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EFFECTS OF VARIOUS CONDITIONS ON THE ALKALINE DEGRADATION OF D-FRUCTOSE AND D-GLUCOSE

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ABSTRACT

Dilute solutions of D-fructose and D-glucose undergo alkaline degradation, and, at temperatures in the range of 30–70°, almost two moles of alkali are consumed per mole of the carbohydrate. The degradation is partly guided by the dielectric constant of the medium; such additives as acetone and urea have specific effects where the reactions are not essentially guided by the medium dielectric. Acetone and urea presumably form complexes with the carbohydrates; this is revealed for the former by the formation of a dark red solution having a spectral band at 320 nm, like that observed earlier in the presence of ethylenediamine.

INTRODUCTION

Alkaline degradation of carbohydrates is a well known phenomenon[1]. The process is complex, and many salient features still remain unexplored, but some interactions of alkalis and other bases with reducing and nonreducing sugars have been reported[2–5]. An initial complex-formation prior to alkaline transformation[6] and degradation has been found. It has also been noted that, under mild conditions, and within a short period of time, complexation is the only process; the sugar undergoes degradation under drastic conditions. Furthermore, formation of complex proceeds better in the presence of polar media; addition of nonpolar solvents diminishes the formation.

The results of detailed investigations of the degradation of D-fructose and D-glucose with sodium hydroxide in the presence of various additives, as well as under different experimental conditions, are now presented, to help broaden our knowledge regarding the stability of simple ketoses and aldoses in an alkaline environment.

EXPERIMENTAL

Materials and methods. — All chemical compounds used were of either BDH Analar or E. Merck *pro analysi* grades. The solvents used were purified by standard procedures. Solutions were made in double-distilled water (specific conductance

1.6×10^{-6} mho.cm^{-1} at 30°), and were kept at constant temperature in a thermostated apparatus having temperature fluctuations in the range $\pm$ 0.1°.

Consumption of alkali was determined by titrating with standard hydrochloric acid. Spectral measurements were made with a Beckman DU Spectrophotometer by following the procedure described earlier[5].

RESULTS

Consumption of sodium hydroxide by D-*fructose and* D-*glucose.* — Two sets of experiments were made. In the first set, a constant concentration of the carbohydrate was allowed to react at constant temperature with various concentrations of sodium hydroxide for a fixed length of time (usually 2 h). At the end of the experiment, the mixtures were analyzed for the unconsumed alkali. The results were expressed as moles of alkali consumed per mole of carbohydrate.

In the second set, various amounts of a carbohydrate were added to a fixed concentration of alkali, and the mixtures were kept at constant temperature for 2 h. The mixtures were then analyzed for the unconsumed alkali, and the results were expressed as the moles of alkali consumed per mole of carbohydrate.

The results are shown in Figs. 1 and 2. Consumption of alkali increased asymptotically with increasing initial concentration, and reached a maximum of 2 moles per mole of D-fructose and 2.2 moles per mole of D-glucose, respectively. For a fixed concentration of alkali, the consumption decreased with increasing carbohydrate content, and almost linear variations, whose extrapolated values (see Fig. 2) almost corresponded to the results obtained from proceeding in the reverse direction, were observed. It was concluded that mixtures containing a low proportion of either

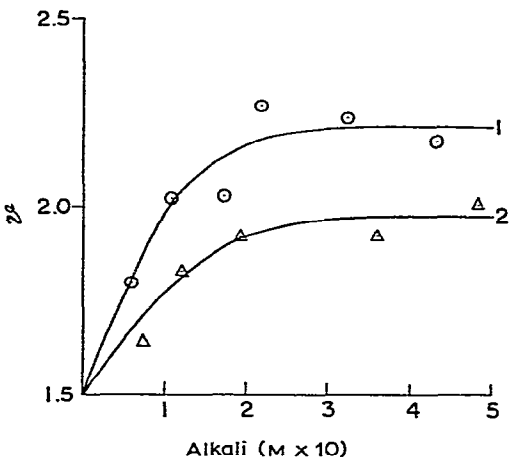

Fig. 1. Consumption of sodium hydroxide per mole of carbohydrate at a fixed concentration of the latter and variable concentrations of the former. (Temp. 70°, time 4 h. Key: curve 1, 11.3 mM D-glucose; curve 2, 10.1 mM D-fructose.)

