STUDY OF D-GLYCERALDEHYDE BY CIRCULAR DICHROISM AND ULTRAVIOLET SPECTROSCOPY*

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The behaviour of D-glyceraldehyde in water, dimethyl sulfoxide, their mixtures and in 1,1,1,3,3,3-hexafluoro-2-propanol was studied by circular dichroism and UV spectroscopy in the 20—80°C temperature range. Fresh-prepared solutions of D-glyceraldehyde exist in a substantial measure in dimeric or oligomeric forms, which passed to a monomeric one. The different character of interaction of solvents with monomeric D-glyceraldehyde is discussed. The bisignate circular dichroic curves are associated with conformational equilibrium of rotamers. The presumption on their spatial arrangement is confronted with the quantum chemical calculation of the rotational strength.

D,L-Glyceraldehyde has, as a crystalline substance in dimeric form, functional groups at the 1,4-dioxane ring in energetically more favourable equatorial positions[1,2]. The syrupy consistence of either D- or L-glyceraldehyde[3] can be rationalized by the inability to form such energetically favourable conformations and their dimeric forms. Since monomerization of trioses and other α-hydroxycarbonyl compounds is a general acid–base catalyzed process[4], one can understand that solvents possessing acid–base properties make this process possible. Processes proceeding by the action of water and other solvents upon D-glyceraldehyde and D-erythrose were studied by circular dichroism (CD) at various temperatures[5]. The less intense positive band at 330 nm was ascribed to the unsolvated, the more intense negative one at 290 nm to the solvated form of D-glyceraldehyde. The intensities of both bands rose with the increase of temperature. They decrease at cooling; nevertheless, they did not reach the original value. Since there is nothing known about the fact that hydroxyl groups absorb at such a long wavelength as anticipated for the hydrated form of D-glyceraldehyde[5], this conclusion has been considered as dubious[6]. Compared were also absorption spectra and CD data of D-glyceraldehyde with those of D-fructose and derivatives thereof[7,8].

As seen, only fundamental data concerning the behaviour of D-glyceraldehyde in the employed solvents have been obtained. We tried to get experimental data enabling to throw more light on the interactions of D-glyceraldehyde with solvents of different character.

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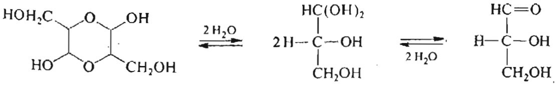
EXPERIMENTAL

D(+)-Glyceraldehyde (~90% syrup, Koch-Light Laboratories) was measured in aqueous solution. In addition to redistilled water, dimethyl sulfoxide (Fluka) and 1,1,1,3,3,3-hexafluoro-2-propanol (Uvasol, Merck) were used as solvents for UV spectroscopy. The non-aqueous solutions were dried with the molecular sieve Potasit 3 (Dimitrov Chemical Works, Bratislava).

The UV absorption spectra were measured with a Specord UV-VIS (Zeiss, Jena) spectrophotometer, the CD curves were recorded with a Roussel–Jouan, model 185, dichrograph. Thermostated cells were employed for measurements of UV and CD spectra of 0·1M solution of D-glyceraldehyde in water in the 20—80°C temperature range at 10°C intervals. Time interval between two measurements was 15 min. Since the values at 80°C had an increasing tendency, the solution was left at this temperature till constant spectral parameters were achieved (2 h). After this time the temperature was allowed to drop to 20°C and afterwards to rise up to 80°C with the difference that the time intervals were 10 min. The 0·1M solution of D-glyceraldehyde in dimethyl sulfoxide was measured analogously; the possible moisture in the solvent and water in the aldehyde (the sample contained approx. 10% water) were removed with the molecular sieve for 2 h. In this case the reaction at 80°C lasted 3 h. Measured were also aqueous-dimethyl sulfoxide 1 : 3, 1 : 1 and 3 : 1 solutions of D-glyceraldehyde in the same way as given for aqueous solutions. The procedure with 1,1,1,3,3,3-hexafluoro-2-propanol was identical with that for dimethyl sulfoxide.

RESULTS AND DISCUSSION

The UV and CD spectra of 0·1M D-glyceraldehyde solution in water, dimethyl sulfoxide, their mixtures and in 1,1,1,3,3,3-hexafluoro-2-propanol were time and temperature dependent (Fig. 1). The values of absorbance (*A*) of D-glyceraldehyde in water, dimethyl sulfoxide and their mixtures rose with increasing temperature. The maximum values in water and its mixtures with dimethyl sulfoxide, obtained at 80°C, dropped with decreasing temperature. This decrease did not follow the original dependence and at the same temperatures the absorbances displayed substantially higher values. After a repeated temperature increase the absorbances at the respective temperatures were virtually identical with those of the preceding measurement. Like findings were obtained at the same temperatures. These facts provided a proof of the existence of two equilibrium reactions the first of which was slow, in comparison with the second one. Evidently, a slow monomerization of the dimeric, or oligomeric forms of D-glyceraldehyde and a rapid equilibration between its free and hydrated forms were involved. The equilibrium decomposition of the one of possible dimeric forms is exemplified by equation (*A*).



