CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION OF ^{13}C NUCLEI IN THE THERMAL DECOMPOSITION OF ORGANIC PEROXIDES

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Carbon-13 NMR spectra of chemically polarized decomposition products were investigated. The polarization is much larger than in proton spectra, positive for radical recombination products and negative for the others. The chemical polarization appears at the very moment of formation of the stable reaction products.

1. INTRODUCTION

Chemically induced dynamic nuclear polarization (CIDNP) phenomena have recently been observed in the course of thermal decomposition of organic peroxides and azo compounds [1-3], during some halogen–metal exchange reactions between alkyllithium and alkyl halides [4,5], as a result of photoexcitation of anthraquinone [6] and in some other photochemically initiated reactions [7-9]. Both enhanced absorption (A) and emission (E) as well as mixed (A/E or E/A) signals from polarized spin multiplets [7-10] have been observed in proton spectra of the diamagnetic products of these reactions.

We have recently been investigating chemically induced nuclear polarization phenomena in ^{13}C NMR spectra at natural abundance of this isotope (1.1%). The thermal decomposition reactions of two peroxides, dibenzoylperoxide (DBP) and acetylbenzoylperoxide (ABP) were studied. It appears that ^{13}C spectra obtained during such reactions provide much more information about the polarization effects than the corresponding proton spectra. The chemical polarization of ^{13}C nuclei is at least an order of magnitude larger than in proton spectra and each polarized carbon atom, including those without attached protons, gives a separate signal. All ^{13}C spectra were obtained at 15.1 MHz on a special spectrometer [11], using frequency sweep, double resonance with total decoupling of all hydrogen nuclei and time sharing to eliminate zero drift and additional non-thermal low-frequency noise. The use of time sharing [12] is essential for successful measurement of very weak NMR signals under adverse experimental conditions, involving rapid and large changes of both sample temperature and composition as well as mechanical vibrations of the sample tube as a consequence of the evoluation of carbon dioxide bubbles. 15 mm o.d. non-rotating sample tubes were used and the sample consisted of 0.3 to 1 g of pure peroxide in 3 ml of cold solvent. The ^{13}C NMR spectrum was scanned each 10 (or 20) seconds and accumulated in a type LP 4050 (Nokia, Finland) [13] multichannel analyser. Only absorption spectra were used to avoid distortion of spin multiplets and relative intensities of spectral lines. The chemical shifts were measured with a frequency counter with a mean error of ± 0.3 ppm. All ^{13}C shifts are given in the carbon disulfide scale ($\delta_{CS_2} = 0$, diamagnetic shifts positive).

2. RESULTS AND DISCUSSION

The thermal decomposition process of a 26% by weight solution of DBP in cyclohexanone at 110°C is depicted in fig. 1. The spectrum was scanned from -18 to $+74$ ppm each 10 sec and accumulated. Both single and double resonance spectra with total decoupling of all hydrogen nuclei were used (figs. 2 and 3). The spectrometer amplification and rf level were chosen so that the signals from unpolarized ^{13}C atoms in the initial DBP and the reaction products did not exceed the noise level. Strong ^{13}C signals were