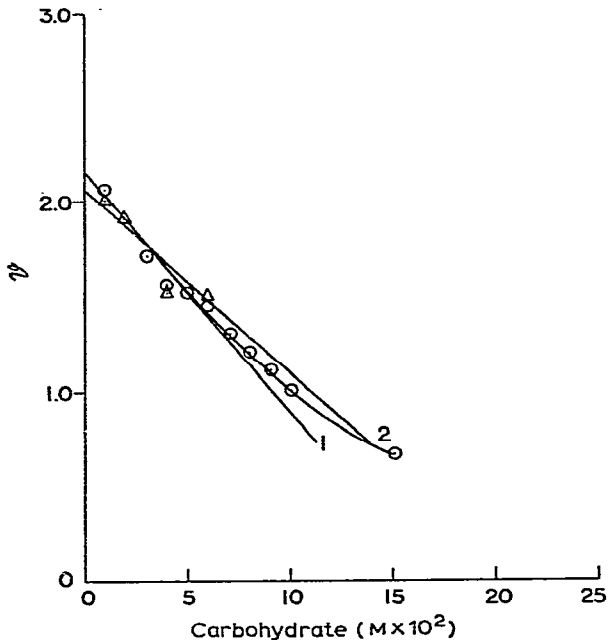

Fig. 2. Consumption of sodium hydroxide per mole of carbohydrate at a fixed concentration (0.1M) of the former and variable concentrations of the latter. (Temp. 70°, time 4 h. Key: curve 1, D-glucose; curve 2, D-fructose.)

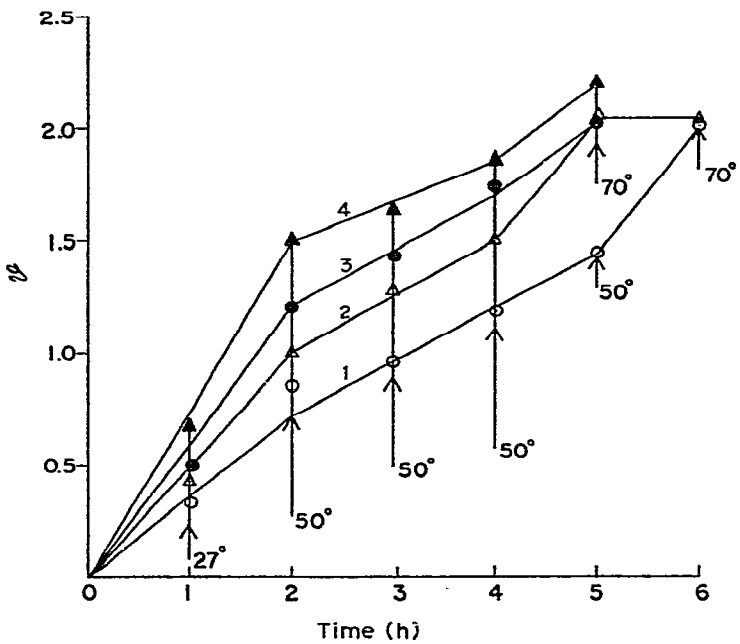

Fig. 3. Consumption of sodium hydroxide per mole of carbohydrate as a function of both time and temperature. (Key: curve 1, 0.01M D-glucose and 0.07M NaOH; curve 2, 0.01M D-fructose and 0.06M NaOH; curve 3, 0.01M D-glucose and 0.46M NaOH; curve 4, 0.01M D-fructose and 0.46M NaOH.)

