[CONTRIBUTION FROM THE TEXTILE FOUNDATION AND THE FRICK CHEMICAL LABORATORY AT PRINCETON UNIVERSITY]

Open-Chain Sugars. I. Absorption in Ultraviolet of D-Glucose and L-Arabinose in Acid Solution

BY EUGENE PACSU AND LEJAREN ARTHUR HILLER, JR.

In 1913 Willstätter and Zechmeister[1] observed that the optical activity of D-glucose in hydrochloric acid increased to a great extent with the concentration of hydrogen chloride. Thus the specific rotations[2] of D-glucose in 41.4 and 44.5% hydrochloric acid were found to be, respectively, +106° and +165°, instead of the constant value of +52.6° in aqueous solution. In a later work Zechmeister[3] published the results of his systematic investigation of this interesting phenomenon. He found that the simple sugars in 42.0% hydrochloric acid at about 6 to 10° possessed the specific rotations: D-glucose, +113.3°; D-galactose, +160.4°; D-mannose, +54.6°; D-fructose, −180.0°; L-arabinose, +202.9°; D-xylose, +96.6°; L-rhamnose, −31.1°. Further increase in the hydrogen chloride content of the solvent resulted in the remarkably high specific rotation of +202° for D-glucose at −12° in 46.7% hydrochloric acid solution. The rates of these rotational changes were generally so rapid that they could not be determined at room temperature. However, they became measurable at 0°, giving, *e. g.*, for D-glucose in 40.6% hydrochloric acid ($[\alpha]^0_D + 96.2°$; *c*, 0.990) $k = 1.6 \times 10^{-2}$ (decimal logarithms, minutes). For comparison, the rate of mutarotation of D-glucose in pure water at 0.7° is given as 7.4×10^{-4}. The reversibility of the process in 40.0% acid was proven when it was found that after neutralization of the various solutions with sodium bicarbonate the sugars were recovered unchanged or nearly so, quantitatively, each of them showing the respective normal value of constant rotation in the corresponding salt solution. Zechmeister also found that, *e. g.*, a 1.5% D-glucose solution in 40.0% hydrochloric acid at 10° remained practically colorless during a twenty-one hour period of time, thus indicating that very little, if any, decomposition had taken place.

For explanation of these experimental facts Zechmeister assumed that in concentrated hydrochloric acid two reactions were taking place with unequal rates: the instantaneous establishment of a new equilibrium between the α- and β-forms of the sugars, and, at sufficiently low temperature, the measurably slow, partial conversion of the latter into "a high-rotating modification." It had already been known for some time from the work of Armstrong and Hilditch[4] that, *e. g.*, D-glucose in 0.1 *N* hydrochloric acid rapidly acquires the ability to reduce potassium permanganate solution, a property which is completely lacking in the aqueous solution of either anomeric form of the sugar. They explained this curious behavior by assuming that a small amount of a new isomer, "γ-glucose," with ethylene oxide ring structure was being formed in acidic solution. This new modification was supposed to be responsible for the potassium permanganate reaction. Zechmeister pointed out that the formation in somewhat larger quantity of such a "γ-sugar" might account for the observed high optical activity and for the measurable rate and the reversible nature of the process. However, he also stated that it was difficult to see how a sugar molecule with ring structure could exist in fuming hydrochloric acid without suffering cleavage of its hemiacetal linkage. He suggested that combination between a hydrogen chloride molecule and the free aldehyde group of the sugar might give rise to a structure with very high optical rotational value.

In connection with our work on the acid-catalyzed degradation of cellulose it became necessary to know the specific rotations of D-glucose in strong mineral acids of various concentrations. We found[5] that solutions of D-glucose in 85% phosphoric acid and in 50.5% sulfuric acid (d^{20}_4 1.40) gave the constant values $[\alpha]^{20}_D + 68.0°$ and $[\alpha]^{20}_D + 61.0°$, respectively, ten minutes after solution. We also found[6] that potassium permanganate in 0.25 *N* sulfuric acid solution selectively attacked cellulose by oxidizing its reducing group to carboxyl group. Since the potential reducing groups of the carbohydrates with ring structures are not oxidized by this reagent in neutral medium, we have concluded that in acidic environment a shift into the open-chain form of the sugars might occur with the formation of carbonyl groups which are then attacked by dilute potassium permanganate. Since it is known from Henri's work[7] that aldehydes possess a characteristic absorption band at the wave length of about 2800 Å., we undertook the measurements in ultraviolet of the acidic solutions of D-glucose to verify our deduction. First we measured at 25° the absorption of a 16% aqueous D-glucose solution ($[\alpha]^{20}_D + 52.9°$) in the ultraviolet region 3100 to 2400 Å., by using a Beckmann photoelectric quartz spectrophotometer. Contrary to the finding of J. E. Purvis[8] and in agreement with statements in the general literature[9]

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[1] R. Willstätter and L. Zechmeister, *Ber.*, **46**, 2401 (1913).