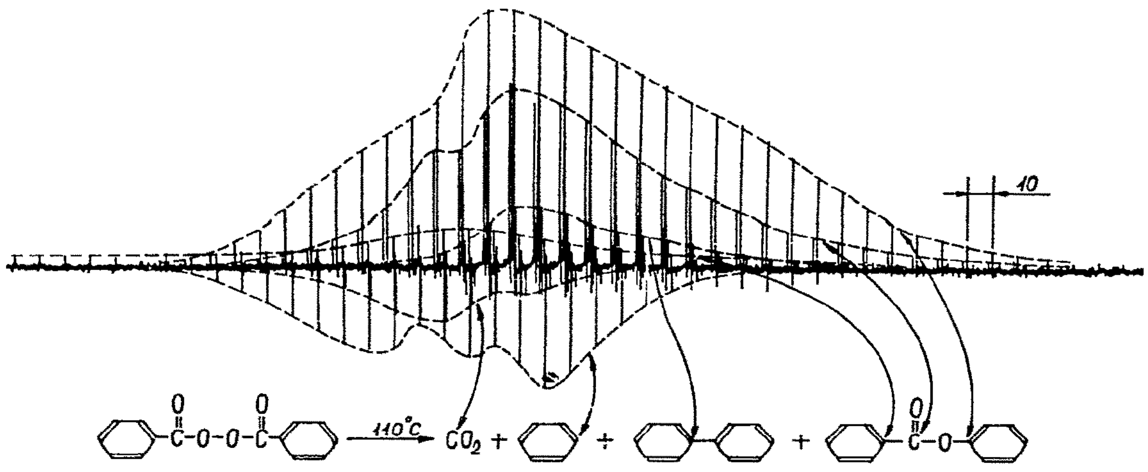

Fig. 1. ^{13}C NMR spectra registered during thermal decomposition of dibenzoylperoxide (1 g in 3ml of cyclohexanone, 110°C, double resonance, spectrum scanned from - 18 to + 74 ppm each 10 sec).

registered only from the polarized carbon atoms during the chemical reaction.

The first step in thermal decomposition of DBP is the formation of free benzoyl radicals that can either form benzoic acid through hydrogen abstraction from the solvent or decompose to polarized carbon dioxide and phenyl radicals. The phenyl radicals can either form benzene through hydrogen abstraction or recombine between themselves to diphenyl or with benzoyl radicals to phenyl benzoate. The secondary free radicals formed from cyclohexanone through hydrogen abstraction also give a slightly polarized product, but no polarized α-benzoyloxy-cyclohexanone [1] is formed.

Of the main reaction products benzoic acid was not polarized, but the quite minor component, phenyl benzoate, gave most of the strong peaks in figs. 2 and 3. These peaks are insensitive to double resonance and so must correspond to unprotonated carbon atoms. The carboxyl carbon absorbs at 28.7 ppm, the substituted carbon atom of the phenyl group at 41.5 ppm and substituted carbon atom of the benzoyl group at 63.2 ppm. The very weak lines at 64.1 ppm and 72.0 ppm that appear only in the double resonance spectrum in fig. 3 belong to carbon atoms in ortho positions of both aromatic rings. The intense negative-going doublet at 59.7 and 70.3 ppm (fig. 2) collapses to one single line at 65.0 ppm in the double resonance spectrum (fig. 3) and belongs to benzene. The other emission line at 68.3 ppm is caused by 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 line at -16.2 ppm belongs to the unpolarized carbonyl group of the cyclohexanone solvent and the emission line at -9.7 ppm to some reaction product of the solvent.

As a rule only the carbon atoms in or adjacent to the reaction center are polarized and the polarization of ^{13}C atoms is positive in radical recombination products, negative in radical decomposition or hydrogen abstraction products. The slight irregularities of reaction kinetics in fig. 1 are apparently caused by chain reactions during the rapid decomposition of DBP in a concentrated solution. The process is much more regular at 90°C, where the benzene emission signal is considerably stronger and the diphenyl peak very markedly reduced.

The thermal decomposition reaction of ABP was studied in a 6% by weight solution in tetrachloroethylene at 110°C. No polarized benzene or chlorobenzene is formed in this solvent. The most intense spectral lines between -18 and +74 ppm belong to carbon dioxide (strong emission line at 67.9 ppm) and methyl benzoate (a very strong absorption line of the carboxyl carbon atom at 26.9 ppm and a weak one, corresponding to the substituted carbon atom of the aromatic ring, at 62.8 ppm). The weak emission line at 55.6 ppm and a very weak absorption line at 65.0 ppm belong to the substituted and ortho carbon atoms of the toluene aromatic ring. The origin of weak lines at 57.0 ppm (A), 62.0 ppm (E) and 72.4 ppm (E) is unclear, but the reaction products between the

Fig. 2. Thermal decomposition of dibenzoylperoxide (^{13}C single resonance spectrum: otherwise conditions as in fig. 1, accumulated signal from 36 passes).