D-fructose or D-glucose respectively consume 2 or 2.2 moles of alkali per mole. The preliminary findings reported earlier[4] also supported this view.

Effect of temperature. — A known mixture of a carbohydrate and the alkali was allowed to react at a series of different temperatures for specified periods of time. At each stage of increase in temperature, the mixture was analyzed for the consumption of alkali. The results, expressed as before, were plotted *vs.* time at different degrees of heating, and are shown in Fig. 3. Significant increase of reaction with respect to both temperature and time was observed; the consumption maxima here at 70° were otherwise approximately equal to that observed for 2 h at 70°. This result supported the view that, within the present experimental conditions, a good approximation of the consumption of alkali by both D-fructose and D-glucose was 2 moles per mole of carbohydrate.

Effect of solvents. — The effects of solvents at different ratios were studied; alcohol, acetone, 1,4-dioxane, and urea were used. The consumption of alkali was again considered as the index. Reactions were conducted at 30 and 60°. The results are plotted in Fig. 4, where the consumption ratio (R) with reference to pure water is given with the dielectric constant. Within the range of composition, the degradation in the presence of alcohol and 1,4-dioxane was less than that in pure water, but the extents were closely similar in the presence of these two solvents; acetone showed some specificity that became prominent at 60°. The effect of dielectric constant in restricting

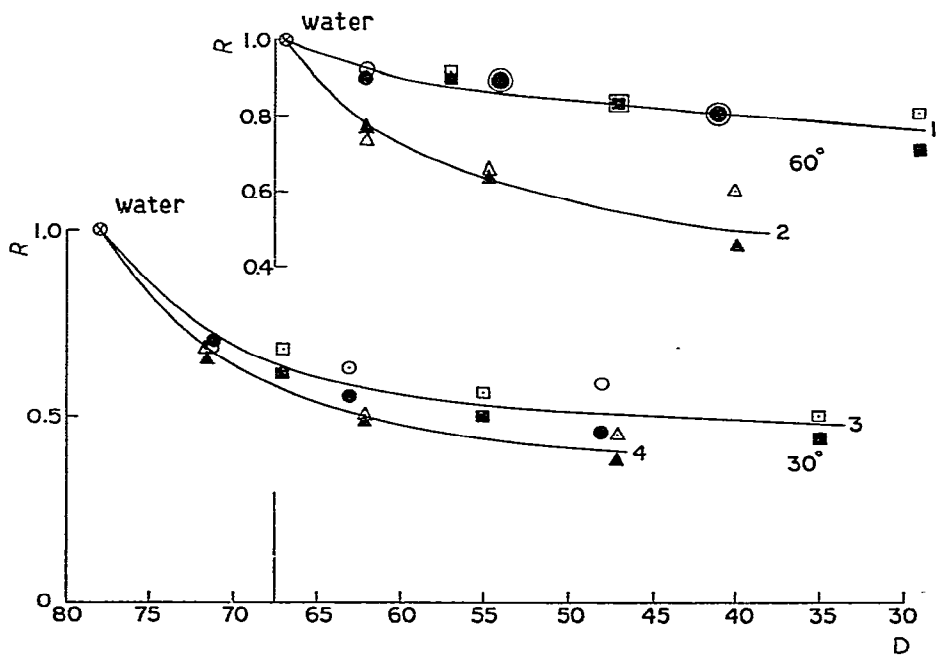

Fig. 4. Plot of the consumption ratio of alkali relative to pure water with the dielectric constant of the medium. (Key: Open and closed symbols refer to D-glucose and D-fructose, respectively. Circle for ethyl alcohol, triangle for acetone, square for 1,4-dioxane, circle with cross for pure water.)

