RELAXATION AND CHEMICAL POLARIZATION OF ^{13}C NUCLEI

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With the increasing use of ^{13}C NMR spectroscopy as an analytical tool the relaxation phenomena of ^{13}C nuclei are also gaining importance. Data about the general character of various ^{13}C relaxation processes are indispensable for the interpretation of double resonance spectra where line intensities are used for the assignment of spectral peaks.

Since the NMR signal at natural abundance of ^{13}C nuclei is very weak, only some special methods can be used for the measurement of relaxation times. The most successful one appears to be a modification of the adiabatic fast passage method equivalent to the $\pi - \pi/2$ pulse sequence, complemented with signal accumulation in a multichannel analyzer and total decoupling of other nuclei /1/. Contrary to tradition the ^{13}C spin-lattice relaxation times T_1 are not very long,but comparable with proton relaxation times /2,3/, ranging for investigated compounds from about 2 sec. (methyl groups of the viscous tert. -butyl alcohol) to 228 sec.(tetrachloromethane) at room temperature (25°C). The characteristic T_1 values for methyl, methylene and methine carbons range from 8 sec . ($C^*H_3CH_2OH$) to 3o sec ($CHCl_3$) at the same temperature. The most important relaxation mechanisms are intramolecular dipole-dipole interaction with nearby protons (but not necessarily with protons on the same carbon atom) and spin-rotation interaction for liquids of low viscosity (CS_2).Some compounds were studied at various temperatures and the nuclear Overhauser effect as well as deuteration were used to gain more insight into the relaxation of ^{13}C nuclei. As always, the presence of halogens leads to a significant decrease of T_2 and an increase of T_1. T_1 values of methyl carbon atoms are 22 sec in $(CH_3)_2CO$, 69 sec in $(CD_3)_2CO$ and 25o sec in $(CCl_3)_2CO$. The range for carbonyl carbons is not so wide, from 25 sec in $(CH_3)_2CO$ to 65 sec in tetramethylcarbamide.

Chemical polarization of ^{13}C nuclei is another relaxation effect that provides much useful information about the CIDNP phenomena in general /4,5/ and also about the excited states and chemistry of the paramagnetic species present in high - energy chemical reactions. The ^{13}C polarization is much larger than in proton spectra and can exceed the limit equal to -o.5 to 1.o times γ_e/γ_N set by the usual dipole -dipole and scalar interactions between the unpaired electron and the nuclei being polarized. Each polarized carbon atom gives a se-

parate signal that is not shifted from the usual values for diamagnetic molecules. The polarized spectrum of dibenzoyl peroxide decomposition at 110°C in 25% cyclohexanone solution was scanned each 1o sec and accumulated. Both single and double resonance with total decoupling of hydrogen nuclei were used and all spectra were ran at 15.1 MHz. Of the main reaction products benzoic acid is not polarized, but the minor (2.5% of Bz_2O_2) component, phenyl benzoate, gave most of the strong peaks in the spectrum. The carboxyl carbon absorbs at 28.7 ppm, the substituted carbon atom of the benzoyl group at 63.2 ppm (from CS_2). The emission lines at 59.7 and 7o.3 ppm belong to benzene and the line at 68.3 ppm to highly polarized carbon dioxide. The central carbon atoms of diphenyl absorb at 52.1 ppm, and just as in the case of phenyl benzoate the other carbon atoms of the molecule are not measurably polarized. The solvent molecules are likewise not polarized. As a general rule only the carbon nuclei in or adjacent to the reaction center are highly polarized and the polarization of ^{13}C is positive in radical recombination products, but negative in radical decomposition or hydrogen abstraction products. The multiplet effect that is so prominent in ^{1}H spectra is very weak in ^{13}C spectra for the cage recombination products and overshadowed by the much stronger energy polarization. At the same time for secondary products, such as the polarized secondary isopropyl iodide, formed outside the solvent cage from the added isopropyl iodide via isopropyl radicals in iodine exchange reactions, the energy polarization is zero, but the multiplet effect is very pronounced, just as in proton spectra /6/. All these results are in accord with the conclusion that chemical polarization appears at the very moment of the formation of stable reaction products and not as the result of dipole-dipole or scalar relaxation processes in the free radical itself, as proposed by many investigators of the phenomenon /4-8/. This point is further illustrated by the very large value of ^{13}C polarization, 16ooo ± 5o % for the 41.5 ppm phenyl benzoate peak. In the absence of oxygen the thermal decomposition of benzoyl peroxide proceeds with the formation of phenyl benzoate as a minor, ≤ 3% product in a solvent cage, as is apparent from the insensitivity of the yield on the presence of radical scavengers /9/. Since the reaction energy is very high, about 7o kcal/mole, the formation and cage recombination of decomposition products must proceed through highly excited radical states with orbital momentum of the unpaired electron to a triplet state and thence to the stable phenylbenzoate molecule. Under appropriate conditions these excited states give rise to intense chemiluminescence /1o,11/. The excited states appear to be comparatively long-lived for high polarization to be achieved that is subsequently transferred to the nearby magnetic nuclei at the moment of the formation of the stable molecule.

REFERENCES

/1/ K.F.Kuhlmann, D.M.Grant and R.K.Harris, J.Chem.Phys. 52, 3439 (197o)
/2/ A.Olivson and E.Lippmaa, Eesti NSV Tead.Akad.Toim., Füüs. Matem. 16, 39o (1967)
/3/ B.K.Hunter and L.W.Reeves, Can.J.Chem. 46, 1399 (1968)
/4/ J.Bargon, H.Fischer and V.Johnson, Z.Naturforsch. 22a, 1551 (1967)
/5/ J.Bargon and H.Fischer, Z.Naturforsch. 22a, 21o9 (1968)
/6/ H.R.Ward, R.G.Lawler and R.A.Cooper, Tetrahedron Lett. 527 (1969)
/7/ M.Cocivera, J.Am.Chem.Soc. 9o, 3261 (1968)
/8/ R.G.Lawler, J.Am.Chem.Soc. 89, 5519 (1967)
/9/ T.Nakata, K.Tokumaru and O.Simamura, Tetrahedron Lett. 33o3 (1967)
/1o/ E.J.Bowen and R.A.Lloyd, Nature 2o1, 18o (1964)
/11/ J.Winkelman and G.Slater, Anal.Biochem. 2o, 365 (1967)