Using the $^{13}$C NMR method, the manifestation of the carbon isotopic effect on the products of the photolysis of an aqueous solution of cyclopentanone is investigated. A relative enrichment by the isotope $^{13}$C of the carbonyl (13%) and α-carbon (6%) atoms of initial cyclopentanone and of the carbonyl atom of pent-4-en-1-ole (11%), as well as the depletion of the carbonyl (15%) and methyl (7%) carbon atoms of valeric acid are revealed. The isotopic effect observed is shown to have a magnetic nature.

Key words: carbon isotopic effect, photolysis, saturated cyclic ketones, biradicals, NMR spectroscopy, kinetic isotopic effect, magnetic isotopic effect.

Investigation of the carbon isotopic effect in photolysis of cyclohexanone in solutions [1] and in the vapor state [2] by the $^{13}$C NMR method has shown that the degree of the enrichment of initial molecules by the isotope $^{13}$C depends on the extent of photolysis and is proportional to the constants of hyperfine interaction on the carbon nuclei in the biradical formed. This result agrees well with the observed effects of chemical polarization of nuclei [3] and points to the magnetic nature of the effect. A carbon isotopic effect of this type has been observed in experiments with cycloheptanone. We attributed the much smaller magnitudes of enrichment to a more intense advancement of chemical reactions that prevented the effective selection of isotopes [4]. Therefore, of certain interest was the study of the possibility for the manifestation of the carbon isotopic effect in photolysis of cyclic ketones, whose decomposition results in the formation of biradicals with a short chain. The large exchange interaction in such biradicals leads to an increase in the distance between energy levels of different multiplicity and strongly impedes singlet-triplet evolution, which is a reason for the enrichment by the magnetic isotope $^{13}$C of an initial molecule that disintegrates from the triplet electronic state.

The aim of the present work was the study of the manifestation of the carbon isotopic effect in photolysis of an aqueous solution of cyclopentanone. The solution of cyclopentanone (0.2 M, 500 m/liter) was exposed to irradiation by a DRSh-500 mercury lamp light that passed through a water light filter. For the photochemical reaction to be conducted more efficiently and for the removal of dissolved oxygen, we irradiated boiling solutions in a quartz flask with a return cooler. The extent to which the reaction had proceeded was controlled by gas-liquid chromatography. Once the 94% cyclopentanone was decomposed (70 hours of photolysis), we separated the initial ketone from the reaction mixture by means of column chromatography on silica gel. Methylene chloride was used as an eluent. Then we dissolved it in CDCl$_3$, to which we added chromium tris-acetylacetonate to decrease the time of relaxation. The spectra were recorded on BS-567 A, AC-200, and MSL-300 spectrometers without decoupling from protons, since in this case the manifestation of the Overhauser effect with delays between pulses that exceed 5T$_1$ is excluded (T$_1$ is the time of the spin-lattice relaxation of carbonyl carbon). To estimate the carbon isotopic
effect, we compared the areas of the absorption peaks of various carbon atoms.

When conducting analyses of this type, it is not advisable to use electron integration, because of the large relative error of measurements. Therefore, we kept records of the signals of separate carbon atoms and determined the area under the contour of the line by the weighing method. The results of measurements showed that the areas of the peaks of the carbonyl and α-carbon atoms, normalized to one carbon atom, are respectively by 13±3% and 6±3% larger than the areas of the peaks of β-carbon atoms.

For determining the efficiency of the separation of isotopes (α), we use the formulas [5]

$$\ln S = (1 - \alpha) \ln (1 - f') ,$$

where \( S = \delta/\delta_0 \) is the ratio of the contents of the isotope \(^{13}\text{C}\) in cyclopentanone after the reaction and before it, respectively; \( 1-f' \) is the degree of the conversion of cyclopentanone molecules determined by molecules containing the isotope \(^{13}\text{C}\):

$$1 - f' = S (1 - f_{\text{exp}}) (1 + \delta_0)/(1 + S\delta_0) ,$$

where \( 1-f_{\text{exp}} \) is the complete conversion of the ketone. Substituting the corresponding values into the formulas, we obtain \( \alpha = 1.04 \pm 0.01 \) for the carbonyl carbon and \( 1.02 \pm 0.01 \) for α-carbon atoms, respectively.

Thus, in our experiments with the photolysis of cyclopentanone we observed an insignificant relative enrichment by the isotope \(^{13}\text{C}\) of the carbonyl and α-carbon atoms in the initial molecule.

In [5] it is shown that the efficient separation of isotopes based on the magnetic isotopic effect must be larger for radical reactions occurring in closed "microreactors," when the following condition is satisfied:

$$K_S - K_{ST} << D/R^2 ,$$

where \( K_S \) is the chemical reaction rate constant; \( K_{ST} \) is the singlet-triplet evolution rate constant in the biradical; \( D \) is the diffusion coefficient for the ends of the biradical; \( R \) is the radius of the "microreactor."

Taking into account that the hyperfine interaction constant for \(^{13}\text{C}\) in acyl radicals is equal to about \( 10^2 \) Oe, we may consider that \( K_{ST} = 3 \cdot 10^8 \) sec\(^{-1}\) [6]. We conducted the photolysis of cyclopentanone under conditions similar to the photolysis of cyclohexanone [1], where a noticeable enrichment of the initial ketone by the isotope \(^{13}\text{C}\) was observed. Therefore, in our opinion, the first condition should be satisfied well.

Using the value of the diffusion coefficient from [5] \( D \sim 5 \cdot 10^{-5} \text{ cm}^2\cdot\text{sec}^{-1} \) and selecting the dimension of the "microreactor" equal to the distance between the ends of the biradical \( (R = 3 \text{ Å}) \), we obtain \( D/R^2 \sim 5 \cdot 10^{10} \) sec\(^{-1}\), which indicates that the second condition is also satisfied.

On the other hand, the insignificant magnitude of the carbon isotopic effect for cyclopentanone agrees well with the known literature data for the kinetic isotopic effect [7].

Thus, the results obtained show that the carbon isotopic effect observed cannot be unambiguously assigned to the magnetic isotopic effect or to the kinetic isotopic effect. However, one of the principal differences in the considered isotopic effects, associated with the fact that the magnetic isotopic effect appears at the stage of recombination of biradicals, whereas the kinetic isotopic effect appears at the stage of the homolysis of cyclopentanone, makes it possible to answer the posed question in studying the manifestation of the carbon isotopic effect on the products of the photolysis of cyclopentanone. However, in the case of the photolysis products, the expected magnitude of the carbon isotopic effect must be smaller than for the initial compound, since in the case of deep photolysis cyclopentanone undergoes several stages of homolysis and the carbon isotopic effect is summed up.

We were able to separate valeric acid and pent-4-en-1-ale from the reaction mixture and analyze them for the content of the isotope \(^{13}\text{C}\) by the above-described technique. Just as in the previous case, the relative error of measurements was \( \pm 3\% \). We assumed that the third carbon atom did not change its natural isotopic composition. Then the relative change in the content of the isotope \(^{13}\text{C}\) (%) for various carbon atoms looks like this: