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A ^{1}H and ^{13}C NMR and UV Study of the State of Hydroxyacetone in Aqueous Solutions

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Abstract—The state of hydroxyacetone in neutral aqueous solutions was studied by ^{1}H and ^{13}C NMR and UV spectroscopy. In the concentration range 0.1–1.41 M, 96–98% of hydroxyacetone exists in the carbonyl form. The content of the hydrated form of hydroxyacetone is 2–4%. No dimeric and polymeric species were detected.

The carbonyl group in aldehydes is highly reactive toward nucleophilic agents. In particular, in aqueous solutions a dynamic equilibrium is attained between the hydrated and free carbonyl compounds. The equilibria between various molecular species and the dynamics of their attainment in aqueous solutions of aliphatic aldehydes, ketones, and some of their derivatives have been studied fairly comprehensively [1–14].

A specific feature of hydroxy carbonyl compounds is the presence of an internal nucleophile, hydroxy group. Therefore, in aqueous solutions of such compounds, there are actually three types of nucleophiles competing for the carbonyl group: external (water and the hydroxy group of a second molecule) and internal (hydroxy group of the same molecule, in cases when an unstrained five- or six-membered ring can be formed) [15–23]. This gives rise to complex equilibria in aqueous solutions, and the solution composition should be studied in each particular case. For example, studies of aqueous solutions of hydroxy aldehydes (glycolaldehyde; *D,L*-glycerinaldehyde) and hydroxy ketones (dihydroxyacetone) revealed formation of various cyclic structures along with the free and hydrated carbonyl species [17–22]. The behavior of hydroxyacetone in aqueous solutions may also be complex.

Studies of the state of compounds in solutions acquire particular importance as applied to biological systems. Hydroxyacetone is the product of radical fragmentation of some lipids of cell membranes; therefore, it attracts our attention. It was shown previously that the reactivity of hydroxy carbonyl compounds in aqueous solutions depends on their structure and can be different for different forms. For example, aldehydes in the carbonyl form rapidly react with hydrated electron but virtually do not react with it when occurring in the hydrated or hemiacetal form [24–26]. Since an equilibrium solution contains all the forms of a carbonyl compound, the reactivity of such a system will depend not only on the content of various species but also on the rates of their mutual transformation. In studies of the homolytic transformations of hydroxyacetone molecules in aqueous solutions, it is necessary to know the composition of the equilibrium mixture, so as to gain insight into the structure of possible radical species and their transformation pathways. Therefore, we performed this study aimed at elucidating the state of hydroxyacetone in aqueous solutions by spectroscopic methods.

Application of UV spectroscopy to studies of aqueous solutions of carbonyl compounds is based on the light absorption in the range 270–290 nm by molecules containing a free carbonyl group, whereas the hydrated and hemiacetal species do not absorb in this range. Hence, comparison of the molar extinction coefficients of hydroxyacetone in aqueous solution and in an aprotic solvent allows evaluation of the content of its carbonyl form in the equilibrium solution, and monitoring of the absorption in time furnishes information on the dynamics of attainment of the equilibrium. As aprotic solvent we chose DMSO, since the isomerization rate of the simplest hydroxy carbonyl compounds (glycolaldehyde, dihydroxyacetone) in this solvent is low [16, 21–23], and the solvent itself does not interfere with monitoring of the absorption at 270–290 nm. Figure 1 shows the UV spectra of solutions of hydroxyacetone in DMSO and water of various concentrations. The absorption maximum in DMSO is about 274 nm, and it shifts toward shorter wavelengths in aqueous solutions. The concentration dependence of the optical density of hydroxyacetone solutions in both water and DMSO follows

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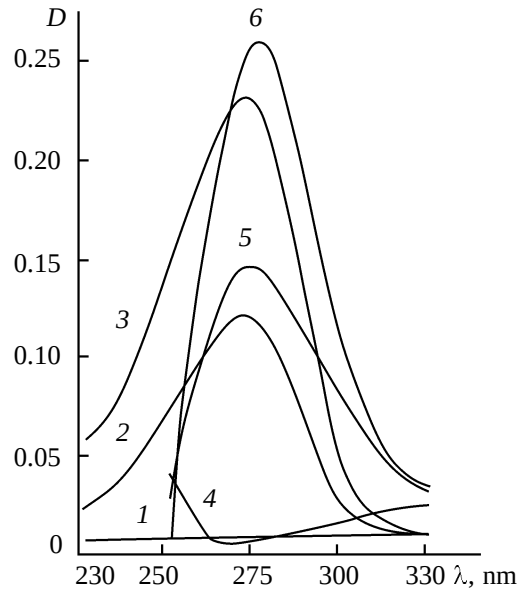


Fig. 1. UV absorption spectra of solutions of hydroxyacetone in (*1–3*) water and (*4–6*) dimethyl sulfoxide. Hydroxyacetone concentration, M: (*1*, *4*) 0, (*2*) 4.9×10^{-2}, (*3*) 9.9×10^{-2}, (*5*) 6.24×10^{-2}, and (*6*) 1.25×10^{-1}.

the Bouguer–Lambert–Beer law; the molar extinction coefficients are given in Table 1.

