THE N^{14} AND C^{13} NMR SPECTRA OF THE ANIONS OF ALIPHATIC NITRO COMPOUNDS

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We investigated the N^{14} and C^{13} NMR spectra of the following mononitroalkane anions (nitromethane, nitroethane, 1- and 2-nitropropanes), gem-dinitroalkanes (dinitromethane and dinitroethane), and trinitromethane in H_2O, CH_3OH, dimethylformamide, dimethylsulfoxide, acetone, and acetonitrile at 25°C in connection with the problem concerning the fine structre of the anions from nitro compounds. The spectra were recorded at frequencies of 4.32 and 15.1 MHz (using double resonance for C^{13}) [1]. The chemical shifts of the N^{14} NMR for nitrocarbanions lie in the range of 20 to 80 ppm (the shift is toward stronger fields from CH_3NO_2), and the shifts of C^{13} in the α-carbon atoms are from 30 to 80 ppm (from CS_2). A relative diamagnetic shift is observed in the N^{14} spectra during the transition from the nitro compounds themselves to their anions: for mononitroalkanes it is 60-100 ppm, for dinitroethane it is 10 ppm: there is no shift for trinitromethane; a relative paramagnetic shift takes place in the C^{13} spectra, which shows there is a double bond on the α-carbon atom. A paramagnetic shift is observed in the C^{13} and N^{14} spectra for the transition from the mononitro to the polynitro carbanions. The observed relations agree with the concepts concerning the change in the charge on the nitrogen atom; other factors evidently play a subordinate role. The N^{14} spectra of all the anions consist of one symmetrical line which narrows drastically with an increase in the number of nitro groups (for example 1,100 Hz for $(CH_3)CNO_2^-$ and 10 Hz for $C(NO_2)_3^-$); these data indicate the nitro groups are equivalent in the anions of polynitro compounds in solutions.

LITERATURE CITED

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