OPTICAL ACTIVITY OF D-GLYCERALDEHYDE IN AQUEOUS SOLUTIONS

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In dilute aqueous solutions, D-glyceraldehyde exists both in the free and hydrated monomeric forms; the equilibrium between them depends on the temperature. The specific rotation of the equilibrium mixture was measured polarimetrically in the temperature range from 20 to 80°C, the concentrations of both forms being determined by ^1H NMR spectroscopy. From these data, the specific rotations of both forms of D-glyceraldehyde in the indicated temperature range were calculated.

The original idea of Fischer about classification of optically active organic compounds[1] was modified by Rosanoff[2,3] so that D(+)-glyceraldehyde was proposed as a better reference model than D(+)-glucose. It is considered a lucky circumstance that the configuration of D(+)-glucose and that of the dextrorotatory glyceraldehyde correspond to reality as was proved experimentally by Bijvoet and coworkers[4]. The absolute configuration of D-glucose and D-glyceraldehyde in Fischer's projection was ascribed to the optical isomer that showed dextrorotation in aqueous solutions. It is known that D-glyceraldehyde exists in various forms in aqueous solutions, each of which contributing to the resulting optical rotation. For example, the observed decrease of the absolute values of the optical rotation of D- and L-glyceraldehyde in aqueous solutions at a decreased temperature was attributed[5] to some reversible chemical changes. Angyal and Wheen[6] showed by ^1H NMR spectrometry that DL-glyceraldehyde in a syrupy state exists in dimeric forms of the type of 1,3-dioxolane and 1,3- or 1,4-dioxane, which in aqueous solutions are in equilibrium with its free and hydrated monomeric forms.

With pure enantiomers of glyceraldehyde, it is possible to study the mentioned equilibria in aqueous solutions not only by ^1H NMR spectrometry[6] but also by using the spectra of circular dichroism[7] and polarimetry. Thus, important data about this principal monosaccharide have been obtained.

EXPERIMENTAL

Apparatus. ^1H NMR spectra of 0·1M D-glyceraldehyde in ^2H_2O were recorded on an FT NMR Jeol FX-100 spectrometer at 20—80°C. The optical rotation values of the solutions in H_2O

were measured at the wave lengths of 589, 546, and 436 nm on a Perkin-Elmer 141 type polarimeter. For comparative purposes, the optical rotation of 0·01M D-glyceraldehyde in H_2O and 0·1M D-glyceraldehyde in ^2H_2O was measured at 589 nm.

Chemicals. D(+)-Glyceraldehyde (Koch-Light Laboratories) was in the form of a syrupy 90% solution in water, $[\alpha]_D^{20} = 12 \pm 2°$ (c 2 in H_2O). Heavy water for NMR spectroscopy was from Merck.

Procedures. Optical rotation values were measured in solutions of D-glyceraldehyde both freshly prepared and stored for 24 h at 50°C. ^1H NMR spectra were recorded with the use of solutions in ^2H_2O stored at the conditions indicated.

Calculations. The concentration ratio of the free and hydrated form of D-glyceraldehyde was determined from ^1H NMR spectra so that the sum of the integrated areas of both signals at each temperature was considered equal to 100% of the total concentration. The ratio of the found concentrations of the free, $[GA]_{exp}$, and hydrated, $[GAH]_{exp}$, forms of D-glyceraldehyde led to experimental values of the equilibrium constant of dehydration, $K_{exp} = [GA]_{exp}/[GAH]_{exp}$, for each temperature. From the linear dependence of log K_{exp} on the reciprocal absolute temperature, evaluated by the least squares method, the values of the reaction enthalpy, ΔH, and entropy, ΔS, for dehydration of D-glyceraldehyde were calculated. These served in turn to calculate the equilibrium constant (K_{calc}) and concentrations of the both forms, $[GA]_{calc}$ and $[GAH]_{calc}$. Whereas ^1H NMR spectrometry enabled us to determine the concentrations of both forms of D-glyceraldehyde, the measured optical rotation values led only to the specific rotations of the mixtures. These were calculated from the equation $[\alpha]_\lambda^t = 100\alpha/lc$, where c denotes concentration in g per 100 ml of solution. The volume change of the solution with the temperature was accounted for by the equation $\alpha_\lambda^{t_0} = \alpha_\lambda^t[1 + \beta(t - t_0)]$, where $t_0 = 20°C$ (reference temperature), t is the temperature of the measurement, and β coefficient of volume expansion of the solution[8].

