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Abstract

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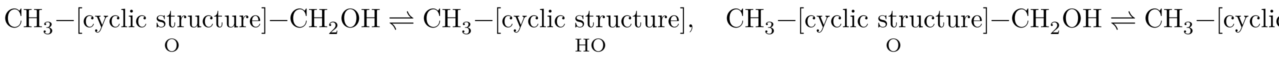
RING-CHAIN TAUTOMERISM

ABSORPTION SPECTRA AND STRUCTURE OF KETO ALCOHOLS IN SOLUTIONS

(Presented by Academician A. N. Nesmeyanov, 30 III 1962)

The existence of ring-chain tautomerism has been proved by physical methods for such compounds as α,β-unsaturated and aromatic γ-keto and γ-aldehydic acids (^{1,2}) and their amides (^{3}), aldehyde alcohols (^{4}), aldoses (^{5}), and halogen anhydrides of some dibasic acids (^{6}). However, the question of the actual structure of a compound with dual reactivity (^{7}) such as γ-acetobutyl alcohol remained open until recently, and in the question of the structure of the simplest representative of the keto alcohols—β-acetopropyl alcohol—uncertainties remained (^{8}). The absorption spectra of solutions of β-acetopropyl alcohol had been studied only in the near infrared region (^{8}), in which it was not possible to observe bands of the cyclic tautomeric form.

In the present work, convincing evidence has been obtained for the ring-chain tautomerism of β-acetopropyl and γ-acetobutyl alcohols, and features of the association of their tautomeric forms have been revealed.



$CH_3-\underset{O}{\text{[cyclic structure]}}-CH_2OH \rightleftharpoons CH_3-\underset{HO}{\text{[cyclic structure]}}$, $CH_3-\underset{O}{\text{[cyclic structure]}}-CH_2OH \rightleftharpoons CH_3-\text{[cycli}$

A detailed study of the actual structure of β-acetopropyl and γ-acetobutyl alcohols is of definite interest, since such keto alcohols may be regarded as models of ketoses (^{9}). To establish the structure and possible tautomeric transformations of β-acetopropyl and γ-acetobutyl alcohols,* we studied, in the region 200-350 mμ, the ultraviolet spectra** of 0.01 M solutions of these compounds and of methyl hexyl ketone as a model compound of the open ketone form, and measured their molar absorption coefficients $\varepsilon_{\max}$ at the maximum of the absorption band associated with the ketone carbonyl group (about 270 mμ).

Table 1

Solvent	Methyl hexyl ketone λ_{max}, mμ	Methyl hexyl ketone ε	Acetopropyl alcohol λ_{max}, mμ	Acetopropyl alcohol ε	Acetopropyl alcohol K_T	Acetobutyl alcohol λ_{max}, mμ	Acetobutyl alcohol ε	Acetobutyl alcohol K_T
Water			268	24.0		270	26.3	
Aqueous alcohol	271	25.5	270	22.5	0.89	270	22.8	0.90
CH_3OH	275	22.3						
C_4H_9OH	276	21.7	275	12.5	0.58	272	18.7	0.86
Dioxane	277	22.2	278	11.5	0.52	275	15.0	0.68
$CHCl_3$	278	22.2	276	9.5	0.43			
CCl_4	281	22.4				275	12.5	0.56
Isooctane	280	22.5	280	9.3	0.42			

* The keto alcohols were synthesized by methods described in the literature ([10,11]) and had constants coinciding with the literature data.

** The ultraviolet spectra were recorded on an SF-4 spectrophotometer. Accuracy of measurements of ε_{max}: $\pm$5%.

The extinction of the keto alcohols proved to be constant over time and close to the extinction of methylhexyl ketone in such polar solvents as water and aqueous alcohol, and significantly lower in the other solvents (Table 1). Since the extinction of methylhexyl ketone is approximately constant in all the solvents used, it may be asserted that the substantial changes in the molar extinction coefficients of β-acetopropyl and γ-acetobutyl alcohols are associated with different positions of the ring-chain tautomeric equilibrium of these keto alcohols in different media. If the extinction of methylhexyl ketone at 270 mμ is taken as equal to the extinction in this same region of the fully open form of the keto alcohols, and the absorption of their cyclic forms is neglected, then the constants of ring-chain tautomeric equilibrium of β-acetopropyl and γ-acetobutyl alcohols in different media can be approximately estimated (Table 1).

