (1826-1909) had used calorimetry to compare the affinities of pairs of acids, by allowing the members of a pair to compete for alkali insufficient to neutralize both. Ostwald, having no access to the sensitive equipment used by Thomsen, made measurements of changes in volume, density and refractive index. In 1878, Ostwald summarized his conclusions as follows(2):

Figure 1. Wilhelm Ostwald

Ostwald's Table of Relative Affinities of Acids (Monobasic) (2)

Nitric acid (taken as standard)	100	Formic acid	3.9
Hydrochloric acid	98	Lactic acid	3.3
Trichloroacetic acid	80	Acetic acid	1.23
Dichloroacetic acid	33	Propionic acid	1.04
Monochloroacetic acid	7.0	Butyric acid	0.98
Glycollic acid	5.0	isoButyric acid	0.92

During his appointment as professor at the Riga Polytechnicum,1882-1887, Ostwald turned his attention from equilibrium methods to ones based upon the measurement of reaction velocities. After first studying the effect of acids on the rate of hydrolysis of acetamide (3) and of methyl acetate (4), he turned to measurements based on the acid-catalyzed "inversion" of the polarimetrically dextro-rotatory cane sugar into the levo-rotatory "invert sugar" (5), an equimolar mixture of the isomeric monosaccharides glucose and fructose. The polarimetry of sugar solutions and the phenomenon of inversion had been described in 1833 by Jean Baptiste Biot (1774-1862) (Fig. 2), Professor of Physics at the Collège de France, and Jean Francois Persoz (1805-1868) (6,7), who obtained his doctorate in the same year and later became Professor of Chemistry in Paris. At that time there was little interest in chemical kinetics.

A pioneer in the field of kinetics was Ludwig Wilhelmy (1812-1864), then a faculty member at Heidelberg, who in 1850 reported a study on the parameters that govern the rate of the inversion of sugar (8). The sugar-HNO_3 solution was placed directly in the polarimeter tube, and changes in the rotation were observed for a day. During this time, the temperature ranged from 14.5° to 18° C. Wilhelmy found that the rate of inversion, dx/dt, was proportional to the concentration of acid and also to the concentration of sugar. He formulated the equation

$$-\frac{dx}{dt} = M.Z.S.$$

where S is the amount of acid, Z the amount of sugar at time t, and M is a constant for this acid. Wilhelmy's paper of 1850 passed unnoticed by most later workers, until, with change of symbols, Ostwald rewrote the integrated form of equation (1) as:

$$\log \frac{b}{b-x} = \log \frac{1}{1-x/b} = a.c.t.$$

Here b signifies the initial amount of sugar and x the amount inverted after passage of time t minutes. The

Figure 2. Jean Baptiste Biot

velocity constant c applies to a particular acid, the specified concentration, a, of which remains unchanged (5).

Ostwald had invented a very effective thermostat which he later described (9). This allowed all experiments to be carried out at 25° C. Constancy of temperature was important, because observations extended over many hours. Ten-mL portions of each 40-50% sugar solution and one-normal acid solution were mixed in a small stoppered vessel. After a suitable time, the liquid was transferred to the polarimeter tube, which was water-jacketed at 25° C. Following polarimetry, the liquid was returned to the thermostatted vessel, returned to the polarimeter after further time lapse, and the sequence continued until termination of the experiment. In this manner, Ostwald determined the inversion velocity constants of more than thirty mainly monobasic acids. Further, he was able to show that the relative values obtained by this technique were in line with those from the methyl acetate hydrolysis studies. In the following year, Ostwald published a second paper on sugar inversion (10). Having been troubled by mold formation in his sugar solution, he found a cure in the addition of camphor to the solution and the use of petroleum-impregnated cork closures. However, his main aim was to show that yet another technique, electrolytic conductivity, afforded results that were in line with those obtained by inversion studies.

In 1887 Ostwald was appointed Professor of Physical Chemistry at Leipzig. He attracted many students

Figure 3. James Walker

from America and Britain. The Scot, James (later, Sir James) Walker (1863-1935) (Fig. 3) was the first of these to earn a Ph.D. under Ostwald's direction. Walker's doctoral research entailed a thorough study of the behavior of weak organic bases. His paper, "Estimation of the Affinities of Organic Bases," is a description of his accomplishments (11). Although the relative strengths of acids could be explored directly, this was not the case for Walker's weak monoacidic bases. To study these, he invoked the phenomenon of *salt hydrolysis*. On dissolution in water, the salt of a weak base undergoes at least partial breakdown into the parent acid and base, or their ions. A determination of the concentration of this acid should provide a measure of the extent of hydrolysis, which will be large with a base of low affinity. This determination cannot be performed by titration with alkali; neutralization of the acid would result in further salt hydrolysis. Walker successfully applied the acid-catalyzed breakdown of methyl acetate used by Ostwald to study organic acids.

