SOLVED PROBLEMS FOR NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY: CHEMISTRY 103

Harold Goldwhite, Professor of Chemistry

Your main reference source is pp. 169 – 182 in "Experiments in General Chemistry", 4^{th}. Edn. Revised, H. Goldwhite and W. Tikkanen.

A useful website with many links is at http://ep.llnl.gov/msds/orgchem/spectroscopy.html

1. Why aren't all proton magnetic resonance signals found at the same frewquency? After all they all arise from the magnetic properties of the same nucleus, namely H.

Answer; the resonance condition $\Delta E = h\nu$ is satisfied when $\Delta E = f\gamma B$ where B is the value of the magnetic field at the H nucleus being observed. B can be regarded as having three components: B_0 the external applied magnetic field; B_1 the field due to electrons circulating near the nucleus being observed; this is called the chemical shift δ; and B_2 the local magnetic field due to other magnetic nuclei (e.g. other H nuclei) near the observed H nucleus; this is called J or spin-spin coupling. So in general differently situated H nuclei resonate at different ν values.

2. How many different chemical shifts do you expect for H nuclei in the following molecules? Where there is more than one chemical shift expected what will be the relative intensities of the different signals?

CH_4 CH_3CH_3 $CH_3CH_2CH_3$ $H_2C{=}CH_2$ $H_2C{=}CHBr$

Answer:

CH_4 All H nuclei are equivalent since the molecule has a regular tetrahedral shape. Equivalent protons have the same chemical shift and do not give rise to J splitting. Only one chemical shift is expected.

CH_3CH_3 The argument is the same as for CH_4 and only one shift is expected. A useful test for magnetic and chemical equivalence is to replace mentally the hydrogens in question by a Cl atom. If you get the same compound then the nuclei are equivalent. Thus $ClCH_2CH_3$ is the same compound as CH_3CH_2Cl.

$CH_3CH_2CH_3$ The two terminal CH_3 groups are magnetically and chemically equivalent and so their hydrogen atoms will all have the same chemical shift. The central CH_2 group is different and will give a resonance signal at a different chemical shift. So two different chemical shifts are expected. Their relative intensities will have the same ratio as the number of H nuclei in the different environments, that is 6:2 or 3:1.

$H_2C{=}CH_2$ All H nuclei in this planar molecule are equivalent. Try the Cl substitution test. Only one chemical shift is expected.

$H_2C{=}CHBr$ Each H nucleus in this planar molecule is different! Try the Cl replacement test – you get three different molecules. So three chemical shifts are expected with intensities in the ratio 1:1:1.

3. What spin-spin coupling patterns do you expect for each distinct set of H nuclei in the following molecules.

CH_3CHCl_2 $CH_3CHClCH_3$ $CH_3OCH_2CH_3$

Answer:

CH_3CHCl_2 There are two different chemical shifts for the H nuclei in this compound. The n+1 rule tells us that for the CH_3 group the single H nucleus in the adjacent $CHCl_2$ group will split its signal into a 1:1 doublet (2 equal peaks). For the $CHCl_2$ group the 3 protons in the adjacent CH_3 group will split its signal into a quartet: four peaks of relative intensities 1:3:3:1. The total intensities of the two signals will be in the ratio 3:1.

$CH_3CHClCH_3$ For the CHCl group the 6 equivalent H nuclei in the two adjacent and equivalent CH_3 groups will give rise to a 7 peak signal (a septet). For the two equivalent CH_3 groups the single H nucleus in the CHCl group will give rise to an equal doublet signal. The total intensities of the two signals will be in the ratio of 1:6.

$CH_3OCH_2CH_3$ The ether oxygen with its bonds means that the magnetic effects of the sets of H nuclei on the two sides of the ether O are not transmitted through it. Thus the 3 H nuclei in the CH_3O group give rise to one unsplit signal. For the OCH_2CH_3 group we expect a1:3:3:1 quartet for the CH_2 group and a 1:2:1 triplet for the CH_3 group. Total intensities for the 3 signals will be in the ratio 3:2:3.