Experimental data obtained from ^1H NMR spectrometry and polarimetry were sufficient to calculate the specific rotations of both forms of D-glyceraldehyde at each temperature. Since the effect of the temperature on the optical rotation[8] is more important than that of volume changes, it would be necessary to calculate four unknowns, namely both specific rotations and their temperature coefficients. However, the solution of four equations corresponding to the measurements at four different temperatures did not yield reliable results. Therefore, we considered the specific optical rotations of the both forms constant in a given temperature interval to obtain a system of two equations

$$[\alpha]_f\, c_f^{t_1} + [\alpha]_h\, c_h^{t_1} = \alpha^{t_1}\,, \tag{1}$$
$$[\alpha]_f\, c_f^{t_2} + [\alpha]_h\, c_h^{t_2} = \alpha^{t_2}\,,$$

where α^{t_1} and α^{t_2} are the measured optical rotations of the mixture at two temperatures chosen, t_1 and t_2, and c with sub- and superscripts denote relative concentrations of the both forms at these temperatures. The chosen temperature differences were 20, 30, and 40°C, the obtained values of the specific optical rotations, $[\alpha]_f$ and $[\alpha]_h$, being ascribed to the mean temperature. Thus, in the temperature intervals 20—40°C, 30—50°C, 40—60°C, ..., the calculated values were ascribed to 30, 40, 50, ... °C.

RESULTS AND DISCUSSION

Our polarimetric and ^1H NMR spectrometric measurements substantiate the slow monomerization of D-glyceraldehyde and the rapid equilibration between its free and hydrated forms, which was proved already by UV spectrometry and circular dichroism[7]. The optical rotation of a freshly prepared aqueous solution of 0·1M D-glyceraldehyde changes not only with the temperature but also with the time, the time of attainment of equilibrium rotation values becoming shorter with increasing temperature. When the solution temperature is increased at 10°C steps at 10 min intervals from 20 to 80°C, the specific rotation changes from about +15° to −15° at 80°C (Fig. 1). If the solution temperature is kept at 80°C, the equilibrium optical rotation value is attained during 30 min. After subsequent lowering of the temperature to 20°C and increasing it again, time-independent optical rotation values were obtained. Their slow changes in freshly prepared D-glyceraldehyde solutions with the time at constant temperature are evidence for monomerization of the dimers[6]. The rapid equilibration of the optical rotation at each temperature, on the other hand, sugests that the monomerization process has been finished and is in accord with the mobile equilibrium between the free and hydrated forms[7]. With the monomer of D-glyceraldehyde, which was obtained by keeping its aqueous solution at 50°C for 24 h, reversible and only temperature-dependent optical rotation values of the mixture of the both forms were obtained. The specific rotations of aqueous solutions of D-glyceraldehyde at three wavelengths and at various temperatures are summarized

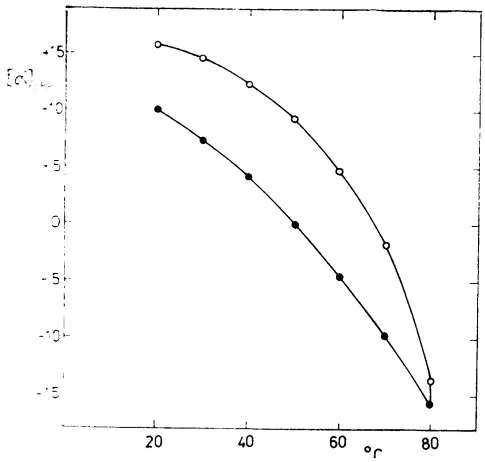

FIG. 1

Dependence of specific rotation of freshly prepared aqueous solution of 0·1M D-glyceraldehyde on increasing (○) and mean value of decreasing and again increasing temperature (●)

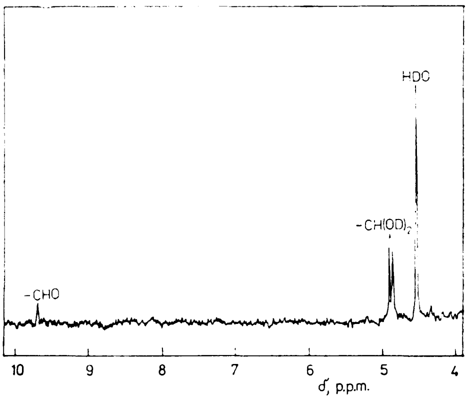

FIG. 2

^{1}H NMR spectrum of 0·1M D-glyceraldehyde in ^2H_2O at 40°C recorded after keeping the solution for 24 h at 50°C in Table I. The values at each temperature are averages from two measurements during increasing and decreasing temperature in the interval 20–80°C and are corrected for the volume change of water with the temperature[8]. The values measured at both concentrations, 0·01 and 0·1 mol/l, are practically the same, evidence that even the more concentrated solution contains in substance only the monomeric form. Practically the same values of optical rotation of D-glyceraldehyde were obtained both in ordinary and heavy water, which enabled us to calculate the specific rotations of both forms in ordinary water from their concentrations determined by the ^{1}H NMR method in heavy water.

