CHEMICAL POLARIZATION OF ^{13}C- AND ^{15}N-NUCLEI IN THERMAL DECOMPOSITION REACTIONS

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C.I.D.N.P. phenomena in proton spectra provide an elegant tool for the study of free radical reactions. Large polarizations and multiplet effects have been found in many cases and a very satisfactory theory of nuclear polarization in reacting radical pairs has been developed by R. Kaptein and G.L. Closs. According to this theory, nuclear polarization is directly proportional to electron spin densities and so carbon and nitrogen NMR spectra should show even larger polarizations and be in general more informative than proton spectra.

This is indeed the case. In the thermal decomposition of dibenzoyl peroxide (*1, 2*) at 110 °C in cyclohexanone, phenyl benzoates is produced in a 2.4 % yield. The enhanced absorption line, corresponding to the polarized substituted carbon atom of the phenol ring, is 21600^{+50}_{-10} times higher than the corresponding signal from the same amount of phenyl benzoate a thermal equilibrium (*3*). The amount of the polarized species B* present at any time can be calculated, using the simple formulae of consecutive reaction kinetics, where

$$A \xrightarrow{K_1} B^* \xrightarrow{T_1^{-1}} B.$$

The first order reaction rate constant K_1 and relaxation time T_1 of any particular polarized line can both easily be measured by scanning the total or partial ^{13}C NMR-spectrum each 10 (or 20) seconds and measuring the pure absorption signal, once with a very weak and non-saturating rf field and then with a completely saturating strong rf field. The signal decay tail gives (preferably on a semilogarithmic amplitude vs. time plot) T_1 in the first case and K_1^{-1} in the second. Chemical polarization thus provides a good new method for the measurement of long relaxation times of even very weak spectral lines in ^{13}C, ^{15}N or other spectra.

It is interesting to note that polarization is high even for the central carbon atoms in symmetrical diphenyl. This line appears in enhanced absorption at 15 MHz and in emission at 10 MHz, even though no other line changes its sign. Of the other reaction products benzoic acid (30 to 32 %) is not polarized, while benzene (31 to 35 %) and CO_2 (25 %) show strong emission. The addition of isopropyl iodide leads, among other products, to polarized iodide that shows a strong multiplet effect in ^{13}C spectra with no net polarization at all.

The thermal decomposition of diazoaminobenzene in cycloheptanone at 170 °C proceeds similarly. While in the proton spectrum only polarized benzene gives a measurable signal, in carbon ^{13}C spectrum there are also strong lines, corresponding to aniline (C_1 in emission, $C_{2,6}$ in absorption), diphenylamine ($C_{1,2,6}$ in absorption), benzene (emission) and diphenyl (absorption). The signal-to-noise ratio is much better than in the case of dibenzoyl peroxide decomposition, despite the much higher temperature, and so the corresponding polarizations may be higher still. Using ^{15}N-enriched compounds, ^{15}N-polarization could be detected. Polarized nitrogen and aniline, as well as some polarized diazoaminobenzene itself, are formed.

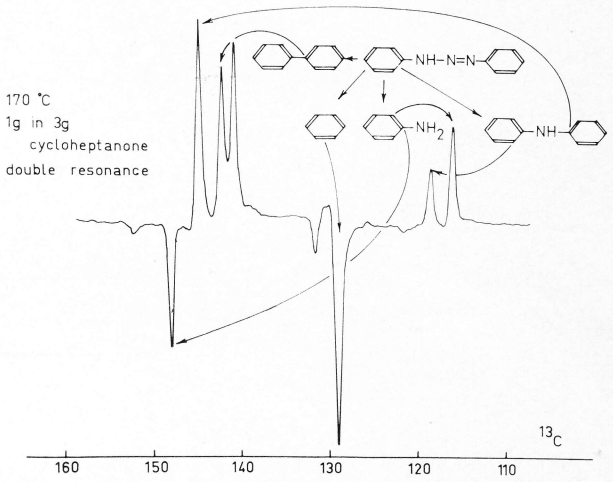

Fig. 1.

A very good example of ^{13}C polarization is provided by the thermal decomposition of 2,6-tert.-butyl benzene 1,4-diazooxide in hexachloroacetone at 110 °C. While only one polarized signal appears in the proton spectrum, all carbons, except that of the end trichloromethyl group of the addition product, are polarized, even in the tert.-butyl groups. The reaction proceeds through the formation of a carbene, and since the signs of all lines are reversed upon the addition of isopropyl iodide (that itself shows a strong net polarization in this case), possibly through carbene in a singlet state.

Very interesting results were obtained with ^{15}N-enriched diazo compounds. On chemical low temperature decomposition both nitrogen atoms and the substituted C_1 carbon of the ring are polarized, presumably because of some reaction of the diazenium radical that may be in equilibrium with the diazonium salt. The same atoms are polarized in the diazo coupling reaction with sodium phenolate in dimethyl sulfoxide and the product, p-hydroxydiazobenzene, is also polarized. This polarization is confined to the

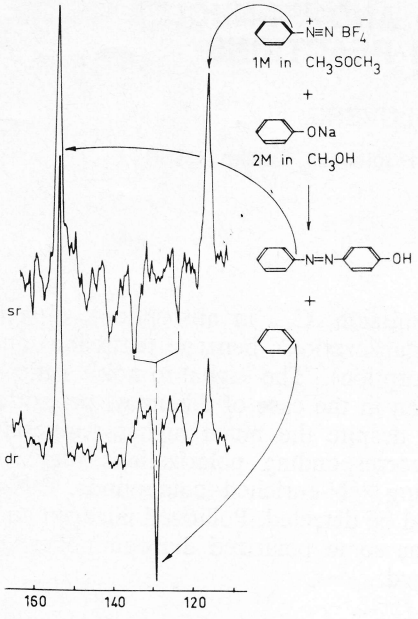

Fig. 2.

same nuclei that are polarized in the diazonium salt and the phenol moiety is not polarized.

All these data lead to the conclusion that C.I.D.N.P. on ^{13}C, ^{15}N, and possibly other and heavier nuclei provides a very good means for the study of free radical reactions and reaction mechanisms in general. The ^{13}C spectra of even quite complicated compounds and reaction mixtures are relatively easy to interpret, particularly through the use of double resonance techniques, and the polarization is very much higher than in proton spectra. After all, it is only logical to look for the unpaired electron there, where it really likes to be.

References

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