[2] All rotations in this paper refer to the sodium light.

[3] L. Zechmeister, *Z. physik. Chem.*, **103**, 316 (1923).

[4] E. F. Armstrong and T. P. Hilditch, *J. Chem. Soc.*, **115**, 1410 (1919); **117**, 1086 (1921).

[5] L. A. Hiller and E. Pacsu, *Textile Res. J.*, **16**, 568 (1946).

[6] L. A. Hiller and E. Pacsu, *ibid.*, **16**, 318 (1946).

[7] V. Henri, "Études de Photochimie," Gauthier-Villars et Cie, Paris, 1919, p. 64.

[8] J. E. Purvis, *J. Chem. Soc.*, **123**, 2519 (1923).

[9] F. Micheel, "Chemie der Zucker und Polysaccharide," Akad. Verlagsges., Leipzig, 1939, p. 218; B. Tollens–H. Elsner, "Kurzes Handbuch der Kohlenhydrate," J. A. Barth, Leipzig, 1935, p. 86.

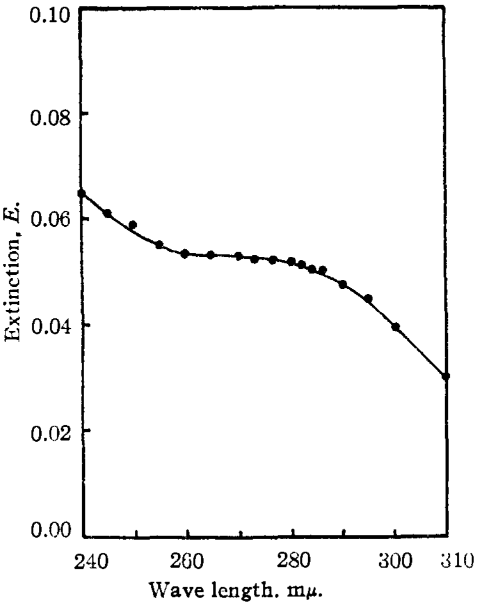

Fig. 1.—Absorption spectrum of a 16% D-glucose solution in water.

we found no selective absorption that would have indicated the presence of the oxo-form of glucose in the aqueous solution (Fig. 1). Then a 17.3% D-glucose solution in 50.5% sulfuric acid (d^{20}_4 1.40) was employed with the result shown in Fig. 2. The absorption became evident ten minutes after dissolution of the sugar and showed a maximum at the wave length 2840 Å. The absorption steadily increased in intensity during the ensuing sixty-nine hours thus indicating that conversion of the non-absorbing cyclo-form of the sugar into the absorbing oxo-form took place gradually.[10] After the maximum intensity had been reached with the extinction value E_∞ = 1.665 the solution began to show a slight discoloration. Ninety-seven hours after the beginning of the experiment the absorption band had shifted slightly to 2880 Å., while only negligible increase (0.005) had occurred in the value of optical density. Since a plot of the difference between the logarithms of $E_\infty - E_0$ and $E_\infty - E_t$ against t time gave a straight line, it was concluded that the conversion of D-glucose with normal ring structure into the carbonyl-containing modification represented a first order reaction. From the slope of the line between the points for one hour and twenty-two hours the rate constant was calculated to be $k = 3.6 \times 10^{-4}$. In a similar experiment the absorption of L-arabinose was determined (Fig. 3). According to Zechmeister the rate of conversion in 40.6% hydrochloric acid of L-arabinose into a high-rotating form was so rapid as to make quantitative measurements even at 0° impossible. We used a 4.0% solution of L-arabinose in 50.5% sulfuric acid and recorded the change in the optical density of the solution with time at the peak of the absorption curve, namely, at the wave length 2840 Å. From a logarithmic plot of the observed data the rate constant was calculated to be $k = 4.5 \times 10^{-4}$.