(*A*)

The concentration decrease of D-glyceraldehyde and the temperature increase result in a shift in favour of the monomeric forms. The increase of temperature noticeably shifted the last equilibrium in favour of the free form of D-glyceraldehyde. We presume that after decomposition of dimeric forms of D-glyceraldehyde virtually only components of the second rapidly establishing equilibrium exist in water and in the mixture of water and dimethyl sulfoxide (equation (*A*)).

Dried dimethyl sulfoxide as solvent also causes an increase in absorbance of D-glyceraldehyde upon elevating the temperature, nevertheless, at 80°C a longer time (3 h) was needed to attain the maximum constant value. This finding indicated that the effect of dimethyl sulfoxide is weaker than that of water. In contrast to aqueous solution, the spectrum of D-glyceraldehyde in dimethyl sulfoxide does not display after monomerization further alteration with temperature (Fig. 1).

This difference consists in the different possibility of influencing D-glyceraldehyde with water or dimethyl sulfoxide. Whereas the nucleophilic attack of water to carbonyl group of D-glyceraldehyde leads to the creation of a spectrally inactive geminal diol at $C_{(1)}$, the effect of dimethyl sulfoxide was reflected in some conformational alterations of the molecule of D-glyceraldehyde only, where the spectral activity of its carbonyl group remained unattacked. The UV spectra of monomeric forms of D-glyceraldehyde in water, dimethyl sulfoxide and their mixtures at 20°C are seen in Fig. 2.

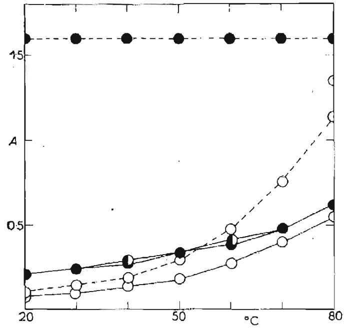


FIG. 1

Dependence of the Absorbance of a Fresh Prepared 0·1M D-Glyceraldehyde Solution on Temperature at 285 nm

In water (———) and dimethyl sulfoxide (-----). ○ Temperature increase, ◐ decrease, ● repeated increase.

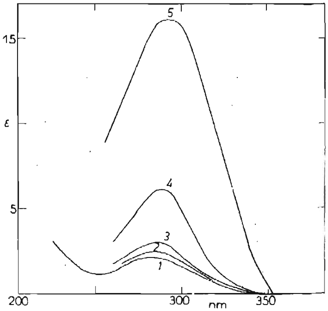


FIG. 2

UV Spectra of Monomeric Forms of D-Glyceraldehyde at 20°C

1 In water, 2 in dimethyl sulfoxide 25%, 3 50%, 4 75%, 5 100%.

The spectrally active moiety of D-glyceraldehyde in water is the smallest one and grows with the increasing concentration of dimethyl sulfoxide. The ratio of hydrated and not hydrated forms of D-glyceraldehyde, or the corresponding equilibrium constant at a certain temperature can be estimated from the real value of the molar absorption coefficient of D-glyceraldehyde in pure dimethyl sulfoxide ($\varepsilon = 16$) and the apparent values measured in water and in mixtures with dimethyl sulfoxide providing that the values of molar absorption coefficients are equal in water and in dimethyl sulfoxide. The same value of the molar absorption coefficient found for the aqueous acetone ($\varepsilon = 16$) backed the correctness of this presumtion[7]. It is evident that differences in the values of spectra (Fig. 2) have a decreasing tendency with the temperature increase, since the equilibrium will be shifted in favour of the not hydrated form of D-glyceraldehyde.

D-Glyceraldehyde in 1,1,1,3,3,3-hexafluoro-2-propanol showed a qualitatively identical behaviour as in dimethyl sulfoxide, *i.e.* the values rose with the increase of temperature and at 50°C they reached their maxima regardless of temperature applied, the difference being only in the position of the maximum and the absorption value. The D-glyceraldehyde absorption maxima in 1,1,1,3,3,3-hexafluoro-2-propanol, water and dimethyl sulfoxide were at λ_{max} 272, 283 and 293 nm, respectively, what

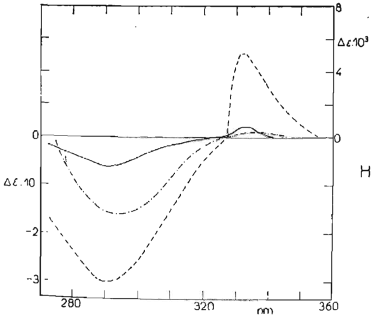


FIG. 3

CD Curves of Monomeric Forms of D-Glyceraldehyde

In water (———) at 20°C, (– – – – –) at 80°C, (–.–.–.–) in dimethyl sulfoxide.

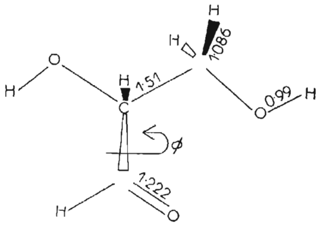


FIG. 4

Molecule of D-Glyceraldehyde with Fundamental Geometric Parameters

In the formulae there are two missing C atoms.

characterizes at the same time the direction of lowering the specific interaction of these solvents with oxygen of the D-glyceraldehyde carbonyl group.