Fig. 3. Thermal decomposition of dibenzoylperoxide (^{13}C double resonance spectrum: conditions as in fig. 1, accumulated signal from 36 passes).

solvent and free radicals are the most probable cause. Three partly overlapping quadruplets and one quintuplet are located in the region between +120 and +220 ppm (fig. 4). The negative-going quintuplet at 198.7 ppm ($J \approx 125$ Hz) can be unequivocally assigned to the highly polarized methane gas. From the two quadruplets with positive polarization the more intense at 142.1 ppm ($J \approx 146$ Hz) belongs to the methyl group of methyl benzoate and the weaker one at 172.2 ppm ($J \approx 132$ Hz) to toluene. Assignment of the intense negative-going quadruplet at 170.2 ppm ($J \approx 132$ Hz) is difficult. The spin–spin coupling constant is too small for the otherwise very probable methyl chloride. All these multiplets give only single lines in double resonance spectra. The multiplet effect [7-10] that is so prominent in proton spectra is overshadowed by the very much stronger energy polarization in ^{13}C spectra. Both positive quadruplets with enhanced absorption show weak multiplet effects (A/E and E/A), but the emission signals are represented by totally symmetric multiplets.

Just as in the previous case only the carbon atoms in or near the reaction center are strongly polarized. The distribution of polarization does not correspond to the probable pattern of electron delocalization in the free radical. The chemical polarization of ^{13}C nuclei is very intense. Even though exact numerical values were not measured, the estimated values are at least an order of magnitude higher than in proton spectra. This point is well illustrated by the good signal to noise ratio in figs. 2 and 3. It is clear that the polarization of ^{13}C nuclei is not a secondary effect, caused by the chemically polarized protons. Complete decoupling of all hydrogen nuclei by a strong perturbing radio-frequency field does not have any measurable effect on the chemical polarization of ^{13}C nuclei in the reaction products, but leads to a significant nuclear Overhauser effect and increase of line intensities in the ^{13}C spectrum of the cyclohexanone solvent only. It is apparent from the figs. 2 and 3 that the collapse of the doublet of polarized benzene is not accompanied by any increase in the total signal intensity. Solvent peaks in the ^{13}C double resonance spectra are slightly diminished while the active process of peroxide decomposition is going on and free radicals provide a competing relaxation mechanism for the ^{13}C nuclei, but the nuclear Overhauser effect in the ^{13}C spectrum of cyclohexanone is never reduced to zero and at no time during the chemical reaction are the solvent molecules chemically polarized. All this is rather different from the usual dynamic polarization experiments where the resulting large nuclear polarization is caused by saturation of the electron resonance signal by a strong microwave field and the solvent protons are always strongly polarized as a result of either dipole-dipole or scalar interaction with the unpaired electron [14].

It is also important to point out that the same free radical (methyl, phenyl or benzoyl) can give stable reaction products with both signs of polarization of the ^{13}C nuclei: positive in the recom-

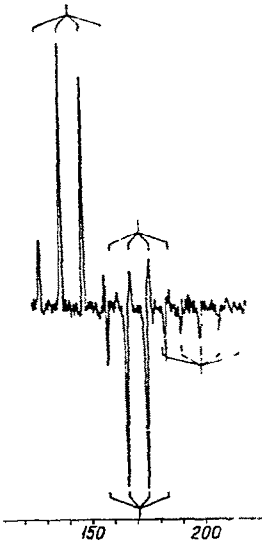

Fig. 4. Thermal decomposition of acetylbenzoylperoxide (^{13}C single resonance spectrum: 0.3 g in 3 ml of tetrachloroethylene, 110°C, spectrum scanned from + 120 to + 220 ppm and accumulated during 30 passes).

bination products (methyl and phenyl benzoate, toluene, diphenyl) and negative in the products of hydrogen abstraction or radical disintegration reactions (methane, benzene, carbon dioxide). The same relationship between the sign of nuclear polarization and the type of chemical reaction occurs in proton spectra, only in this case the recombination products give emission lines and hydrogen abstraction reactions lead to enhanced absorption. The rule is not absolute, however, and benzene provides an exception where the polarization of both ^{13}C and ^{1}H nuclei is negative.

It appears that the chemical polarization of ^{13}C nuclei as well as the CIDNP phenomena in proton spectra [1-10, 15] are not caused by Overhauser-type relaxation processes in single free radicals [1,2], but rather arise at the moment of formation of the stable diamagnetic reaction products as a result of electron–electron and electron–nucleus interactions in elementary acts of chemical reaction accompanied by the formation and disappearance of free radicals.

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