HYDROGEN BONDING OF ALCOHOLS TO PYRIDINE AND SOME PYRAZINES

J. E. HOUSE, JR.
Illinois State University, Normal

ABSTRACT.—The O-H stretching frequencies of several alcohols have been determined when these alcohols were hydrogen bonded to the nitrogen heterocycles pyridine (Py), methylpyrazine (MP), 2,5-dimethylpyrazine (DMP), 2-chloro-3-methylpyrazine (CMP), and *trans*-2,5-dimethylpiperazine (DMPip). From the stretching frequency shifts, the order of decreasing acid strength of the alcohols is found to be methyl > n-propyl ~ n-butyl > i-propyl ~ t-butyl ~ cyclohexyl. The order of decreasing base strength of the heterocycles is DMPip > Py > DMP > MP > CMP, in accord with pK_b values. A linear relationship was obtained between $\Delta\nu_s$ for hydrogen bonded methyl alcohol and the pK_b valuesof the first four bases.

Intermolecular hydrogen bonds can exist between hydrogen atoms in one molecule and electronegative atoms in another. This is a type of Lewis acid-base interaction, with the hydrogen functioning as an acid. Alcohols are known to hydrogen bond to many bases (Pimentel and McClellen, 1960, pp. 375-382). When the hydroxyl hydrogen of an alcohol is attracted to a base and forms a hydrogen bond, there is a slight weakening and lengthening of the O-H bond. There are several experimental methods for studying such systems. For a complete review of these methods and the chemistry of the hydrogen bond, see Pimentel and McClellen (1960).

Such a change in the nature of the O-H bond is easily seen from changes in the position and intensity of peaks in the infrared spectrum attributed to the O-H bond (Pimentel and McClellen, 1960, p. 70). A change in the stretching frequency of the O-H bond is observed, with the shift toward lower wave numbers upon forming the hydrogen bond. There have been numerous attempts to relate the shift, $\Delta\nu_S$, to enthalpy of formation of the hydrogen bond (Pimentel and McClellen, 1960, p. 82), the equilibrium constant for its formation (ibid., p. 96), the pK value of the base (ibid., p. 90), and the internuclear distances (ibid., p. 85).

In the work reported here, the stretching frequency shift has been determined when several alcohols are hydrogen bonded to some nitrogen heterocycles, pyridine, 2-methylpyrazine, 2,5-dimethylpyrazine, 2-chloro-3-methylpyrazine, and *trans*-2,5- dimethylpiperazine. These determinations were made in dilute CCl_4 solutions using a large excess of base to prevent bonding between alcohol molecules and restrict the interaction to one molecule of alcohol for each molecule of base.

Experimental

The alcohols used in this work were of reagent grade and were checked for purity by determining the indices of refraction using an Abbe Refractometer. These alcohols were used without further purification. The pyrazines and *trans*-2,5-dimethylpiperazine were obtained from Wyandotte Chemical Corp. These compounds and the pyridine were checked for water or other O-H bond containing impurities by examination of infrared spectra of dilute CCl_4 solutions. There were no peaks attributable to O-H bond stretching bands. Spectra obtained using materials which had been dried for several days over P_2O_5 were identical, with a complete absence of O-H stretching bands.

In all solutions in which the alcohols and bases were hydrogen bonded, the alcohol concentration was 0.040 molar and the base concentration was 0.50 molar. The solvent was Fisher Spectral Grade CCl_4. The large excess of base was used to assure hydrogen bonding to only one of the potential electron donor atoms in each molecule of base. The alcohol concentration was chosen because at higher concentrations, appreciable amounts of the alcohols exist as dimers or higher aggregates. Peaks corresponding to these species were found at concentrations of 0.08 molar or higher. No such peaks were found at the concentration used.

The infrared spectra in the range 3000-3800 cm^{-1} were obtained using a Perkin-Elmer Model 12C Infrared Spectrophotometer with a sodium chloride prism and a slit width of 0.014 mm. All spectra were obtained using a cell of 1.0 mm path length with sodium chloride windows. The spectrophotometer was calibrated by a standard method (Downie, et. al., 1953) using the polystyrene peaks at 3060, 2924, and 2850 cm^{-1}, the ammonia peaks at 3219, 3336, and 3414 cm^{-1}, and the water peaks at 3881, 3740, and 3619 cm^{-1} (Plyler, et. al., 1960, 1950). Stretching frequencies were first obtained for the alcohol alone in CCl_4, then with alcohol and base present.

Results

The O-H stretching frequencies for the alcohols with and without base present are shown in Table 1. The literature values for the alcohols with no base present are those from Kuhn (1952).

