

Effect of Pressure on the Frequency of the O—H Band in Butanol Solutions*

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The infrared spectra of dilute solutions of normal butanol have been observed in the 3-micron region at pressures from 10 to 12 000 atmospheres. The sharp "monomeric" O—H band shifts toward lower frequencies as the pressure increases. If we define $\Delta\nu$ as the shift in frequency from its value at one atmosphere and 25°C in each solvent, $\Delta\nu$ at the maximum pressure varies from 11 cm⁻¹ in 2, 3 dimethyl butane to 41 cm⁻¹ in *n*-propyl iodide. The frequency shift is found to be a linear function of the square of the density and the polarizability of solvent bonds, though this latter relationship is not quantitative. The shifts are plausibly explained as due to van der Waals' forces between the O—H bond and the solvent. The pressure causes a large increase in the polymerization of the alcohol, from which the change of volume on polymerization is estimated to be -4.64 cm³/mole in the 1 to 5820 atmosphere range, and -2.47 cm³/mole in the 5820 to 11 330 atmosphere range.

TWO of the older problems of molecular spectroscopy are the shift in the infrared vibration band when a molecule is transferred from the vapor into solution and the effect of hydrogen bonding on the O—H band in solution. In our present study, the effect of pressure to 10 000 atmospheres on the O—H band of *n*-butanol in dilute solutions, we have sought results throwing light on both the foregoing problems.

Several papers¹⁻⁴ serve to define the problem. To summarize: It was observed that the O—H band in alcohols and acids consists of a very sharp peak at the fundamental frequency around 3600 cm⁻¹ and an extremely broad band centered around 3300 cm⁻¹. The relative intensities of the two bands is strongly dependent on concentration, temperature, and the nature of the solvent, as is their exact frequency. Chemical intuition has led to the assignment of the broad, low-frequency band to molecules associated by hydrogen bonding and the sharp band to the free molecules. Attempts to correlate the frequency shifts with macroscopic properties of the solvents have not been very convincing, at least from the standpoint of obtaining an exact mechanistic picture of the cause of the shift. West and Edwards⁵ correlated the frequency shift in HCl with the dielectric constant of the solvent in terms of a continuum theory (Appendix A). Gordy and Stanford⁶ showed that the frequency shift in CH₃OD was independent of the dipole moment of the solvent but correlated nicely with the "tendency of a solvent to acquire protons from a hydroxyl group" as measured by its basicity. Finally, Wulf, Liddel, and Hendricks,⁷ observed the effect of *ortho*-substituents of phenol on

the O—H frequency and noted good correlation with the polarizability of the *ortho*-group.

Our present study represents an effort to extend the scope of observations on the frequency shift in the hydroxyl group. We have compressed various alcohol solutions to 10 to 12 000 atmospheres pressure and have observed the effect of decreasing intermolecular distance on the O—H frequency at densities otherwise unobtainable and at constant temperature.

EXPERIMENTAL PROCEDURE

High-grade commercial compounds were used as solvents with no further purification other than drying over magnesium perchlorate. The alcohols were Eastman "White Label" brands, and these were used without purification.

The concentration of all solutions reported here was $\frac{3}{4}$ volume percent alcohol (with one exception). We chose this concentration for two reasons: (1) A $\frac{3}{4}$ % solution yielded a sharp, intense O—H band with a cell length of 1 to 2 mm. The window separation for all of our runs was in this range. (2) In CS₂ solution, the broad polymer band was plainly visible but not very intense at this concentration. These conditions therefore seemed suitable for making observations on the effect of pressure on the polymer band.

The following criteria governed our choice of solvents: (1) Transparency in the 3 μ region. (2) Ability to remain a liquid at 10 000 atmospheres pressure and room temperature. (3) Noncorrosiveness in contact with the steel bomb. Thus two of the best solvents as tested by conditions (1) and (3), benzene and carbon tetrachloride, were decisively ruled out by condition (2). Toluene represented a compromise, inasmuch as it froze at 8500 atmos. Our final choices were 2, 3, dimethyl butane (2, 3, DMB), CS₂, toluene, *n*-propyl bromide (*n*PrBr), and *n*-propyl iodide (*n*PrI). The objective was to vary the physical and chemical properties of the liquids as much as possible within the limits of our criteria.

The bomb was not thermostatted. The contents were assumed to be at room temperature throughout a run.

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¹ R. M. Badger and S. H. Bauer, J. Chem. Phys. 5, 605, 839 (1937).

² J. J. Fox and A. E. Martin, Proc. Roy. Soc. (London) A162, 419 (1937).

³ Errera, Gaspard, and Sack, J. Chem. Phys. 8, 63 (1940).

⁴ W. Gordy, J. Chem. Phys. 7, 93 (1939); 9, 215 (1941).

⁵ W. West and R. T. Edwards, J. Chem. Phys. 5, 14 (1937).

⁶ W. Gordy and S. C. Stanford, J. Chem. Phys. 8, 170 (1940).

⁷ Wulf, Liddel, and Hendricks, J. Am. Chem. Soc. 58, 2287 (1936).

Since the band position was independent of the time after compression, this condition was at least practically fulfilled. Furthermore, the experiments were carried out in an air conditioned room, in which the day-to-day temperature variation was small.

