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THE CIRCULAR DICHROISM OF SOME α-HYDROXYALDEHYDES

T. M. Feeley, M. K. Hargreaves and D. L. Marshall
Department of Chemistry, West Ham College of Technology,
London, E.15.

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The chemistry of the α-hydroxycarbonyl compounds, glycolaldehyde, DL-glyceraldehyde and 1,3-dihydroxyacetone has been adequately documented (1,2). The crystalline forms of these compounds are dimeric with the 1,4-dioxan structure and the dimers dissociate into monomeric forms in aqueous solution. Less information is available about D-(+)- and L-(-)-glyceraldehyde. Baer and Fischer (3) have observed that refrigeration of aqueous solutions of D-(+)- or L-(-)-glyceraldehyde substantially reduces the optical rotation. The original rotation can be regenerated by suitable treatment. These authors conclude that the "mutarotation" is not due to racemisation but may be attributed to one or more of three possible equilibria.

We have examined the circular dichroism of D-(+)-glyceraldehyde in a number of solvents (Figures 1, 2; Table I). In aqueous and in methanolic solution at room temperature only one peak at ca. 290 nm. is apparent. With increasing temperature, a second band appears near 330 nm. In aqueous solution buffered at pH 4 and pH 6 the trends are similar; at pH 12 condensation occurs leading to total loss of optical activity. When dioxan, dimethyl sulphoxide or N-methylformamide are employed as solvents both bands are present over the whole temperature range.

The presence of two peaks in the range 280 nm. to 330 nm. on the dichrogram of a compound containing only a carbonyl chromophore may be interpreted (4, 5, 6) as involving an equilibrium between (a) a solvated and an unsolvated species, (b) an associated and an unassociated molecule, or (c) two conformations. The distinction between these two possibilities will be difficult unless conformational homogeneity is required as in the case of the bridged bicyclics or unless temperature dependent circular dichroism measurements are inconsistent with the solvational equilibrium hypothesis.

In the case of D-(+)-glyceraldehyde, the 330 nm. peak may be assigned to the unsolvated monomeric form and the 290 nm. peak to the solvated species. An inspection of Table I reveals that as the temperature is raised the ellipticity of both bands increases. This may be attributed to the dissociation of the dimer to the solvated and unsolvated monomeric forms. That the dimer is initially present is indicated by molecular weight measurements (Table II); this species dissociated into monomer during the course of several days. However, it is not possible to determine the degree of solvation from the molecular weight determinations. Since we are dealing with an equilibrium between three species, it is understandable that the peak due to the solvated form grows with rise in temperature since its actual concentration increases. At the

Table I

The C.D. of D-(+)-Glyceraldehyde

Solvent, and conc. of solute g./l.	T°C	330 nm. Extremum $\Delta\epsilon \times 10^3$	290 nm. Extremum $\Delta\epsilon \times 10^3$
Water	25	—	-42.8
11.221	31	+0.905	-52.5
	43	+1.51	-108
	61	+3.67	-219
	78	+5.86	-291
	29^x	+1.48	-97
Methanol	22	—	-5.39
27.564	34	+0.991	-5.95
	54	+1.01	-7.6
	25^x	+0.739	-5.91
Dimethyl	25	+3.72	-19.4
Sulphoxide	41	+8.29	-52.8
18.19	60	+14.6	-93.6
	80	+29.0	-184
	90	+43.5	-243
	22^x	+26.8	-200
N-methyl	22	+7.2	-97.9
Formamide	28	+5.8	-97.8
18.76	43	+5.87	-80
	68	yellow decomposing	
Dioxan	22	+1.9	-17.1
3.568	41	+2.9	-30
	59	+4.94	-48.4
	72	+5.52	-49.1
	85	+6.11	-53.9
	25^x	+2.54	-43.1

x After cooling the heated solution for at least 12 hours.

Table II

M.Wt. in Water at 37°C of D-(+)-Glyceraldehyde

Time (days)	Conc. mole/l.	Calcd.M.Wt. / Actual M.Wt.
0	0.102	1.82
3	"	1.33
4	"	1.21
5	"	1.08

Table III

The C.D. of D-(+)-Glyceraldehyde in Water-Dimethyl Sulphoxide Mixture at 22°C

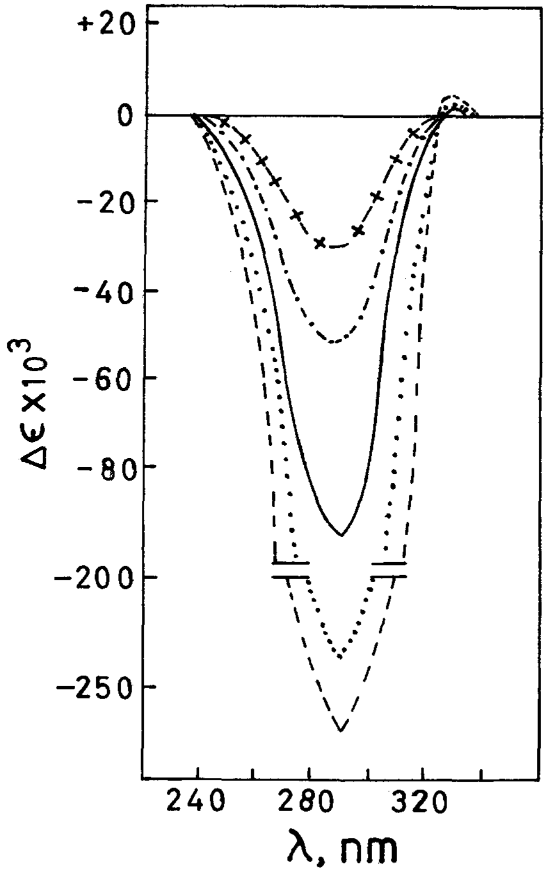
H_2O:DMSO. Ratio Vol./Vol.	Conc. g./l.	330 nm. Extremum $\Delta\epsilon \times 10^3$	290 nm. Extremum $\Delta\epsilon \times 10^3$
2:8	10.67	+1.41	-16.5
4:6	15.82	+0.593	-12.6
6:4	11.75	+0.479	-14.7
8:2	9.8	—	-14

