

Intramolecular Interaction between Hydroxyl Group and π -Electrons.
II¹⁾. Limitation of the Interaction by Chain-length in
 *ω -Hydroxy-1-alkenes**

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Recent studies on the intermolecular interaction between the hydroxyl group and aromatic nucleus have led some authors to examine the O-H stretching absorption band in the infrared region with compounds which are considered to possess possible intramolecular interaction between the hydroxyl group and aromatic nucleus. The first of these examples was found by Trifan and his co-workers in α -hydroxyethylferrocene and β -phenylethyl alcohol²⁾. However, the phenomenon, splitting of the O-H stretching band, had been known for some years, although those authors who investigated the matter were not quite aware of the cause. That is to say, O-H stretching bands were found by Wulf³⁾ in 2-hydroxybiphenyl, by Fox and Martin⁴⁾ in benzyl alcohol and by Barnard and his collaborators⁵⁾ in cumene α -hydroperoxide.

Quite recently Goldman and Crisler⁶⁾ have also reported the existence of two O-H stretching bands in the first overtone vibrational region in some β -phenylethyl alcohol derivatives, but these examples mentioned here are all limited to the participation of an aromatic nucleus in the interaction as a hydrogen acceptor. Therefore, the authors felt that it was necessary to know whether a conjugated π -electron system, such as an aromatic ring, is really indispensable to this interaction and carefully investigated the O-H stretching absorption of ω -hydroxy-1-alkenes.

Although the only known example of the intermolecular interaction between the hydroxyl group and isolated double bond was the result of Lüttke and Mecke⁷⁾ who found it in cyclohexene and phenol, it turned out to be true that the intramolecular interaction between the hydroxyl group and π -electrons of an isolated double bond does exist, the result being in agreement with that obtained by Baker and Shulgin⁸⁾ who published a paper on the interaction in *o*-propenylphenol and *o*-allylphenol during the preparation of this paper.

Experimental

Measurement and Calculation.—The infrared absorption was measured with a Perkin Elmer Model 112-G Double Pass High Precision Grating Infrared Spectrometer⁹⁾, the spectral slit width being 1.0 cm^{-1} in the region required. Eastman-Kodak spectro grade or redistilled carbon tetrachloride was used as a solvent. A quartz absorption cell 2 cm. in length was used and the concentration of the solution was $0.0025\sim 0.0032\text{ mol./l.}$ at which dilution the association of the solute is negligible. The temperature was $28.0\sim 28.5^\circ\text{C.}$

The integrated intensities of the two bands were calculated according to the equations

$$A = \pi/2 \cdot \Delta\nu_{1/2} \cdot \log_e(I_0/I)_{\max}$$

$$\log_e(I_0/I) = a/[(\nu - \nu_0)^2 + b^2]$$

$$a/b^2 = \log_e(I_0/I)_{\max}$$

$$2b = \Delta\nu_{1/2}$$

given by Ramsay¹⁰⁾, where A is the integrated intensity, $\Delta\nu_{1/2}$ the half-width, ν_0 the amount expressed by wave number at the band center and a and b are parameters. Because of the presence of two bands, four parameters had to be used.

Materials.—Allyl alcohol obtained from a commercial source was purified by redistillation using

1) Part I: M. Ōki, H. Iwamura and Y. Urushibara, *This Bulletin*, **31**, 769 (1958).

* Added in proof: After the submission of this article P. von Schleyer, D. S. Trifan and R. Bacskaï have reported in a brief note that they observed two O-H stretching absorptions with allyl alcohol and 3-buten-1-ol [*J. Am. Chem. Soc.*, **80**, 6691 (1958)].

2) D. S. Trifan, J. L. Weinmann and L. P. Kuhn, *J. Am. Chem. Soc.*, **79**, 6566 (1957).

3) O. R. Wulf, *ibid.*, **58**, 2290 (1936).

4) J. J. Fox and A. E. Martin, *Trans. Faraday Soc.*, **36**, 897 (1940).

5) D. Barnard, K. R. Hargrave and G. M. G. Higgins, *J. Chem. Soc.*, **1956**, 2845.

6) I. M. Goldman and R. O. Crisler, *J. Org. Chem.*, **23**, 751 (1958).

7) W. Lüttke and R. Mecke, *Z. Electrochem.*, **53**, 241 (1949).

8) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958).

9) For calibration of the wave number, see: S. Mizushima et al., *J. Japan. Chem. (Kagaku no Ryoiki)*, Extra Ed., No. 28, Nankodo, Tokyo (1957) p. 1.

10) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

carbon tetrachloride for removal of water¹¹), b.p. 96.0~96.3°C. 3-Buten-1-ol and 5-hexen-1-ol were prepared by action of formaldehyde on the corresponding alkenylmagnesium bromides and the physical constants were as follows: 3-buten-1-ol b.p. 113~113.5°C, n_D^{25} 1.4185 (lit.¹²) b.p. 112~114°C, n_D^{25} 1.4189; 5-hexen-1-ol, b.p. 72.0~72.2°C/19.5mm., n_D^{30} 1.4353 (lit.¹³) b.p. 155.6~156.0°C/718mm., n_D^{30} 1.4364. 4-Penten-1-ol and 10-undecen-1-ol were prepared by lithium aluminum hydride reduction of the corresponding carboxylic acids and the following physical constants were obtained: 4-penten-1-ol, b.p. 63°C/3.0mm., n_D^{25} 1.4292 (lit.¹⁴) n_D^{20} 1.4299; 10-undecen-1-ol, b.p. 95.5~96°C/3.5mm., n_D^{20} 1.4462 (lit.¹⁵) n_D^{19} 1.4506).