We found that the carbonyl absorption of a freshly prepared solution of hydroxyacetone in DMSO does not change in time. This means that either the equilibrium is attained very fast, or the carbonyl form is the only form of the compound in solution. Since isomerization and monomerization of dimeric species of hydroxy carbonyl compounds in this solvent were observed experimentally [16, 21–23], we concluded that such species were absent from the very beginning. Hence, the observed absorption apparently belongs to the single species, monomeric carbonyl form of hydroxyacetone, and the molar extinction coefficient of this species is 22.7 ± 0.8 l mol^{-1} cm^{-1} (Table 1).

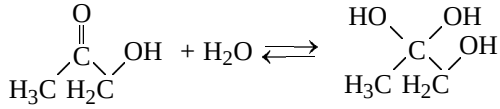
Table 1. Spectral characteristics of solutions of hydroxyacetone in water and dimethyl sulfoxide

Solvent	Molar extinction coefficient, l mol^{-1} cm^{-1}	λ, nm
DMSO	20.7 ± 1.4	274.7
	24.0 ± 1.3	273.9
	23.5 ± 1.6	272.5
Average	22.7 ± 0.8	273.7
H_2O	22.3 ± 0.7	269.5
	25.0 ± 1.6	269.5
	20.2 ± 0.9	269.5
Average	21.9 ± 0.5	269.5

In aqueous solutions of hydroxyacetone, the optical density did not change in time either; therefore, the absorption in this case was also assigned to the monomeric species. The molar extinction coefficient of hydroxyacetone in aqueous solution is 21.9 ± 0.5 l mol^{-1} cm^{-1}, coinciding within experimental error with that in DMSO. Hydration of the carbonyl group in aqueous solution appreciably decreases the apparent extinction coefficients of carbonyl compounds, because the hydrated species do not absorb in this range [6, 11–13]. Therefore, we can conclude that the content of hydrated hydroxyacetone species in aqueous solution is insignificant.

Rich information on the state of hydroxyacetone in aqueous solutions is furnished by NMR spectroscopy, since this method allows simultaneous monitoring of the existing species and measurement of their concentrations. Figure 2a shows the ^{1}H NMR spectrum of a 0.1 M aqueous solution of hydroxyacetone. Along with the HDO signal, the spectrum contains two strong singlets at 1.92 and 4.15 ppm assignable to the methyl and methylene protons of nonhydrated hydroxyacetone molecules. The ratio of the integral intensities of these signals is 3 : 2 with a high accuracy. In the range of hydroxyacetone concentrations in D_2O from 0.1 to 1.41 M, the spectrum was similar. The ^{1}H NMR spectrum of hydroxyacetone in an aprotic solvent, $CDCl_3$, consists of three singlets at 2.09 (CH_3), 3.27 (OH), and 4.19 ppm (CH_2) (Table 2); their intensity ratio is 3 : 1 : 2. The spectrum does not vary in time and is not altered on adding *p*-toluenesulfonic acid.

Hydration of hydroxyacetone molecules [reaction (1)] results in transformation of the carbonyl group into a *gem*-diol group, affecting the chemical shifts of protons at adjacent carbon atoms:



(1)

For example, the chemical shift of the methylene protons in the hydrated form of glycolaldehyde, $HOCH_2CH(OH)_2$, is 3.25 ppm [19], i.e., the signal is shifted upfield by 1.0–1.1 ppm relative to the nonhydrated species (4.30 ppm). Therefore, it can be expected that the signals of the methylene group in the hydrated form of hydroxyacetone will be located in the range 3.2–3.3 ppm. Indeed, all the spectra contain a weak singlet at 3.25 ppm, assignable to the methylene protons of the hydrated hydroxyacetone

