"Amplifying" Effect of Hydrogen Bonding on the Correlation of Frequencies of O–H Stretching Vibrations of Phenols with Hammett Substituent Constants

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Summary The OH stretching frequencies measured for dilute solutions of various phenols in acetonitrile have been correlated with Hammett substitution constants.

IT has been known for many years[1,2] that the frequencies of stretching vibrations of monomeric phenolic hydroxy-groups can be related to Hammett σ constants, provided that there is not substitution at the *ortho*-position. Low values of the ρ constant and considerable scatter of the experimental ν_{OH} values along the regression line gave rise to rather sceptical conclusions on the usefulness of i.r. data for the estimation of pK or σ constants,[3] and the opinion has been advanced[4] that substituent effects can be discussed only qualitatively in terms of i.r. spectroscopic data.

Having studied substituent effects in systems with hydrogen bonding,[5,6] we have established that in the case of the properties affected by hydrogen bond formation—n.m.r. chemical shifts, ionization constants, and frequencies of out-of-plane deformation vibrations—the effect of substituents on the hydrogen bond strength must be taken into account, as well as their direct effect on the reaction centre. So, in systems with intermolecular hydrogen bonding, constant a in the equation defining the dependence of the property studied (I) on the Hammett substituent constants (σ), $I = I_0 + a\sigma$, is considered as including the Hammett ρ constant and a term (c) characterizing the effect of substituents on the hydrogen bond strength, so that $a = \rho + c$.[5] As the formation of the hydrogen bond causes a shift of ν_{OH} to lower values, the constant c should be negative (substituents with $\sigma > 0$ strengthen the hydrogen bond, thus causing a shift of ν_{OH} to lower values) and further, because the ρ constant is negative in the case of phenols too ($-13{\cdot}4$ cm^{-1}, solutions of phenols in CCl_4[2]) the absolute value of the experimentally observed constant a should be higher than the value of ρ observed in inert solvents.

We have measured the frequencies of the stretching vibrations for the OH groups of ten phenols dissolved in acetonitrile (1% solutions) and obtained a correlation of ν_{OH} with Hammett substituent constants. The Hammett equation has the form $\nu_{OH} = 3402 - 66{\cdot}6\,\sigma^-$, the correlation coefficient and standard deviation being 0·986 and ± 7·4 cm^{-1}. The reaction constant is five times higher than for phenols in CCl_4. The contribution of the H-bond term c to the constant a is consequently large, and makes the i.r. correlation comparable with the correlation of the n.m.r. chemical shifts of OH protons of phenols with Hammett substituent constants.[7]

Frequencies of OH *stretching vibrations of phenols measured in acetonitrile solutions and substituent constants used for the correlation*

Substituent	σ^-	ν_{OH} (cm^{-1})
4-NH_2	−0·66	3439
4-OH	−0·37	3422
4-CH_3	−0·17	3415
3-CH_3	−0·07	3412
-H	0·00	3409
3-OH	0·12	3402
4-Cl	0·23	3379
3-Cl	0·37	3374
3-NO_2	0·71	3346
4-NO_2	1·27	3319

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