Similarly to the case of DL-glyceraldehyde[6], we made use of the difference in the magnetic resonance adsorptions of the H 1 proton of the free and hydrated form of D-glyceraldehyde to determine their ratio in heavy water at the given temperatures. Since in the case of a single enantiomer (D-glyceraldehyde) the possible number of dimers is lower than with the racemic DL-glyceraldehyde[6], the concentration used was much lower, and the spectra were recorded only after 24 h of monomerization at 50°C, only an equilibrium mixture of the free and hydrated forms was found in solution. This is documented by Fig. 2. In the spectrum at lower intensities of the external magnetic field, besides the signal of H^2HO only signals of the dublet of the hydrated form of D-glyceraldehyde at $\delta = 4{\cdot}92$ with $J_{1,2} = 4{\cdot}5$ Hz and the singlet of the aldehydic hydrogen at $\delta = 9{\cdot}65$ are observable. In the case of DL-glyceraldehyde under different conditions, the spectrum shows, besides the mentioned signals, also those corresponding to the dimeric forms[6].

The experimental and calculated relative concentrations of the free and hydrated forms of D-glyceraldehyde and the corresponding equilibrium constants are given

TABLE I

Specific rotations of aqueous solutions of D-glyceraldehyde

Temperature °C	0·1 mol l^{-1}, H_2O			0·01 mol l^{-1}, H_2O	0·1 mol l^{-1}, ^2H_2O
	λ_{589}	λ_{546}	λ_{436}	λ_{589}	λ_{589}
20	9·9	11·6	16·1	10·0	10·2
30	7·2	8·2	9·5	7·9	7·3
40	3·9	4·1	1·0	4·5	4·2
50	0·0	− 0·8	− 9·0	0·0	0·0
60	− 4·5	− 6·5	−20·5	− 4·5	− 4·6
70	− 9·6	−12·7	−33·4	−10·2	− 9·7
80	−15·8	−20·3	−48·4	—	−15·7

in Table II. The reaction enthalpy and entropy for dehydration of the hydrated form were determined from the dependence of log K on $1/T$ by the least squares method as $\Delta H = 32{\cdot}6\ \text{kJ mol}^{-1}$ and $\Delta S = 82{\cdot}0\ \text{J K}^{-1}\ \text{mol}^{-1}$.

The experimental specific rotations of the mixture of both forms in aqueous solution (Table I) and their calculated relative concentrations (Table II) were used in calculating the mean optical rotations of both forms (Table III).

TABLE II

Experimental and calculated relative concentrations of free and hydrated forms (%) and equilibrium constants of dehydration for 0·1M D-glyceraldehyde in ^2H_2O

Temperature °C	$[GA]_{exp}$	$[GAH]_{exp}$	K_{exp}	$[GA]_{calc}$	$[GAH]_{calc}$	K_{calc}
20	3·3	96·7	0·03	2·9	97·1	0·03
30	4·1	95·9	0·04	4·4	95·6	0·05
40	6·9	93·1	0·07	6·6	93·4	0·07
50	11·0	89·0	0·12	9·1	90·9	0·10
60	14·6	85·4	0·17	13·0	87·1	0·15
70	16·4	83·7	0·20	17·5	8·25	0·221
80	20·9	79·1	0·26	22·4	77·6	0·29

TABLE III

Calculated mean specific rotations of free and hydrated forms of D-glyceraldehyde in aqueous solution at three wave lengths

Temperature °C	$[\lambda]_{589}$		$[\lambda]_{546}$		$[\lambda]_{436}$	
	$[\alpha]_f$	$[\alpha]_h$	$[\alpha]_f$	$[\alpha]_h$	$[\alpha]_f$	$[\alpha]_h$
30	−147	14·6	−184	17·4	−380	27·9
35	−144	14·5	−181	17·3	−374	27·7
40	−139	14·0	−167	16·8	−355	26·6
45	−124	13·3	−157	15·8	−326	24·9
50	−118	12·8	−149	15·2	−311	23·8
55	−113	12·1	−141	14·3	−294	21·8
60	−109	11·4	−136	13·3	−283	19·7
65	−108	10·8	−134	12·6	−278·	18·1
70	−108	10·8	−133	12·3	−277	17·6

It follows from the results that the free (nonhydrated) form of D-glyceraldehyde in aqueous solutions is laevorotatory and its hydrated form is dextrorotatory. The specific rotations of D-glyceraldehyde in water given in the literature are the effective values of the rotations of all dimeric and both monomeric forms, the ratio of which depends on the concentration of D-glyceraldehyde, temperature, and time elapsed from the preparation of the solution. The laevorotation of the free form proved in aqueous solutions is in formal agreement with the rotations of the closely related acids with the same configuration, namely D(−)-glyceric and D(−)-lactic acid.

It can be concluded that relations between optical rotation and structure of compounds may often be complicated by the circumstance that the optical activities of the individual compounds in the system investigated are unknown. The case under study suggests that the assumption of Rosanoff[2] that D-glyceraldehyde in aqueous solutions is dextrorotatory and L-glyceraldehyde laevorotatory refers not to the free but to the hydrated forms of these compounds.

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