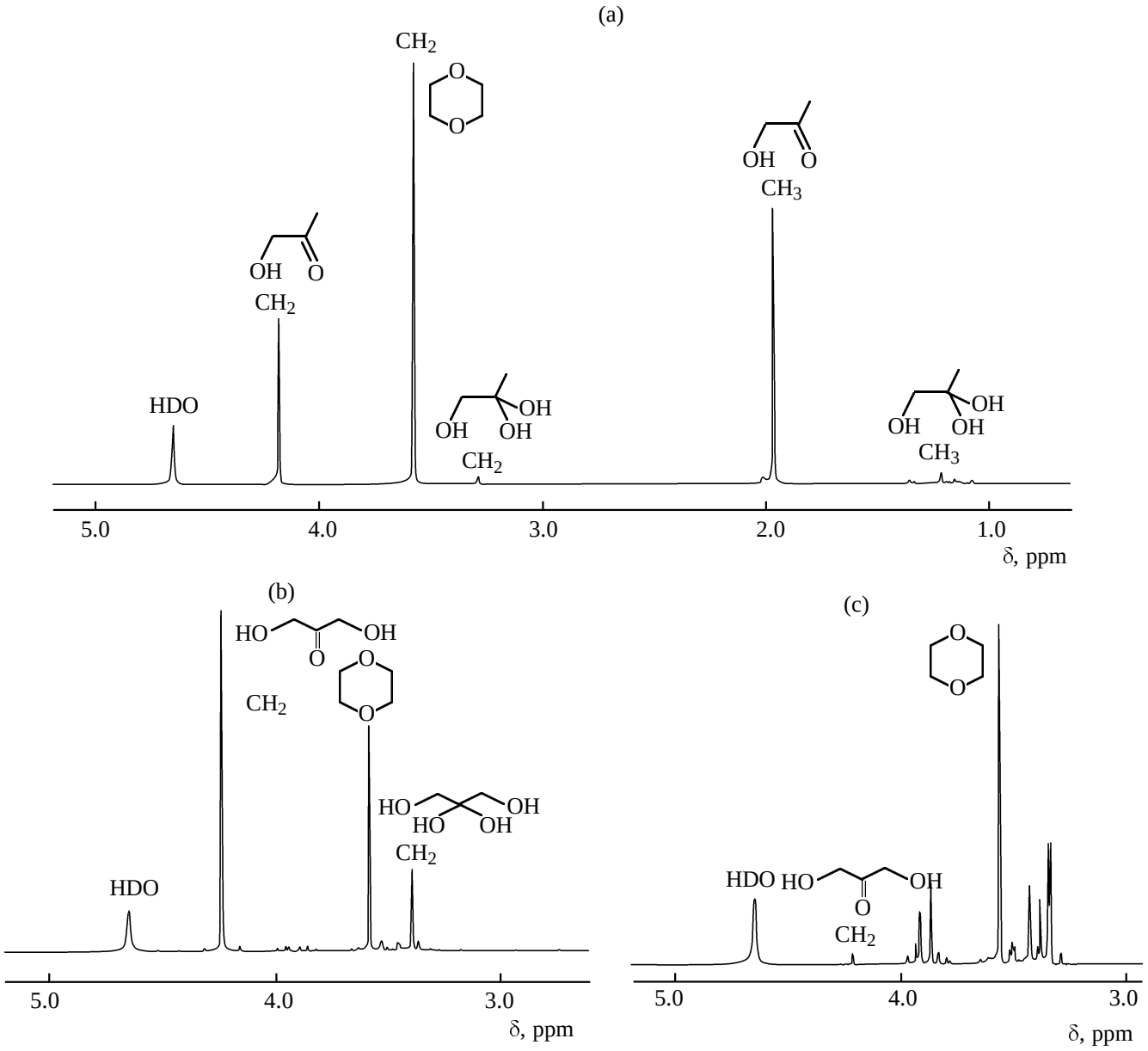


Fig. 2. ^{1}H NMR spectra of (a) hydroxyacetone and (b, c) dihydroxyacetone in D_2O: (a, b) after attainment of the equilibrium and (c) immediately after dissolution. Concentration of hydroxy carbonyl compound, M: (a) 0.1–1.4, (b) 0.1, and (c) 1.0.

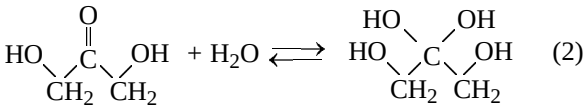
species, and the corresponding weak singlet of methyl protons at 1.21 ppm. The content of the hydrated hydroxyacetone species in aqueous solution, estimated from the ratio of the integral intensities of the corresponding methylene signals, is as low as 2%; this value is consistent with the UV data.

The assignment of the signal at 3.26 ppm to the HO $CH_2C(OH)_2CH_3$ prtons is confirmed by the ^{1}H NMR spectrum of a 0.1 M solution of dihydroxyacetone in D_2O after attainment of the equilibrium (Fig. 2c). Apart from the signals of HDO and 1,4-dioxane (internal reference), the spectrum contains two singlets with the chemical shifts of 4.20 and 3.35 ppm (intensity ratio 3.35 : 1). Since there are virtually no other signals in the spectrum, they should be assigned to the methylene protons of the free and hydrated forms of dihydroxyacetone. The chemical shifts are close to those of the respective signals in the spectrum of hydroxyacetone. The relative content of the hydrated form of dihydroxyacetone in equilibrium 0.1 M solution is 23%; this value is considerably higher than the relative content of the hydrated form of hydroxyacetone and is consistent with data of [23].

Table 2. Signal assignment in the ^1H and ^{13}C NMR spectra of the free and hydrated forms of hydroxyacetone and dihydroxyacetone (0.1 M solutions)

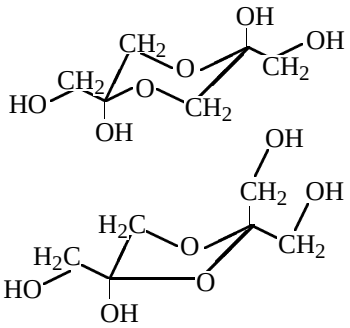
Compound	Solvent	Form	δ, ppm	δ_C, ppm
Hydroxyacetone	D_2O	Free	1.92 s (3H, CH_3), 4.15 s (2H, CH_2)	24.80 (CH_3), 66.50 (CH_2), 212.45 (C=O)
		Hydrated	1.21 s (3H, CH_3), 3.26 s (2H, CH_2)	23.50 (CH_3), 65.00 (CH_2), 95.44 [$C(OH)_2$]
	$CDCl_3$	Free	2.09 s (3H, CH_3), 3.27 br.s (2H, OH), 4.19 s (2H, CH_2)	25.00 (CH_3), 67.00 (CH_2), 210.05 (C=O)
Dihydroxyacetone	D_2O	"	4.26 s (4H, CH_2)	69.32 (CH_2), 214.73 (C=O)
		Hydrated	3.35 s (4H, CH_2)	66.32 (CH_2), 97.80 [$C(OH)_2$]

The ^{13}C NMR spectrum of free hydroxyacetone consists of the signals at 24.80 (CH_3), 66.50 (CH_2), and 212.45 ppm (C=O), and the spectrum of the hydrate consists of the signals at 23.50 (CH_3), 65.00 (CH_2), and 95.44 ppm [$C(OH)_2$] (Table 2). The signal assignment is consistent with data of [27]. The ^{13}C NMR spectrum of an equilibrium 0.1 M solution of dihydroxyacetone in D_2O also contained signals of the free [69.32 (CH_3) and 214.73 ppm (C=O)] and hydrated {66.32 (CH_2) and 97.80 ppm [$C(OH)_2$] forms (Table 2).



(2)

The ^1H NMR spectrum of a 1.0 M solution of dihydroxyacetone contained, along with the above-mentioned singlets, also multiplets at 3.8–4.0 and 3.2–3.6 ppm (Fig. 2c). These signals should be assigned to cyclic hemiacetal dimers [16, 22, 23]:



Since in the spectra of hydroxyacetone solutions such signals are absent even at a concentration as high as 1.4 M, we can conclude that hydroxyacetone exists in solutions exclusively in the monomeric form.

Thus, our experimental data show that hydroxyacetone in aqueous solutions exists as a monomer, with the relative content of the carbonyl and hydrated forms being 96–98 and 2–4%, respectively. The equilibrium is apparently attained within several minutes (during the time of solution preparation).

EXPERIMENTAL

Hydroxyacetone (Merck) was used without additional purification. The main substance content, according to chromatographic analysis, was no less than 98%. Dihydroxyacetone (Merck) was vacuum-dried and stored in an inert atmosphere. Solutions were prepared volumetrically in distilled water or in analytically pure grade dimethyl sulfoxide (DMSO).

The UV spectra were recorded on a Specord M-40 spectrophotometer in 1–10-mm quartz cells. The ^1H and ^{13}C NMR spectra were taken on a Bruker AM-250 spectrometer (working frequency 250 and 62.9 MHz, respectively) at room temperature. The deuterium content in D_2O was 99.7 at. %. The chemical shifts were determined relative to the signals of HDO (δ 4.65 ppm) and 1,4-dioxane (δ 3.65, δ_C 67.45 ppm), and also of $CDCl_3$ (δ 7.26, δ_C 77.00 ppm). The ^{13}C signals were assigned using the DEPT technique: CH and CH_3 (+), CH_2 (–), and C (0).

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