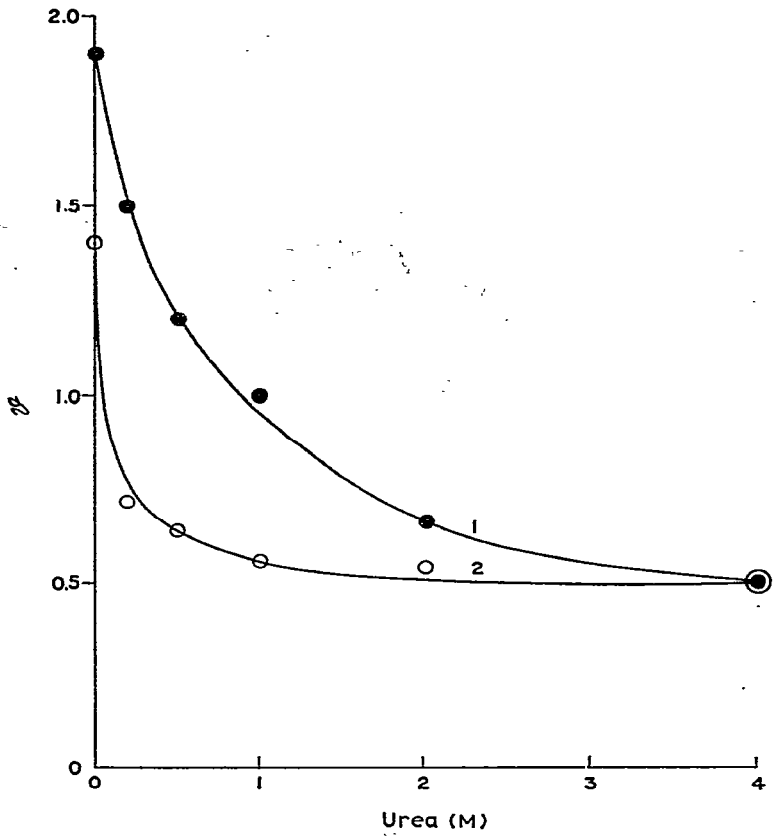

Fig. 5. Consumption of alkali per mole of carbohydrate in the presence of urea. (Temp. 50°, time 2 h. Key: curve 1, 0.01M D-glucose and 0.2M NaOH; curve 2, 0.05M D-glucose or D-fructose and 0.1M NaOH.)

the reaction is not, therefore, a general phenomenon. When the results were compared with those for urea (see Fig. 5), much more specificity was observed. Although ϑ was expressed in molarity, the rapid decrease in the lower range could not be due to the dielectric effect, as urea is known to increase the dielectric constant of water. The specificity occurred almost equally for D-fructose and D-glucose.

Spectra of the degraded solutions. — Ultraviolet absorption spectra of solutions of degraded D-fructose and D-glucose exhibited peaks at 285 nm that confirmed the earlier observations of ring opening by the action of alkali, to form free aldehydic and ketonic groups that usually register maximum absorption at ~280 nm. That acetone imparted some specific effects was observed from the spectra, where a new, red-shifted band had appeared at 320 nm. With the addition of alkali and acid, the intensity of the band changed in opposite directions, and this phenomenon was observed to be reversible; the results have been incorporated in Fig. 6. Moreover, for comparison, spectra of the reactants in the presence of ethylenediamine and urea were also recorded. Keeping all other conditions the same, the absorbances at 320 nm