The values obtained in this work were slightly lower than those of Kuhn. This is because they were determined at 0.040 molar instead of 0.005 molar as were Kuhn's. It has been pointed out that the "free" O-H stretching frequency should be determined at 0.02 molar or less to be really "free" (Pimentel and McClellan, 1960, p. 79).

From the data in Table 1 are found the shifts in stretching frequency, $\Delta\nu_s$, shown in Table 2. Because of the difficulty in determining some of the maxima from rather broad peaks and the difficulty of calibration due to the dispersion of NaCl in this region, the values in Table 2 are probably no better than ± 5 cm^{-1}.

Table 1.—Alcohol O-H Stretching Frequencies in cm^{-1} for Alcohols Hydrogen Bonded to Pyridine (Py), Methylpyrazine (MP), 2,5-Dimethylpyrazine (DMP), 2-Chloro-3-methylpyrazine (CMP), and *Trans*-2,5-dimethylpiperazine (DMPip).

Base	Alcohol					
	Methyl	n-Propyl	i-Propyl	n-Butyl	t-Butyl	Cyclohexyl
None[1]	3642	3626	3620	3632	3614	3610
Py	3341	3341	3365	3360	3364	3356
MP	3394	3390	3406	3401	3403	3383
DMP	3377	3381	3385	3380	3395	3398
CMP	3432	3442	3439	3444	3437	3438
DMPip	3261	.....	.....	.....	.....	.....

[1] Kuhn (1952)

Table 2.—Stretching Frequency Shift in cm^{-1} of the O-H Bond for Alcohols Hydrogen Bonded to Pyridine (Py), Methylpyrazine (MP), 2,5-Dimethylpyrazine (DMP), 2-Chloro-3-methylpyrazine (CMP), and *Trans*-2,5-dimethylpiperazine (DMPip).

Base	Alcohol					
	Methyl	n-Propyl	i-Propyl	n-Butyl	t-Butyl	Cyclohexyl
Py.....	301	285	255	272	250	254
MP.....	248	236	214	233	211	212
DMP....	265	245	235	252	219	224
CMP.....	210	184	181	188	177	172
DMPip...	381	.....	.....	.....	.....	.....

Discussion

In considering the stretching frequency shifts shown in Table 2 there are two factors to be kept in mind; namely the acidity of the alcohol and the basicity of the heterocycle. The strength of the hydrogen bond is reflected by the relative acid strength and base strength of the interacting molecules and hence the O-H stretching frequency shift. Thus the strongest interaction is between methyl alcohol and *trans*-dimethylpiperazine. The weakest interaction is between 2-chloro-3-methylpyrazine and the secondary or tertiary alcohols. The acidity of the alcohols is reflected by choosing a particular base and noting $\Delta\nu_S$ as the series of alcohols is considered. Looking at the series of alcohols and comparing $\Delta\nu_S$ for each base in turn, it is apparent that methyl alcohol is the strongest acid and t-butyl, cyclohexyl, or i-propyl is the weakest. The order of decreasing acidity of all the alcohols is methyl > n-propyl ~ n-butyl > i-propyl ~ t-butyl ~ cyclohexyl. Chandra and Sannigrahi (1965) found that toward electron donors the acid strength of the alcohols decreases in the order primary > secondary > tertiary. Ketelaar (1953, p. 264) has shown that this is also the order of decreasing alkyl group electronegativity. Kuhn (1952) has found for the interaction of alcohols with ether, the order of decreasing acidity of the alcohols is methyl > n-butyl > sec-butyl > t-butyl. In fact, the ratio of $\Delta\nu_S$ for methyl alcohol to that for t-butyl when both are interacting with ether was found to be 1.18. However, Kuhn (1952) reports shifts for methyl and n-butyl which were almost identical; they are 151 and 150 cm^{-1} respectively. From the values reported here, the value for n-butyl seems too high.

The ratios of $\Delta\nu_S$ (methyl)/$\Delta\nu_S$ (alkyl) are shown in Table 3. The data in Table 3 show that if all the bases are considered, there is a reasonably constant value of $\Delta\nu_S$ when each alcohol is compared to the $\Delta\nu_S$ for methyl. This indicates that the acid strength of each alcohol is constant toward all the bases and that no steric factors are involved. These factors are important only when the alcohols are functioning as bases. The data in Table 3 also indicate that the ratio of the stretching frequency shift for methyl alcohol compared to that of n-butyl should be

Table 3.—Ratios of $\Delta\nu_s$ for Methyl Alcohol to $\Delta\nu_s$ of Other Alcohols Hydrogen Bonded to Nitrogen Heterocycles.