Table 2

Substance	K_{max}	K_{max}	K_{max}
Substance	$CHCl_3$	CCl_4	C_8H_{18}
Methylhexyl ketone	372	304	276
Acetopropyl alcohol	212	204	177
Acetobutyl alcohol		152	74

Comparison of the molar extinction coefficients ε and the tautomeric-equilibrium constants K_τ given in Table 1 shows that in water and aqueous alcohol acetopropyl and acetobutyl alcohols are present (completely or predominantly) in the open form, and in the other solvents as a mixture of two forms.

The existence of ring-chain tautomerism of acetopropyl and acetobutyl alcohols was confirmed in the present work by measuring and comparing the molar extinction coefficients K^*_{max} of the keto alcohols and methylhexyl ketone at the maximum of the absorption band at 1710 cm^{-1} (stretching vibrations of C=O).

The results of measurements of the molar extinction coefficients K_{max} of methylhexyl ketone and the keto alcohols in 0.05 M solutions are given in Table 2.

The extinction coefficients K_{max} of β-acetopropyl alcohol in chloroform, carbon tetrachloride, and isooctane, and the extinction coefficients of γ-acetobutyl alcohol in carbon tetrachloride and isooctane, are much lower than the molar extinction coefficients of methylhexyl ketone (Table 2), which confirms the results obtained by the UV-spectroscopic method and proves the existence of ring-chain tautomerism of the keto alcohols.

A study, in the 3800–2000 cm^{-1} region, of the concentration dependence of the intensities of the absorption bands of the keto alcohols and model compounds in carbon tetrachloride also confirmed this conclusion and made it possible to establish certain features of the association of the tautomeric forms of the keto alcohols. δ-Hydroxyvaleraldehyde was used as a model compound for the cyclic form of the keto alcohols. It was shown that the latter exists in carbon tetrachloride and carbon disulfide completely in the cyclic form of α-hydroxytetrahydropyran. In the IR spectra of the indicated solutions of this compound, no noticeable absorption was observed at 1730 cm^{-1} (stretching vibrations of the C=O group of aldehydes), and we found all the frequencies of the skeletal vibrations [12] of tetrahydropyran (1080, 1045, 1035, 1015, 875, and 820 cm^{-1}). n-Butyl alcohol was used as a model compound for the open form.

The concentration dependences of the intensities in the absorption spectra of acetopropyl alcohol, acetobutyl alcohol, δ-hydroxyvaleraldehyde of the aldehyde and n-butyl alcohol were studied* in solutions of decreasing concentration (0.5, 0.1, 0.05, and 0.005 M) under the obligatory condition $C \cdot d =$ const, where C is the concentration of the solution and d is the thickness of the absorbing layer. For 0.5 M solutions of the compounds listed (Fig. 1), an intense and broad absorption band is observed with a maximum at 3425 cm^{-1} for γ-acetobutyl alcohol, 3430 cm^{-1} for β-acetopropyl alcohol, 3400 cm^{-1} for α-oxytetrahydropyran, and 3360 cm^{-1} for n-butyl alcohol (stretching vibrations of OH groups participating in the formation of hydrogen bonds).

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* Measurements of K_{max} were carried out on a sealed, dried IKS-12 instrument at a constant spectral slit width of 9 cm^{-1}. Accuracy of measurements of K_{max} $\pm$3%.

Fig. 1

Figure 1: Fig. 1

Fig. 1. IR spectra of solutions: I –γ-acetobutyl alcohol, II –β-acetopropyl alcohol, III –α-oxytetrahydropyran, IV –n-butyl alcohol. Concentration: a – 0.5 M, b –0.1 M, v –0.05 M, g –0.005 M.