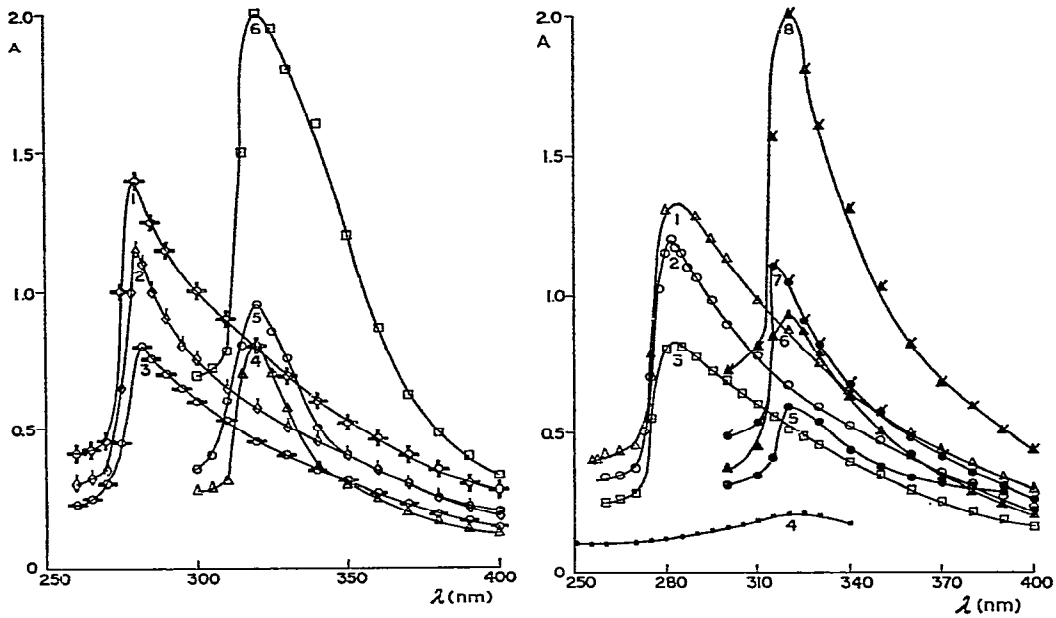

Fig. 6A. Spectra of alkali-treated D-fructose in water and acetone–water. [Reaction temp. 50°, time 4 h. Key: curve 1, product of 0.01M D-fructose and 0.1M NaOH diluted to have final strength for carbohydrate (3 mM) in excess alkali (2.5M); curve 2, same in water; curve 3, same in excess HCl (4M); curve 4, product of 0.05M D-fructose and 0.1M NaOH diluted to have final strength for carbohydrate (0.28 mM) in 33 mM HCl in 1:1 acetone–water; curve 5, same in absence of HCl; curve 6, same, in 33 mM NaOH.]

Fig. 6B. Spectra of alkali-treated D-glucose in water and acetone–water. [Reaction temp. 50°, Time 4 h. Key: curve 1, product of 0.05M D-glucose and 0.05M NaOH diluted to have final strength for carbohydrate (3 mM) in excess NaOH (~3M); curve 2, same in water; curve 3, same in excess HCl (~4M); curve 4, spectrum of D-glucose–ethylenediamine complex (*cf.*, ref. 5); curve 5, product of 1 at 0.36mM for carbohydrate in 7:3 acetone–water; curve 6, product of 1 at 3.6 mM for carbohydrate in 1:1 acetone–water and 0.5M HCl; curve 7, composition of 6 in the absence of added alkali or acid; curve 8, composition of 6 in 0.5M NaOH.]

were observed to vary linearly with concentrations of the sugars in acetone–water. Lines 1 and 2 in Fig. 7, for 50% acetone, show that initial concentrations of unknown samples could be estimated from these calibration lines.

DISCUSSION

By the action of sodium hydroxide, both D-fructose and D-glucose undergo degradation, and consume more alkali as the ratio of alkali to carbohydrate increases, and the maximum consumption is, on average, almost two moles of alkali per mole of carbohydrate. The decrease in the consumption in the presence of larger proportions of the carbohydrates, and the Langmuirian curves[7] with respect to the initial strength of the alkali, indicated different modes of reaction and carbohydrate–base complexation. Quantitative evidence in favor of such complexation had been given[4,5];