Table IV

The C.D. of D-Erythrose

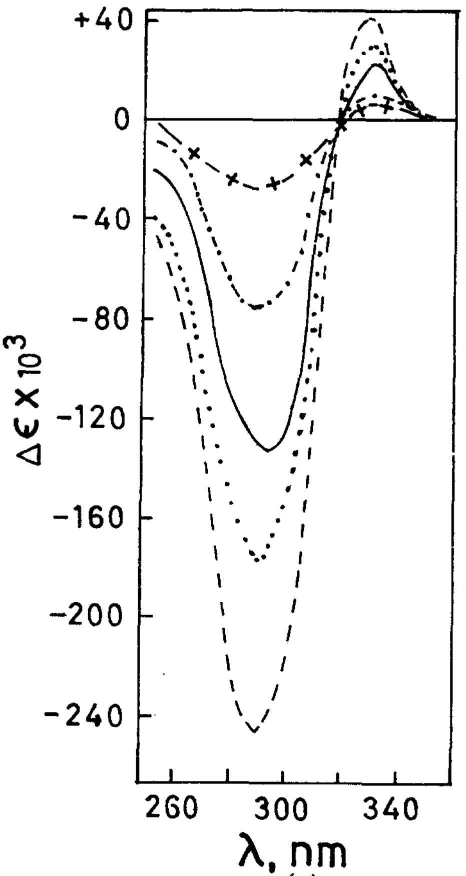
Solvent, and conc. of solute g./l.	T°C	330 nm. Extremum $\Delta\epsilon \times 10^3$	290 nm. Extremum $\Delta\epsilon \times 10^3$
Dimethyl	22	+3.35	-26.8
Sulphoxide	57	+8.62	-93.1
10.754	72	+10.5	-124
	some decomposition		
Water			
10.086	22	—	-41.1
	32	—	-66.2
	54	—	-97.5
	71	—	-129
	75	—	-144
	22^x	—	-71.4

FIG. 1



Circular dichroism of D-(+)-glyceraldehyde in water: -+- (25.5°), -•- (31°), — (43°), ••• (61°) and ---(77°).

FIG. 2



Circular dichroism of D-(+)-glyceraldehyde in DMSO: -+- (25°), -•- (41°), — (60°), ... (80°) and --- (90°).

same time, of course, the population of the free aldehyde increases.

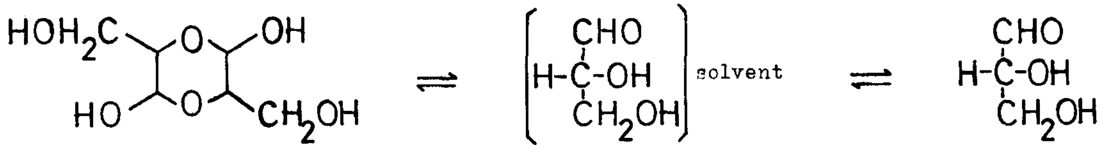


Table I, also, shows that on cooling heated solutions of D-(+)-glyceraldehyde, the value of the ellipticity does not return to its original point. Furthermore, unheated solutions on standing display increased circular dichroism with time; the exact position of the equilibrium has not been determined. The circular dichroism of D-(+)-glyceraldehyde in water-dimethyl sulphoxide mixtures is summarised in Table III. It may be observed that as the concentration of water is increased, the ellipticity of the longer wavelength band decreases, apparently due to the complete solvation of the free monomer. It is well known (7) that aldehydes are strongly hydrated in aqueous solutions. The behaviour of D-(+)-glyceraldehyde in mixed solvents supports the view that the longer wavelength band is not due to a decomposition product. The circular dichroism of synthetic L-(-)-glyceraldehyde gives mirror image results as is to be expected.

Table IV demonstrates that the circular dichroism of D-erythrose in aqueous solution is characterised by a single peak, whereas in dimethyl sulphoxide solution two peaks are present. These preliminary observations are indicative of a solvational equilibrium. However, since in dimethyl sulphoxide solution both bands increase in intensity upon elevation of temperature, it appears that a form other than solvated or unsolvated monomer is present. Work is in progress to determine its nature.

In conclusion, although as in other literature (4, 5, 6) we use the terms solvated and unsolvated monomer, we do so with some reservation, since an equilibrium between two differently solvated species cannot be excluded.

Experimental. Circular dichroism measurements were carried out on a Roussel-Jouan Dichrograph. Molecular weight determinations were performed on a Mechrolab Osmometer, Model 301A. D-(+)-glyceraldehyde was purchased from Koch-Light Laboratories. L-(-)-glyceraldehyde was obtained from Fluka Ltd. We found that some samples of D-(+)-glyceraldehyde from other sources had properties inconsistent with literature values and therefore had different circular dichroic properties.

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