Base	Alcohol				
	n-Propyl	i-Propyl	n-Butyl	t-Butyl	Cyclohexyl
Py	1.06	1.18	1.11	1.20	1.18
MP	1.05	1.16	1.07	1.18	1.17
DMP	1.07	1.13	1.05	1.21	1.18
CMP	1.14	1.16	1.12	1.19	1.22
Ave.	1.08	1.16	1.09	1.20	1.19

about 1.09 instead of the value of 1.00 found from Kuhn's data (1952).

Arbitrarily assigning the acid strength of methyl alcohol a value of 1.00, the following relative acid strengths are found from the relative O-H stretching shifts: methyl, 1.00; n-propyl, 0.925; n-butyl, 0.917; i-propyl, 0.862; cyclohexyl, 0.840; and t-butyl, 0.833.

It is also apparent from TABLE 3 that if the series of alcohols is considered with each base in turn, without exception the order of decreasing base strength of the heterocycles is DMPip > Py > DMP > MP > CMP. The corresponding pK_b values of the first four of these are 4.31 (Hall, 1956), 8.82 (Butler, 1964), 12.15 (Chia and Trimble, 1961), and 12.55 (Chia and Trimble, 1961). Apparently no pK_b value for CMP has been reported. It is seen that the order of decreasing base strength as determined by the pK_b values is the same as that measured by $\Delta\nu_S$ of the alcohols bonded to these bases. A plot of $\Delta\nu_S$ for hydrogen bonded methyl alcohol vs pK_b for the four bases where pK_b has been determined, is linear. This plot is shown in FIGURE 1.

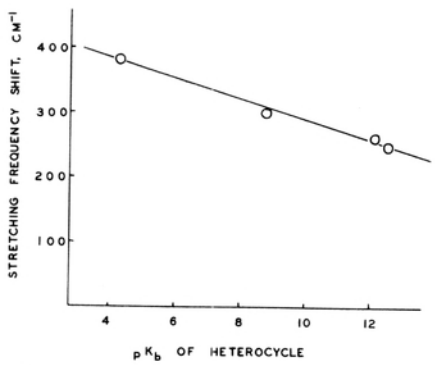

FIGURE 1.—A plot of O-H stretching frequency shift for hydrogen bonded methyl alcohol vs. pK_b of the heterocyclic bases.

It has been suggested that a linear relationship may exist between pK_b of a series of bases and the Δ_s of an alcohol hydrogen bonded to these bases if they are similar (Pimentel and McClellan, 1960, p. 91). FIGURE 1 shows that even though there are structural differences in the heterocycles used, they are similar enough that such a linear relationship exists. As can be seen from TABLE 2 and the pK_b values there is a very large

difference in the basicities of the heterocycles but less than a factor of two in the stretching frequency shifts.

Acknowledgments

This work was supported in part by the Faculty Research Fund of Western Kentucky State College while the author was at that institution. The author also expresses his appreciation to Mr. E. A. Barnhardt who helped obtain some of the spectra and to the Wyandotte Chemical Corp. who supplied the pyrazines.

Literature Cited

Butler, J. N. 1964. Ionic Equilibrium. Addison-Wesley Pub. Co., Inc., Reading, Mass. xi + 547 pp.

Chandra, A. K., and A. B. Sannigrahi. 1965. Hydrogen Bonding Properties of Alcohols. J. Phys. Chem. 69:2494-9.

Chia, A., and R. F. Trimble, Jr. 1961. Acid-Base Properties of Some Pyrazines. J. Phys. Chem. 65:863-6.

Downie, A. R., M. C. Maggon, T. Purcell, and B. Crawford. 1953. The Calibration of Infrared Prism Spectrophotometers. J. Opt. Soc. Amer. 43:941-51.

Hall, H. K. 1956. Potentionmetric Determination of the Base Strengths of Amines in Nonprotolytic Solvents. J. Phys. Chem. 60:63-70.

Ketelaar, J. A. A. 1953. Chemical Constitution. Elsevier Pub. Co., Amsterdam viii + 398 pp.

Kuhn, L. P. 1952. The Hydrogen Bond. I. Intra- and Intermolecular Hydrogen Bonds in Alcohols. J. Am. Chem. Soc. 74:2492-9.

Pimentel, G. C., and A. L. McClellan. 1960. The Hydrogen Bond. W. H. Freeman and Co., San Francisco xii + 475 pp.

Plyler, E. K., and C. W. Peters. 1950. Wavelengths for Calibration of Prism Spectrophotometers. J. Res. Nat. Bur. Stand. 45:462-8.

———, A. Danti, B. R. Blaine, and E. D. Tidwell. 1960. Vibration-Rotation Structure in Absorption Bands for Calibration of Spectrophotometers from 2-16 Microns. J. Res. Nat. Bur. Stand. 64A:29-48.

Manuscript received May 23, 1966.