The details of the high-pressure apparatus are described elsewhere.⁸ We present a schematic drawing, Fig. 1, to show the arrangement of low- and high-pressure ends, ring seals, and windows. The windows are similar to those used previously for high-pressure scintillation counting.⁹ The use of sapphire windows limits this bomb to the spectral region between 4μ and 0.2μ . The high-pressure end was calibrated against the readings on a Bourdon gauge in the low-pressure end by means of a Manganin gauge. The gauge, not in place during spectroscopic runs, was inserted through the bottom plug. The pressures reported are considered accurate to ± 25 atmos.

The spectrometer used was a Perkin-Elmer Model 112. The external optics were replaced by an arrangement of two spherical mirrors allowing an image of the globar source to be focused on the sample in the bomb. Because of the $\frac{1}{4}$ -inch hole at the end of the window plugs, there was still a considerable loss of radiation and it was found necessary to work at a fairly large slitwidth for this region (0.10 mm) and high gain. The resulting high noise level was partially smoothed by using a slow amplifier response and slow sweeping speed. Since we were interested in a small spectral region containing a single, intense band, no important errors were introduced by this procedure.

Most of the radiation path was swept clear of water vapor by a rapid flow of air from the laboratory supply line. The air was dried by CaCl_2 and a liquid nitrogen trap. However, the 20 cm of exposed path in our present set up caused considerable absorption by the intense rotation-vibration band of water vapor in this region. Since we determined frequencies from the position of the absorption maximum, some error in the absolute values and in the frequency shifts was undoubtedly caused by the water vapor. In one case we performed a point-by-point subtraction of the water vapor band from the alcohol O-H band and found one or two wave number changes in ν and in $\Delta\nu$. It was our feeling that the errors introduced by the subtraction procedure outweighed any gain in accuracy so obtained.

A LiF prism was used, calibrated by the rotational lines of the water vapor. Our estimate of the accuracy of frequency determinations, based on repeated observations, is $\pm 2 \text{ cm}^{-1}$ in the value of ν and $\pm 1 \text{ cm}^{-1}$ in $\Delta\nu$.

EXPERIMENTAL RESULTS AND DISCUSSION

The data which we obtained are all presented in Table I. The results on *t*-butanol, 2% *n*-butanol, and

⁸ E. Fishman and H. G. Drickamer, *Ind. and Eng. Chem.* (to be published).

⁹ R. C. Koeller and H. G. Drickamer, *J. Chem. Phys.* **21**, 267 (1953).

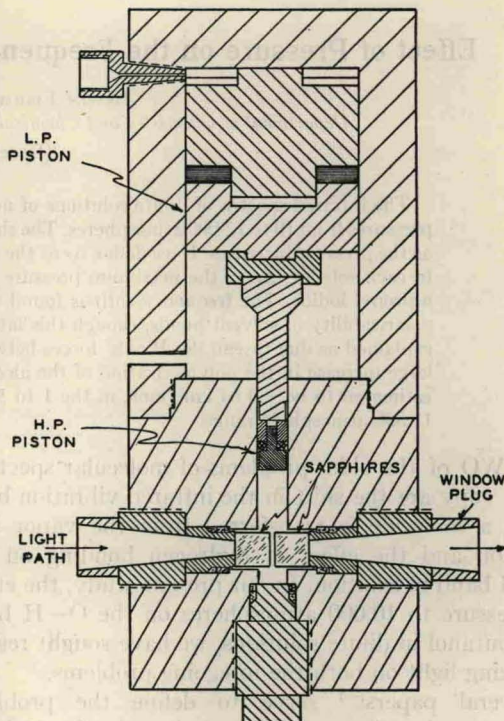


FIG. 1. Cross section of spectroscopic bomb.

methanol were obtained to determine the importance of the alkyl radical of the alcohol and the concentration on the frequency shifts. Comparison of these results with the *n*BuOH in the same solvent show the existence of some effects due to the alkyl radical; however, they are not large and will be considered outside the scope of subsequent discussion.

There does not appear to be a record of the vapor phase spectrum of *n*BuOH in the 3-micron region. The vapor phase spectrum of ethanol was reported with a central frequency of the O-H band at 3640 cm^{-1} ,¹⁰ which ought to be close to the value for butanol. We find a frequency of 3648 cm^{-1} in 2, 3, DMB solution and this represents our best estimate of the O-H frequency in the unperturbed alcohol molecule. From the data in Table I, it is apparent that the greater the displacement of the O-H band from 3648 cm^{-1} at one atmosphere in a particular solvent, the greater is the pressure-induced shift. For subsequent discussion we define $\Delta\nu$ as the shift in frequency from its value at 1 atmosphere and 25°C for each solvent; therefore the values of $\Delta\nu$ only indirectly reflect the difference in frequency in going from solvent to solvent, as indicated.

Since pressures of the order of 50 000 atmos are probably required to bring about significant compression of ordinary chemical bonds, it is clear that the frequency shifts reported are brought about by intermolecular effects, not by deformation of the molecules. Using

¹⁰ J. Errera and P. Mollet, *Compt. rend.* **204**, 259 (1937).