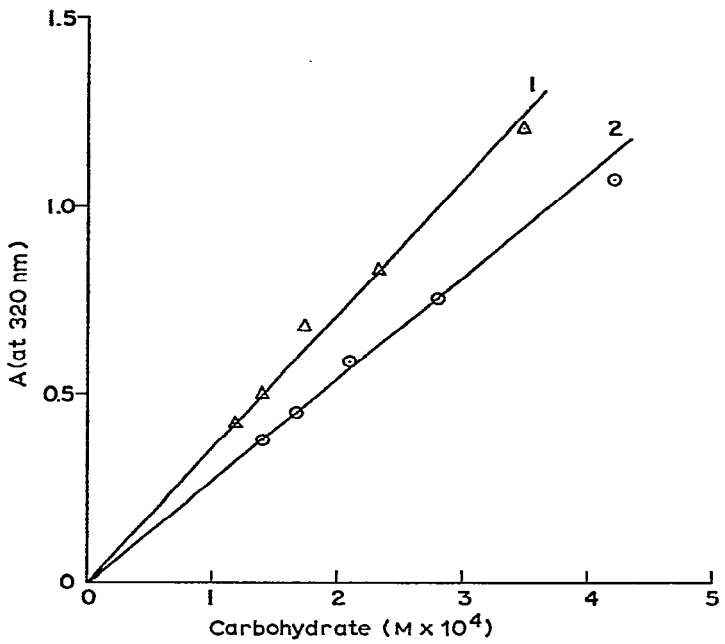

Fig. 7. Absorbance of alkali-treated carbohydrate at 320 nm, plotted as a function of the carbohydrate concentration in 1 :1 acetone–water. (Reaction temp. 50°, time 4 h. Key: line 1, D-glucose in 106 mM NaOH; line 2, D-fructose in 0.10M NaOH.)

complexation under mild conditions was observed, followed by degradation on (*a*) prolonged treatment with alkali, or (*b*) shorter treatment with a large excess of base at higher temperatures. The results given in Fig. 3 show that, in the lower range of temperature, the rate of consumption of alkali (a reflection of degradation) was much lower than that at higher temperatures. A further conclusion was that, at elevated temperature (70°) also, the maximum consumption amounted to a mole ratio of about two, as already mentioned. This was then taken as the extent of alkali consumption for dilute solutions (10mM) of D-fructose and D-glucose in an alkaline solution of concentration as high as 0.5M.

The complexation of carbohydrates with alkalis has been observed to be dependent on the types of solvent mixtures used[4]. At equal dielectric constant, 1,4-dioxane is a much more decomplexing solvent, and it was considered that hydroxylic would be more favorable than nonhydroxylic solvents. On the other hand, for the degradation process, the effect of solvent polarity (rather than solvent type) becomes more important when 1,4-dioxane and ethyl alcohol are the additives. Acetone, although much more polar than 1,4-dioxane, causes significant suppression, indicating some specific effect of this compound. In this regard, the effect of urea was surprising. At ~2M urea, the degradation was checked 80%, although the dielectric constant increased with the addition of this amide. A specific, rather than an electrostatic, effect was then the major factor; this may be due to the protection of the vulnerable

H^+ ion affecting C-1 in D-glucose and C-2 in D-fructose through complexation[4,5] with urea, as this amide deactivates hydrogen ions by such complexation[8,9].

The specific effect of acetone was also prominent, and was observed by the formation of complex molecules revealed through the appearance of a red-shifted band at 320 nm for the alkaline solutions. The intensity of the band increased with increase in acetone, and was reversibly interchanged by addition of acid or alkali; the results shown in Fig. 6 demonstrate this effect. In the presence of water, 1,4-dioxane, and ethyl alcohol, alkaline solutions showed a band[10] at 285 nm that, for ethylenediamine[5,10], was at 325 nm. In Fig. 6, these results have been included for ready comparison. Spectral indication was not, however, obtained in the case of urea, and the dramatic action of urea was not observed when thiourea was used instead, proving that the $> C = O$ group is vital.

At constant concentration of alkali and constant temperature, absorbances at 320 nm in acetone–water showed a Beer's law validity with respect to the variation of carbohydrate content. Under precise conditions, then, such a procedure may have potentiality for estimation of simple carbohydrates.

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