The UV spectra provided information mainly on the chemical behaviour of D-glyceraldehyde, whilst data from the CD spectra threw light at the spatial arrangement of its molecule. All CD spectra showed two dichroic bands in the 280 – 335 nm region of opposite sign belonging to the $n \rightarrow \pi^*$ electronic transition of the carbonyl group. Differences in the CD spectra of D-glyceraldehyde were consistent with those of UV spectra and depended on the solvent, reaction time and temperature. As anticipated, in aqueous solution and in mixtures of water and dimethyl sulfoxide both dichroic bands were temperature dependent, nonetheless in a pure dimethyl sulfoxide virtually no differences were observed in the 20 – 80°C temperature range (Fig. 3). Feeley and coworkers[5] did not solve the irreversibility of the CD spectra of D-glyceraldehyde with temperature, even though they evidenced a considerable decrease of its molecular weight at 37°C in relation to time. The intensity ratios of the long- and short-wave dichroic bands were found to be 1 : 157 for 1,1,1,3,3,3-hexafluoro-2-propanol, 1 : 109 for water and 1 : 5·3 for dimethyl sulfoxide; they did not undergo alteration with temperature. The mentioned relations are evidently associated with the conformational equilibrium of rotamers at the bond of the carbonyl chromophore on the residue of the D-glyceraldehyde molecule. The difference in the order of magnitude in the intensity ratios and their temperature stability led to a presumption that the energy difference among rotational isomers is noticeably great. The increase of the proton-donating ability of the solvent leads to a relatively high increase of the short-wave band with a negative sign. This major band belongs, therefore, to conformers energetically stabilized by solvation with protogenic solvents. They are, however, in a substantial excess in the thermodynamic equilibrium.

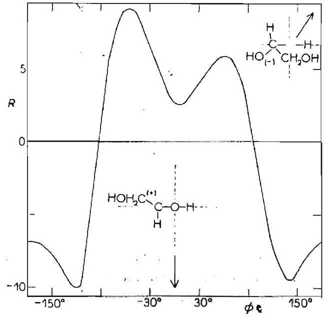


FIG. 5

Dependence of the Rotational Strength R [10^{40} cgs] on Bond Rotation

In the upper formula there is missing O atom.

The spatial arrangement of the respective conformers can theoretically be cleared by a quantum chemical calculation of rotational strength and therefore, the isolated D-glyceraldehyde molecule of fundamental geometric parameters shown in Fig. 4 was investigated. The rotational strength was calculated on the basis of CNDO/2 (Del Bene–Jaffe) wave functions in a gradient formalism by a method already described[9]. The aim of the calculation was to find the relation among the orientation of the carbonyl chromophore, the residue of the molecule and the sign of the Cotton effect. The orientation of the carbonyl group was altered with the rotation around the $C_{(1)}$ to $C_{(2)}$ bond from 0° to ±180° in 10s intervals. The geometry of the dihydroxyethyl residue was constantly oriented in the antiperiplanar position of the hydroxyl groups involved. Geometry shown in Fig. 4, with the orientation of the carbonyl group plane perpendicular to the $C_{(2)}$-bond was the starting point of rotation. Fig. 5 displays the relationship of the calculated rotational strengths on the rotation around the bond. The overall course revealed the range of the positive Cotton effect sign to be $\varphi \sim 0° \pm \pm 90°$ and that of the negative Cotton effect $\varphi \sim 180° \pm 90°$. The octant projections for $\varphi = 0°$ and $\varphi = 180°$, in accordance with the octant rule of the carbonyl chromophore[10], are given just for illustration. The calculation of the rotational strength of the isolated molecule provided evidence that both dichroic bands of opposite sign belong to the conformational equilibrium of the rotational isomers in the molecule of D-glyceraldehyde. The found conformational regions shall also be valid for conformers in solution.

REFERENCES

1. Hall L. D.: Carbohyd. Res. *4*, 429 (1967).
2. Gardiner D.: Carbohyd. Res. *2*, 234 (1966).
3. Baer E., Fischer H. O. L.: J. Amer. Chem. Soc. *61*, 761 (1939).
4. Bell R. P., Baughan E. C.: J. Chem. Soc. *1937*, 1947.
5. Feeley T. M., Hargreaves M. K., Marshall D. L.: Tetrahedron Lett. *1968*, 4831.
6. Maier G. D., Kusiak J. W., Bailey J. M.: Carbohyd. Res. *53*, 1 (1977).
7. Avigad G., Englard S., Listowsky I.: Carbohyd. Res. *14*, 365 (1970).
8. Swenson C. A., Barker R.: Biochemistry *10*, 3151 (1971).
9. Maloň P., Bystrický S., Bláha K.: This Journal *43*, 781 (1978).
10. Moffit W., Woodward R. B., Moscowitz A., Klyne W., Djerassi C.: J. Amer. Chem. Soc. *83*, 4013 (1961).

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