[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Integrated Intensity of the O–H Stretching Band in Aliphatic Alcohols

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RECEIVED SEPTEMBER 12, 1956

The integrated intensity of the infrared band due to the O–H stretching vibration is determined for a number of aliphatic alcohols in carbon tetrachloride solution. The intensity is very sensitive to variations in the electron-withdrawing or donating properties of the alkyl groups attached to the hydroxyl group, and is highest when the group is most electronegative. The observed results are strongly indicative of a positive sign for the bond moment derivative, $(\partial\mu/\partial r)$, for the O–H bond.

Introduction

Although intensity measurements on series of compounds in solution have been yielding much interesting information,[2,3] very little work has been done on many of the common functional groups. Barrow has measured the intensities of a few aliphatic alcohols in various solvents for the purpose of determining the effect of hydrogen bonding on the intensity of the O–H band.[4] In the present work the intensities of the O–H band for a large number of aliphatic alcohols have been determined in order to assess the sensitivity of this quantity to changes in the electronic properties of the alkyl groups attached to the hydroxyl, and to determine what property of the groups causes the variations.

The intensity of absorption due to a molecular vibration which is infrared active is proportional to the square of the first derivative of the electric moment with respect to the vibration coördinate, $(\partial\mu/\partial r)^2$. For the O–H stretching vibration the hydrogen may be considered as vibrating against a stationary mass which is the rest of the molecule, the vibration coördinate being the O–H bond axis. The group moment of the O–H group, if the contribution of the C–O bond moment is neglected, is made up of three parts: the contribution from the O–H bond due to partial ionic character, the hybridization moment from unshared electron pairs on the oxygen, and the overlap moment of the O–H bond. In considering intensities, however, it is only the changes which occur in the magnitude of these contributions as the O–H bond stretches which are important. The overlap moment is not large, and it is to be expected that changes in its magnitude due to change in the O–H distance will be small. The contribution to the moment from unshared electron pairs on the oxygen is appreciable,[5] but it is unlikely that a motion of the hydrogen atom along the O–H bond axis would cause an appreciable change in the hybridization of the oxygen orbitals, so that the change in hybridization moment is also probably small. It is therefore assumed that the observed intensity is due largely to a change in the O–H bond moment brought about by a change in the degree of ionic character in the bond.

Experimental

Materials.—Propargyl alcohol, 3-butyn-2-ol and 2-methyl-3-butyn-2-ol were obtained from the Farchan Laboratories, Cleveland, Ohio. Cyclopentanol was obtained from Arapahoe Chemical Co., Boulder, Colo., and 2,2,2-trichloroethanol was obtained from K and K Laboratories, Long Island City, N. Y. The remaining compounds were Eastman White Label materials. Each was thoroughly dried and fractionated by use of an efficient packed column. The refractive indices of the purified materials (Table II) were in agreement with accepted literature values in all cases where these were available. No absorption bands attributable to water were observed in the spectra of the alcohols.

Fresh bottles of reagent grade carbon tetrachloride were used without further purification.

Apparatus and Method.—A Perkin-Elmer Model 21 double beam spectrometer with sodium chloride prism was employed. A sodium chloride-window cell of 0.494 mm. thickness, determined by the interference fringe method,[6] was employed. A mechanical slit width of 0.015 mm., corresponding to a spectral slit width of about 6 cm.$^{-1}$, was used. The instrument was operated with the sample cell in the sample beam and nothing in the reference beam. The region of interest was scanned slowly, first with pure solvent in the cell, and then with solution. There was no observable absorption due to solvent at the cell thickness employed. A curve of optical density *vs.* frequency was made up from the data, and the areas under the curve in the interval 75 cm.$^{-1}$ on either side of band maximum determined with an Ott compensating planimeter. The integrated intensity is then calculated from the equation

$$A = \frac{1}{cl}\int_{\nu_0 - 75\ \text{cm.}^{-1}}^{\nu_0 + 75\ \text{cm.}^{-1}} \log (I_0/I)\, d\nu$$

To this value of the intensity must be added a correction for the residual area lying outside the limits of integration.[7] This wing correction is most reliably applied when the shape of the band approximates that of a Lorentz type of curve. In the present case the absorption bands were almost exactly of this shape, and the corrections were accordingly made.

The concentration range employed was from 0.09 to 0.01 *M*, with most of the samples (at least one sample for each alcohol) being about 0.06 *M*. At the higher concentrations there was some evidence of hydrogen bonding, although it did not appear to be extensive. In order to determine whether there would be an appreciable dependence of intensity on concentration, a sample of the alcohol having the most intense band, β-trichloroethanol, was successively diluted in the range 0.0645 to 0.0129 *M*. The results of the measurements on the four samples are shown in Table I. It is seen that there is no regular dependence of the intensity on the concentration. If a concentration dependence were to be found in this case it is expected that the intensity would be highest for the most dilute sample. In any case since the alcohols were all measured in solutions of about the same concentration, any concentration effects which might be present would not affect the relative values appreciably.

At least two samples of each alcohol were measured; if the two values for the correct intensities did not agree to within 0.02 intensity unit,[8] further measurements were made on new samples.

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[8] An intensity unit is defined as 1×10^4 mole^{-1} liter cm.$^{-2}$.