Results and Discussion

The actual O-H stretching absorption curves of the alcohols are shown in Fig. 1 and the data of the two bands divided by the Ramsay's equations are given in Table I, in which, for the convenience of the discussion, the bands are named I and II rather than interacted and free.

As is seen from Fig. 1, the only example which showed two distinct bands is 3-buten-1-ol which can undoubtedly be said to possess intramolecular interaction between the hydroxyl group and π -electrons of the double bond.

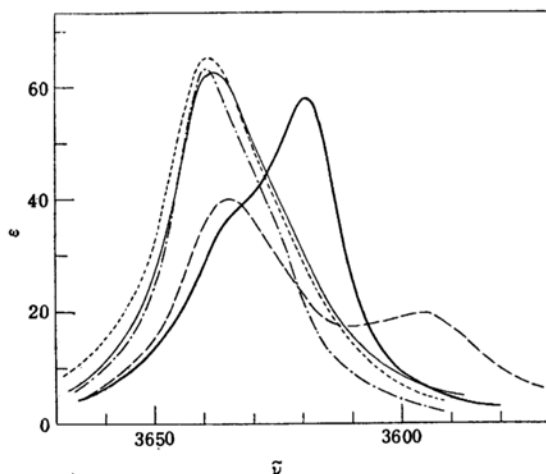


Fig. 1. ν_{O-H} absorption of ω -hydroxy-1-alkenes.

— allyl alcohol, - - - 3-buten-1-ol,
 - - - 4-penten-1-ol, ····· 5-hexen-1-ol,
 - · - · 10-undecen-1-ol

TABLE I. O-H STRETCHING ABSORPTION BANDS OF ω -HYDROXY-1-ALKENES

[CH ₂ =CH(CH ₂) _n OH]					
<i>n</i>		ν_{\max} (cm ⁻¹)	$\Delta\nu_{1/2}$ (cm ⁻¹)	$A \times 10^{-4}$ (mol. ⁻¹ , liter·cm ⁻²)	$\Delta\nu_{\max}$ (cm ⁻¹)
1	I	3619.4	16.4	2.87	15.4
	II	(3634.8)	(23.4)	(2.29)	
2	I	3596.1	32.2	1.93	39.1
	II	3635.2	24.0	3.27	
3	I	(3624.5)	(24.0)	(1.76)	14
	II	3638.3	20.8	4.03	
4	I	(3626.0)	(17.2)	(1.15)	13
	II	3639.2	20.8	4.45	
9	I	(3628.5)	(18.8)	(1.78)	12
	II	3640.0	15.8	2.94	

The lower homolog of 3-buten-1-ol, allyl alcohol, was spectroscopically studied by Flett¹⁶ in its O-H stretching region and reported to have a single band at 3620 cm⁻¹. However, the present authors' result with the instrument of high resolution shows that allyl alcohol possesses two bands at 3619.4 cm⁻¹ and 3634.8 cm⁻¹, the latter corresponding to the normal vibration of aliphatic primary alcohols and is reminiscent of the result obtained by Fox and Martin⁴) with benzyl alcohol. Since this kind of curve for O-H stretching vibration is obtained only with allyl alcohol or benzyl alcohol, the band at ca. 3620 cm⁻¹ may be attributed to the interaction between π -electrons and the hydroxyl group.

Comparison of the curves for allyl alcohol and 3-buten-1-ol reveals that the number of internally interacted molecules is greater in allyl alcohol than in 3-buten-1-ol, provided that the absorption intensity of a molecule is equal in both free and interacted forms. This assumption is based on the fact that the sum of two integrated intensities is almost the same in the two compounds. This phenomenon seems to be rather striking, because it is a common concept that the difference in wave number corresponds to the energy¹⁷), but can be explained in either of the following two ways. Firstly, the interactions occurring in allyl alcohol and in 3-buten-1-ol may be different in nature and, secondly, unfavorable entropy change in 3-buten-1-ol may limit the number of the internally interacted molecules, in spite of the greater stabilization in energy term. Although, as far as the present data are concerned, it is not clear which is the real cause, the accumulated data

11) O. Kamm and C. S. Marvel, "Org. Synth.", Coll. Vol. I. John Wiley & Sons, Inc., New York (1948), p. 43.

12) E. D. Amstutz, *J. Org. Chem.* **9**, 310 (1944).

13) V. P. Gol'mov, *Zhur. Obshchei Khim.*, **22**, 2132 (1952); *Chem. Abstr.*, **48**, 1240 (1954).

14) M. S. Kharash and C. F. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).

