

2.3: Some Factors Which Influence delta

In general, the chemical shift parameter δ will be a function of the electron density around the nucleus, since the electrons are directly involved in the diamagnetic shielding which acts to attenuate the applied magnetic field. Specific solvent and bulk diamagnetic susceptibility effects will also be important in determining δ . Temperature is not usually very important unless a change in temperature causes marked changes in some type of association equilibrium. For example, the O-H resonance line of ethanol moves toward the CH₂ and CH₃ lines with increasing temperature probably because of changes in the concentrations of the various hydrogen-bonded species.¹ A similar effect is noted when ethanol is diluted with carbon tetrachloride.² At low concentrations, the O-H absorption appears between that of the methylene and methyl groups. Extrapolation of the position of the O-H line as a function of concentration to infinite dilution indicates that in such circumstances the O-H line would be at higher fields than even the CH₃ absorption.

Table 2-1. Typical Proton δ Values ($\times 10^6$) for Pure Liquids with Approximate Variations for Different Compounds *

$-\text{SO}_3\text{H}$	-6.7 ± 0.3	H_2O	(0.00)
$-\text{CO}_2\text{H}$	-6.4 ± 0.8	$-\text{OCH}_3$	$+1.6 \pm 0.3$
RCHO	-4.7 ± 0.3	$-\text{CH}_2\text{X}$	$+1.7 \pm 1.2$
RCONH_2	-2.9	$\equiv\text{C}-\text{H}$	$+2.4 \pm 0.4$
ArOH	-2.3 ± 0.3	$\begin{array}{c} \\ =\text{C}-\text{CH}_3 \end{array}$	$+3.3 \pm 0.5$
ArH	-1.9 ± 1.0	$-\text{CH}_2-$	$+3.5 \pm 0.5$
$=\text{CH}_2$	-0.6 ± 0.7	RNH_2	$+3.6 \pm 0.7$
ROH	-0.1 ± 0.7	$\begin{array}{c} \\ -\text{C}-\text{CH}_3 \\ \end{array}$	$+4.1 \pm 0.6$

* Data from L. H. Meyer, A. Saika, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953).

In some cases, a temperature effect on chemical shifts may result from changes in amplitude of torsional vibrations with temperature. An example is 1,1,2,2-tetrafluoro-3-phenylcyclobutane, which shows substantial changes in the chemical shifts of the fluorine atoms as the temperature is increased or decreased because of changes in the amplitudes of vibration of the fluorines with respect to each other and the aromatic ring at the 3-position.³

Studies of the proton resonance absorptions of a wide variety of organic compounds have revealed that the resonance lines for similarly located hydrogens appear at comparable applied magnetic fields. This fact permits setting up a table of δ values for various types of protons as is shown in Table 2-1. The line positions for a given species of hydrogen are seen to occur over a moderate range of values as would depend on the electrical and shielding effects of substituent groups as well as bulk diamagnetic shielding influences produced by the other molecules in the sample. Recent work has shown that variations in δ because of the latter factor can be minimized by extrapolating the line positions to infinite dilution in a suitable common solvent^{4a} or by using internal standards.^{4b} For best results, internal standards should be chosen to be of such nature that any bulk diamagnetic shielding effects are expected to influence the resonances of the sample and standard to the same degree. The internal standard procedure is very convenient and has been shown by Chamberlain^{4b} to narrow the range of variations in δ values for many of the individual types of proton resonances listed in Table 2-1 to less than $\pm 0.2 \times 10^6$.

Some idea of the magnitude of solvent effects on chemical shifts is provided by the data of Table 2-2 which show the change in δ for methyl protons in a variety of compounds between pure liquid and extrapolated to infinite dilution in carbon tetrachloride.⁵ In general, the changes are large and irregular enough to suggest need for considerable caution in interpreting pure liquid spectra. Changes of chemical shift in some solvents appear to parallel changes in bulk diamagnetic susceptibility.

A cursory examination of Table 2-1 might lead one to believe that there is a relationship between the δ value of a proton and its acidity. This is not an unreasonable idea, since the electron density is important in determining both the diamagnetic shielding and the ease of removal of the proton by bases. Thus, a sulfonic acid proton appears at very low fields as would be expected if the electron density and diamagnetic shielding of the acidic proton were small. Carboxyl protons come at higher fields while water and alcohol protons are near the center of the table. Furthermore, the very weakly acidic amine and hydrocarbon protons come at the end of the table, corresponding to high electron densities and high diamagnetic shielding. However, closer inspection of Table 2-1 shows a number of groups, the proton δ values of which cannot be fitted into any simple acidity scale. Thus, aldehydic hydrogens appear at quite low fields, as do aromatic hydrogens. In contrast, the relatively strongly acidic acetylenic hydrogens come at rather high fields.

Table 2-2. Change in δ for Methyl Protons between Pure Liquid and Infinite Dilution in Carbon Tetrachloride *

Compound	δ (pure liquid)	δ (infinite dilution in CCl_4)	Δ
CH_3NO_2	+1.19	+0.48	-0.71
CH_3F	2.10	0.53	-1.57
$\text{CH}_3\text{OC}_6\text{H}_5$	1.83	1.09	-0.74
CH_3OH	1.85	1.39	-0.46
CH_3OCH_3	2.63	1.55	-1.08
CH_3Cl	2.10	1.74	-0.36
CH_3Br	2.02	2.10	+0.08
CH_3I	2.00	2.60	+0.60
CH_3CN	3.14	2.89	-0.25
$(\text{CH}_3)_4\text{C}$	4.35	3.84	-0.51

* Data from Allred and Rochow.⁵

1 J. T. Arnold and M. E. Packard, J. Chem. Phys., 19, 1608 (1951).

2 A. D. Cohen and C. Reid, J. Chem. Phys., 25, 790 (1956).

3 Unpublished experiments by W. D. Phillips and coworkers.

4a A. A. Bothner-By and R. E. Giick, J. Clzem. Phys., 26, 1651 (1957); 4b N. F. Chamberlain, Anal. Chem., 31, 56 (1959).

5 A. L. Allred and E. G. Rochow, J. Am. Chem. Soc., 79, 5363 (1957).