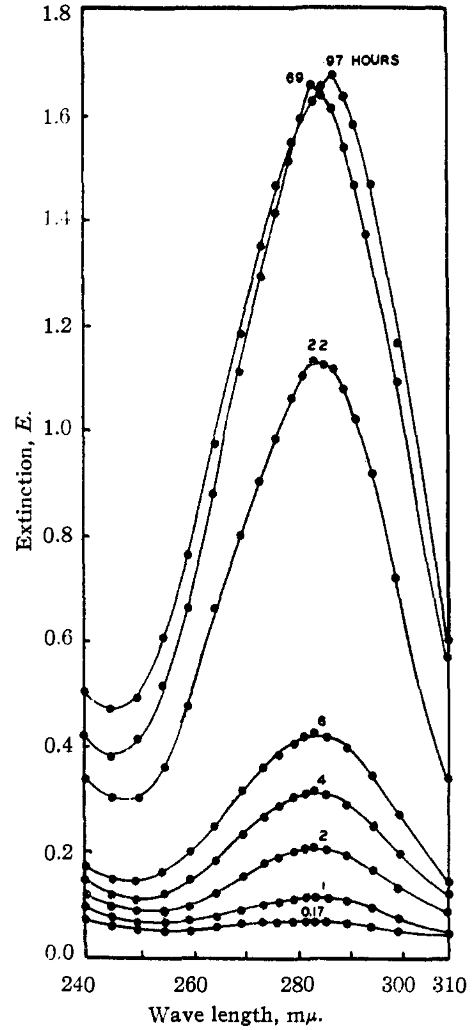

Fig. 2.—Change with time of the absorption spectrum of a 17.3% D-glucose solution in 50.5% sulfuric acid.

It has been stated above that the rotational value of D-glucose in 50.5% sulfuric acid, $[\alpha]^{20}D$ + 61.0°, was obtained about ten minutes after the sugar had first come into contact with the solvent. For an explanation of the fact that the optical rotation remains constant while the absorption develops, it may be assumed that two processes are taking place in the acid solution. The first reaction is probably the reversible formation of an

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[10] The absence of hydroxymethylfurfural was demonstrated when 100 cc. of a twenty-two hours old 10% glucose solution in 50.0% sulfuric acid was, after dilution, extracted with ether and the concentrated ether layer was tested with resorcinol dissolved in concentrated hydrochloric acid with negative result. For comparison, 5 cc. of a 1% sucrose solution in 1 *N* sulfuric acid was boiled for three minutes and then extracted with ether; the ether extract gave a very strong positive test for hydroxymethylfurfural with the same reagent. Also, the absence of levulinic acid in the aged glucose solution was proved by the negative outcome of the iodoform test carried out on the aqueous residue of the moist ether extract.

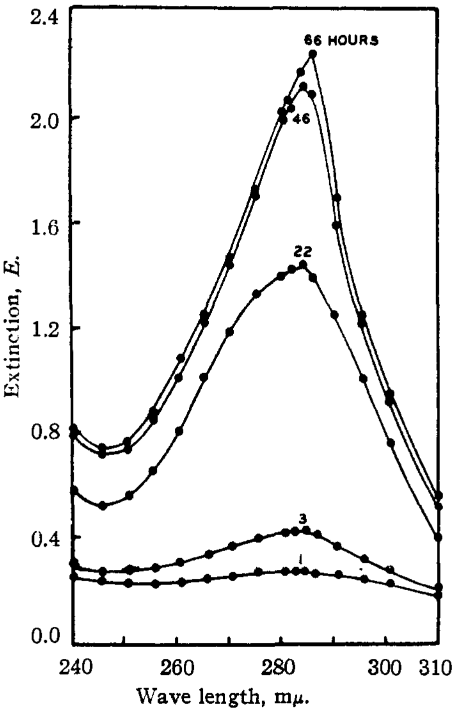
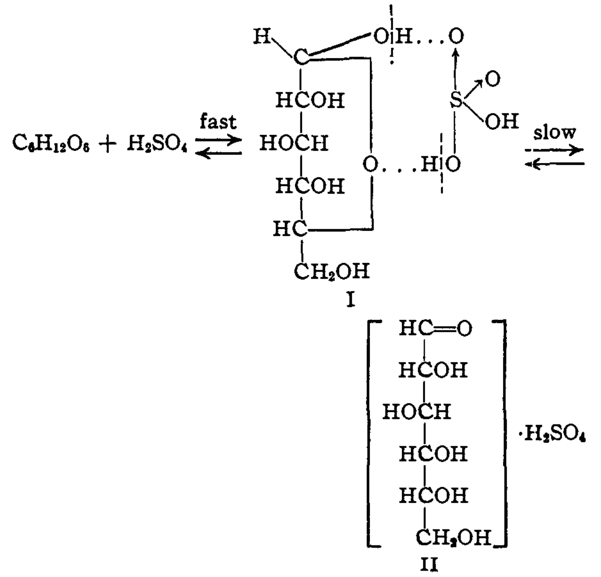


