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N. M. POMERANTSEV, V. A. KHRAMCHENKOV, L. V. SUMIN, and A. V. ZIMIN

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Abstract

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NUCLEAR MAGNETIC RESONANCE SPECTRA OF IRRADIATED PERFLUOROOCTADIENE AND PERFLUORODODECADIENE

(Presented by Academician V. A. Kargin, November 17, 1960)

In the study of radiation-chemical processes occurring as a result of irradiation of organic systems, the use of infrared spectroscopy and nuclear magnetic resonance (NMR) methods gives very valuable results ([1]). However, interpretation of IR spectra is difficult (especially for complex molecules) because of the overlap of absorption bands characterizing individual functional groups in the molecule. In NMR spectra, the lines characterizing these groups are clearly distinguishable, which makes the solution of the question of the presence of individual functional groups more reliable.

We have obtained magnetic-resonance spectra of F^{19} nuclei for unirradiated and Co^{60}-irradiated (integral dose $\sim 10^{22}$ eV $\cdot$ g^{-1}) perfluorooctadiene and perfluorododecadiene. The spectra were recorded at room temperature using an apparatus that will be described in a separate article. The chemical shift was measured relative to the F^{19} line of the CF_3 group of trifluoroacetic acid. The chemical-shift values δ, plotted on the scales of Figs. 1 and 2, are determined by the expression

$$\delta = \frac{H_{\text{std}} - H_{\text{sample}}}{H_{\text{std}}} \cdot 10^5,$$

where H_{std} is the resonance value of the field for the standard, and H_{sample} is the resonance value of the field for fluorine of the given functional group.

The theoretical and experimental data published in the literature on chemical shifts for fluorocarbon compounds make it possible to unambiguously interpret the spectra given above. It may be considered established that, for fluorine-containing compounds, the chemical shift of F^{19} nuclei is determined mainly by the type of chemical bond. For spherically symmetric F^- ions, the paramagnetic term in the expression for the chemical shift is absent. The presence of a covalent bond leads to the appearance of this term and to displacement of the

Fig. 1. Magnetic resonance spectrum of F^{19} nuclei for unirradiated (1) and irradiated (2) perfluorooctadiene

Figure 1: Fig. 1. Magnetic resonance spectrum of F^{19} nuclei for unirradiated (1) and irradiated (2) perfluorooctadiene

Fig. 2. Magnetic resonance spectrum of F^{19} nuclei for unirradiated (1) and irradiated (2) perfluorododecadiene

Figure 2: Fig. 2. Magnetic resonance spectrum of F^{19} nuclei for unirradiated (1) and irradiated (2) perfluorododecadiene

absorption lines toward weaker fields ([2],[3]). For fluorocarbon compounds containing no atoms other than carbon and fluorine, it has been established that the absorption lines for F^{19} nuclei of CF groups are located in relatively strong fields. In weaker fields are located the lines of CF_2 groups, and the lines due to F^{19} nuclei of CF_3 groups are located in still weaker fields ([4]).

On the basis of the considerations presented above, the spectra of unirradiated perfluorooctadiene and perfluorododecadiene are interpreted as follows. The strong band in the region $\delta = 5.5$ is assumed to consist of a series of unresolved lines belonging to F^{19} nuclei of $-CF_2-$groups in the molecules

$CF_2 = CF—(CF_2)_4—CF = CF_2$

and

$CF_2 = CF—(CF_2)_8—CF = CF_2$.

The relatively weak line ($\delta = 1.8$) is assumed to be due to F^{19} nuclei of the terminal $= CF_2$ groups. The line due to CF, which is expected to be located in a stronger field than the line of F^{19} nuclei of $-CF_2-$groups, was not observed, apparently because of its low intensity. The above assignment of the spectral lines is confirmed by considerations based on an estimate of the line intensities.

The spectra of irradiated perfluorooctadiene and perfluorododecadiene differ from the spectra of the unirradiated compounds by the presence of a line located in relatively weaker fields than the lines of the unirradiated samples. According to what was said above, this line, by its position, should be assigned to the CF_3 group, which was also detected by IR spectroscopy.

Some changes in the shape of the band belonging to the F^{19} nuclei of the $-CF_2-$groups are probably explained by the appearance of a branched structure

Fig. 1. Magnetic resonance spectrum of F^{19} nuclei for unirradiated (1) and irradiated (2) perfluorooctadiene

Fig. 2. Magnetic resonance spectrum of F^{19} nuclei for unirradiated (1) and irradiated (2) perfluorododecadiene

and may be interpreted with better resolution of the lines constituting this band. It should be noted that the line width for the irradiated samples is greater than for the unirradiated ones. This is explained by the viscosity of the irradiated samples and imposes a limit on the possible resolution. It should be expected that measurements at higher temperatures will yield spectra with better resolution.

Physical-Chemical Institute
named after L. Ya. Karpov

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Note: Figure translations are in progress. See original paper for figures.