THE CHEMICAL POLARIZATION OF THE PROTON SPINS IN THE ^{13}C CONTAINING MOLECULES

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Relative enhancement coefficients due to the chemical polarization were measured for the $^{12}CH_3$ and $^{13}CH_3$ PMR lines in the decomposition products of the acetyl-benzoyl peroxide. These coefficients were found to be equal within experimental errors of 30-50%.

The complex nature of the chemical polarization is not fully understood at present. Certain experimental results seem to be mutually contradictory, such as for example, the data concerning the sign reversal of the ^1H and ^{13}C polarization in the products of the decomposition of benzoyl and acetyl-benzoyl (ARP) peroxides [1-3]. The proton polarization of the ^{13}C containing molecules has not been formerly investigated.

The present study was undertaken with a view to establishing a mutual dependence or independence of the ^{13}C and ^1H polarization processes. We measured the relative enhancement due to the chemical polarization of the methyl lines and their ^{13}C satellites in the PMR spectrum of the ABP decomposition products (CH_3Cl and $CH_3O\underset{\underset{O}{\|}}{C}C_6H_5$).

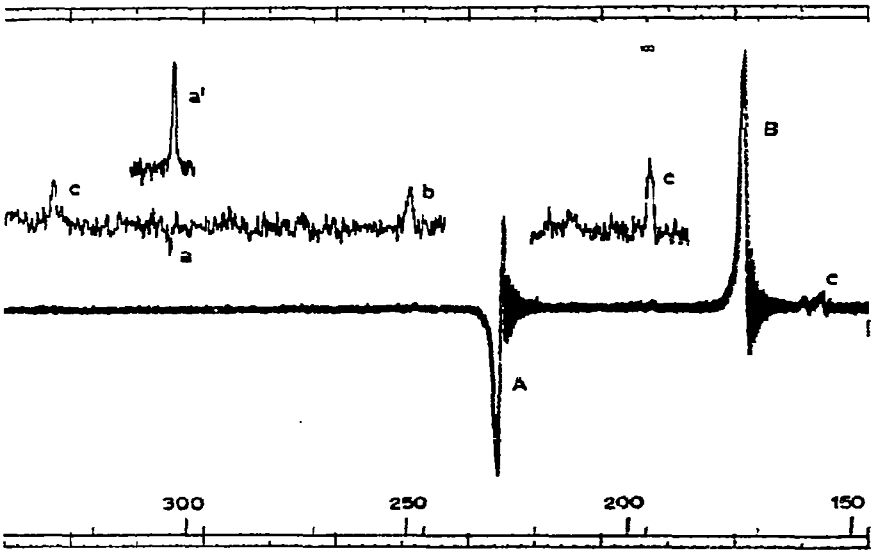

Fig. 1. The spectrum part of the ABP decomposition products taken in the course of the reaction (calibrated in Hz relative to TMS).
A, B - $^{12}CH_3$ lines in methyl benzoate and CH_3Cl respectively (tenfold record).
a, b - respective $^{13}CH_3$ lines by the use of 137-fold accumulation.
a' - ^{13}C satellite of the methyl benzoate OCH_3 line (for comparison).
c - nonidentified lines.

The reaction was carried out in the 0.3 N ABP solution in CCl_4 at 73°C. These conditions were most suitable for the application of the signal accumulation method. HNDS was used as an internal NMR standard. The experiment was performed on the Varian DA-60-IL instrument equipped with the spectra accumulator C 1024. 137 spectra were accumulated in all in the course of the decomposition of two ABP solution portions. The spectra were run at a sweep width of 250 Hz and a sweep time of 100 sec.

The observed $^{13}CH_3Cl$ and $O^{13}CH_3$ signal intensities are equal to 18 ± 7 and 12 ± 7 mm on the chart of recorder respectively (see fig. 1). Only low field satellites were observed. The high field satellites were shut out by other intensive signals. The above intensities would be equal to 29 ± 3 and 14 ± 3 mm respectively if ^{13}C did not affect the proton polarization. The agreement was almost within the limit of experimental errors.

This result was not unexpected since the polarization effects are small for both ^{13}C and ^{1}H. The value of the chemical polarization enhancement is of the order of magnitude $E = 10^3$ but the absolute value of the polarization is of the order of magnitude $P = 5 \times 10^{-3}$.

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