Fig. 3.—Change with time of the adsorption spectrum of a 4.0% L-arabinose solution in 50.5% sulfuric acid.

addition complex (I) between the anomeric forms of D-glucose and the acid molecule, which event proceeds with an unmeasurably high rate. The observed rotational value of $[\alpha]^{20}_{\mathrm{D}} + 61.0°$ would correspond to the optical activities of the components in the equilibrium mixture. This fast reaction would then be followed by a comparatively slow process which essentially consists of the opening of the ring structure in complex (I) to give rise to the carbonyl form of the sugar (II). Although this phase of the reaction becomes noticeable by the sensitive method of absorption measurement, yet the concentration of (II) is probably so small under our experimental conditions that the presence of this form remains undetected when the much less sensitive polarimetric method is employed.



Zechmeister postulated that the rotational value, $[\alpha]^{0}_{\mathrm{D}} + 62.0°$, obtainable by extrapolation to 0 time from the rate constant, $k = 1.6 \times 10^{-2}$, corresponded to a new equilibrium between the α- and β-form of D-glucose in the moment of dissolution of the sugar. In support of this argument he pointed out that this extrapolated value lies between the known specific rotations of the two anomeric forms. However, it seems to us more likely that the acid molecules play a decisive role in this reaction which, according to our assumption, should generally be initiated by the formation of molecular compounds like (I) between the sugar and acid molecules.

According to Zechmeister's experiments neutralization of the concentrated hydrochloric acid solutions of the sugars by sodium bicarbonate restored the constant specific rotations which were shown by the respective sugars in sodium chloride solutions of corresponding concentrations. We had, therefore, expected that after neutralization of our sulfuric acid solution with sodium bicarbonate the characteristic carbonyl band would

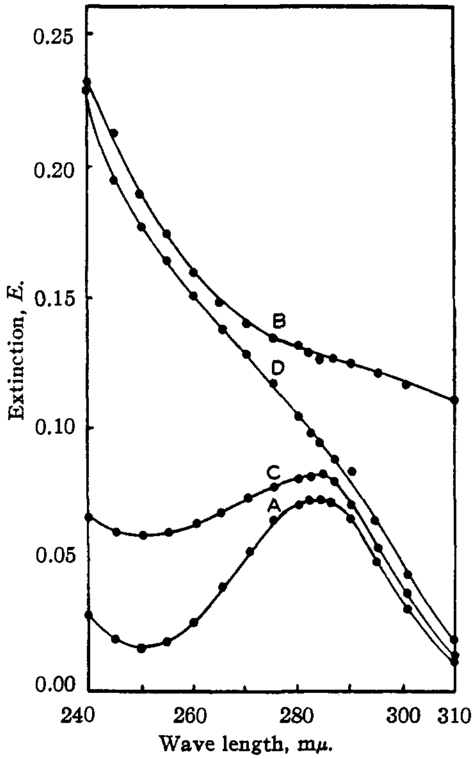


Fig. 4.—Disappearance of peak in neutralized D-glucose solution (2%): A, 1 day of standing; B, 1 day of standing + 2 drops alkali; C, 8 days of standing; D, 16 days of standing.

disappear and the solution would show the general absorption as has been found for D-glucose in neutral solution (Fig. 1). Pertinent experiments have revealed the remarkable fact that this is only true if the solution, after treatment with sodium bicarbonate, becomes slightly alkaline. In slightly acidic solution, however, the assumed open-chain form of the sugar persists for a comparatively long period of time. It is seen in Fig. 4 (C) that eight days after "neutralization" the slightly acidic solution still exhibited the characteristic absorption at 2840 Å., although the peak was not as sharp as that measured after the first day (A). It took altogether sixteen days until the absorption band completely disappeared in the slightly acidic solution (D). On the other hand, addition of two drops of dilute alkali to the one-day old solution resulted in the immediate disappearance (B) of the peak at 2840 Å.