With gradual dilution of the solutions of the ketone alcohols, a noticeable weakening of the absorption intensity in the region of 3400 cm^{-1} is observed (Fig. 1b, v, g), along with the appearance of appreciable absorption in the region of 3500 cm^{-1}. This new absorption band at 3520 cm^{-1} is clearly visible in the 0.005 M solution of γ-acetobutyl alcohol and in the 0.05 M solution of β-acetopropyl alcohol. The absorption of ketone alcohols in the region of 3500 cm^{-1} could be due to stretching vibrations of hydroxyl groups either in dimers of open forms, or in dimers of cyclic forms, or in monomers of open forms with intramolecular hydrogen bonds.

The last two possibilities must be excluded. Indeed, if intramolecular hydrogen bonds were present in the open forms of γ-acetobutyl and β-acetopropyl alcohols, one would expect a decrease in frequency and a broadening of the band of the C=O stretching vibrations of the ketone alcohols in comparison with ketones. Such a decrease in the frequency of the C=O stretching vibrations reaches in some cases 50 cm^{-1} (13).

In studying the absorption of ketone alcohols in the region of 1700 cm^{-1}, no such shift or broadening was found, which indicates the absence of intramolecular hydrogen bonds in β-acetopropyl and γ-acetobutyl alcohols. In addition, in the presence of intramolecular hydro-

···bonds in keto alcohols in the region of the stretching vibrations of the OH groups, there would be a single absorption band corresponding to the OH group participating in the formation of an intramolecular hydrogen bond, the intensity of which would not change upon dilution of the solutions ([14]). Such an absorption band is not observed for the keto alcohols (Fig. 1), which also indicates the absence of intramolecular hydrogen bonds in β-acetopropyl and γ-acetobutyl alcohols. The absorption of keto alcohols in the region of 3500 cm^{-1} is also not associated with the stretching vibrations of hydroxyl groups in dimers of the cyclic forms. From consideration of Fig. 1 it is evident that the formation of dimers does not occur for α-oxytetrahydropyran. In the IR spectra of its solutions, no absorption is observed at 3500 cm^{-1}, which might be expected in the presence of dimeric molecules. From the literature data it is known ([15]) that dimer formation also does not occur in solutions of γ-oxyvaleraldehyde, which has a cyclic structure. The absence of dimers of α-oxytetrahydropyran and γ-oxyvaleraldehyde makes it possible to assume, with justification, the absence of

* The IR spectra of solutions of the listed compounds were recorded by R. B. Teplinskaya on an IKS-2 instrument.

dimers of the cyclic forms of keto alcohols.

In this connection, the absorption band of γ-acetobutyl and β-acetopropyl alcohols at 3520 cm^{-1} may be assigned to the stretching vibrations of hydroxyl groups in dimers of the open forms of these keto alcohols.

Simultaneously with the decrease in intensity of the absorption band in the region of 3400 cm^{-1} and with the appearance, in the case of γ-acetobutyl and β-acetopropyl alcohols, of absorption at 3520 cm^{-1}, the intensity of absorption in the region of 3600 cm^{-1} increases for all four substances upon dilution of the solutions. Narrow absorption bands in this region correspond to stretching vibrations of free hydroxyl groups in monomer molecules ([13]). Since for the stretching vibrations of the OH groups of monomers of primary alcohols an absorption band is observed in the interval 3630-3620 cm^{-1}, the band at 3630 cm^{-1} observed in the spectra of solutions of β-acetopropyl and γ-acetobutyl alcohols can reliably be assigned to the stretching vibrations of the OH groups of monomers of the open form of these keto alcohols. The position of the other absorption band of the keto alcohols (3590 cm^{-1}) proves to be close to the position of the absorption band of α-oxytetrahydropyran in dilute solution (3600 cm^{-1}). In this connection, the band of the keto alcohols at 3590 cm^{-1} may be assigned to the stretching vibrations of OH groups in monomers of their cyclic forms, and the appearance, for β-acetopropyl and γ-acetobutyl alcohols, of two bands in the region of 3600 cm^{-1} may be regarded as confirmation of the presence of two tautomeric forms.

Thus, for β-acetopropyl and γ-acetobutyl alcohols, in contrast to the previously investigated δ-keto acids ([16],[17]), ring-chain tautomerism occurs.

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