After receipt of his Ph.D. degree in July, 1889, Walker returned to Edinburgh as assistant to Alexander Crum Brown (1838-1922), where the two worked on the electrosynthesis of organic dibasic acids, whose dissociation constants Walker then determined. In 1895, Walker returned to the area of his doctoral studies but now made use of the sugar-inversion method in this reexamination of the affinities of organic bases (12). As in the Leipzig experiments, the acid arose from the hy-

drolysis of the weak-base hydrochloride. However, this method appeared to be inferior to the conductometric, and possibly to the methyl acetate method. Unlike the latter approach, the sucrose method was applicable to a wide range of affinities. Salt hydrolysis ranged from 2% for pyridine to 97% for thiourea. Because of the uncertainties of this method, affinity constants were not reported. However, the velocity constants followed a sequence similar to that noted at Leipzig.

Joseph Ellis Trevor (1864-1941) (Fig. 4), an American student in Ostwald's laboratory, after making a successful study of double-salt formation (13), turned his attention to the measurement of the small degrees of "hydrogen dissociation" (i.e., the very low acidities) of acid sodium salts, such as sodium hydrogen maleate (14). At least in Ostwald's laboratory, the ionic theory had become fully accepted. Accordingly, the hydrogen ion was considered to be the actual catalyst in the inversion of sugar. Trevor pointed out that the solution of such a salt may contain the ionic species Na^+, H^+, HX^-, and X^{2-}, and therefore dismissed conductometry as a possible means of acidity determination.

A polybasic acid has at least two dissociation constants. Thus for the dibasic maleic acid, $K_1 = 1 \times 10^{-2}$ and $K_2 = 3 \times 10^{-7}$, so that the acidity of the monosodium salt is much lower than that of the free acid. Working at 25° C with various weak acids, Ostwald had needed very
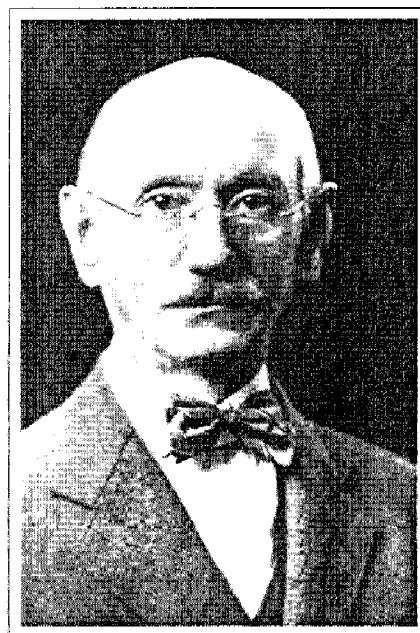

Figure 4. Joseph Ellis Trevor

long times to get extensive inversion of sugar. Trevor realized that, at this temperature, inversion by his acid salts would be impossibly slow. Knowing that the rate
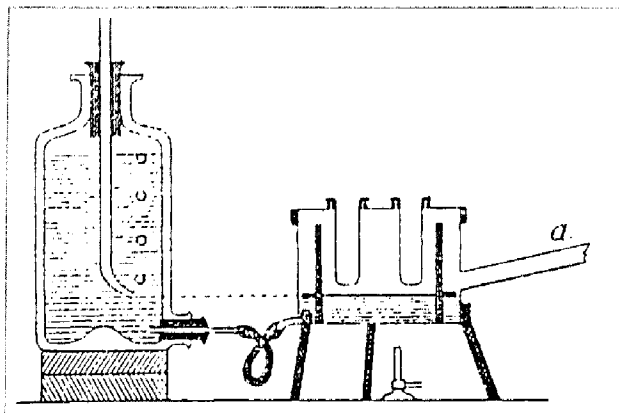
Figure 5. Trevor's steam bath