In view of the present theory of mutarotation[11] these facts can not be interpreted readily. Further investigations are necessary before the significance of our observations to the true mechanism of mutarotation can be evaluated. We have already made initial attempts to isolate the postulated open-chain form of D-glucose by using superconcentrated hydrochloric acid solutions. So far we have not been able to isolate the free sugar in crystalline form, but we have succeeded in obtaining an amorphous acetate as the single product which, unlike the α- and β-pentaacetate, in chloroform solution shows strong selective absorption at the wave length of 2840 Å. The investigation is being continued.

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[11] T. M. Lowry, "Rapports sur les Hydrates de Carbon," Xième Conférence de l'Union Internationale de Chimie, Liége, 1930.

Summary

It has been found that D-glucose and L-arabinose in 50.5% sulfuric acid solutions show strong absorption at wave length 2840 Å. which is characteristic for carbonyl-containing compounds. After neutralization with sodium bicarbonate the slightly acidic solution still exhibits this band which, however, instantaneously disappears on rendering the solution barely alkaline. A possible mechanism is suggested for explanation of the behavior in strong acids of sugars with ring structures by assuming the formation of molecular compounds between the acid molecules and the open-chain forms of the sugars.

From D-glucose in superconcentrated hydrochloric acid solution an amorphous acetate has been obtained which compound, unlike the α- and β-pentaacetate, in chloroform solution exhibits strong absorption at 2840 Å.

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Preparation of α-Carbalkoxyalkyl Methacrylates by Pyrolysis of the Corresponding α-Acetoxyisobutyrates

BY E. M. FILACHIONE, M. L. FEIN, J. H. LENGEL AND C. H. FISHER

In an earlier paper[2] it was demonstrated that α-carbalkoxyalkyl methacrylates[3] (II) can be made in satisfactory yields by pyrolyzing the corresponding α-acetoxyisobutyrates (I, R = Me or H; R′ = Me or Et).

$$\underset{\text{I}}{CH_3COOC(CH_3)_2COOCH(R)COOR'} \xrightarrow[550^\circ]{450\text{ to}}$$

$$\underset{\text{II}}{CH_2{=}C(CH_3)COOCH(R)COOR'} + CH_3COOH$$

The present paper records results obtained in a further study of the pyrolysis method of preparing methacrylates (II). The additional esters made pyrolytically are the methacrylates of allyl glycolate and of allyl, methallyl, tetrahydrofurfuryl, benzyl and β-chloroethoxyethyl lactates.

The α-acetoxyisobutyrates (I) used in the pyrolysis experiments were prepared in high yields by treating allyl glycolate and several lactic esters (allyl, methallyl, tetrahydrofurfuryl, benzyl and β-chloroethoxyethyl) with α-acetoxyisobutyryl chloride. The resulting acetoxyisobutyrates (Table I) were decomposed by passage through a Pyrex glass tube heated at about 450° (Table II).

Although the esters (I) pyrolyzed had three esterified carboxyl groups, decomposition occurred preferentially at the acetate group, the principal products being acetic acid and the corresponding methacrylates (II, yields, 65–85%). On the basis of these and earlier[2] findings, it is concluded that the pyrolysis method is generally useful for the preparation of methacrylates (II) of alkyl glycolates and lactates. Presumably the method is useful also for preparing esters (II) in which R is ethyl or higher, but less suitable for esters (II) in which R′ is a secondary or tertiary alkyl group. It is anticipated that only relatively low yields of carbalkoxyisopropyl methacrylates ($CH_2{=}C(CH_3)$-$COOC(CH_3)_2COOR$) would be obtained in the pyrolysis of $CH_3COOC(CH_3)_2COOC(CH_3)_2COOR$,

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] E. M. Filachione, J. H. Lengel and C. H. Fisher, THIS JOURNAL, 68, 330 (1946).

[3] C. E. Rehberg, M. B. Dixon and C. H. Fisher, *ibid.*, 67, 208 (1945); I. E. Muskat and F. Strain, U. S. Patent 2,384,119, Sept. 4, 1945.