15) P. Chuit, F. Boelsing, J. Hausser and G. Malet, *Helv. Chim. Acta*, **9**, 1074 (1926).

16) M. St. C. Flett, *Spectrochim. Acta*, **10**, 210 (1957).

17) See, e.g., R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

in this laboratory suggest that the former is the preferable cause.

Higher homologs of 3-buten-1-ol, 4-penten-1-ol and 5-hexen-1-ol, possess an unsymmetric band, fatter at the smaller wave number side, and the band can be divided into two, assuming that the band is an overlapping of two symmetric bands which are expressed by the Lorentz function. The smaller peaks (band I) at ca. 3625cm^{-1} may be attributed to the presence of the hydroxyl group and π -electrons interaction but the minor peak (band I) also appears in 10-undecen-1-ol in which the intramolecular interaction is improbable in respect of the entropy increase. Moreover, these three curves are quite similar and suggest that the minor peaks do not represent the intermolecular interaction, since it is not plausible to consider that the same extent of intramolecular interaction between the hydroxyl group and π -electrons exists in these three compounds. In other words, this kind of interaction can not be found in higher homologs than 4-penten-1-ol. The origin of the minor peaks (bands I of 4-penten-1-ol, of 5-hexen-1-ol and of 10-undecen-1-ol) will be dealt with in the following paper.

It may seem to be rather strange that the interaction takes place up to 3-buten-1-ol in the homologs studied, in contrast with the finding of Baker and Shulgin who reported the existence of the interaction both in *o*-propenylphenol and *o*-allylphenol, the latter being an analog of 4-penten-1-ol. But the explanation can be given by considering the difference in proton donating ability of phenolic and alcoholic hydroxyl groups and the favorable structure of the phenols in which O-

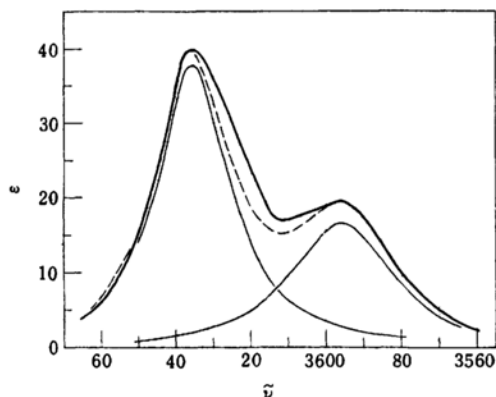


Fig. 2. $\nu_{\text{O-H}}$ absorption of 3-buten-1-ol.

— observed curve
 --- divided bands
 ---- calculated curve

C-C-C bonds are fixed *cis*. The representative cases are under investigation.

It might also be mentioned here that, as shown in Fig. 2, the calculated band area of 3-buten-1-ol does not quite agree with the observed one. Namely, the computed value is always lower than the observed one at the valley of the band for 3-buten-1-ol, while that for the others

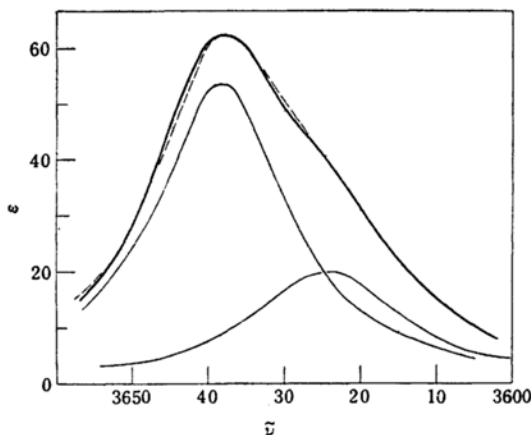


Fig. 3. $\nu_{\text{O-H}}$ absorption of 4-penten-1-ol.

— observed curve
 --- divided bands
 ---- calculated curve

agree, as shown in Fig. 3 (taking 4-penten-1-ol as an example). The cause of the disagreement is unknown but is quite understandable if one considers that another absorption band exists in this compound at about 3626cm^{-1} corresponding to those in the higher homologs.

In closing, the authors would like to mention the terminology of this interaction. Although many authors^{2,6,8}) used "hydrogen bonding", "interaction" is the present authors' choice, since the definition of the hydrogen bonding was discussed at the international symposium¹⁸⁾ on the hydrogen bonding and an agreement that the interaction between a hydrogen donating group and an electron pair of an atom was hydrogen bonding, was reached. The interaction discussed here undoubtedly resembles the hydrogen bonding, but is still distinguishable from the hydrogen bonding because of the participation of the π -electrons of a double bond which are not on the same atom, although they overlap.

Summary

Infrared absorption was measured with

18) See: *Angew. Chem.*, **67**, 755 (1957).

five ω -hydroxy-1-alkenes in the 3μ region, using an instrument of high resolution and the following results were obtained.

1) Intramolecular interaction between the hydroxyl group and π -electrons was found in allyl alcohol and in 3-buten-1-ol.

2) Interactions which occur in allyl alcohol and in 3-buten-1-ol may be of a different kind.

3) Higher homologs also possess two O-H stretching absorption bands but these bands can not be associated with the intramolecular interaction.

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