of inversion increases with temperature, Trevor made the obvious choice of working at 100° C. For this purpose, he devised the constant water level steam bath shown in Fig. 5. From a trial with $0.01N$ succinic acid, he found that the rate of inversion of sugar was about 4000 times faster at 100° than at 25° C. If inversion at 100° C solved one problem, it created another. For successful polarimetry, the solution had to be cooled down to 20° C, the temperature of the jacketed polarimeter tube. Corrections for inversion that occurred while the temperature was changing had to be elucidated. Further, since the strong acid HCl was to be used as the reference standard, a way to arrest the very fast inversion at 100° C had to be found. Trevor sterilized his approximately 13% sugar solution by boiling, then added camphor or naphthalene as preservative. He showed that the solution underwent no polarimetric change after being kept in the steam bath for 80 minutes. Inversions were carried out in steamed-out hard glass test tubes, closed by rubber stoppers , each with a short length of capillary tubing as a vent. Each tube contained 10 mL each of solutions of sugar and of the acid. The steam bath could hold about seven of these tubes. After a suitable time, a tube was transferred to a thermostated bath operating at 20° C and left there for 15 minutes. Although this period sufficed to bring the tube contents to 20° C, the acidity of many of the salts was so low that hourlong periods in the thermostat caused no further inversion. Preliminary experiments were made with lactic acid, so that a correction could be obtained for the inversion that occurred while the temperature of the reaction mixture was rising to 100° C.

Having tested his proposed technique by determining the inversion velocity constants of monosodium succinate and monosodium-*m*-phthalate, Trevor turned to the determination of the degrees of "hydrogen dissocia-

tion" in solutions of these and of other sodium acid salts. He determined the molar velocity constant of HCl, his "standard," at dilutions ranging from 200 to 3200 L per mole. In such solutions, 100% dissociation could be assumed with confidence, and the rate of inversion was low enough to allow samplings to be made with reasonable accuracy. As a sample tube was removed from the thermostat, one mL of concentrated sodium acetate solution was added. This destroyed the acidity by forming undissociated acetic acid and thus arrested the inversion. Experiments in glass tubes, confirmed and extended by runs in silver tubes, gave the mean value 17.92, with a maximum deviation of 0.6%, as the molar velocity constant of HCl at 100° C. If this value represents 100% dissociation, the degree of dissociation of another acid could be assessed from the ratio of its inversion rate to that of HCl . The acid salt solutions were prepared by titrating a measured volume, V cc, of a standard solution of the appropriate acid with NaOH, to form the disodium salt. A second V cc of acid was then added, and the resulting solution, of known concentration of the monosodium salt, was diluted as required.

Trevor suspected that the principal uncertainty in his experiments with acid salts was in the exact proportionality between inversion velocity and degree of dis-
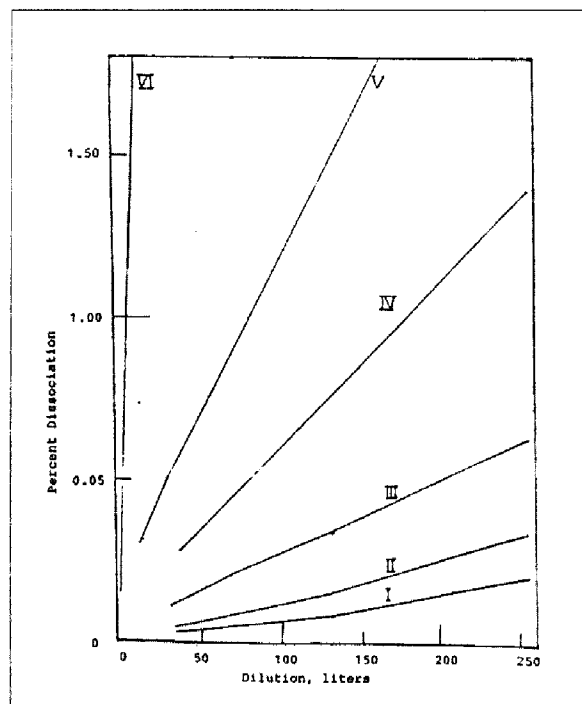

Figure 6. Percent dissociation of the monosodium salts of dibasic acids: I, suberate; II, succinate; III, citraconate; IV, mesaconate; V, fumarate; VI, acetic acid (for comparison).

sociation. He attributed this uncertainty to the unknown influence of the nonelectrolyte, sugar, on the dissociation of an acid. The results of Trevor's extensive determinations are indicated by the curves in Fig. 6. These show the relationship between the degree of dissociation and the dilution of solutions of the various acid salts. For comparison, the rocket-like curve of acetic acid, the typical "textbook" weak acid, is included. Trevor believed that his value of 0.03%, at $v = 32$ L, for monosodium suberate was the smallest degree of dissociation that had ever been measured. He noted that a conductometrically obtained value of 0.04% at $v = 14.4$ had been reported for p-cresol (15).

Thus a common natural substance sugar played a key role in a variety of investigations which led to the development of chemical kinetics and support of the ionic theory.

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