No attempt was made to determine accurately the frequencies of band maxima. Although it is possible to obtain accurate and reproducible absorption curves in this region of the spectrum using sodium chloride optics and a linear wave length drive, the uncertainty in the frequency of band maximum is too large to permit comparisons of one alcohol with another.

Results

The results of the intensity measurements on thirteen aliphatic alcohols are shown in Table II. The first column after the name of the compound lists the observed intensities, A', in units of 1 × 10^4 mole^{-1} liter cm.$^{-2}$; the second lists the corrected intensities, the third lists the half-intensity widths, $\Delta\nu_1/_2$, in units of cm.$^{-1}$. Since the corrections applied to the intensities were of about the same magnitude for all the alcohols, the values of corrected intensities are relatively accurate to within about 0.02 to 0.03 intensity unit. The absolute accuracy of the values is difficult to evaluate, but in view of the symmetrical shape of the bands, the corrected values are probably within 10% of the absolute values.

TABLE I

VARIATION OF INTENSITY WITH CONCENTRATION FOR SOME SAMPLES OF 2,2,2-TRICHLOROETHANOL

Concn., M	Cor. intensity
0.0645	0.92
.0323	.94
.0258	.92
.0129	.91

TABLE II

RESULTS OF THE MEASUREMENT OF THE O–H BAND INTENSITY FOR THIRTEEN ALIPHATIC ALCOHOLS. REFRACTIVE INDICES OF THE PURIFIED MATERIALS ARE ALSO SHOWN

Compound	A'^a	Cor. intensity^a	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	n^{20}D
Methanol	0.45	0.54	39	1.3320
n-Propyl alcohol	.44	.52	40	1.3856
sec-Butyl alcohol	.38	.46	40	1.3968
t-Butyl alcohol	.34	.39	30	1.3870
Cyclopentanol	.44	.50	33	1.4530
Cyclohexanol	.38	.44	34	1.4651
Benzyl alcohol	.54	.66	45	1.5404
Allyl alcohol	.48	.58	42	1.4128
Propargyl alcohol	.59	.69	34	1.4283
3-Butyn-2-ol	.56	.66	36	1.4250
2-Methyl-3-butyn-2-ol	.52	.59	29	1.4212
3-Chloro-1-propanol	.63	.74	38	1.4474
2,2,2-Trichloroethanol	.76	.92	40	1.4850

^{a} In units of 1 × 10^4 mole^{-1} liter cm.$^{-2}$.

Discussion

Examination of the data in Table II reveals that the O–H intensity is strikingly sensitive to structural changes; the ratio of the highest to the lowest intensity is over 2.5. The manner in which it varies with the nature of the alkyl group permits a correlation to be made between the intensity and the electronic properties of the group.

In the series of simple aliphatic alcohols (methanol through *t*-butyl alcohol) the intensity decreases as the electron-donating power of the alkyl group increases, and as the polarizability increases.[9] Successive substitution of methyl groups for hydrogen on the α-carbon atom in propargyl alcohol also results in a decreasing intensity. In the series propargyl, allyl and *n*-propyl alcohols the intensity decreases as the electron-donating power increases and the polarizability decreases. These results indicate that the factor which is largely responsible for the intensity variations is the static inductive effect rather than a polarizability effect which is called into play as the O–H bond stretches. If the polarizability (inductomeric) effect was the determining factor, groups with the largest polarizabilities should give rise to the most intense bands, and this is not observed to be the case. The large increase in intensity which results from substitution of chlorine for hydrogen on the β-carbon atom in *n*-propyl alcohol is an indication of how sensitive the intensity is to the inductive properties of the alkyl group. Another interesting example is afforded by the difference between cyclopentanol and cyclohexanol; the higher value for cyclopentanol is in agreement with the view that the strained ring systems possess a greater electron-withdrawing power than the unstrained systems.[10]

It is interesting to observe that the value of intensity obtained for benzyl alcohol leads to the conclusion that the inductive properties of the phenyl group are closer to those of the ethynyl than to the vinyl linkage, whereas the properties of phenyl and vinyl groups are usually considered to be about the same.[9] It may be that polarizability effects are large enough in the case of the phenyl group to cause a slightly increased value of intensity. The order observed here for the electron-withdrawing power of the ethyl, vinyl, phenyl and ethynyl groups has been attributed by Walsh to the change in hybridization in the carbon orbital which binds the alkyl group to some other group.[11]

A series of simple aliphatic alcohols comparable to that studied here also has been observed by Barrow[4]; a comparison of results is difficult, however, since he did not report the interval of integration, or whether a wing correction had been applied. Francis, using a grating spectrometer of high resolving power, has obtained a value for *n*-propyl alcohol of 0.46, in good agreement with the uncorrected value of 0.44 given here.[12]

There is some question as to whether the sign of $(\partial\mu/\partial r)$ is positive or negative. If its sign were positive, corresponding to greater degree of ionic character as the O–H bond stretches, it is to be expected that for a series of alcohols R–O–H, the intensity would be highest when the group R–O is most electronegative, or when the group R– is most electron-withdrawing. Since this proves to be the case, it appears that the sign is positive. It is assumed in the above argument that the hydrogen atom is at the positive end of the bond dipole; if the hydrogen atom were at the negative end, as suggested by some theoretical work,[5] then the sign of $(\partial\mu/\partial r)$ would be negative by the same argument.

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